Iridium Based Ultramicroelectrodes

DEVELOPMENT AND USE IN ELECTROCHEMICAL ANALYSIS

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Electrochemical methods of analysis are of practical advantage in many areas. These include use for determining relevant values in trace-metal pollution studies and remediation; understanding the roles these metals play in biological systems and medicine; characterising materials in the microelectronics industry; developing new energy technologies; and even in fields such as archaeology and forensic science. The direction of research in this area of electrochemistry has been shaped by the increasing demands on analytical chemistry in general to provide the means to accurately determine and characterise traces of heavy metals in the environment. Many of these metals, such as lead, cadmium, arsenic, thallium, zinc and copper, can weave their way through the food chain in the marine and terrestrial environment and eventually accumulate in the vital organs of larger organisms. In humans their toxic effects have been manifested through links to cancer and heart diseases.

Total trace-metal concentrations in natural water samples can be found by various analytical techniques, such as atomic absorption spectroscopy, X-ray fluorescence, neutron activation, and anodic stripping voltammetry. However, as is shown in the Table, the sensitivity which can be achieved with anodic stripping voltammetry (ASV) is unsurpassed, not to mention the low cost of the instruments and ease in sample handling. An additional consideration is that analysis of a water sample for its total trace-metal concentration alone does not necessarily provide the information needed to predict its toxicity. The distribution of an element into its various physicochemical forms, that is its speciation, is also of paramount importance (1). For example, copper in the ionic (Cu^{2+}) or labile ($CuCl_2$) forms is highly toxic, while in the non-labile (CuEDTA) form it is not. Electrochemical methods can offer versatile and efficient approaches for both the measurement and characterisation of dissolved trace-metal species (2, 3).

Anodic stripping voltammetry (ASV) is one of the most sensitive electrochemical techniques (4), and has been used for or is applicable to over 30 metals. The remarkable sensitivity of ASV is obtained through a two step process: [a] a so-called predeposition step, where a cathodic potential is applied at a small film/drop of mercury so that the metal ions in solution are electrochemically reduced and concentrated into the mercury; [b] after a given period of time the applied potential is slowly scanned in the anodic direction, resulting in a peak current at the oxidation potential of the metal, proportional to its concentration.

The most critical component in this technique is the mercury drop or film electrode on which the ASV analysis takes place. There have been two types of electrodes routinely used with ASV, the hanging-mercury-drop electrode (HMDE) and the mercury-film electrode (MFE). The HMDE, a drop of mercury less than 1 mm in diameter suspended from a glass capillary, faces several problems. These are the undesirability of working with bulk mercury, its relative "massiveness" with respect to internal diffusion leading to low resolution or prolonged analysis times, and the uncontrolled solution hydrodynamics and diffusion at its surface during the deposition step. The MFE consists of a flat inlaid disc substrate on which a thin (1–100 μm) film of mercury is electrodeposited. The substrates utilised are either [i] an inert material such as glassy carbon, graphite or carbide, on all of which a "mercury droplet film" forms (5) (even though these type of electrodes have been successfully used for many years for quantitative work, their

Comparison of Analytical Techniques				
Metal	Detection limits, ppb			
	ASV	AA	ICP	NA
Cu	0.5	2	2	2
Sn	0.2	200	3	30
Zn	0.4	0.5	1	2
Hg	0.5	500	50	3
Bi	0.05	40	50	100
Cd	0.005	20	1	5
Pb	0.01	15	20	500
Sb	0.1	30	200	7
Tl	0.01	80	50	—

ASV: Anodic Stripping Voltammetry, ICP: Inductively Coupled Plasma, AA: Flame Atomic Absorption, NA: Neutron Activation

characteristics are far from those of an ideal MFE); [ii] the metals platinum, gold, or silver, all of which dissolve into the mercury (6–8), forming intermetallic compounds with the metals being analysed or eventually converting the film to an amalgam-film, thus severely limiting the utility of such electrodes in studies of fundamental electrochemistry where only mercury electrodes are suitable. It has seemed that finding an "appropriate" substrate on which to form a mercury film has been, to the frustration of many electrochemists, an unattainable goal!

Iridium as a Suitable Substrate

About five years ago, in an attempt to find a more suitable substrate on which to deposit mercury we noticed that although the deposition of mercury on platinum, gold, silver, nickel, and carbon was well documented in the literature, the same could not be said for iridium. A literature search going back 30 years found only four articles dealing with mercury deposition onto iridium, and these were concerned with mercury as a poison for hydrogen or oxygen adsorption. There were and are several reasons for the lack of interest in using iridium as an electrode in electroanalytical techniques. Although iridium is similar to the other noble metals, it is substantially harder, more inert, and was less available and more expensive. These properties made it difficult to

mount, and make electrical connections with; and it was generally overlooked because of its high cost. These problems do not exist to the same extent today thanks to improved electrode fabrication techniques and the drop in price differential between platinum, gold, and iridium.

Using data from both theoretical calculations (9) and experimental studies (10), we concluded that iridium was indeed a viable substrate for the formation of a mercury film or semisphere. We showed that this noble metal possesses two properties which make it ideal for this use; first its solubility in mercury is less than 10^{-6} per cent by weight; and second, mercury can be electroplated onto iridium discs (1–4 mm dia.) in such a way as to give a uniform film or semispherical coverage. We also found that the electrode behaved according to thin film theory and could be used for analysis (11).

Ultramicroelectrodes

Ultramicroelectrodes (UME), which are typically less than 10 μm in size, have been shown to possess several unique properties for electrochemical analysis, and in the past few years have rapidly become routinely used in many laboratories (12). As with larger electrodes, the most common types are prepared either from platinum, gold, or carbon fibre. Platinum UMEs have been fabricated down to diameters as small as 0.003 μm and in various geometries such as disc (13, 14), cylindrical

(15), and conical (16). Typical carbon fibre electrodes have diameters in the range of 5–20 μm and are similarly used, either as fibres of 1–5 μm length or as discs (12).

Attempts have been made by several groups at fabricating micron sized mercury UMEs on platinum (17–19) and carbon fibre substrates (20). As with the larger electrodes, the dissolution of the platinum in the mercury was found to give intermetallic interferences in the analyses (18). However, the advantages of a mercury UME were clearly evident.

Until recently the only attempt at fabricating an iridium based mercury UME had been made using a 127 μm diameter iridium wire (21). However, because of its rather large size, its characteristics were not those of a micron range UME. No attempts at fabricating iridium UMEs of less than 127 μm have been recorded in the literature to date. This is most likely because of the commercial unavailability of finer iridium wire, probably caused by difficulties in drawing iridium to less than 127 μm.

An Iridium Ultramicroelectrode

Over the past year we have attempted several procedures for fabricating an UME from commercially available 127 μm diameter iridium wire. The most successful technique developed has been to electrochemically etch the 127 μm diameter iridium wire in a molten salt mixture consisting of sodium chloride and sodium nitrate at 350°C using a square wave potential of ±5 volts at 10Hz, applied between the iridium wire and a platinum crucible containing the melt (22). The resulting iridium wire, with a diameter in the 5–20 μm range, is sealed in a 0.1 mm glass capillary, with the tip then being made plane and polished. The iridium UME, shown in Figure 1, can then be used directly, or as a substrate for the deposition of the mercury. The mercury adheres well and is stable for long periods of time. These electrodes have been characterised by optical microscopy, cyclic voltammetry, and chronoamperometry, and have been shown to exhibit microelectrode behaviour. By applying the technique of square wave anodic stripping voltammetry, (23), these
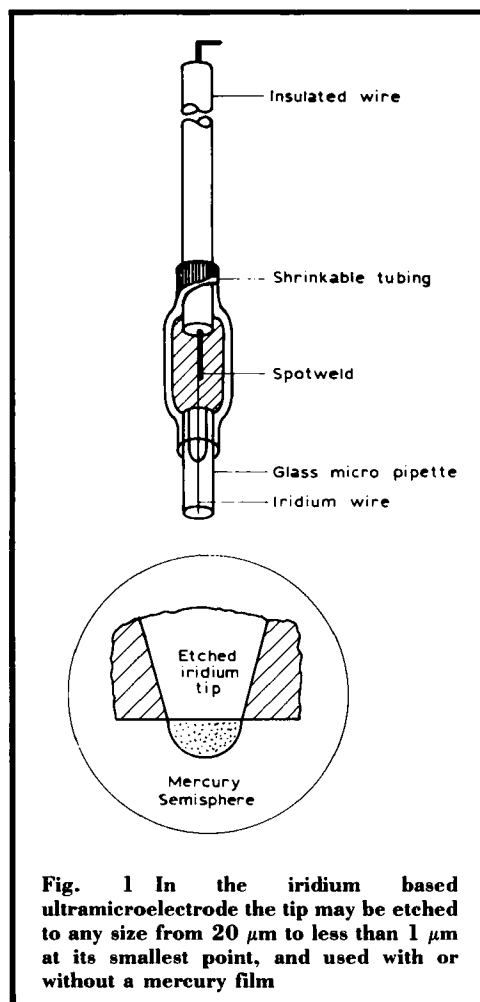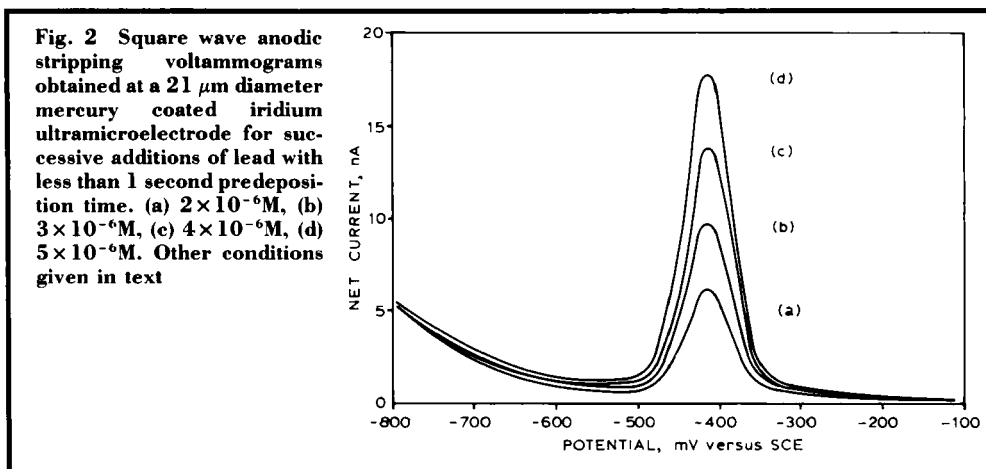

Fig. 1 In the iridium based ultramicroelectrode the tip may be etched to any size from 20 μm to less than 1 μm at its smallest point, and used with or without a mercury film

mercury UMEs have been used to determine lead at molar concentrations of 10^{-4} to 10^{-9} M (24). For example, in a solution containing 10^{-6} M Pb(II) with no separate predeposition step, the mercury UME gave excellent results. A typical analysis with standard additions is shown in Figure 2. The Pb(II) analysis was carried out in 0.1M HClO$_4$, with a square wave frequency of 30Hz, step height of 5mV, pulse amplitude of 25 mV, and with no stirring or deoxygenation.

Because of the unique properties of ultramicroelectrodes, they can be used in analyses with sample volumes in the microlitre range; without stirring of the solution; without

Fig. 2 Square wave anodic stripping voltammograms obtained at a 21 μm diameter mercury coated iridium ultramicroelectrode for successive additions of lead with less than 1 second predeposition time. (a) 2×10^{-6}M, (b) 3×10^{-6}M, (c) 4×10^{-6}M, (d) 5×10^{-6}M. Other conditions given in text

deoxygenation; and because of the small volume of mercury, a very short or even no predeposition time of the metal into the mercury is required. The iridium based micro mercury electrode appears to be a stable and rugged mercury electrode with potential uses for in situ and in vivo electrochemical analysis.

Conclusion

As shown by the initial work with iridium, it possesses many desirable properties for use as an electrode material either in pure form or as

substrate for mercury. The renewed interest, and recent advances in working and fabricating micro iridium structures, appear to augur well for the increasing use of iridium as an electrode material in both electroanalytical and other electrochemical techniques.

In addition to this, the ability of iridium to hold several layers of mercury on its surface through attractive forces and not by chemical bonding, makes it therefore a unique candidate for further studies in several areas of interface and surface science.

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