AN IRIDIUM BASED MERCURY FILM ELECTRODE

PART II. COMPARISON OF MERCURY-FILM ELECTRODE BEHAVIORS: THEORY VERSUS REALITY

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ABSTRACT

An experimental study of a 2 mm diameter iridium based mercury film rotating disk electrode (IrMFE) is presented. Using anodic stripping voltammetry and test ions of cadmium, lead and zinc, the effects of Hg film thickness on peak potential, half-width and peak height are compared with the predictions given by the De Vries and Van Dalen theory. The response of the Ir-MFE was found to be theoretical for Hg film thicknesses less than 1 μm. Application of this classical theory to real Hg film electrodes, on any type of substrate, is found to be inappropriate when the Hg film thickness begins to exceed 1 μm. It is also shown that the stripping peak characteristics at a semi-spherical film electrode can be estimated by assuming that it is composed of a large number of annular flat films. The individual responses of the flat films can be summed to give the overall semi-spherical response.

INTRODUCTION

As was discussed in Part I [1] of this series of papers, most mercury film electrodes present some drawbacks for use in anodic stripping voltammetry (ASV) techniques, either because they are in fact composed of mercury droplets (e.g. mercury "films" on glassy carbon) or the support dissolves in mercury (e.g. Pt, Au, and Ag) and forms intermetallic compounds with the test ion. None of these electrodes are usable for speciation studies. The drawback of the latter is obvious and that of the former results from the fact that the classical thin-film theory of De Vries and Van Dalen [2,3] is not rigorously applicable. In addition, it has been demonstrated recently [4] that the morphology of the mercury layer can have

significant effects on the current response when pulsed voltammetric techniques of higher frequency are used (e.g. differential or square-wave voltammetry). For these reasons, it has been difficult to test thin-film theories in a wide range of experimental conditions, and in particular, effects of film thickness.

It has been shown [1] that the preparation of a true mercury film electrode is feasible on an iridium substrate, that Ir does not dissolve in Hg, and that the iridium mercury film electrode (Ir-MFE) is sufficiently stable to be used under normal experimental conditions. The above advantages of the Ir-MFE allow us to test the De Vries and Van Dalen theory [2,3] in more ideal conditions than is possible with other types of Hg film electrodes.

We first describe the work done for characterization of the Ir-MFE in terms of the experimental ASV current–potential parameters. A comparison is made with other types of MFEs as well as with the theoretical predictions of De Vries and Van Dalen [2,3]. With the results from this work and from the literature, it will be shown that the above MFE theory does not, and cannot, apply to real MFEs with thicknesses greater than about 1 μm.

EXPERIMENTAL

Instrumentation

The electrochemical system has been described previously [5]. It consists of a microcomputer controlled potentiostat (Motorola Exorset + Tacussel PRG5), a custom built medium-exchange/flow-through plexiglas cell, and an inverted polarizing microscope (Leitz Epivert) allowing in-situ observation and photography of the electrode surface.

The working electrode assembly was a Tacussel EDI-55442 rotating disk electrode (RDE) with a 1 cm Teflon tip into which a 2 mm dia. $\times$ 10 mm long iridium cylinder (99.9% purity, Heraeus GmbH) was press-fitted. The electrodes were polished initially with diamond spray pastes (Surfex, Metzger & Co., Switzerland) of decreasing size down to 1 μm, until a mirror like surface could be seen under the microscope at 250 $\times$. After polishing, the electrode was rinsed with diamond spray solvent (Blue Diamond Spray Solvent, Metzger & Co.). Deposition of mercury films was done as described previously [1]. The electrode was rotated at 1500 rpm during the experiments unless indicated otherwise. The counter electrode was a 2 mm dia. $\times$ 2 cm long Pt rod. The reference electrode, to which all potentials are referred, was a SCE (238 mV vs. SHE) filled with a saturated NaCl solution and equipped with a 0.1 M NaNO$_3$ bridge.

Reagents

All chemicals used were analytical reagent grade (Merck). The metal-ion solutions were prepared from their nitrate salts. The Hg(II) used for film formation, was prepared by dissolution of triply distilled mercury in nitric acid, followed by dilution with 0.1 M HClO$_4$ to give 10^{-3} M Hg(II).

All solutions were prepared with 18 MΩ water from a Millipore brand ion-exchange system.

High-purity (99.95%) nitrogen gas (Carbagas) was used to purge oxygen from solutions and to maintain a nitrogen blanket during experimentation.

Experimental tests on the mercury film were made by using the Pb^{2+}/Pb^0, Cd^{2+}/Cd^0, and Zn^{2+}/Zn^0 systems. From the literature it is known that these three systems behave reversibly. This was confirmed by our results with the Ir-MFE. Therefore, in the following discussion they will be taken together for the interpretation of the data. Note in particular, that since the Zn system behaves like Pb and Cd, we can also assume that no intermetallic compounds are formed between Zn and Ir.

EVALUATION OF THE Ir-MFE PARAMETERS

There are several parameters which play an important role in the analytical use of any mercury film electrode. This is especially true in speciation applications where a comparison of experimental data with a rigorous theory is a necessary prerequisite. These include the ASV parameters, such as scan rate, deposition time, peak stripping current, and deposition potential, and the physical parameters of the mercury film, such as film thickness or concentration of the reduced metal in the film.

The experiments to test these effects were carried out using mercury films of several thicknesses (0.1 to 52.0 μm) prepared according to previously described procedures [1], and using as test ions Pb(II), Cd(II), and Zn(II). The peak potential is given as the difference $E_p - E_{1/2}$, where the values of $E_{1/2}$ used for Cd(II), Pb(II), and Zn(II) are -580 mV, -382 mV, and -1000 mV, respectively.

Deposition time

One important condition in an ASV analysis is that the peak current should be directly proportional to the concentration of reduced metal in the mercury film. This was tested by measuring the peak current as a function of deposition time using:

(i) 4×10^{-6} M Cd(II), with a deposition potential of -900 mV vs. SCE, and a mercury film of 1 μm, and

(ii) 2×10^{-6} M Zn(II), with a deposition potential of -1300 mV vs. SCE, and a mercury film of 32 μm.

In both cases the electrolyte was 0.1 M KNO$_3$, the rate of rotation (ω) 2000 rpm, and the scan rate (v) 40 mV/s.

The results are linear plots with an intercept at (0, 0), confirming the theoretical dependence of peak current on the concentration of the reduced metal in the film, and also confirming that the saturation point is not attained for either Cd or Zn under these conditions.

The relationship between current response and concentration of analyte was verified by measuring the peak stripping current as a function of Cd(II) concentration in the sample solution. Using 1×10^{-6} M to 1×10^{-7} M Cd(II) in 0.1 M

KNO_3, with a deposition time of 100 s at a potential of -900 mV, $v = 20$ mV/s, and $\omega = 2000$ rpm, the results show that the peak current is linear with respect to concentration of Cd(II), with a sensitivity of 2.5 $\mu A/\mu M$ and a correlation coefficient of 0.998.

Scan rate

For bulk mercury electrodes, such as the HMDE, the peak stripping current is proportional to the square root of the scan rate, $v^{1/2}$. For mercury film electrodes the theory of De Vries and Van Dalen [2,3] predicts that i_p is a function of v^α, where α is nearly 0.5 for a thickness of $l > 100$ μm and approaches a limiting value of 1.0 at $l < 10$ μm.

Figure 1 shows a log–log plot of the peak current as a function of scan rate, using test ions of Pb(II), Zn(II), and Cd(II), and for Hg film thicknesses of 2, 8, and 32 μm. Evaluating the slope of the log (i_p) vs. log(v) plot, the exponent of the scan rate, α was found to be ca. 1.0 for all thicknesses. This value is in agreement with the theory [2] for *thin* mercury films. It is interesting to note, however, that these values were obtained even though the other peak parameters (see below) are those normally found with bulk mercury or thick film electrodes.

The variation of the peak potential and half-width with scan rate is shown in Fig. 2a, b. The half-width increased with scan rate as expected, but the increase occurred with thinner films and slower scan rates than predicted by theory [2,3]. It appears that the mercury films behave as though they are 2–3 times thicker in terms of these parameters, even though in terms of others, such as for i_p vs. v, they behave as expected.

Film thickness

In an ASV experiment, the thickness of the mercury film (l) can have a direct effect on the peak potential (E_p), and half-width $(b_{1/2})$, of the stripping peak. The
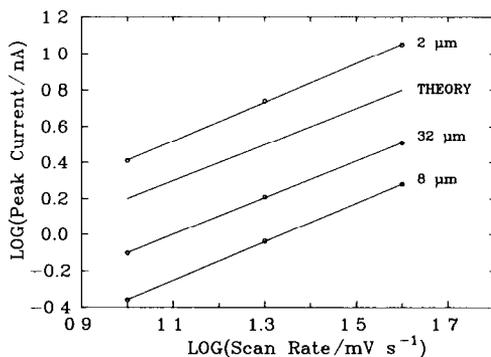

Fig. 1. Log–log dependence of the peak current (i_p) on the scan rate (v), for different film thicknesses. Theoretical curve is for $\alpha = 1$.
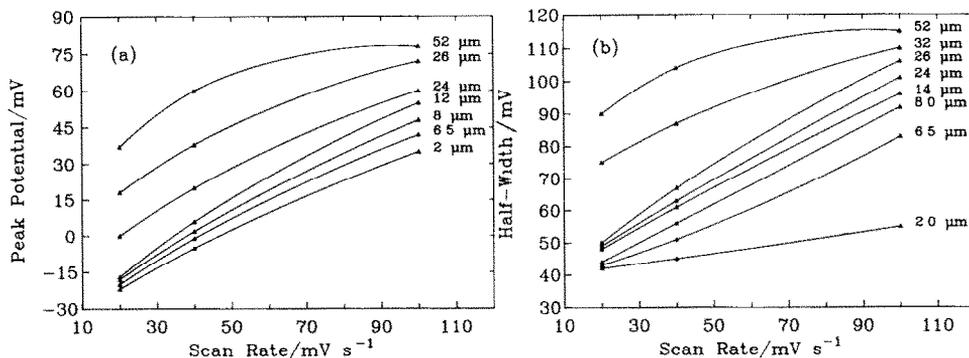
Fig. 2. Effect of scan rate on ASV; (a) peak potential, and (b) peak half-width, for the film thicknesses indicated.

results of varying this parameter are summarized in Fig. 3a, b and discussed in more detail below.

THIN MERCURY FILM BEHAVIOR: THEORY VS. REALITY

The basic theoretical equations of ASV current–potential curves for mercury film electrodes were derived by De Vries and Van Dalen in 1964–65 [2,3], with some contributions made by Roe and Toni [6] a year later. For the reasons given in the introduction, during the past 20 years the theory has been tested only for certain special conditions and electrodes and, as we will show, may not apply to "real world" mercury film electrodes.

The only investigations which attempted to verify the theory specifically were those of Roe and Toni [6], Perone and Brumfield [7], and the group of Stojek Ostapczuk and Kublik [8,9]. Many studies have compared results with theory, but
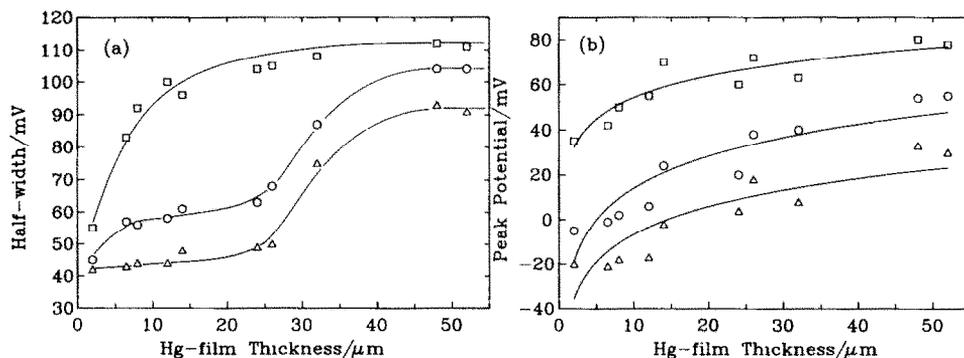

Fig. 3. Effect of mercury film thickness on ASV; (a) peak half-width and (b) peak potential. $v(\triangle)$ 20; ($\bigcirc$) 40; ($\square$) 100 mV/s; solid curves are best spline fit.

TABLE 1

Compilation of experimental results found in the literature for various Hg film thicknesses and on different substrates

l /µm	Elect. subst.[a]	Test ion	$[M^{2+}]$ /mol l⁻¹	[KCl] /mol l⁻¹	t(dep) /s	v /mV s⁻¹	$b_{1/2}$ /mV	$(E_p - E_{1/2})$ /mV	Ref.
7.2	Pt	Pb²⁺	1.2×10^{-5}	0.1	50	20	47	−8	10
4.8	Pt	Pb²⁺	1.2×10^{-5}	0.1	50	20	45	−14	10
2.8	Ni	Cd²⁺	5.0×10^{-5}	1.0	120	18	48	−25	6
2.0	Ag	Cd²⁺	2.0×10^{-6}	0.2	60	20	40	−36	9
1.8	Pt	Pb²⁺	1.2×10^{-5}	0.1	50	20	43	−28	10
1.0	gr	Cd²⁺	5.0×10^{-5}	0.1	600	19	40 [b]	−110	7
1.0	Ag	Pb²⁺	2.0×10^{-7}	0.1	–	20 [b]	38	−42	8
0.6	Pt	Pb²⁺	1.2×10^{-5}	0.1	50	20	42	−40	10
0.01	GC	Pb²⁺	2.0×10^{-7}	0.1 [c]	300	20	36	−100	11
0.01	gr	Pb²⁺	5.0×10^{-5}	0.2	600	13	35	−123	12
0.004	gr	Cd²⁺	1.0×10^{-4}	0.2	600	13	38	−134	12
0.002	gr	Cd²⁺	2.5×10^{-7}	0.1 [d]	180	13	39	−139	12
0.002	gr	Pb²⁺	2.5×10^{-8}	0.1 [d]	180	13	38	−134	12

[a] gr: graphite, GC: glassy carbon.
[b] Estimated.
[c] KNO_3.
[d] pH 4.

usually as an evaluation of the usefulness of their mercury films for total concentration analysis, i.e. for applications where an exact and rigorous correspondence between theory and practice, is not necessary.

Table 1 shows a compilation of the results found in the literature for the values of stripping peak current, peak potential, and peak half-width, along with the electrolytes, ions, and mercury film thicknesses used. Even though it was difficult, we have attempted to find data which are of the same nature for each study, to allow an approximate comparison. The data from Table 1, along with those from this work and the expected theoretical response, are shown graphically in Fig. 4a, b.

The studies can be divided into two groups: those using mercury films $< 1 \mu m$ with carbon substrates; and those using mercury films $> 1 \mu m$ with metal substrates.

There are two important differences that should be noted between these two groups:

(i) For all carbon substrates, the authors claim to have made mercury films of 0.002 to 1.0 μm, and that the characterizing parameters (i.e. half-width, peak current and potential) were generally as predicted by theory.

(ii) For all metal substrates, mercury film thicknesses of 1 to 52 μm were used, and the characterizing parameters generally acted as though the films were much thicker than they really were.

This second point is especially evident for the values of the half-width, $b_{1/2}$. For example, the data from Cox [10] for films of 1 to 7 μm, give values of $b_{1/2}$ of 45–58 mV, which correspond to mercury films of 5 to 20 μm according to the theory of De Vries and Van Dalen [2,3]. In fact, Cox [10, page 58] stated that "... it appears that the mercury film electrode behaves as though the film is considerably thicker than calculated, the 7.2 μm film behaves as the 25 μm film should ...". However, he made no comments or interpretations as to the reasons.
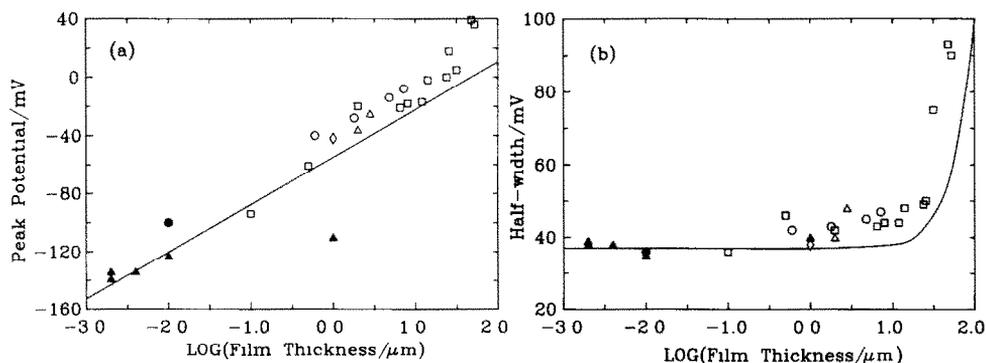

Fig. 4. Comparison of data from both the literature and this work with the theoretical predictions [2,3] for the effect of mercury film thickness on: (a) peak potential, and (b) peak half-width. $v = 20$ mV/s; (———) Theory; (●) GC, (▲) graphite, (○) Pt, (△) Ni, (□) Ir, (◇) Ag.

The true form of a mercury film

We believe that the reason for the above deviation of experimental values from theoretical values is that no such thing as a true mercury film with consistent thickness can exist with deposition of a mercury layer ca. > 1 μm.

Direct substrate–mercury interactions can bind a monolayer of mercury atoms to the surface, and one would estimate that long-range attractive forces could probably also keep at least another 100 layers relatively well attached to the surface. However, mercury having a very low viscosity (0.0156 N s m^{-2}, 20°C) and very high surface tension (480 mN m^{-1}) will, when left on its own, tend to a spherical shape. Taking the radius of the mercury atoms to be 0.157 nm [13], we can estimate roughly that a monolayer is ca. 0.0003 μm, and so we need about 3400 layers for a 1 μm film and more than 1×10^5 layers for a 30 μm film. It therefore seems evident that the bulk of mercury for films > 1 μm is free to take on a natural semi-spherical form.

For equal volumes of mercury deposited as a flat film or a semi-spherical film, the relationship between the thickness of the flat film, (l_f), and the maximum thickness of the semi-spherical film, (l_s), can be written as:

$$\left(\pi l_s/6\right)\left(3r^2 + l_s^2\right) = \pi r^2 l_f \tag{1}$$

with the parameters defined as shown in Fig. 5a, b. For values of $l_f < 100$ μm eqn. (1) simplifies to $l_s = 2l_f$. The maximum thickness is approximately two times greater than that assumed if we had a flat film. At the same time, the decreasing thickness of the film towards the edge of the substrate results in an area where the thickness will always approach zero, regardless of the maximum thickness.

An additional factor which could complicate matters at this point is that in terms of hydrodynamic flow, the Levich theory [14] may not be strictly applicable to a semi-spherical film. In the present case, however, it will be assumed that for films
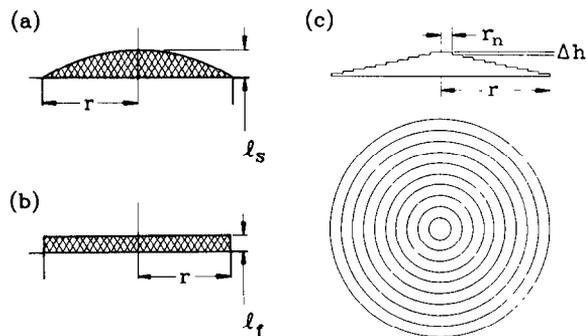

Fig. 5. Relationship between; (a) an equivolume semi-spherical film; and (b) a flat film. (c) Approximation of the semi-spherical film by annular flat films. (Not to scale.)

with a maximum thickness of 52 μm and a substrate diameter of 2000 μm, the hydrodynamic flow at the surface will approximate that of a flat surface.

Comparison of experiment and theory for $l > 1$ μm

For the $E_p - E_{1/2}$ and $b_{1/2}$ data in Table 1 and Fig. 4a, b, the experimental values for films > 1 μm behave as though the films are thicker than given, irrespective of the fact that the data are taken from different studies and for different electrode materials and metal ions. At the same time, the i_p vs. v data (Fig. 1) indicate complete thin-film behavior, i.e. as though $l \ll 10$ μm.

To understand these results better we must take into account the fact that a semi-spherical film will behave as a thicker film at the center of the disk and also as a thinner film at or near the edges. We should then expect that the observed behavior of a "supposed flat film" of thickness l_f, but actually semi-spherical with a thickness l_s, should be a composite of behaviors exhibited by flat films with thicknesses ranging from l_s to almost zero.

There are currently no theoretical equations available for calculating the voltammetric stripping response at a semi-spherical film. However, some of the characteristics can be estimated by assuming that: (i) the semi-spherical film is composed of a large number of annular flat films, and (ii) for a film with a very large ratio of diameter to thickness (e.g. 2000 : 40) the semi-spherical shape can be approximated by a cone. As shown in Fig. 5c, the annuli in this case are taken to be of equal radial width ($r_n = r/10$) and of equal difference in thickness ($\Delta h = l/10$). The area of the annuli, however, increases slowly with increasing radius and must be taken into account for each calculation. The classical thin-film theory [2,3] is then used to calculate the peak response for each annulus; the sum of the peaks being taken as the "equivalent" response for the approximated semi-spherical film. The results of using the above procedure are shown in Fig. 6. For an assumed flat film with $l = 20$ μm, $r = 1$ mm, $n = 2$, and using a stripping scan rate of 20 mV/s, theory predicts a $b_{1/2}$ of 38 mV and a $E_p - E_{1/2}$ of -8 mV. On the other hand, combining the ten peaks for annuli with thicknesses of 40 μm ($l_s = 2l_f$) through 4 μm ($l_s/10$), $n = 2$, $v = 20$ mV/s, and appropriate area, we obtain $b_{1/2} = 48$ mV and $E_p - E_{1/2} = 2$ mV, for a semi-spherical film. The calculated values are in good agreement with the experimental data (Fig. 4). As the film thickness increases (i.e. the ratio diameter/thickness decreases) the divergence from the De Vries and Van Dalen theory should become greater. As the film thickness decreases, the ratio increases, and the two methods should give similar results.

The above description, however, is only an approximation since diffusion can also occur horizontally in the mercury film, especially at slower scan rates and thicker films. The metal oxidized near the edges can thus be replaced by new metal from the thicker center of the film. During the scan, this process may allow oxidation from the thinner part of the film to continue at potentials more positive than would normally be the case, resulting in a shift of the stripping peak to more positive values.
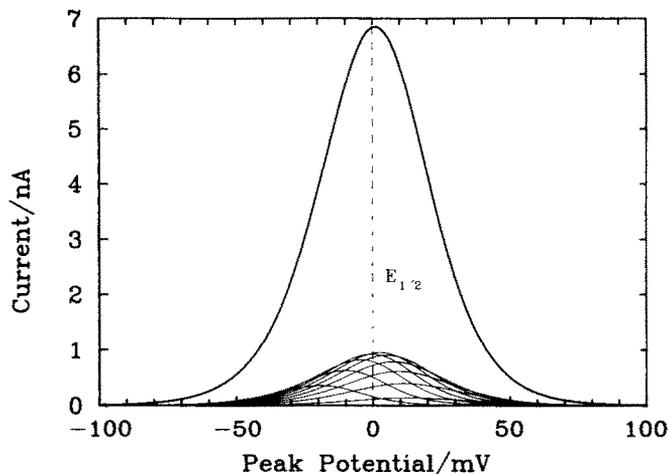
Fig. 6. Approximation of the stripping peak for a 40 μm thick semi-spherical mercury film, by combining the stripping peaks of ten annular flat films (conditions given in text).

The actual shape of an ASV peak, made using a semi-spherical film, could be calculated exactly if the appropriate diffusion equations were solved. Such calculations must be done in order to compare results with theory rigorously. The calculations, though, are no simple matter and have been left for subsequent research.

Comparison of experiment and theory for l < 1 μm

In contrast to the above results, the behavior of mercury films < 1 μm, on both our iridium substrate, and the glassy carbon or graphite substrates used in the literature studies cited, was in good agreement with theory [2,3]. This is to be expected with thinner mercury films on iridium, since we approach the thickness of mercury at which it is easier to maintain a true film due to the interactive forces between the mercury atoms and iridium substrate [15].

In the case of mercury films on glassy carbon, we know the surface is covered not by a true film, but by a very large number of mercury droplets [16]. For the deposition of the mercury equivalent to a flat film < 0.1 μm, these droplets are small enough and close enough in comparison with the diffusion layer thickness to act effectively as a flat surface, and thus agreement with theory is to be expected.

CONCLUSION

We have shown that application of the classical thin-film theory to MFEs of more than approximately 1 μm in thickness is inappropriate since the mercury film assumes an increasingly semi-spherical form beyond that point.

In addition, the work described here shows that the Ir-MFE is useful in obtaining true mercury films without intermetallic compound formation. Although this condition is not necessary for application of ASV to measurements of total trace metal concentrations, it is a characteristic of utmost importance when ASV peak response is to be compared with a well-founded theory, as is the case for speciation studies. We feel that the ability to form real mercury films, without the solvation and amalgamation of the substrate, is of importance in the application of voltammetric techniques to the elucidation of complicated trace metal speciation problems. We have shown here that the Ir-MFE responds as expected under typical voltammetric conditions and techniques used in trace metal determinations.

ACKNOWLEDGEMENTS

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