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Trace detection of mercury using boron-doped diamond electrodes

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TRACE DETECTION OF MERCURY USING BORON-DOPED DIAMOND ELECTRODES

Latha Ramakrishnan

**Thesis submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Electrical Engineering**

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2004**

**Keywords: Mercury Detection, Boron-doped diamond electrodes, DPV, Standard
addition method**

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ABSTRACT

Trace Detection of Mercury using Boron-Doped Diamond Electrodes

Latha Ramakrishnan

This Project was undertaken to develop electrochemical techniques using Boron-doped Diamond (BDD) electrodes for the purpose of detecting mercury in solutions in the ppb-ppt range. Differential Pulse Voltammetry (DPV) was used successfully to develop calibration curves for mercury detection in standard solutions in the ppb-ppt range, followed by using these curves for mercury measurements in unknown samples. DPV experiments were performed in nitrate, thiocyanate and chloride media. Investigation in the chloride medium is important since practical samples always contain chloride impurities. The formation of calomel in chloride medium is avoided on the BDD surface by the co-deposition of 3ppm of gold during DPV detection. Excellent linear calibration plots have been obtained in all media for ppb ranges. Mercury in the 0.1-50 ppb range has been detected in real samples (KCl impinger solutions) prepared from flue gas released by a pilot-scale coal fired combustion facility. A portable instrument has also been used for the detection of mercury efficiently. BDD mounted in rotating disk electrode (RDE) system together with gold co-deposition has been demonstrated to detect mercury with higher sensitivity and reproducibility. Standard additions method was used for the analysis of unknown samples.

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DEDICATION

I dedicate this work with lots of love and affection to my parents Ms. Lakshmi and Mr. Ramakrishnan, as I would never have come this far without their infinite encouragement and guidance through all phases of my life. Also I would like to dedicate this work to my sisters Subashini and Geetha who have always been a great source of motivation and inspiration.

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1. INTRODUCTION

Detection of trace levels of mercury in the environment has been a highly important and challenging analytical problem. Mercury is highly toxic and it is found sometimes in undesirable amount in the environment. The maximum permissible concentration (MPC) of mercury in drinking water as set by the EPA is 2ppb. The action levels for other heavy metals are lead- 15ppb, Copper- 1.3ppm, Cadmium – 5ppb, Arsenic – 10ppb and Antimony – 6ppb. In comparison to other metals, mercury has a very low permissible level. Humans are affected primarily by eating contaminated fish and the potential hazards are: kidney damage, brain damage, lack of motor skills, impaired cognitive skills, difficulty speaking and hearing, cardiovascular problems and impairment of immune and reproductive systems [1].

It is important to be able to detect mercury down to the range of 100 ppt to 6 ppb. Since mined coal contains trace amounts of mercury, coal-burning power plants are a significant source of mercury emissions. Other sources include industrial processing, residential and commercial combustion. Power generation contributes 37% of man-made mercury to the environment. Current methods used for mercury detection includes cold-vapor atomic fluorescence spectrometry (CV-AFS) [2], cold-vapor atomic absorption spectrometry (CV-AAS) [3], and inductively coupled plasma-mass spectrometry (ICP-MS) [4]. These methods require relatively large sample volumes for analysis and considerable time between sample collection and analysis. Therefore, these techniques are not suitable for on-line monitoring.

The detection of mercury in solutions, using anodic stripping voltammetry (ASV) has been reported on several different electrodes, including graphite [5], carbon paste [6, 7], glassy carbon [8, 9], modified glassy carbon [10], gold [11, 12], platinum [13], modified gold [14] and gold-plated glassy carbon [15]. Gold electrodes and glassy carbon electrodes are the most popular electrodes currently employed for mercury detection. Gold electrodes require electrochemical pretreatment and surface polishing quite regularly due to the strong amalgam formation with mercury. In many cases, the surface of the glassy carbon electrode needs to be modified by coating it with metals like gold and copper for mercury deposition. The lowest detection limit reported on a glassy carbon electrode is 5×10^{-14} mole/l (0.017ppt) using thiocyanate as the supporting electrolyte [8]. However longer deposition times like 40 mins for concentrations 5×10^{-14} to 10^{-12} mole/l (0.017ppt to 0.35ppt); 30 minutes for 10^{-12} to 10^{-9} mole/l (0.35ppt to 350ppt) and 20 minutes for 10^{-9} to 10^{-7} mole/l (350ppt to 35ppb) were required. The electrode required extensive pretreatment and polishing as well. It is time consuming and complicated to use these electrodes in on-line monitoring units, which require quick analysis of samples. It is thus required to use an electrode, which requires minimum pretreatment and polishing, shorter deposition times and high mechanical strength. One such electrode is the Boron-Doped Diamond (BDD) electrode, which is used in this work.

Diamond is the strongest material on earth and makes an excellent electrode after being doped with boron. In recent years, boron-doped diamond (BDD) electrodes have attracted considerable attention for electro analytical detection of variety of analytes including trace metals [16, 17-18]. BDD electrodes are superior for such applications due

to their excellent properties such as chemical inertness, corrosion resistance, durability, good electrical conductivity, low background current and large potential window between oxygen and hydrogen evolution [19-20]. This thesis work describes the successful detection of mercury down to ppt levels using BDD electrodes and in shorter deposition times compared to any other electrode currently used for mercury detection. The unique properties of BDD electrodes make them the proper choice for on-line monitoring units in coal-fired power plants.

Several electrolytes have been used so far to study the pattern of mercury deposition on BDD electrodes. It was found necessary to add a known amount of gold solution to co-deposit with mercury to minimize the calomel formation in the chloride medium and to improve the reproducibility in nitrate and per-chloric acid medium. The gold thus co-deposited could be removed by holding the electrode at a positive potential of about 1V for 2 minutes after every experiment and using fresh gold solution for the next experiment. The lowest concentration detected so far in real samples using BDD is 5.3 ppt, which is far less than the EPA regulations. The deposition time ranges from 30 to 60 seconds for 2 to 30ppb, 60 to 120 seconds for 2ppb to 10ppt and it also depends on the morphology of the electrode and other experimental conditions. On average, it would take 7 minutes of run time for one experiment and 10 minutes on the whole for the analysis of a sample including the electrode-cleaning step, which is a reasonable time for an on-line monitoring unit.

Three types of BDD electrodes with different morphology and manufacturing procedure were used in this work. Both stationary and rotating electrode setups were tested and the later was found to be more reproducible and linear. Differential Pulse

Anodic Stripping Voltammetry (DPASV) was used for the analysis. Calibration plots were made with standard concentrations of mercury in different electrolytes in both ppb and ppt range and a discussion of the results is presented. A hand held portable potentiostat 'PalmSens' was tested for use in on-line monitoring units. Real samples obtained from coal fired power plants and some water and fish samples were analyzed using standard additions method and the results were compared with Cold-Vapor Atomic Absorption Spectrometry (CV-AAS) analysis performed in two Analytical Labs. The effect of other metals such as copper and manganese on the detection of mercury was also investigated. Details of these results and their discussion are presented in the following chapters.

2. BACKGROUND

2.1. Overview

This chapter gives a background on BDD electrodes and electrochemical detection of mercury using these electrodes, including the various pulsing techniques and analysis of unknown samples using the standard addition method. Also given are the potential applications of BDD electrodes in analysis of other trace metals and then the advantages over other electrodes.

2.2. Boron-Doped Diamond (BDD) electrodes

2.2.1. General Aspects

Pure, undoped diamond is a good insulator (resistivities in the range of 10^{10} to 10^{12} Ω cm) [21] with a large band gap (5.4 eV). Therefore it is not immediately usable as an electrode material in electrochemistry. Diamond is a cubic lattice structurally, constructed from sp^3 -hybridized rings with each carbon atom bonded to four neighbours. The stacking sequence is ABCABC with every third plane identical. The electrical properties of diamond electrode can be varied by different doping processes, making them an attractive choice for several applications.

It has long been recognized that boron doping of diamond single crystals, either natural or synthetic, [21] leads to semiconducting behaviour. The boron dopant atoms form a band located ~ 0.35 eV above the valence band edge. At room temperature, some of the valence band electrons are thermally promoted to the boron acceptors, leaving free electrons in the dopant band and holes in the valence band to support the flow of current.

BDD thin films possess a rough, polycrystalline morphology with grain boundaries at the surface and a small-volume fraction of nondiamond carbon impurity. The electrical conductivity of the film surface and the bulk is consequently influenced by the boron-doping level, the grain boundaries and the impurities [22]. If the doping level is increased, the acceptor level widens to form a band, which can eventually approach within a few meV from the conduction band, at which point the material becomes metallic [23]. Boron acts as an electron acceptor due to an electron deficiency in its outer shell giving p-type semiconducting properties to diamond. Based on the pioneering work of Angus and coworkers [24], it became possible to produce electrically conductive boron-doped diamond films by use of the chemical vapour deposition (CVD) technique, providing conductivity sufficient for electrochemical and sensor applications.

Ramesham et al [25] have reported that the resistivity of CVD polycrystalline diamond thin films can be decreased to ca. $10 \Omega \text{ cm}$ after boron-doping. Okano et al [26] [27] have reported that the resistivity of CVD thin films can be reduced to ca. $0.01 \Omega \text{ cm}$ after boron doping at a B/C ratio of ca. 1000 ppm. The electrical and magnetic properties of the BDD films used in this work are described in a recent paper by Manivannan et al [28] which shows room temperature resistivity $\sim 0.007 \Omega \text{ cm}$. Boron doping of sp^2 hybridized carbon materials has also been shown to produce more oxidation resistant materials [29-31].

2.2.2. Electrochemical properties and applications

The use of diamond electrodes in electrochemistry was pioneered by Iwaki et al. [32]. Pleskov et al. [33, 34] have reported the photoelectrochemical properties of undoped polycrystalline diamond thin films. In work of Fujishima et al, the potential of diamond

in electrolytic processes was demonstrated [35-37]. However, Swain et al were the first to demonstrate the great potential of BDD electrodes in analytical electrochemistry [38] and showed that BDD provides number of advantages over carbon, glassy carbon, and metal electrodes. These advantages include: i) an order of magnitude lower background current density; ii) a large potential window (as much as 4 V in aqueous solution) which allows the resolution of many different species; iii) very low capacitance, which results in relatively small charging current, thus providing higher sensitivity; and iv) chemical inertness and stability without any pretreatment.

Swain et al [39] have described the various factors, which contribute to the low background and capacitance of the diamond electrodes. These include the relative absence of electroactive carbon-oxygen functionalities on the hydrogen-terminated diamond surfaces, lower density of surface electronic states near the Fermi level caused by the semimetal-semiconductor nature of BDD and the presence of more “electrochemically active” sites separated by more insulating regions.

BDD has a wide potential window for solvent-electrolyte electrolysis in conventional aqueous media. In other words, a large overpotential exists for the evolution of chlorine [40, 41], oxygen and hydrogen [41, 19]. The working potential window (potentials at which the anodic and cathodic currents reach 50 A (250 A/cm^2)) is 3.5 V for diamond and 2.5 V for glassy carbon [39]. Figure 2.1 shows the working potential window for different electrodes. A possible explanation is the absence of requisite surface sites needed for the adsorption of reaction intermediates on diamond [42, 43].

Figure 2.1: Working potential windows

Working potential windows for different electrodes in the electrolyte 0.5M H₂SO₄, at a scan rate of 200mV/sec. [3]

The above-mentioned features of BDD electrodes make them very suitable for use in electrochemical trace metal analysis. A particularly attractive feature of these electrodes is the avoidance of use of mercury for metal analysis. Generally, for practical applications, the electrode should be robust enough to withstand high voltage pulse amplitude and faster potential sweep rates, detection limits below 10⁻¹⁰ M should be achievable, the technique should be adaptable for the rapid quantification of trace metals at distributed and/or remote locations, provide reproducible results and linear stripping peaks and should be less prone to interference such as those due to adsorption. BDD electrodes satisfy these conditions as well making them the best choice for trace metal analysis.

2.2.3. Advantages of BDD electrodes

The BDD electrodes have the following advantages: Hardness, low coefficient of friction; Unmatched mechanical strength; Durability and electrical conductivity; Chemical inertness, low background currents and wide potential window; Low capacitance; Stable against various pulsing conditions (for pulsed electrochemical detection); Breakdown Voltage >200 V; Highly sensitive surface; No need for mechanical grinding and polishing, chemical or electrochemical pretreatment.

2.2.4. Previous work using BDD

Several experiments for bulk deposition and trace metal analysis of different metals have been conducted on BDD electrodes. This section focuses on the work done so far on trace metal analysis using these electrodes.

2.2.4.1. Trace metal Deposition

Mercury-free detection of lead at levels upto 1ppb has been demonstrated at a bare diamond electrode [44-18]. In their initial studies, simple Cyclic Voltammetry (CV) at the diamond electrode was measured for relatively high lead concentrations. This work concluded that, under certain circumstances, specifically at high metal concentrations in solution, it is difficult to use anodic stripping technique for quantification of metals at diamond electrodes. These results indicated that Pb was not completely stripped from the electrode during a single anodic scan, which was in agreement with results reported by others [46, 47]. All have reported an excess charge for the cathodic deposition compared to the anodic oxidation.

Although this phenomenon has not yet been completely explained, one likely explanation is that the deposited particles may only be weakly attached to the hydrophobic, hydrogen terminated surface [48] or only well attached at specific nucleation sites [49, 50].

Figure 2.2: Model of Metal deposition on Diamond

Model explaining the observed behavior for metal deposition on diamond. [51]

The model shown in figure 2.2 explains that if the particles are too large to be visible by scanning electron microscopy (i.e., $>0.1 \mu\text{m}$), they are too large to be completely oxidized during the positive voltammetric sweep. However at relatively low lead concentrations, i.e., those of most interest for public health, Manivannan et al [51] have shown that it is possible to deposit and quantitatively strip small amounts of lead, demonstrating the feasibility of trace analysis.

An SEM image (Fig. 2.3) shows the morphology of the metallic lead that deposits on the diamond surface when the solution concentration is relatively high. Lead was deposited for 2 minutes (Fig. 2.3c) and 10 minutes (Fig. 2.3d) at -0.7 V vs. SCE. It is clear that metal islands deposit on the BDD crystal planes as well as on the grain boundaries. It should be noted here that these metallic deposits are of the type that cannot be quantitatively stripped [51].

Figure 2.3: SEM images of BDD electrodes

(a, b) SEM images of bare BDD; (c) electrochemical nucleation of lead metal is observed; (d) lead deposited electrochemically all over the diamond facets. [51]

In anodic stripping voltammetry, it is a requirement that the deposited metal be completely removed from the electrode surface. An experiment was done in the lab to

study the behaviour of stripping of lead when in small concentrations in the solution using Differential Pulse Voltammetry. Figure 2.4 shows the stripping of lead, the first scan being performed after the deposition of lead, and the second scan immediately following the second scan. It is clear that the lead deposited on the BDD surface has been completely removed.

Figure 2.4: DPV of lead on a BDD surface

DPV scans of 1.5×10^{-6} M lead on BDD (a) after 3 minutes of deposition at -1.0 V vs. SCE, (b) without deposition.

2.2.4.2. Trace Metal analysis

2.2.4.2.1. Single metal Analysis

2.2.4.2.1.1. Lead

Trace analysis of lead on BDD electrodes has been reported by Manivannan et al [18].

DPASV technique was used under different measurement conditions. The sweep rate and

deposition time were varied. The experiment was carried out with 2min deposition time at -1.0 V vs. SCE, for Pb concentrations from 4×10^{-7} to 2×10^{-6} M in 0.1 M KCl (pH 1), with a sweep rate of 20 mV s^{-1} . A much lower concentration of 4×10^{-9} M was detected using a higher deposition time of 15 minutes and a sweep rate of 200 mVs^{-1} . Both the conditions were found to be equally sensitive. However, it was found that it was difficult to strip all of the metal deposited on the BDD surface as the sweep rate was increased. A detection limit of 400ppt was obtained using LSV for lead [52]. This is sufficiently sensitive for public health applications, considering that the maximum allowable concentration in drinking water is 50ppb. Figure 2.5 describes the stripping of Lead on a diamond surface.

Figure 2.5: Stripping of lead from Diamond surface [52]

Ramesham et al have carried out analyses in the range of mM concentrations of lead, copper, cadmium and silver using differential pulse voltammetry [53]. Various other groups [54-56], have examined the deposition of metals at diamond electrode surfaces for electrocatalysis applications.

2.2.4.2.2. Several Metal Analysis

Real world samples usually contain several trace metals, all of which can be detected using anodic stripping voltammetry. Manivannan et al [51] have demonstrated that individual stripping peaks can be observed during simultaneous multi-element detection analysis at a BDD electrode (Figure 2.6).

Figure 2.6: DPV of multiple metal stripping from BDD surface

Differential pulse anodic stripping voltammetry of a mixture of Zn, Cd, Pb and Cu ions (5×10^{-7} M) in 0.1 M KCl (pH 1) at a BDD electrode. [51]

Experiments have been performed to try to understand the interactions between Pb and Cd during anodic stripping voltammetric analysis. It was found the stripping peak of Cadmium in the presence of Lead was 55% less than what was obtained in pure Cd^{2+} solutions. The decrease in the peak currents for Cd was explained on the basis of the proposed formation of an alloy of Pb and Cd. It has been demonstrated that by using 3D plots for Cadmium and Lead, good approximations can be obtained for both the concentrations [57].

Prado et al [58] have reported the simultaneous detection of lead and copper in aqueous solution using anodic stripping voltammetry (ASV) at BDD electrode. Voltammetry and AFM imaging were used to show that, while both metals nucleate as their pure phases on BDD, the copper nuclei, which form more easily than those of lead, act as favorable sites for the subsequent nucleation and growth of lead; the latter acts to inhibit hydrogen evolution on the copper surface. ASV at BDD electrodes provides the basis for a method of independent detection of Cu and Pb via conventional standard addition procedures [59, 60].

Manivannan et al [52] have used lower concentrations of lead (down to ca. 10 nM lead) in the presence of various concentrations of copper (0 to 100 nM). Contrary to the results of Prado et al., [58] they observed no evidence for hydrogen evolution catalyzed by copper deposits and thus no evidence for the inhibition thereof with the subsequent deposition of lead. This discrepancy was explained to be most likely due to the lower metal concentrations used. They have also demonstrated that, even though lead-copper alloy does indeed form during electrodeposition, it does so predominantly at higher pH, and the mutual interference can largely be avoided by adjusting the pH to low values (pH 1-3). They have also experimented with the use of so-called masking agents, which are designed to form complexes selectively with copper, so that the electrodeposition of the latter is impeded. This strategy was found to be promising, with the most effective masking agent being a water-soluble, metal-free porphyrin, which can indeed form a complex with copper much more easily than with lead [52].

2.3. Trace detection of mercury

Current methods for trace detection of mercury include cold-vapor atomic fluorescence spectrometry (CV-AFS) [4], cold-vapor atomic absorption spectrometry (CV-AAS) [5], and inductively coupled plasma-mass spectrometry (ICP-MS) [6]. These methods are not suitable for onsite monitoring considering the requirement of extensive sample preparation and longer times for analysis. Electrochemical detection techniques are thus of major interest and is discussed in detail in this section.

2.3.1. Electrochemical Detection of Mercury

Electrochemical stripping analysis is an attractive, powerful tool for detecting trace metals due to its simplicity and sensitivity in the simultaneous measurement of multiple elements at detection levels from ppb to ppt. In addition, the added features of portability, low power requirement, and the suitability for automatic on-line monitoring emphasize its great power for rapid, inexpensive analysis of trace metals in applications such as field-testing. Higher detection limits are obtained as the metal is deposited directly on the electrode. The electrodes used so far for the electrochemical detection of mercury include gold, glassy carbon and other modified carbon electrodes and iridium electrodes. This section discusses briefly the work done using gold and glassy carbon electrodes for the detection of mercury.

2.3.1.1. Gold Electrode

Given the high affinity of mercury towards gold, Gold electrodes are widely used for the detection of mercury. Different types of gold electrodes have been used. Solid gold

electrodes [61, 8] are less commonly used than fibre gold [62] and plated gold electrodes [63-65].

The detection limits obtained using gold electrodes are as follows: Andrews et al [66] obtained a detection limit of 0.02ppt for Hg(II) by anodic differential pulse stripping voltammetry on a rotating gold disc electrode (the method was not applicable to real samples). Sipos et al [67] applied the same technique for simultaneous determination of mercury and copper in natural water and wine. They used a twin gold electrode for the determination of Hg(II) below 100ppt. Huiliang et al [68-70] have determined mercury and other elements in a flow system with potentiometric stripping on a gold fibre working electrode, with a detection limit of 45ppt (10 min deposition time). This method was proved to be useful in tap water [68] and certified urine standard [69]. Other methods include adsorption of volatilised mercury metal on a gold disc and subsequent voltammetric stripping in thiocyanate solution [71], with a detection limit of 30ppt. A study using alternating current anodic stripping voltammetry on a rotating gold disc electrode has been reported [72, 73]. Recently, Bonfil et al [74] reported a detection limit of 0.171 ppt (120 sec deposition time) on a rotating gold disk electrode. 10mM HNO₃, 10mM NaCl was used as the electrolyte and the method has been successfully applied for the determination of mercury in urine.

The major disadvantages of solid gold electrodes are the structural changes of the gold surface that take place due to amalgam formation with mercury and the time consuming and complex electrochemical pretreatment required to achieve reproducibility [64]. Gold electrodes usually have a higher background current when compared to other electrodes. This would result in broad peaks during stripping hindering the analysis of the

analyte. Bonfil et al [74] suggested Subtractive Anodic Stripping Voltammetry (SASV) to reduce the background current, thereby enhancing the mercury-stripping peak.

2.3.1.2. Glassy Carbon Electrode

Glassy carbon, because of its hardness (Shore hardness of 100), good electrical conductivity, high hydrogen over-potential and chemical inertness, has found a considerable use in electrochemistry. It is a recently developed electrode material [75, 76]. Gunasingham et al [77] have done extensive work based on the deposition of metallic mercury on a glassy carbon surface. Allen and Johnson investigated the use of bare glassy carbon electrode and noted that deposition of mercury from very dilute solutions occurs only when a second metal cation, which can co-deposit with Hg, such as Cu or Au, is present in the solution [78]. Glassy carbon is usually modified by coating with gold, crown ether and other metals, which aid in deposition of mercury. The USEPA method 7472 for Hg(II) determination involves electrochemical deposition of a thin gold film on a glassy carbon electrode. This method lengthens the analysis time and significantly increases the cost of analysis.

Turyan and Mandler have reported selective determination of levels $<10^{-12}$ M of mercury using a glassy carbon electrode spin-coated with 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Kryptofix-222). The deposition time was 5 minutes in this case [10]. The lowest detection limit reported on a glassy carbon electrode is 5×10^{-14} mol l⁻¹ (0.017ppt) using thiocyanate as the supporting electrolyte [8]. The deposition time in this case was 40 minutes for concentrations 5×10^{-14} to 10^{-12} mol l⁻¹ (0.017ppt to 0.35ppt); 30 minutes for 10^{-12} to 10^{-9} mol l⁻¹ (0.35ppt to 350ppt) and 20 minutes for 10^{-9} to

$10^{-7} \text{ mol l}^{-1}$ (350ppt to 35ppb). This method was useful for determining mercury levels in drinking water.

2.4. Pulsing Techniques

The electrode is maintained at a potential at which the metal is expected to deposit. The potential is then positively swept to oxidatively dissolve the deposited metal. In the simplest implementation of this technique, the potential sweep is an unadorned potential ramp. In many cases, however, one or another type of pulse program is used. The pulse variables include the nature of the excitation waveform (pulse, differential pulse, square wave) and its amplitude, and the current sampling regime. These variables determine the specific voltammetric method, e.g., differential pulse stripping voltammetry (DPSV), and Osteryoung square-wave stripping voltammetry (OSWSV). A comparison of the various electroanalytical techniques (figure 2.7) shows that stripping voltammetry is usually several orders of magnitude more sensitive for trace metal analysis than the others [79].

Figure 2.7: Comparison of Pulsing techniques

Comparison of different pulsing techniques employed for trace metal detection with respect to their achievable detection limits. [79]

2.4.1. Anodic Stripping Voltammetry

Anodic stripping voltammetry is the most popular stripping technique used for trace metal detection. In the anodic stripping voltammetry (ASV) of metals in aqueous solution, the metal ionic species are first deposited (reduced) electrolytically onto an inert electrode at a constant applied potential. For Mercury, this potential is about -200mV to -100mV.

Figure 2.8: Schematic representation of deposition and stripping of Cd, Pb and Cu

As a specific example, Fig 2.8 shows schematically what happens when Pb^{2+} , Cd^{2+} , Cu^{2+} are deposited from solution as Pb, Cd, and Cu. A potential ramp is then applied in the positive direction, which will cause the deposited metals to be stripped (oxidized) from the electrode at characteristic potentials, E_p . Rectangular voltage pulses with adjustable pulse height and width are usually super imposed on this voltage ramp. This allows the separation of the charging current from the Faradaic current component, which is proportional to the concentration of the analyte. Since E_p is different for

different species, simultaneous detection of several metallic species is possible. For mercury E_p is of the range 200-300mV depending on the supporting electrolyte. Clearly, for the technique to work properly, the species must adhere to the electrode surface and be in electrical contact with it. This section describes the stripping techniques currently employed for trace metal analysis in detail.

2.4.1.1. Linear Stripping Voltammetry (LSV)

This technique is similar to CV, but the electrode potential is held at a particular potential before scanning. Fig 2.9 shows a typical potential-time sequence used in linear scan anodic stripping experiment along with the resulting voltammogram.

Figure 2.9: Sequence of Linear Anodic Stripping Voltammetry

Potential-time sequence used in linear scan anodic stripping experiment along with the resulting voltammogram. [80]

square wave cycle, once at the end of the forward pulse and once at the end of the reverse pulse. Since the square-wave modulation amplitude is very large, the reverse pulses cause the reverse action of the product (of the forward pulse). The difference between the two measurements is plotted vs. the base staircase potential. Fig 2.11 shows a typical excitation signal for square wave stripping voltammetry.

Figure 2.11: Waveform for Square wave Voltammetry

Square-wave waveform showing the amplitude, E_{sw} ; step height, ΔE ; square-wave period, τ ; delay time, T_d ; and current measurement times, 1 and 2. [79]

2.5. Standard additions method

The Standard Addition Method is a useful calibration technique for analyzing unknown samples when the sample matrix affects the analyte signal. In most of the unknown samples, the matrix effects caused due to other possible elements in the sample are

unknown. Assuming a linear change in response for an increased concentration of an analyte, the response of the analyte is measured before and after several successive additions of the analyte to a sample of unknown analyte concentration. Plotting response (ordinate) by the amount of standard added (abscissa), the analyte concentration is found by fitting a line to the data and finding the intercept on the abscissa. Generally, two to three additions of standard are required to assure linearity. The linearity of the first two additions is the most important in determining the unknown concentration of the analyte. In applying the standard addition method, it is important to add small volume of concentrated standard to the sample solution in order to minimize volume change and thereby making volume corrections unnecessary [81].

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Overview

This chapter gives the details of the experimental setup and procedures. Also given are the results obtained in various electrolytic media using different types of BDD electrodes, the rotating disc electrode technique and the unknown samples. The results obtained using a portable PalmSens potentiostat in comparison to lab potentiostat are also given.

3.2. Experimental

3.2.1. Electrode and Instrumentation

Three types of BDD electrodes, Type A, B and C, were used in the experiments performed so far (Fig 3.1). Type A electrodes were made at the University of Tokyo with methanol/acetone mixture as the carbon source. Type B was a free standing film purchased from Harris International Inc. Type C BDD films on silicon were synthesized at the Naval Research Laboratory. The microcrystallites in these polycrystalline films were in the range of 5-10 μm .

Figure 3.1: (a) Type A, (b) Type B and (c) Type C electrodes

For the Rotating Disk Electrode (RDE) experiments, a 6mm diameter Type B electrode was used to mount on a Pine instrument rotator (Fig 3.2). A 2mm diameter Type B electrode was fixed on a stainless steel base and mounted on a rotating base rod made with peek material (fig 3.3) for use on a portable rotating disk electrode setup.

Figure 3.2: Rotating Disk electrode on a Pine Instrument rotator

Figure 3.3: Electrode used in a portable rotating disk electrode setup

3.2.1.1. Stationary Electrode Set-up

The experiments in the stationary electrode set-up were conducted in a specially designed three-electrode configuration ‘O’- ring type cell as shown in Figure 3.4. The working electrode (BDD) is at the bottom of the cell on top of a brass plate from which connections are made out to the potentiostat. An ‘O’ ring is present between the cell and the electrode to ensure a leak free system. Reference and counter electrodes are inserted

from the top end of the cell. A platinum wire was used as the counter electrode and a Saturated Calomel Electrode (SCE) was used as the reference electrode. The supporting electrolyte used was 0.2M acetate buffer (pH=5). The reference electrode was stored in a highly concentrated KCl solution when not in use. Disposable pipettes were used for eliminating air bubbles in the surface and for proper mixing of the solution. Nitrogen gas was also used in certain cases for mixing.

Figure 3.4: Stationary electrode setup using ‘O’-ring type cell [23]

A Hokuto Denko potentiostat/galvanostat (Model HZ-3000) was used for potential control in most of the cases (fig 3.5.). A BAS-Epsilon, B-100W Potentiostat was also used. The potentiostat is connected to a personal computer.

Figure 3.5: Hokuto Denko potentiostat/galvanostat (Model HZ-3000)

3.2.1.2. Rotating Disk Electrode Set-up

Figure 3.6: Rotating Disk Electrode set-up

In case of rotating disk experiments, the working electrode was mounted on a rotator (Pine instruments), the speed of which can be varied over a range of 0-5000 RPM using a

speed controller (MSRX, Pine instruments). The working electrode was then mounted on a disk shaft connected to the rotator (fig 3.6.). Connections to the potentiostat (HZ-3000) were drawn from the rotator. A simple 100mL glass beaker was used as a cell in this case. The reference and counter electrodes were inserted using stands.

3.2.1.3. Portable Rotating Disk Electrode Set-up

In the Portable Rotating Disk Electrode Set-up, a portable rotator/speed controller unit was connected to a portable potentiostat ‘PalmSens’, the later was controlled by a pocket pc. A typical setup of a portable unit is given in (fig 3.7)

Figure 3.7: A Portable Rotating Disk Electrode set-up

3.2.2. Reagents and Samples

All supporting electrolytes and standard solutions were of analytical reagent grade. De-ionized water from Labchem Inc., was used throughout this work for rinsing and solution preparing purposes. Mercury and Gold solutions were prepared by diluting 1000mg/l (in 10% nitric acid) standard stock solutions manufactured by SPEX Industries Inc., The samples obtained from coal-fired power plants were prepared by the method invented by Mendelsohn, et al (United States Patent: 5,900,042).

3.2.3. Procedure

In case of the stationary working electrode setup, the working electrode (1.5x1.5cm) was carefully placed on top of a polished brass plate and the cell was mounted on top of the electrode with the use of mounting screws until it was tight enough. An 'O'-ring was placed between the cell and the electrode. The counter and reference electrodes were inserted from the side ends of the cell. The set up is shown in figure 3.4. The cell was rinsed with de-ionized water before use. 10 mL of working electrolyte was then added from the top aperture of the cell. The solution was mixed using a disposable pipette going all the way down to the electrode surface to ensure the absence of air bubbles. Connections were made out to the potentiostat.

In the case of the rotating disk electrode (RDE), a special Type B BDD electrode of 6mm diameter was attached to a stainless steel disk, which can be attached to a rotating disk electrode rotator by Pine instruments. A 100mL glass beaker was used as the cell. The reference and counter electrodes were inserted using stands. The electrode

was rotated at the required speed during deposition and was held stationary during the stripping phase.

The potentiostat was controlled using a computer. The pulsing technique was chosen from the given menu. In most of the cases, Differential Pulse Voltammetry (DPV) was used. The initial and final potential, scan rate, deposition time and the pulsing parameters were set and the experiment was run. During the end of the run, the software plots the graph between the obtained differential current and the respective potential. The same procedure was repeated for additions of known amounts of mercury to the electrolyte and the working conditions were kept constant for different runs of the same experiment. The individual graphs were then plotted together and formatted using Origin 6.0 software (Microcal, MA, USA) for analysis.

3.2.4. Standard additions method

For analyzing unknown samples, the standard addition method was used. The first run was conducted with 10mL of the sample and a known amount of gold solution. The successive runs were performed with known additions of mercury. The base to peak current of the scans was plotted against the concentration of Hg, with the sample assumed to have zero mercury concentration. These plots were made from ppt to ppb range for each of the samples and the most linear plot was selected for calculating the concentration of the unknown sample. Linearity in the increase in peak currents indicates the correct concentration range of the sample. For example, if the original unknown concentration of mercury present in the solution is in the range of 2-4ppb, if ppt range of mercury is added to the solution, the peak current does not change as the amount of mercury added is too small compared to that present in the sample. On the other hand if

the unknown concentration present in the sample is of the range of 200 to 600 ppt, then ppb additions of mercury would result in a sudden rise in the peak current on the first addition after which the plot is linear indicating the presence of too little mercury. Thus selecting a correct working range is of utmost importance. The plot is then extrapolated to the negative axis to obtain the actual concentration of the sample.

3.2.5. Electrode Cleaning

After the end of each experiment, the setup was washed with de-ionized water and then a blank run was conducted. If necessary, the electrode was cleaned using few drops of aqua regia (1part of conc.HNO₃ : 3 parts of conc.HCl) to dissolve the gold alloy and other residues present on the surface. Alternatively, the electrode was conditioned by holding at 1 volt for 2 minutes in a slightly acidified fresh electrolyte. In the case of analyzing the unknown samples, it was found that more conditioning time was required, ranging from 2 to 10 minutes, the ideal being 5 minutes, at 1 volt in most of the cases. Most of the samples obtained from the coal power plants were found to have copper. Copper forms an alloy with gold and mercury and the stripping of this alloy to give a fresh surface would require more conditioning.

3.3. Results

3.3.1. Calibration Plots

3.3.1.1. Nitrate Medium

Figure 3.8: DPV of Mercury in Nitrate medium

(A) DPV scans for mercury in 0.1M KNO₃ (pH=1), (a) 4ppb Hg (b) 6ppb Hg (c) 10ppb Hg (d) 14ppb Hg (e) 22ppb Hg. Other conditions were: deposition time = 30 sec, deposition potential = -0.1V vs. SCE, scan rate = 50mV/sec, (B) Calibration plot based on the 0.55V peak.

An experiment with 0.1M KNO₃ as electrolyte was conducted for mercury additions of 2 – 30 ppb. 3ppm of gold solution was added to the electrolyte. The DPV scans are shown in Figure 3.8. A Type A electrode was used. Two stripping peaks at 0.24V and 0.55V were observed. The peak at 0.55V was dominant indicating that most of the mercury present was stripped as Hg²⁺. The peak at 0.24V is believed to result from free mercury on the surface that is due to one electron stripping of Hg⁰ to Hg⁺ state. This is explained later in detail. The presence of gold limits the possibility of mercury stripping in its +1 state thereby reducing calomel formation due to little amounts of

chloride present in the solution. A calibration plot based on the 0.55V peak in fig 3.8(A) is shown in Figure 3.8(B).

3.3.1.2 Thiocyanate Medium

Thiocyanate is a good complexing agent that can overcome the effect of chloride and form a complex with mercury. Work has been done using this electrolyte on electrodes like glassy carbon [8]. The only disadvantage is the requirement of higher deposition times (even up to 10 mins) for lower mercury concentrations (less than 2 ppb), which is the main range of interest. It was not necessary to add gold solution. A type B electrode was used and the DPV scans for 50 to 250 ppb of Hg in 0.1M KSCN are shown in Figure 3.9.

Figure 3.9: DPV of Mercury in Thiocyanate medium

(A) DPV scans for Hg^{2+} in a range 50ppb to 250ppb in 1M KSCN (pH=3), (a) Blank 1M KSCN (b) + 50ppb Hg, (c) + 100ppb Hg, (d) + 150ppb Hg, (e) + 200ppb Hg, (f) + 250ppb Hg. Deposition time = 360 sec, Deposition potential = -0.5V vs. SCE, Scan rate = 50mV/sec. Type B stationary electrode. (B) Calibration plot based on the 0.25V peak.

The deposition potential and time are -0.5V and 360secs respectively. Square wave anodic stripping voltammetry was tried using BAS-100W potentiostat. The results were almost the same. One experiment in the range of 10 to 50 ppb with a deposition time of 9 minutes was conducted but the scans were not linear. A rotating disk electrode was tried in the range 2 to 10 ppb for a deposition time of 2 minutes and the results are shown in Figure 3.10. In this case linearity was a problem. The peak suddenly rose after 6 ppb. It can be noted that when using rotating disk electrodes, noticeable stripping peaks could be obtained for concentrations above 4 ppb even with low deposition time like 2 minutes.

Figure 3.10: DPV of Mercury in Thiocyanate medium (RDE)

DPV scans for Hg^{2+} in the range of 2 to 10 ppb in 1M KSCN (pH=3), using RDE. (a) 1M KSCN + 2ppb Hg (b) + 4ppb Hg, (c) + 6ppb Hg, (d) + 8ppb Hg, (e) + 10ppb Hg. Other conditions include: Speed = 2500 RPM, Deposition time = 120 sec, Deposition potential = -0.5V vs. SCE, Scan rate = 50mV/sec.

3.3.1.3. Perchloric acid Medium

A number of experiments were conducted both in ppb and ppt ranges using perchloric acid (HClO_4) on BDD electrodes. 3ppm of Gold solution was added to the electrolyte.

Both 6mm and 2mm BDD electrodes were tried. Figures 3.11 and 3.12 show the ppb and ppt range calibration plots obtained for additions of mercury in 0.1M HClO₄ on a BDD electrode.

Two peaks, at 0.2V (peak 1) and 0.55V (peak 2), were observed. Peak 2 increased linearly with mercury additions and is clearly shown in fig 3.11(B). The results were highly reproducible when the experiment was repeated later. The peak 1 has been established to be a characteristic of gold in the HClO₄ medium in Reference [82]. During the first run (supporting electrolyte + gold) the peak 1 is observed. As there was no mercury in this case, the peak 1 is attributed to the background due to gold addition.

Figure 3.11: DPV of Mercury in Perchloric acid medium (1)

(A) DPV scans for Hg²⁺ in a range 2ppb to 12ppb in 0.1M HClO₄ (pH=1) using RDE, (a) 0.1M HClO₄ + 3ppm gold, (b) 2ppb Hg, (c) 4ppb Hg, (d) 6ppb Hg, (e) 8ppb Hg, (f) 10ppb Hg, (g) 12ppb Hg. Deposition time = 60 sec, Deposition potential = -0.1V vs. SCE, scan rate = 50mV/sec, speed = 2500rpm. Calibration plot obtained from the peak heights of 0.55V peak is shown in figure 3.11(B).

On comparing the ppb and ppt range experiments, both cases show 2 peaks but peak 1 is stronger in ppt range than in ppb. This may be due to the higher deposition times in the ppt range of experiments. In both cases, the background increases in every

run. However, since only the base to peak height is considered, the change in background does not affect the calibration. Figure 3.12(B) shows the calibration plot for 200ppt to 5000ppt of Hg additions. It is noted that the plot is linear even over the wide range of calibration.

Figure 3.12: DPV of Mercury in Perchloric acid medium (2)

(A) DPV scans for Hg^{2+} in a range 200ppt to 5ppb in 0.1M HClO_4 (pH=1) with 3ppm gold added. (a) 200ppt Hg (b) 600ppt Hg, (c) 1ppb Hg, (d) 3ppb Hg, (e) 5ppb Hg. Other Conditions were: deposition time = 120 sec, deposition potential = -0.1V vs. SCE, scan rate = 50mV/sec, speed = 2500rpm, Type B rotating disk electrode. (B) Calibration plot obtained for the peak heights of 0.55V peak.

Figure 3.13: DPV of Mercury in Perchloric acid medium (3)

(A) DPV scans for Hg^{2+} in a range 4ppb to 14ppb in 0.1M HClO_4 (pH=1) with 3ppm Au added. (a) 4ppb Hg (b) 6ppb Hg, (c) 8ppb Hg, (d) 10ppb Hg, (e) 12ppb Hg, (e) 14ppb Hg. Other conditions were: deposition time = 120 sec, deposition potential = -0.1V vs. SCE, scan rate = 50mV/sec , speed = 2500rpm , type B 2mm diameter rotating disk electrode. (B) Calibration plot obtained for the peak heights of the 0.55V peak.

Figure 3.14: DPV of Mercury in Perchloric acid medium (4)

(A) DPV scans for Hg^{2+} in a range 200ppt to 800ppt in 0.1M HClO_4 (pH=1) with 3ppm Au added. (a) 200ppt Hg (b) 400ppt Hg, (c) 600ppt Hg, (d) 800ppt Hg. Other conditions were: deposition time = 150 sec, deposition potential = -0.1V vs. SCE, scan rate = 50mV/sec , speed = 2500rpm , type B 2mm diameter rotating disk electrode. (B) Calibration plot obtained for the peak heights of the 0.55V peak.

A 2mm BDD electrode was also used and calibration plots were obtained for ppb and ppt ranges (Figs 3.13 & 3.14 respectively) in 0.1M HClO₄. The results were similar to those in a 6mm BDD electrode. However, higher deposition times were required in case of 2mm electrode. All the experiments in HClO₄ medium show an increased background in each run.

3.3.1.4. Chloride Medium

For practical applications, it is important to be able to detect mercury in chloride media since most practical samples contain some chloride. Gold solution was added in all the experiments to limit the formation of calomel. Initially, the experiments were carried out using the stationary electrode setup and later the rotating disc electrode was also used to improve the method. This section gives a description of experiments carried out in chloride media.

3.3.1.4.1. Stationary electrode set up

Type A, B & C electrodes were tried in this set up. The experimental details are similar to those described earlier.

Figure 3.15 shows the DPV scans obtained using Type A electrode with 1M KCl and 3ppm Au added to the solution. Figure 3.16 shows the DPV scans obtained on a Type B electrode with 1M KCl and 3ppm Au added to the solution.

Type C electrodes were also tested. Two kinds of these electrodes, one with oxygen and the other without oxygen during preparation were tested. The results obtained were similar except for minor differences and DPV scans obtained using 1M KCl with 3ppm gold addition is shown in figs 3.17 & 3.18. It should be noted that the behavior of

this electrode is similar to that of the type B electrodes, except that the relative heights of the two peaks are somewhat different.

Figure 3.15: DPV of Mercury in Chloride medium (Type A electrode)

DPV scans for Hg^{2+} in a range 2ppb to 30ppb in 1M KCl (pH=1) with 3ppm Au added. (a) 4ppb Hg, (b) 6ppb Hg, (c) 8ppb Hg, (d) 10ppb Hg, (e) 12ppb Hg, (f) 14ppb Hg. Other conditions were: deposition time = 30 sec, deposition potential = -0.1V vs. SCE, scan rate = 50mV/sec , type A electrode.

Figure 3.16: DPV of Mercury in Chloride medium (Type B electrode)

DPV scans for Hg^{2+} in a range 2ppb to 30ppb in 1M KCl (pH=1), 3ppm Au added. (a) 2ppb Hg, (b) 6ppb Hg, (c) 10ppb Hg, (d) 14ppb Hg, (e) 22ppb Hg, (f) 30ppb Hg. Deposition time = 30 sec, Deposition potential = -0.1V vs. SCE, scan rate = 50mV/sec . Type B electrode.

Figure 3.17: DPV of Mercury in Chloride medium (Type C electrode (1))

DPV scans for Hg^{2+} in a range 2ppb to 22ppb in 1M KCl (pH=1) with 3ppm Au added. . (a) 2ppb Hg, (b) 6ppb Hg, (c) 10ppb Hg, (d) 14ppb Hg, (e) 22ppb Hg. Other conditions were: deposition time = 30 sec, deposition potential = -0.1V vs. SCE, scan rate = 50mV/sec, type C electrode without oxygen.

Figure 3.18: DPV of Mercury in Chloride medium (Type C electrode (2))

DPV scans for Hg^{2+} in a range of 2 to 22ppb in 1M KCl (pH=1) with 3ppm Au added. (a) 2ppb Hg, (b) 6ppb Hg, (c) 10ppb Hg, (d) 14ppb Hg, (e) 22ppb Hg. Other conditions were: deposition time = 30sec, deposition potential = -0.1V vs. SCE, scan rate = 50mV/sec, type C electrode with oxygen.

3.3.1.4.2. Rotating Disc Electrode (RDE)

Type B electrodes were used for RDE studies. Both 6mm and 2mm diameter electrodes were tried. This section describes all the ppb and ppt range experiments done using these electrodes.

The following experiments were performed using a 6mm diameter electrode. Figure 3.19 show the DPV scans obtained using 1M KCl as the electrolyte with 3ppm of gold addition and with variation of speed from 1000 to 2500 RPM. It is noted that only one peak is observed in chloride media in the case of a rotating disc electrode in contrast to two peaks observed using the stationary electrodes. This shows that the free mercury stripping is reduced with rotation of the electrode or the uniformity of gold coating is improved with rotation and so does the mercury-gold alloy resulting in most of the mercury in the solution being stripped in the Hg^{2+} form. However the peak currents for different concentrations appear to saturate after 1500 rpm as can be seen from Figure 3.19. Figures 3.19 (A, B, C & D) are consecutive experiments on the same electrode with different rotation speeds, viz. 1000, 1500, 2000 and 2500 rpm respectively. Thus rotating disc electrodes are more convenient than stationary electrodes, as it is easier to deal with single peaks than two peaks when it comes to calibration plots.

Figures 3.19: DPV of Mercury in Chloride medium (RDE)

DPV scans for Hg^{2+} in 1M KCl (pH=1) with 3ppm Au added. (a) 2ppb Hg, (b) 6ppb Hg, (c) 10ppb Hg, (d) 14ppb Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.2V vs. SCE, scan rate = 50mV/sec, type B rotating disc electrode.

Figure 3.20: DPV of 5ppb of Mercury in Chloride medium in RDE with different speeds

DPV scans for different speeds from 500 to 2500 rpm for Hg^{2+} of concentration 5 ppb Hg in 1M KCl (pH=1) with 3ppm Au added: (a) 500rpm, (b) 1000rpm, (c) 1500rpm, (d) 2000rpm, (e) 2500rpm. Other conditions were: deposition time = 30 sec, deposition potential = -0.2V vs. SCE, scan rate = 50mV/sec, type B RDE.

It was also observed that the peak currents increase with speed until a specific speed (1500rpm) and remains almost constant for higher speeds. Figures 3.20 and 3.21 shows the DPV scans for 1M KCl electrolyte with 3ppm gold addition containing 5ppb and 20ppb of mercury respectively. The speed was increased from 500 to 2500 RPM and a linear increase in peak currents with speed was observed.

Figure 3.21: DPV of 20ppb of Mercury in Chloride medium in RDE with different speeds

DPV scans for different speeds from 500 to 2500 rpm for Hg^{2+} of concentration 20 ppb Hg in 1M KCl (pH=1) with 3ppm Au added: (a) 500rpm, (b) 1000rpm, (c) 1500rpm, (d) 2000rpm, (e) 2500rpm. Other conditions were: deposition time = 30 sec, deposition potential = -0.2V vs. SCE, scan rate = 50mV/sec, type B RDE.

Since most of the unknown samples were found to have less than 2ppb of Hg, experiments in ppt ranges were necessary. Experiments in different ranges like 10-100ppt, 100-900ppt, 50-500ppt, 200-800ppt, were performed. Figures 3.22 (A & B) show the respective DPV scans for 200-800ppt and 50-500ppt in 1M KCl with 3ppm gold addition. Good linearity was observed for 5 to 6 runs as shown and then they saturate (not shown). Real time applications require the testing of unknown samples using the standard additions method. In these cases 3 to 4 additions of standard mercury are enough to get a calibration plot. So the saturation observed above would not affect the detection of mercury in unknown samples.

Figure 3.22: DPV of ppt range of Mercury in Chloride medium using RDE

DPV scans for Hg²⁺ in 1M KCl (pH=1) with 3ppm Au added. A: (a) 100ppt Hg, (b) 200ppt Hg, (c) 300ppt Hg, (d) 400ppt Hg, (e) 500ppt Hg. B: (a) 50ppt Hg, (b) 100ppt Hg, (c) 150ppt Hg, (d) 200ppt Hg, (e) 250ppt Hg, (f) 350ppt Hg. Other conditions were: deposition time: (A) 60 sec, (B) 90 sec, deposition potential: (A) -0.2V, (B) -0.1V vs. SCE, scan rate: (A) 50mV/sec (B) 75mV/sec, speed= 2500 rpm, type B RDE.

In order to check the reproducibility of all these experiments, calibration plots were made for repeated measurements on the same electrode. Figure 3.23 shows the peak current versus Hg concentration measurements carried out for four consecutive measurements on the same electrode (6mm dia). The experimental conditions are as given in figure 3.19 and the RDE speed was 2000rpm. The calibration plot is linear for all the cases. However, the slopes are different indicating some surface modification of the electrode after each experiment.

Figure 3.23: Consecutive DPV calibration plots on a same electrode

Four consecutive DPV calibration plots for 2-14 ppb of mercury concentrations in 1M KCl (pH=4). 3ppm gold standard solution was added and deposition time = 60 sec with deposition potential = -0.1V vs. SCE, Type B electrode and rotation speed = 2000rpm.

Similar experiments in ppb and ppt range were conducted on a 2mm electrode. Figure 3.24 shows the DPV scans in 1MKCl for different rotation speeds. The peak currents remain almost constant for different speeds. However the peak currents obtained are much smaller when compared to those using the 6mm electrode. Figure 3.25 shows the DPV scans obtained for 10 to 50 ppt of Hg in 1M KCl using a 2mm diameter electrode. Good linearity with concentration was observed.

Figures 3.24: DPV of Mercury in Chloride medium using 2mm RDE

DPV scans for Hg^{2+} in 1M KCl (pH=1) with 3ppm Au added for different speeds (a) 2ppb Hg, (b) 4ppb Hg, (c) 6ppb Hg, (d) 8ppb Hg, (e) 10ppb Hg, (f) 12ppb Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.2V vs. SCE, scan rate = 50mV/sec, 2mm Type B RDE.

Figure 3.25: DPV of ppt range of Mercury in Chloride medium using 2mm RDE

DPV scans for 10ppt to 50ppt Hg^{2+} concentrations in 1M KCl (pH=1) with 1.5ppm gold standard solution added, (a) 10ppt, (b) 20ppt, (c) 30ppt, (d) 40ppt, (e) 50ppt. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, Type B rotating disc electrode and rotation speed = 2000rpm.

3.3.2. Portable Potentiostat

Both standard calibration curves in Chloride media and standard additions method for unknown samples were conducted using a portable potentiostat ‘PalmSens’. A typical calibration plot obtained in 1M KCl for Hg additions of 2 to 12 ppb is shown in Fig 3.26. Under similar conditions, an experiment using the lab potentiostat was performed and the results are shown in Fig 3.27 for comparison. This portable unit was tested mainly for use in online monitoring at power plant sites, where a reliable and compact unit is required for quick and easy testing of samples. Several samples were tested using this instrument and a comparison with the results obtained from the HZ-3000 potentiostat and their calibration plots are shown in Figures 3.28 and 3.29 respectively. The Palm sens detected a concentration of 123 ppt and the HZ-3000 detected a concentration of 183 ppt which is a fair agreement considering the very low concentration range of Hg in the sample.

Figure 3.26: DPV of Mercury in Chloride medium using portable potentiostat

(A) DPV scans for Hg^{2+} for concentrations: (a) 2ppb Hg, (b) 4ppb Hg, (c) 6ppb Hg, (d) 8ppb Hg, (e) 10ppb Hg, (f) 12ppb Hg in 1M KCl (pH=1) with 3ppm Au added and the other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 25mV/sec. Type B RDE with Portable Palm Sens unit and speed = 2500 rpm. (B) Calibration plot from part A.

Figure 3.27: DPV of Mercury in Chloride medium using lab potentiostat

(A) DPV scans for Hg^{2+} for concentrations: (a) 2ppb Hg, (b) 4ppb Hg, (c) 6ppb Hg, (d) 8ppb Hg, (e) 10ppb Hg, (f) 12ppb Hg in 1M KCl (pH=1) with 3ppm Au added. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 50mV/sec, speed = 2500rpm, rotating disc electrode. (B) Calibration plot from part A.

Figure 3.28: DPV for an unknown sample using portable potentiostat

(A) DPV scans and (B) Calibration plot for an unknown Sample with 200 to 800ppt standard additions of Mercury with 3ppm of gold solution added. (a) Sample with 3ppm of gold (b) + 200ppt of Hg, (c) + 400ppt of Hg, (d) + 600ppt of Hg, (e) + 800ppt of Hg. Other conditions: deposition time = 120 sec, deposition potential = -0.2V vs. SCE, scan rate = 25mV/sec, speed = 2500rpm. Unknown Concentration = 123ppt

Figure 3.29: DPV for an unknown sample using lab potentiostat

(A) DPV scans and (B) Calibration plot for an unknown Sample with 200 to 800ppt standard additions of Mercury with 3ppm of gold solution added. (a) Sample with 3ppm of gold (b) + 200ppt of Hg, (c) + 400ppt of Hg, (d) + 600ppt of Hg, (e) + 800ppt of Hg. Other conditions: deposition time = 120 sec, deposition potential = -0.2V vs. SCE, scan rate = 50mV/sec, speed = 2500rpm. Unknown Concentration = 183ppt

3.4. Discussion and Analysis

3.4.1 Mechanism of Hg stripping on BDD electrodes in the presence of gold

All the experiments done so far for the detection of mercury show two peaks. Experiments on different electrolytes were conducted to verify the presence of the two peaks. All the other media, except for the thiocyanate medium, show two peaks. To explain this behavior, experiments on a gold rotating disc electrode were also conducted and are explained later. This section describes the mechanism for stripping of mercury from the BDD electrode surface in the presence of gold, based on the results obtained so far.

A standard solution of mercury was prepared by diluting 1000ppm Hg(II) to 1ppm and was used for all the experiments. Mercury in the electrolyte is in its +2 state. When a cathodic potential is applied to the electrode, the mercury reduces to metallic state (Hg^0) by accepting 2 electrons from the electrode. The mercury to be detected is thus now on the electrode surface. During stripping, an anodic potential sweep from -100 to 700 mV is applied to the electrode and the mercury present in the surface oxidizes by releasing 2 electrons to the electrolyte thereby giving rise to a current, which is proportional to the amount of mercury stripped.

In the case of gold addition, the mercury that deposits on the surface could form an alloy with gold. As mercury strips from this alloy, it oxidizes in its +2 state. This is the ideal case. But due to other factors such as the amount of gold added, the uniformity of gold deposition, the amount of mercury present in the solution and the surface area of the

electrode, the entire amount of mercury present in the solution doesn't form an alloy with gold resulting in free mercury deposited on the electrode surface and on top of the gold-mercury alloy. This free mercury strips to its +1 oxidation state. Thus one can observe 2 peaks during the stripping phase. The following equations explain the deposition and stripping of mercury on the electrode surface.

In the presence of an anion such as chloride in the electrolyte media, the surface mercury which strips to its +1 oxidation state forms calomel with the chloride ions. This compound is insoluble in the electrolyte. Thus during further runs, this affects the stripping peak of mercury. In other words, due to calomel formation, all of the mercury present in the electrolyte is not available for detection. Thus addition of gold is essential to prevent or to at least limit the formation of calomel (Hg_2Cl_2).

Figure 3.30 shows the deposition and stripping of mercury on a BDD surface in the presence of gold on the application of a pulse. Mercury deposits along with gold at the potential of -100mV forming gold-mercury alloy on the surface together with free mercury. During stripping, the free mercury strips first at about 200mV in its +1 oxidation state and the mercury from gold-mercury alloy strips around 300 to 350mV. The stripping peaks were found to shift from their positions depending on the chloride concentration.

Figure 3.30: Stripping of Mercury from BDD surface

3.4.2. Comparison with Gold Electrode

Detection in chloride and other media on BDD electrodes involved the addition of gold solution. It was therefore critical to compare the behavior of gold electrode and BDD electrode with gold addition. A 6mm diameter gold electrode was used to mount on a pine rotator. Prior to mounting, the electrode was polished using 600 grit emery sheet and then with 5microns alumina powder and finally using 0.5microns alumina powder on a polishing cloth to get a mirror like finish. The electrode was then rinsed with deionized

water and immersed in an ultrasonic bath for few minutes and rinsed again with deionized water.

An experiment was conducted using 10mM NaCl and 10mM HNO₃ as the working electrolyte (Fig 3.31). As established earlier [74], two peaks were observed at 0.3V and 0.55V vs. SCE respectively. The peak at 0.3V was a broader peak and the peak at 0.55V increased linearly with mercury additions. Subtractive DPV was also performed to get a sharp peak at 0.55V. For this, a DPV with 0 sec deposition time was run before the original run and the results were subtracted before plotting.

Figure 3.31: DPV scans for 10mM NaCl + 10mM HNO₃ on a rotating gold disk electrode

(a) Blank 10mM NaCl + 10mM HNO₃ (b) + 2ppb of Hg, (c) + 4ppb of Hg, (d) + 6ppb of Hg, (e) + 8ppb of Hg, (f) + 10ppb of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.4V vs. SCE, scan rate = 50mV/sec, speed = 2500rpm.

Under similar conditions, an experiment using a BDD rotating disk electrode with the same electrolyte was conducted for comparison (fig 3.32). Two peaks, first at 0.25V and the second at 0.5V, were observed. The shift in peak positions when compared to those on gold electrodes may be due to the electrode surface and the addition of gold. The

first peak didn't increase linearly while the second peak showed a linear increase with mercury additions. The peak currents obtained were less than those in the gold electrode due to the properties of BDD. It should be noted that the 2nd peak was absent in both the cases during the first run (blk electrolyte and electrolyte + gold solution respectively) and on successive runs, in both the cases, peak2 started to increase linearly. Peak 1 on the gold electrode didn't show as much increase as is seen on the BDD electrode. This may be due to lesser amount of gold present in the case of BDD, thereby increasing the free mercury on the surface.

Figure 3.32: DPV scans for 10mM NaCl + 10mM HNO₃ on a rotating BDD electrode

DPV scans for 10mM NaCl + 10mM HNO₃ on a rotating BDD electrode with 3ppm of gold added. (a) Blank 10mM NaCl + 10mM HNO₃ (b) + 3ppm Au, (c) + 2ppb of Hg, (d) + 4ppb of Hg, (e) + 6ppb of Hg, (f) + 8ppb of Hg, (g) + 10ppb of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 50mV/sec, speed = 2500rpm.

To compare the results obtained in the chloride media, an experiment using 1MKCl was conducted on the gold rotating disk electrode. The electrode was conditioned by holding at +0.8V for 5 minutes. The electrode was then checked for background and an experiment with mercury additions of 2 to 42 ppb was conducted (Fig 3.33).

The result obtained was comparable with that on a BDD electrode under similar conditions. Two peaks were obtained, the first at 0.28V and the second at 0.35V, which is similar to the explanation given earlier (free mercury stripping and mercury-gold alloy stripping) using BDD.

Figure 3.33: DPV scans for 1M KCl on a rotating gold disk electrode

(a) Blank 1M KCl (b) + 2ppb of Hg, (c) + 6ppb of Hg, (d) + 10ppb of Hg, (e) + 22ppb of Hg, (f) + 32ppb of Hg, (g) + 42ppb of Hg. Deposition potential = -0.4V, final potential = 0.8V. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm.

3.5. Other factors affecting mercury detection

3.5.1. Electrode type

Three types of electrodes Type A, B and C were tested so far in the lab. In all cases, two peaks (1 & 2) were observed. As explained in Section 2, there are 2 forms of mercury that strip from the surface, Hg^+ and Hg^{2+} , giving rise to peaks 1 and 2 respectively. On comparing Type A and B electrodes, the 1st and 2nd peaks remain in the same position but 1st Peak dominates in Type A and 2nd peak dominates in Type B. Types C show a similar

behavior to that of type B. The type A electrode has a rough surface and has a greater number of grain boundaries while type B has a smooth mirror like surface and has lesser grain boundaries compared to type A. Thus it can be explained that there is a non-uniform deposition of gold on Type A electrodes resulting in more free mercury depositing between the grains giving rise to a dominant 1st peak. In the case of Type B electrodes, the surface is smooth and there are more chances for uniform gold deposition resulting in more mercury-gold alloy formation and hence a dominant 2nd peak. Type B electrodes are more advantageous than Type A when considering the linearity of 2nd peak, which is essential for calibration. Moreover if the surface mercury is more, i.e., if more mercury strips to the +1 oxidation state, it results in more calomel formation complicating further measurements. Thus Type B electrodes were used for rotating disk experiments and testing of unknown samples.

3.5.2. Addition of gold

Experiments without the addition of gold were also carried out. But there was no stripping peak for mercury especially in chloride media. In thiocyanate media, gold addition was not required as thiocyanate forms a strong complex with mercury. Conversely when gold was added, the stripping peak for mercury started to decrease in thiocyanate media. Gold addition was necessary in case of chloride, nitrate and perchloric acid media. The amount of gold added also played a vital role. Several experiments using different concentrations of gold were tried and 3ppm was chosen to be the appropriate level. However for the ppt range of experiments, a lesser amount of gold (1.5ppm) was sufficient to obtain linear peaks. The peaks start saturating for higher levels of gold (more than 5 ppm).

4. ANALYSIS OF UNKNOWN SAMPLES

4.1. Overview

Several samples with unknown concentrations of mercury were tested for mercury. Mercury concentrations down to 5.3 ppt could be detected using the rotating disc electrode technique. The standard addition method was used for the analysis. This chapter discusses in detail the results obtained for the unknown samples using rotating disc electrodes and the effect of copper on the stripping peak for mercury. Also given are the results obtained using stationary BDD electrodes on different samples.

4.2. Sample Preparation

Samples from coal fired power plants

The samples obtained from coal-fired power plants were prepared by the method proposed by Mendelsohn, et al (United States Patent: 5,900,042). The samples fall under categories such as Potassium Permanganate ($\text{H}_2\text{SO}_4\text{-KMnO}_4$), Hydrogen Peroxide ($\text{HNO}_3\text{-H}_2\text{O}_2$), Probe Rinse and Potassium Chloride (KCl) depending on the form of the mercury captured. Mercury in its elemental form (mercury in its zero oxidation state Hg^0) is captured in acidified hydrogen peroxide and potassium permanganate impinger solutions (this is gaseous Hg^0). In its oxidized state (Mercurous or Mercuric oxidation states: Hg_2^{1+} and Hg^{2+} , respectively), mercury is captured in aqueous potassium chloride impinger solution (this is gaseous Hg^{2+}). The composition of the impinger solutions are as given below:

KCl Absorbing Solution (1 mol/L)

$\text{HNO}_3\text{-H}_2\text{O}_2$ Absorbing Solution (5% v/v HNO_3 , 10% v/v H_2O_2)

H₂SO₄–KMnO₄ Absorbing Solution (4% v/v KMnO₄, 10% v/v H₂SO₄)

Water samples

Water Samples from ponds that receive the exhaust from coal-fired power plants were analysed as such with acidification to attain a stable pH (1-3).

Fish Samples

Fish from ponds that receive the exhaust from mines were analyzed for mercury. The solutions were prepared from the muscle tissue of the fishes using EPA approved method 245.5.

4.3. Copper Interference

The samples obtained from coal-fired power plants were found to contain copper. Copper has a stripping potential near 0.25V, which is close to that of mercury. Copper is proven to have positive effects on mercury stripping [9, 83]. The presence of copper in the solution tends to enhance the deposition of mercury on the surface.

To identify the presence of copper and or manganese, an experiment with standard additions of copper and manganese in a sample was performed. Figure 4.1 shows the DPV scans obtained for a sample, using a stationary type B BDD electrode. A standard solution of Manganese, prepared from Manganese nitrate was used as a standard addition to the sample. As we can observe, the addition of manganese did not affect the stripping peak for mercury indicating the absence of manganese. In the same solution, copper was then added and the DPV scans are as shown in figure 4.2.

During run one, the composition was Sample + 7ppm Gold solution + 8ppb Mercury + Manganese. A known volume of copper was then added in run 2. A high concentration (40ppb) of mercury was added during run 3. It is noted that there are two

peaks, one at 0.18V (peak 1) and the other at 0.49V (peak 2). Figure 4.2(B) clearly shows peak2. The peak 1 increases in run 2 on the addition of copper indicating its presence. Moreover peak 2 decreases in run 2 indicating that the mercury present in the solution is too little compared to the amount of copper and thus has formed an alloy with copper and gold. In run 3, peak 2 increases indicating that there is enough mercury in the solution to form an alloy with gold present in the solution.

Figure 4.1: DPV peak currents for an unknown sample (obtained from coal-fired power plant) with standard additions of Manganese solution.

(a) Sample, (b) Sample with 3ppm of gold + 8ppb of Hg, (c) b + 2ppm of Gold, (d) c + 2ppm of Gold, (e) d + 1st addition of Manganese, (f) e + 2nd addition of Manganese. Other conditions were: deposition time = 60 sec, deposition Potential = -0.1V vs. SCE, scan rate = 100mV/sec, stationary type B electrode.

Figure 4.2: Explanation of Fig 4.1.

(A) (a) curve f from Figure 4.1 (b) + Copper, (c) + 40ppb of hg and (B) Peak 2 of (A). Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, stationary type B electrode.

In the analysis made so far, gold solution has been added to the sample to deposit mercury. So in samples that contain copper, there are three metals: gold, mercury and copper involved. In most of the cases, two peaks were observed, peak1 near 0.2V and peak2 at 0.35V. On addition of copper without adding mercury to the sample, peak 1 increased. This shows that the peak 1 corresponds to the stripping of copper in the solution. On the addition of mercury alone, in the presence of gold, both the peaks 1&2 increased linearly, peak 1 showing more increase than peak 2. This shows that the sample already has some amount of copper in it and it forms an alloy with gold and mercury and strips at the position of peak1. Mercury also forms an alloy with gold that strips at peak 2. It is also been noted that mercury finds increased affinity towards copper and gold rather than only gold.

4.4. Standard Additions Method

Both Rotating disk and stationary Type B electrodes were used in the testing of the samples. Two batches of samples obtained from coal fired power plants and water and fish samples from ponds that receive exhaust from coalmines were tested. The results obtained were compared with Cold Vapor Atomic Absorption Spectrometry (CVAAS) done by the National Research Center for Coal and Energy (NRCCE), West Virginia University and Department of Energy (DOE). This section discusses these results and the effect of copper and gold addition on the analysis of the samples.

4.4.1. Range of Calibration

The range used for calibration plays a vital role in the case of standard additions method as known concentrations are added to an unknown concentration and the linearity in the peak increase is taken into account. A value obtained for the unknown concentration from a ppb range of additions of mercury will be different from a ppt range of additions and the linearity will also vary. Moreover as Copper is present in almost all the samples, it is critical to choose a proper range of calibration. All the samples were analyzed in both ppb and ppt range. In certain cases of ppt range of experiments, the peak 2 was absent completely and peak 1 increased linearly. In the case of ppt ranges of mercury, there is so little mercury in the solution that all of it forms an alloy with copper and gold alone and strips as peak 1. The samples were first analyzed in the ppt range and then in the ppb or the next level in ppt range depending on the linearity. A specific example of a sample analyzed is given below:

Figure 4.3: DPV peak currents for Sample 4 with 200 to 800ppt standard additions of Mercury

(A) DPV peak currents for Sample 4 with 200 to 800ppt standard additions of Mercury with 3ppm of Gold solution added. (a) Sample, (b) Sample with 3ppm of gold, (c) + 200ppt of Hg, (d) + 400ppt of Hg, (e) + 600ppt of Hg, (f) + 800ppt of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm, rotating disc electrode. (B) Calibration plot based on the 0.2V peak.

Figure 4.3 shows 200-800 ppt standard addition plot for this sample. It is noted that the increase in peak current is not linear with concentration. The next lower level 100-400 ppt was tried and the result is shown in figure 4.4. There is a sudden rise in the peak and the increase is linear after the first addition, which means that the sample is not in the range of calibration of the experiment. The first and second additions play a vital role in the standard additions method and if the first 2 additions are not linear, then it indicates an incorrect working range. The next lower range 20-80 ppt was tried (figure 4.5) and the same behavior was observed. The next lower range 10-40 ppt was tried (figure 4.6) and in this case, the first 2 additions were linear and then the peak started to saturate. The first 2 points were taken for calibration. A ppb range of experiment was also

conducted on this sample and the result is as shown in figure 4.7. As the concentration of mercury is very low, both the peaks are not linear.

Figure 4.4: DPV on Sample 4 with 100 to 400ppt standard additions of Mercury

(A) DPV peak currents and (B) Calibration plot for Sample 4 with 100 to 400ppt standard additions of Mercury with 3ppm of Gold solution added. (a) Sample, (b) + 3ppm of gold, (c) + 100ppt of Hg, (d) + 200ppt of Hg, (e) + 300ppt of Hg, (f) + 400ppt of Hg. Other Conditions: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 244ppt.

Figure 4.5: DPV on Sample 4 with 20 to 80ppt standard additions of Mercury

(A) DPV peak currents and (B) Calibration plots for Sample 4 with 20 to 80ppt standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 20ppt of Hg, (c) + 40ppt of Hg, (d) + 60ppt of Hg, (e) + 80ppt of Hg. Other conditions: deposition time = 60 sec, deposition Potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 83ppt.

Figure 4.6: DPV peak currents for Sample 4 with 10 to 20ppt standard additions of Mercury

(A) DPV peak currents and (B) Calibration plot for Sample 4 with 10 to 20ppt standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold (b) + 10ppt of Hg, (c) + 20ppt of Hg. Other conditions: deposition time = 120 sec, deposition Potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 45ppt.

Figure 4.7: DPV peak currents for Sample 4 with 2 to 10ppb standard additions of Mercury

(A) DPV peak currents and (B) Calibration plot for Sample 4 with 2 to 10ppb standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 2ppb of Hg, (c) + 4ppb of Hg, (d) + 6ppb of Hg, (e) + 10ppb of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm, rotating disc electrode.

From the above example it is clear that the range of calibration plays a vital role in determining the concentration. All the samples were thus analyzed in different ranges and finally one range was selected for calibration depending on linearity. 2 to 3 ranges of experiments were performed in most of the cases.

4.4.2. Effect of gold addition

As noted earlier, it is necessary to add gold for mercury to deposit on. Copper was present (though in different concentrations) in all the samples obtained from the coal-fired power plants. Copper helps in the deposition of mercury by forming an alloy with gold and mercury. The amount of gold added to the solution had to be varied to reduce the background in certain samples. The amount of gold added thus played a role in the

analysis of unknown samples. In solutions with very low concentrations of mercury and higher concentrations of copper, an increase in the background was noticed for the normal concentration of gold. In such cases, the amount of gold added to the solution had to be decreased, which improved the linearity. A specific example is discussed below:

Figure 4.8 shows the 200-800 ppt standard additions plot on this sample. 3ppm of gold solution was added in this case. Good linearity was observed in this case but the background was higher. In an attempt to reduce the background, an experiment with lower concentration of gold (1.5ppm) was performed (Figure 4.9) with a deposition time of 90 seconds. The background reduced and the plots were linear too. The peak obtained at 210mV was taken for calibration.

Figure 4.8: DPV peak currents for Sample 2 with 200 to 800ppt standard additions of Mercury

(A) DPV peak currents and (B) Calibration plot for Sample 2 with 200 to 800ppt standard additions of Mercury with 3ppm of Gold solution added. (a) Sample, (b) Sample with 3ppm of gold, (c) + 200ppt of Hg, (d) + 400ppt of Hg, (e) + 600ppt of Hg, (f) + 800ppt of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm, rotating disc electrode. Unknown concentration = 825ppt.

Figure 4.9: DPV peak currents for Sample 2 with 200 to 600ppt standard additions of Mercury

(A) DPV peak currents and (B) Calibration plot for Sample 2 with 200 to 600ppt standard additions of Mercury with 1.5ppm of Gold solution added. (a) Sample, (b) Sample with 1.5ppm of gold, (c) + 200ppt of Hg, (d) + 400ppt of Hg, (e) + 600ppt of Hg. Other conditions were: deposition time = 90 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm, rotating disc electrode. Unknown concentration = 250ppt.

4.4.3. Batch 1 (Stationary BDD electrodes)

Four samples, Sample 1 to 4 were analyzed. Both ppb and ppt range experiments were conducted and the most linear curves, which were taken for calibration as discussed in the previous section, are shown from figures 4.10-4.13. Table 4.1 shows the comparison with results by CVAAS analysis.

Figure 4.10: Standard additions method on Sample A

(A) DPV peak currents and (B) Calibration plot for Sample A with 500 to 1500ppt standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 500ppt of Hg, (c) + 1000ppt of Hg, (d) + 1500ppt of Hg. Other conditions were: deposition time = 30 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, stationary Type B electrode. Unknown concentration = 0.61ppb.

Figure 4.11: Standard additions method on Sample B

(A) DPV peak currents and (B) Calibration plot for Sample B with 2 to 8ppb standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 2ppb of Hg, (c) + 4ppb of Hg, (d) + 6ppb of Hg, (e) + 8ppb of Hg. Other conditions were: deposition time = 30 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, stationary Type B electrode. Unknown concentration = 0.58ppb.

Figure 4.12: Standard additions method on Sample C

(A) DPV peak currents and (B) Calibration plot for Sample C with 3 to 6ppb standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 3ppb of Hg, (c) + 6ppb of Hg. Other conditions were: deposition time = 30 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, stationary Type B electrode. Unknown concentration = 6.26ppb.

Figure 4.13: Standard additions method on Sample D

(A) DPV peak currents and (B) Calibration plot for Sample D with 2 to 4ppb standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 2ppb of Hg, (c) + 4ppb of Hg. Other conditions were: deposition time = 30 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, stationary Type B electrode. Unknown concentration = 2.5ppb.

Table I Results of Batch (I) samples (Stationary electrode)

Sample	Standard Addition Method (Conc. in ppb)	<i>CVAA Test Results</i> (Conc. in ppb)	
		<i>NRCCE</i>	<i>DOE</i>
A	0.61	0.24	0.43
B	0.58	0.7	0.27
C	6.26	6.3	3.0
D	2.50	5.1	2.7

Comparison of DPV results by standard addition method on a stationary B electrode and CVAAS analysis (from National Research center for Coal and Energy (NRCCE), West Virginia University and Department of Energy (DOE)) on the first batch of KCl impinger samples obtained from a pilot-scale combustion facility collected during coal burning.

4.4.4. Batch 2 (Rotating Disk electrodes)

On comparison with the stationary electrode, a rotating disk electrode proved to be more effective considering the linearity and reproducibility. The second batch of samples obtained was analyzed using the RDE. Figures 4.14-4.23 give the calibration plots for the samples and Table 4.2 shows the comparison with CVAAS analysis.

Figure 4.14: Standard additions method on Sample 1

(A) DPV peak currents and (B) Calibration plot for Sample 1 with 200 to 800ppt standard additions of Mercury with 3ppm of Gold solution added. (a) Sample, (b) +3ppm of gold (c) + 200ppt of Hg, (d) + 400ppt of Hg, (e) + 600ppt of Hg, (f) + 800ppt of Hg. Other conditions: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 0.532ppb.

Figure 4.15: Standard additions method on Sample 2

(A) DPV peak currents and (B) Calibration plot for Sample 2 with 200 to 600ppt standard additions of Mercury with 1.5ppm of Gold solution added. (a) Sample, (b) + 1.5ppm of gold (c) + 200ppt of Hg, (d) + 400ppt of Hg, (e) + 600ppt of Hg. Other conditions: deposition time = 90 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 0.25ppb.

Figure 4.16: Standard additions method on Sample 3

(A) DPV peak currents and (B) Calibration plot for Sample 3 with 200 to 600ppt standard additions of Mercury with 3ppm of Gold solution added. (a) Sample, (b) + 3ppm of gold (c) + 200ppt of Hg, (d) + 400ppt of Hg, (e) + 600ppt of Hg. Other conditions: deposition time = 90 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 0.43ppb.

Figure 4.17: Standard additions method on Sample 5

(A) DPV peak currents and (B) Calibration plot for Sample 5 with 100 to 300ppt standard additions of Mercury with 1.5ppm of Gold solution added. (a) Sample, (b) + 1.5ppm of gold (c) + 100ppt of Hg, (d) + 200ppt of Hg, (e) + 300ppt of Hg. Other conditions: deposition time = 120 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 200ppt.

Figure 4.18: Standard additions method on Sample 6

(A) DPV peak currents and (B) Calibration plot for Sample 6 with 200 to 600ppt standard additions of Mercury with 1.5ppm of Gold solution added. (a) Sample, (b)+ 1.5ppm of gold (c) + 200ppt of Hg, (d) + 400ppt of Hg, (e) + 600ppt of Hg. Other conditions: deposition time = 120 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 0.3ppb.

Figure 4.19: Standard additions method on Sample 7

(A) DPV peak currents and (B) Calibration plot for Sample 7 with 100 to 300ppt standard additions of Mercury with 3ppm of Gold solution added. (a) Sample, (b) + 3ppm of gold (c) + 100ppt of Hg, (d) + 200ppt of Hg, (e) + 300ppt of Hg. Other conditions: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 94ppt.

Figure 4.20: Standard additions method on Sample 8

(A) DPV peak currents and (B) Calibration plot for Sample 8 with 200 to 600ppt standard additions of Mercury with 3ppm of Gold solution added. (a) Sample, (b) + 3ppm of gold (c) + 200ppt of Hg, (d) + 400ppt of Hg, (e) + 600ppt of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 0.12ppb.

Figure 4.21: Standard additions method on Sample 9

(A) DPV peak currents and (B) Calibration plot for Sample 9 with 2 to 6ppt standard additions of Mercury with 1.5ppm of Gold solution added. (a) Sample, (b) + 1.5ppm of gold (c) + 2ppt of Hg, (d) + 4ppt of Hg, (e) + 6ppt of Hg. Other conditions: deposition time = 120 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 5.3ppt.

Figure 4.22: Standard additions method on Sample 10

(A) DPV peak currents and (B) Calibration plot for Sample 10 with 2 to 8ppb standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 2ppb of Hg, (c) + 4ppb of Hg, (d) + 6ppb of Hg, (e) + 8ppb of Hg. Other conditions: deposition time = 60 sec, deposition potential = - 0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 1.97ppb.

Figure 4.23: Standard additions method on Sample 11

(A) DPV peak currents and (B) Calibration plot for Sample 11 with 2 to 8ppb standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 2ppb of Hg, (c) + 4ppb of Hg, (d) + 6ppb of Hg. Other conditions: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm. Unknown concentration = 1.78ppb.

Table II Results of Batch (II) samples

Sample	Standard Additions Method (ppb)	CVAAS Results (ppb)	
		NETL	NRCCE
1	0.53	0.41	0.41
2	0.25	0.39	0.37
3	0.43	0.41	0.38
4	0.045	0.02	<0.07
5	0.20	0.21	0.26
6	0.30	0.18	0.19
7	0.09	0.09	0.11
8	0.12	0.12	0.16
9	0.0053	0.0044	<0.07
10	1.97	1.94	<0.07
11	1.78	1.78	<0.07

Comparison of DPV results by standard addition method on a rotating disc B electrode and CVAAS analysis (from National Research center for Coal and Energy (NRCCE), West Virginia University and Department of Energy (DOE)) on the second batch of KCl impinger samples obtained from a pilot-scale combustion facility collected during coal burning.

The values obtained for unknown concentrations using standard additions method and CVAA analysis (NETL) as shown in the above table is plotted in Figure 4.24. Excellent one-to-one correspondence is observed. The Rotating disc electrode technique (BDD electrodes) is thus a promising technique for applications in onsite monitoring units.

Figure 4.24: Comparison of CVAAS and Standard Additions Method

Comparison plot of the concentrations determined by the standard addition and CVAA methods (Table 2).

The solid line represents one-to-one correlation between the two methods.

4.4.5. Samples from other Environmental Resources

Water samples from ponds that receive exhaust from mines and fish samples from river were analyzed for mercury. The following figures show the calibration plots of standard additions method obtained on these samples. Table 4.3 summarizes the results and compares it with CVAA results.

Figure 4.25: Standard additions method on Water Sample1

(A) DPV peak currents and (B) Calibration plot for Water Sample1 with 200 to 600 ppt standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 200ppt of Hg, (c) + 600ppt of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm, rotating disc electrode. Unknown concentration = 417ppt.

Figure 4.26: Standard additions method on Water Sample2

(A) DPV peak currents and (B) Calibration plot for Water Sample2 with 2 to 6 ppb standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 2ppb of Hg, (c) + 4ppb of Hg, (d) + 6ppb of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm, rotating disc electrode. Unknown concentration = 287ppt.

Figure 4.27: Standard additions method on Fish Sample 1

(A) DPV peak currents and (B) Calibration plot for Fish Sample 1 with 2 to 6 ppb standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 2ppb of Hg, (c) + 4ppb of Hg, (d) + 6ppb of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm, rotating disc electrode. Unknown concentration = 2ppb.

Figure 4.28: Standard additions method on Fish Sample 2

(A) DPV peak currents and (B) Calibration plot for Fish Sample 2 with 2 to 6 ppb standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 2ppb of Hg, (c) + 4ppb of Hg, (d) + 6ppb of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm, rotating disc electrode. Unknown concentration = 2.84ppb.

Figure 4.29: Standard additions method on Fish Sample 3

(A) DPV peak currents and (B) Calibration plot for Fish Sample 3 with 2 to 6 ppb standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 2ppb of Hg, (c) + 4ppb of Hg, (b) + 6ppb of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm, rotating disc electrode. Unknown concentration = 1.4ppb.

Figure 4.30: Standard additions method on Fish Sample 4

(A) DPV peak currents and (B) Calibration plot for Fish Sample 4 with 2 to 6 ppb standard additions of Mercury with 3ppm of Gold solution added. (a) Sample with 3ppm of gold, (b) + 2ppb of Hg, (c) + 4ppb of Hg, (b) + 6ppb of Hg. Other conditions were: deposition time = 60 sec, deposition potential = -0.1V vs. SCE, scan rate = 100mV/sec, speed = 2500rpm, rotating disc electrode. Unknown concentration = 2ppb.

Table III Results of Environmental samples

Sample	Standard Addition Method (Conc. in ppb)	CVAA Test Results (Conc. in ppb)
Water Sample 1	0.42	0.32
Water Sample 2	0.29	0.46
Fish Sample 1	2.0	2.0
Fish Sample 2	2.84	1.4
Fish Sample 3	1.4	2.0
Fish Sample 4	2.0	2.3

Comparison of DPV results by standard addition method on a stationary type B electrode and CVAAS analysis (from National Research center for Coal and Energy (NRCCE), West Virginia University) on the water and fish samples obtained from mine exhaust and river respectively.

5. CONCLUSIONS AND FUTURE DIRECTIONS

5.1. Summary and Conclusions

Trace detection of mercury using Boron-doped diamond electrodes was studied using DPASV on stationary and rotating disc BDD electrodes. Experiments were conducted using different electrolytic media, the majority being done in the chloride media. Promising results were obtained using perchloric acid and thiocyanate media as well. It was essential to add gold solution in all the cases except for the thiocyanate media. Linear calibration plots were obtained in both ppb and ppt range of mercury additions.

In the case of stationary electrode, two peaks were obtained, one for the free surface mercury and the other for the mercury-gold alloy. This problem was resolved by using a rotating disc electrode in which the electrode was made to rotate at a constant speed during deposition and the electrode was held stationary during the stripping or the measurement phase. Excellent linearity was observed in most of the cases. Before the start of each experiment, electrode cleaning was found to be necessary as a trace of gold was found to remain on the surface during the start of a new experiment. The cleaning procedure might be electrochemical (holding the electrode at 1.0V for 2 minutes), or chemical (cleaning of the surface using few drops of aqua regia for 1 minute).

Though rotating disc electrodes produced reasonably good results, in consecutive experiments, the stripping currents obtained for the same concentration was not constant. Several experiments were conducted to study this behavior. This may be due to an unexplained surface change of the electrode due to the addition of gold at the start of every experiment. Gold deposition may not be constant under the same conditions in different experiments, thus leading to a different background current in each experiment

and hence causing a difference in the stripping current. However, excellent linearity was obtained in the same experiment for mercury additions, which is the most important criteria for the analysis of unknown samples.

Several unknown samples were tested on both stationary and rotating disc electrodes using the standard addition method. The lowest concentration detected was 5.3ppt ($15.42 \times 10^{-12}\text{M}$) using a rotating disc electrode with the addition of 1.5ppm of gold solution for a deposition period of 120 seconds. Most of the samples obtained from the coal fired power plants contained copper, which was found to improve the detection of mercury in the sample by the formation of alloy with gold and mercury. In cases of absence of copper, mercury-gold alloy was used for the detection of mercury. The same electrode cleaning procedure as described before was used after each experiment. However, in certain cases, a prolonged cleaning time of 5 minutes was necessary considering the other metals such as copper in the unknown sample. Excellent correlation was obtained when the results were compared with CVAA method. A portable potentiostat was also used for analyzing unknown samples and gave comparable results as those with the normal potentiostat. Calibration plots were also made using the portable unit and excellent linearity was observed.

BDD electrodes thus provide a leading edge over other electrodes currently used for mercury detection due to their various advantages, the most important being the minimal pretreatment and deposition time requirements.

5.2. Future work

Detailed surface studies can be done to understand the changes occurring in the surface due to the formation of mercury-gold alloy. This would make it possible to ascertain the reasons for obtaining different calibration plots (as shown in fig 3.17) each time when the electrode is used. This would also result in ways to calculate a single current for a given concentration thereby minimizing the working time on each sample by using a single run of the sample to determine its concentration. Flow injection cells, wherein the sample in a constant flow hits the electrode surface using a controlled potential technique such as chronoamperometry resulting in a current, which is proportional to the concentration of mercury in the sample. Promising results were obtained in thiocyanate and perchloric acid media, which can be probed further to obtain constant current for the same concentration.

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