Determination of Trace Mercury (Hg(II)) by Anodic Stripping Voltammetry at a Gold Electrode

A Look at Different Techniques, Common Background Electrolytes, and Electrode Surface Cleaning Procedures

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Electrochemical determination of aqueous Hg(II) at a 1.6 mm solid gold electrode is described. Background current, baseline behavior, technique, experimental time, background electrolyte, and surface cleaning procedures were examined for the quality of data. Three acid media (HNO_3, $HClO_4$, and HCl) showed satisfactory performance. The potential window allowed by HCl was narrower than for the other two electrolytes. Electrochemical surface cleaning, as well as controlling the amont of Hg deposited onto the gold surface by lowering the deposition time, were necessary for maintaining better reproducibility and linearity. Excellent sensitivity was observed with just a 10 second deposition time in the 100 - 400 ppb Hg(II) concentration range.

As a highly toxic metal in the environment, the determination of trace Hg(II) is important. Atomic absorption and inductively coupled plasma spectroscopic methods are currently widely used. Many publications on this subject focus on electrochemical methods (anodic and potentiometric stripping voltammetry) at a variety of electrode materials. Glassy carbon, gold-plated glassy carbon, screen-printed carbon, platinum (Pt) and gold (Au) have all been utilized in these investigations.

The use of a bare glassy carbon electrode was investigated by Allen and Johnson and they noted that deposition of Hg onto this electrode 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 (1). Early work on the use of a wax-impregnated graphite electrode was reported by Perone and Kretlow (2). The USEPA method 7472 for Hg(II) determination involves electrochemical deposition of a thin gold film on a glassy carbon electrode. Accumulation of Hg vapor on an Au-plated glassy carbon electrode followed by voltammetric determination has been the subject of a recent publication (3). Simultaneous determination of arsenic (As) and Hg was performed on a gold-plated glassy carbon electrode as recently reported by Viltchinskaia, et al. (4). Disposable screen-printed carbon electrodes with a coating of Au were used by Wang and Tian in potentiometric stripping voltammetry for the determination of trace quantities of inorganic Hg as well as organic mercury compounds such as dimethylmercury (5).

The determination of Hg(II) at Pt by anodic stripping voltammetry has been studied by many people (6,7). Different surface species formed between Pt and Hg give rise to multiple peaks that interfere with the analysis. These multiple peaks have been proposed to be due to varying amounts of Hg plating, i.e., more or less than a monolayer. Careful control of deposition time, depending on the sample concentration, is therefore necessary.

The use of solid gold electrodes for on-site Hg analysis in soil samples was proposed recently (8). A good correlation between the results from the solid 1 mm Au electrode and the EPA method with the Au-plated glassy carbon electrode has been indicated here. The EPA method requires deposition of Au onto the carbon electrode, which lengthens the analysis time and significantly increases the cost of analysis. The acceptance of a solid Au electrode for this analysis has been slow, probably due to the strong interaction between Hg and Au (6). A remedy to this situation can be electrochemical cleaning of the electrode after a single use as suggested by Hsi, et al. (9). This procedure is very easy to perform and can conveniently be integrated into fully automated systems. Continuous use of a gold electrode with a better cleaning procedure could make the procedure more adaptable

to field, clinical, or other applications. Since this procedure does not require degassing of the sample, automation could easily be achieved.

In this work, the use of a solid Au electrode for Hg determination is carefully investigated in terms of the effect of background electrolyte, electrode surface cleaning procedure, and the choice of stripping technique.

Experimental

As supporting electrolytes, three highly pure, concentrated acids (HNO_3, $HClO_4$ and HCl) were used as received after dilution by a factor of 100 with water. The mercury solutions used here were prepared by spiking each supporting electrolyte with a diluted (10 ppm) 1000 ppm Hg(II) standard (Certified Atomic Absorption Standards, Fisher Scientific Company, Fair Lawn, NJ) with water. All glassware was stored in a 1.0 M HNO_3 acid bath and rinsed with water before use. De-ionized water was used throughout this work for rinsing and solution preparation purposes.

The instrument used for potential control in all the experiments was the BAS 100B/W Electrochemical Workstation (BAS, West Lafayette, IN). The Linear Scan Stripping Voltammetry (LSSV), Osteryoung Square Wave Stripping Voltammetry (OSWSV) and Differential Pulse Stripping Voltammetry (DPSV) techniques available with this instrument were used as the ASV methods. Other techniques such as Cyclic Voltammetry (CV), Osteryoung Square Wave Voltammetry (OSWV) and Linear Scan Voltammetry (LSV) were also used. The gold electrode used was first polished with alumina slurry, rinsed with methanol, followed by water, then stored in 6 M HNO_3 overnight. Cleaning of the electrode after each use was achieved by holding the electrode at an oxidative potential, at least 200 mV greater than the stripping peak potential of Hg, for a predetermined time based on the performance in each supporting electrolyte or scanning to extreme positive potentials (1.5 V).

Results and Discussion

Background Current Behavior

Based on the literature, the measurement of an analytical signal for Hg(II) on a gold surface has been somewhat hindered by the baseline (background current) behavior. The definition of a good baseline for the Hg peak has been difficult due to the appearance of multiple peaks or the broadness of the Hg peak. These problems result from the nature of the deposit on the electrode, i.e., the amount deposited and/or the type of interaction between the two materials (6).

The background current behavior for all three different electrolytes employed here was first examined by cyclic voltammetry with slow potential scan rate (20 mV/sec.). In the potential window from 0 to +1.2 V, HNO_3 and $HClO_4$ produced similar voltammograms where other activities due to oxidation of the surface and/or the formation of surface species with the electrolyte were not visible. On the other hand, HCl medium showed sharply rising background current starting around +0.90 V in the oxidative direction and a corresponding reduction peak at about +0.65 V. This activity is possibly due to oxidation of chloride ions and oxidation of the gold surface (9). The stripping peak for Hg is reported to appear between +0.50 and 0.70 V and hence the potential window in a chloride medium is still suitable for the analysis.

Out of three ASV techniques in use, LSSV, DPSV, and OSWSV, the last two techniques are popular because of their ability to enhance the analytical signal by removing nonfaradaic current. In the case of OSWSV, faradaic current due to kinetically slower O_2 reduction is also reduced by virtue of its inherent speed. In the potential window specified above for the Hg determination, the reduction of O_2 would not be of concern, but other electrochemical activities such as that seen at +0.40 V (**F1**) could be enhanced by OSWSV or DPSV. Therefore, careful selection of the technique is necessary.

In order to investigate the baseline behavior, LSV, DPV and OSWV were used in all three blank-background electrolytes. The voltammograms obtained in HNO_3 are shown in **F1**. These have similar features as in the other two electrolytes as well. However, the potential

F1

Voltammetry in blank electrolyte (0.15 M HNO_3). Scan rates for both LSV and DPV were 20 mV/sec., whereas that for OSWV was 60 mV/sec.
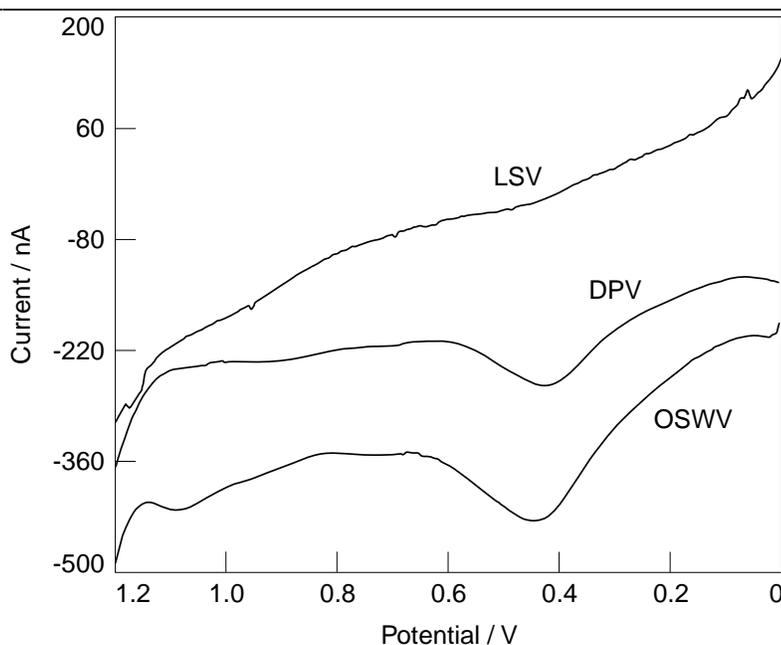
F2

Stripping voltammograms in $HClO_4$ from three different techniques. Scan rates for both LSSV and DPSV were 20 mV/s, whereas that for OSWSV was 60 mV/sec. Deposition time = 10 sec. Deposition potential = +0.30 V End potential = +1.5 V
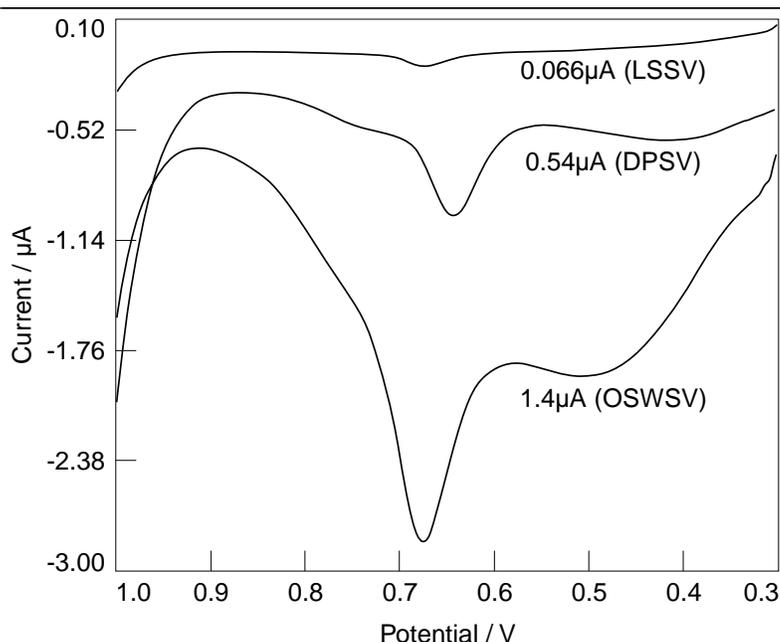
F3

Stripping voltammograms (LSSV) with different deposition times in $HClO_4$. Scan rate = 20 mV/sec. Deposition potential = +0.30 V End potential = +1.5 V
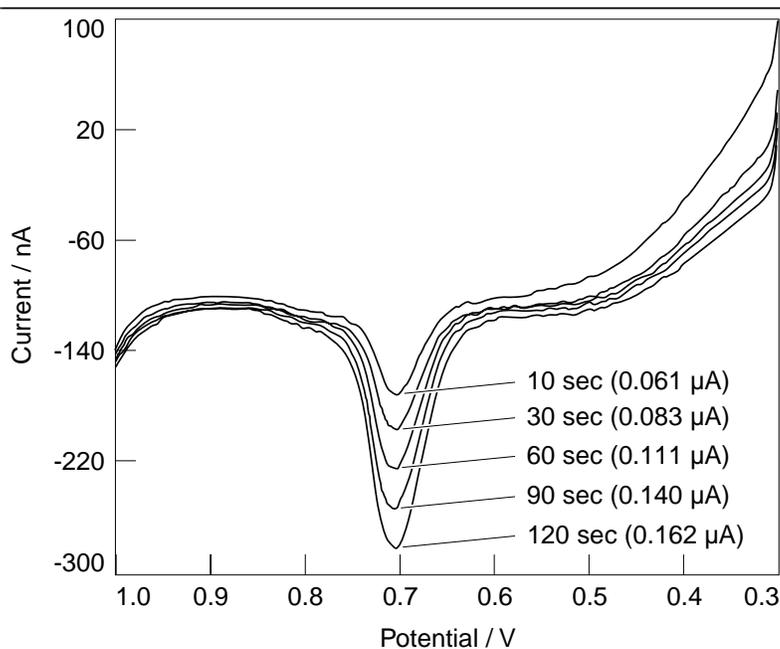
window allowed was narrower in the case of HCl (see above). The scan rate for both LSV and DPV was 20 mV/sec. The default scan rate for OSWV (60 mV/sec.) was used. The background current difference in the first two compares well in terms of the faradaic-current-enhancement property of DPSV. The slope in the baseline in the case of LSV is due to the change in charging current during the potential scan. It is important to notice, though, the difference in background current magnitude and the features exhibited. The broad peak around +0.40 V, a characteristic of gold, is prevalent in both DPSV and OSWV, whereas this activity is not visible or dominant in the case of LSV (5). Increased background current in OSWV can partially be assigned to the difference in scan rate. All other features in the voltammogram are similar between DPSV and OSWV except that the latter case starts to show another electrochemical activity around +1.1 V. The peak around +0.40 V is bound to introduce a slope negative to the Hg(II) peak that would hinder the data analysis.

Therefore, based on the baseline behavior, LSV or LSSV with a 20 mV/sec scan rate would be a reasonable choice for the analysis.

Behavior in Different Electrolytes with Added Hg(II)

Baseline and Peak Current

The stripping voltammograms were compared in all three electrolytes chosen with added Hg(II) (100 ppb). The baseline behavior observed in the $HClO_4$ medium with LSSV, DPSV, and OSWSV is compared in **F2**. All three electrolytes showed similar baseline behavior around the Hg peak. The LSSV and DPSV output had a scan rate of 20 mV/s and hence we can compare the actual difference in background current between linear and pulse voltammetry. These experiments were done with no stirring and only a 60 sec deposition time. The current is, of course, greater in both pulse techniques as expected along with enhanced background signal as well. In the case of LSSV, the current for both Hg(II) and other background is lower, but a peak current of 0.066 μA for 100 ppb Hg(II) shown here with only 60 sec. deposition time in an unstirred solution is quite satisfactory for all analytical purposes. Increased deposition time would provide higher current. The complexity in baseline behavior can be lowered by choosing the LSSV technique. As can be seen in **F2**, the peak measurement in both pulse techniques would be erroneous due to the difficulty in drawing a consistent baseline from run to run. A background subtraction method has also been suggested to remove the broad peak at +0.40 V and other artifacts in order to improve the data analysis with pulse techniques (5).

Peak Potentials

The stripping voltammograms with different deposition times of all three electrolytes gave satisfactory peak currents at 100 ppb Hg concentration in an unstirred condition. The peak potentials in HNO_3 and $HClO_4$ were ca. +0.70 and 0.65

Potential Window (mV)	Average Peak (μA) (n=5)	RSD (%)
300-900	.143	15
	.137	17
	.145	15
300-1,500	.128	7
	.123	9
	.144	12

V, whereas that in HCl was +0.52 V, more than 150 mV negative. The greater difference in HCl medium could be due to the complexation between Hg and chloride acting as a driving force for oxidation and hence lowering the oxidative potential. Chloride medium has been suggested as the most suitable chemical stripping solution in potentiometric determination of mercury at gold electrodes (10). The difference in peak potentials between DPSV and the other two techniques is an inherent property of DPSV (11).

Deposition Time and Linearity

Deposition of Hg onto a gold surface should be carefully controlled to avoid saturation and maintain linearity with increased loading. The greater solubility of Hg in gold compared to other metals could result in non-linear performance. The solution described above with 400 ppb Hg was utilized to investigate the effect of the length of deposition time. The peak currents obtained from LSSV experiments with 10, 30, 60, 90, and 120 sec. in unstirred solutions were examined. A set of stripping voltammograms obtained in this range in $HClO_4$ is shown in **F3**. Note the fairly flat baseline around the peak response. Linear regression of the first four readings resulted in a correlation coefficient of 0.9995, whereas all five readings together gave 0.9965. It appears that the saturation point and the nonlinearity for 400 ppb Hg concentration at this particular electrode is approaching around 120 sec. deposition time. As described above, the current observed, even

for 60 sec deposition time in unstirred solution for 100 ppb Hg, is quite satisfactory. A stirred solution would give increased current but would also quicken the arrival of the saturation point. It is necessary, therefore, for the analyst to have an idea where the nonlinearity appears in the concentration range in question. The linearity observed in LSSV mode for a concentration range of 100 - 400 ppb Hg with 10 sec. plating time in an unstirred condition was excellent, with a correlation coefficient of 0.9993.

Electrode Cleaning

Many people have shown the importance of electrode cleaning after a single Hg determination at a gold surface in order to maintain linearity. This is achieved more conveniently by electrochemical means. A recent publication on Hg determination at a gold electrode by pulse amperometry indicates a decrease in the Hg signal in the absence of cleaning (9). This work concerns the behavior of a gold electrode in a chromatographic mobile phase containing $HClO_4$, KCl and acetonitrile in determination of organic mercury (methyl-Hg) where fouling of the electrode by acetonitrile is also present. Here, a relatively large positive potential (1.8 V) is applied to remove adsorbed species and deposited Hg after a single determination. Other methods have also been described (5, 10, 12).

The need for electrode cleaning in all three electrolytes employed here was examined by performing repetitive stripping voltammetry with different positive end potentials, i.e., 0.90 and 1.5 V in

LSSV mode with 20 mV/s scan rate. **T1** illustrates the relative standard deviation (RSD) observed in these two ranges. In this experiment, 10 runs, five in each potential window, were done at a time. Then a 60 sec. potential step to +1.5 V was applied for removing any accumulating Hg. This procedure was repeated three times. The data suggests definite improvement in RSD in the runs with more positive end potential where average RSD is less than 10%, whereas in the other case it was above 15%.

The stripping experiments following this finding were designed to start a 60 sec. cleaning procedure after each run. Both $HClO_4$ and HNO_3 showed sufficient cleaning, but HCl required longer cleaning times with increased loading. This is somewhat contradictory to behavior observed by the authors in reference 10. A clear explanation for the need for longer cleaning time is not available at the present time. It can be speculated that the Hg being stripped from the gold electrode causes calomel to form on the surface and the effective removal of this complex requires a longer oxidation time. This procedure, therefore, could lengthen the experimental time in the case of HCl. Comparable performance with 60 sec. cleaning time was found with HNO_3 and $HClO_4$.

Conclusion

The use of a 1.6 mm solid gold electrode was described in terms of type of the background electrolyte, potential range applicable, technique, deposition time, linearity, and electrochemical cleaning procedure. All three media show satisfactory performance. The potential range in HCl is narrowed due to the activity of chloride ions. Among the three popular stripping modes, LSSV with a 20 mV/s scan rate was found to be a good choice when baseline behavior and reproducibility are considered. The experiment with other techniques would require

background subtraction integrated into the data analysis. The determination of Hg(II) at a gold electrode is always hindered by the incomplete removal of previously deposited Hg. In order to eliminate this drawback, an electrochemical cleaning procedure between runs is essential. Gold electrodes provide good sensitivity for Hg(II). Knowledge of the concentration range, careful selection of deposition time, and necessary pre-cleaning would help facilitate proper use of this technique.

References

1. R.E. Allen and D.C. Johnson, Talanta 20 (1973) 799.
2. S.P. Perone and W.J. Kretlow, Anal. Chem. 37 (1965) 968-970.
3. M. Korolczuk, Fresenius' J. Anal. Chem. 357 (1997) 389-391.
4. E.A. Viltchinskaia, L.L. Ziegman, D.M. Garcia, and P.F. Santos, Electroanalysis 9 (1997) 633.
5. J. Wang and B. Tian, Anal. Chim. Acta. 274 (1993) 1-6.
6. M.Z. Hassan, D.F. untereker, and S. Brukenstein, J. Electroanal. Chem. 42 (1973) 161.
7. G.D. Robbins and C.G. Enke, J. Electroanal. Chem. 23 (1969) 343 .
8. D.F. Foust and J.Y. Gui, American Environmental Laboratory, April, (1997) 17.
9. T.S. Hsi and J.S. Tsai, J. Chin. Chem. Soc. 41 (1994) 315.
10. D. Jagner, M. Josefson, and K. (r(n, Anal. Chim. Acta., 141 (1982) 147.
11. J. Wang in "Stripping Analysis" VCH Publishers, Inc., Deerfield Beach, Florida, 1985.
12. L. Sipos, P. Valenta, H.W. Nurnberg, and M. Branica, J. Electroanal. Chem. 77 (1977) 263.