

# Quantification of Mercury in Flue Gas Emission Using Boron-Doped Diamond Electrochemistry

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## Abstract

The detection of toxic trace metals in the environment is a highly important yet challenging analytical problem. Because of the growing awareness of environmental mercury pollution and its high toxicity, it is becoming more urgent to develop highly sensitive techniques for the detection of Hg (1). Spectroscopic techniques such as 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) have been used successfully for the detection of mercury. However, all of these techniques require relatively large sample volumes for analysis and are also not suitable for on-line monitoring.

In this project, we are developing a new technique utilizing Boron-doped diamond (BDD) films to electrochemically detect mercury dissolved in solution via the initial deposition of metallic mercury, followed by anodic linear sweep voltammetry in the range from  $10^{-10}$  M to  $10^{-5}$  M. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques were employed. The extremely low background current for BDD electrodes compared to glassy carbon (GC) provides a strong advantage in trace metal detection. CV peak currents showed good linearity in the micromolar range. A detection level of  $6.8 \times 10^{-10}$  M was achieved with DPV in 0.1 M  $\text{KNO}_3$  (pH = 1) for a deposition time of 20 minutes. Reproducible stripping peaks were obtained, even for the low concentration range. A comparison with GC shows that BDD is superior. Linear behavior was also obtained in the mercury concentration range from  $10^{-10}$  M to  $10^{-9}$  M (5).

Boron-doped diamond films were deposited on conductive silicon substrates by use of microwave-assisted plasma-enhanced chemical vapor deposition (6). An O-ring type three-electrode electrochemical cell was used. A saturated calomel electrode (SCE)

and a platinum wire were used as the reference and counter electrodes, respectively. An auxiliary platinum quasi-reference electrode was used along with the SCE to decrease noise. A Hokuto-Denko Model HZ-3000 potentiostat was used for all of the electrochemical measurements. The supporting electrolyte used was 0.1M KNO<sub>3</sub>, acidified with 0.05M HNO<sub>3</sub> (pH = 1). The mercury solutions were prepared from Hg(NO<sub>3</sub>)<sub>2</sub> (from Fisher and Aldrich) with ultrapure water and ca. 0.05M HNO<sub>3</sub>. It was found to be unnecessary to remove oxygen from the solutions, due to the high overpotential for oxygen reduction (6). This is also an advantage for trace metal detection using diamond electrode. However, in a series of sequential measurements with increasing Hg concentrations, in which aliquots of Hg<sup>2+</sup> stock solution were added, the electrolyte was mixed between additions by use of N<sub>2</sub> gas bubbling in order to save time.

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

Several other problems need to be solved before this technique becomes useful for practical applications. First is the effect of chloride ions on the detection current since the real samples from coal fired power plants will have significant amount of chloride. Although, the chloride ions enhance the sensitivity, they also form Hg<sub>2</sub>Cl<sub>2</sub> at the electrode surface which affects the sensitivity and reproducibility. We are experimenting with different procedures (e.g. co-deposition of gold) to overcome the effect of the chloride problem so that reproducible calibration curves for mercury detection in the presence of chloride ions can be obtained. The co-deposition of gold enhances the nucleation sites for mercury since it has a great affinity to form amalgam with mercury. Results of these procedures along with the appropriate calibration curves will be presented.

## References:

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