ADSORPTIVE STRIPPING VOLTAMMETRY IS INTERESTING: IS IT USEFUL?

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ABSTRACT

Voltammetric investigation of a chemical species after accumulation on a hanging mercury drop electrode can be very interesting chemically. Histidine-containing peptides, for example, are frequently found to have accumulated as copper(I) complexes. The mechanism of adsorption can be altered by modifying the HMDE, for example with polyaminoacids. Chemical transformations can be observed to be occurring on the electrode surface, particularly during repeated cycles in cyclic voltammetry.

But is adsorptive stripping voltammetry (AdSV) useful analytically? It is an accepted method for the determination of at least eight trace metals in seawater and other water samples. Its acceptance is partly owing to the ease of destroying organic interferences by means of UV irradiation. But what about the determination of organics? Here, usually, some form of separation is required, and the use of solid phase extraction cartridges seems to be particularly appropriate.

Keywords: adsorptive cathodic stripping voltammetry, peptides, polyaminoacid films, modified electrodes, analytical technique.

Introduction

The average industrial analytical chemist prefers not to use voltammetry. It is a complementary technique, which he will use only if nothing else works. Adsorptive stripping voltammetry (AdSV) is a very simple technique using modern forms of the hanging mercury drop electrode (HMDE). The problem with this electroanalytical technique is still the lack of selectivity and the problem of interferences. AdSV is ideal for trace metals in seawater, because UV irradiation can be used to remove trace organics that would interfere. Van den Berg and coworkers, in particular, have produced some neat methods to overcome other difficulties, such as interferences between metals. Solid phase extraction cartridges have been used effectively with AdSV. AdSV with the HMDE can be used conveniently to study bioinorganic problems. The use of modified HMDEs provides interesting chemistry and could provide selectivity. Preliminary studies with modifiers for HMDEs can be extended for use with solid electrodes in sensor devices.

Determination of metals

Anodic stripping voltammetry (ASV), in which metal ions are accumulated by reduction to an amalgam and then determined by reoxidation, was the common voltammetric method for determining copper, lead, cadmium and zinc: it is still the 'blue book' method for determining cadmium and lead [1]. At levels of these metals found in blood the HMDE can be used, but at the levels in seawater a rotating mercury film electrode has to be used owing to difficulties caused by diffusion of amalgam into, and away from the surface of, the mercury drop.

In AdSV metal ions are determined by reduction after accumulating them as a metal complex on an HMDE: here there is no problem with diffusion into the drop, and modern HMDEs are extremely convenient to use. Another advantage of AdSV is that it is applicable to a far wider range of metal ions. "Blue book' methods are available for the determination of copper and vanadium as catechol complexes, zinc with APDC, nickel and cobalt with DMG, uranium with 8-hydroxyquinoline, aluminium with DASA, and iron with 1-nitroso-2-naphthol [1,2]. The determination of aluminium is an indirect method as it is the ligand that is reduced. Determinations can usually be made at about the 10^{-9}M level, but even lower detection limits can be reached if the reduction of the metal complex is coupled with an oxidant in solution in a catalytic reoxidation: such methods are currently available for chromium, molybdenum, titanium and platinum [2].

Van den Berg and coworkers have introduced some neat methods of overcoming some metallic interferences. Tin is usually determined as the tropolone complex, but molybdenum is more plentiful in seawater, and is also accumulated and interferes. ASV cannot be used as the lead peak is too close. In the recommended method [3] tin amalgam is accumulated at -0.8V, tin is reoxidised to form instantly the adsorbed tropolone complex, and the tin is determined reductively before the molybdenum has time to accumulate. Total chromium [4] is determined by means of the catalytic DTPA complex reaction. At the accumulation potential chromium(VI) is reduced to chromium(III) and the chromium(III)-DTPA complex is adsorbed and is determined by reduction to chromium(II) at -1.27V. The chromium(III)-DTPA complex relaxes to an electroinactive form, and if DTPA is added to the sample solution containing chromium(III) and chromium(VI), the chromium(VI) can be determined as above after the original chromium(III)-DTPA complex formed has become inactive [4]. With UV irradiation selenium(VI) is reduced to selenium(IV), and this can be accumulated and determined as copper(I) selenide [5].

Mlaker and Branica have showm that uranium can be determined using a mixed ligand complex with TBP and 2-thenoyltrifluoroacetone [6].

Determination of organics

If an adsorbed substance is reversibly reduced, then it may be possible to accumulate it in the reduced state. This has been illustrated by van den Berg in determining nitrite in seawater by reacting it with sulphanilamide which is then coupled with 1-naphthylamine: either the azo or the hydrazo compound can be accumulated, although accumulation of the azo compound is more favourable in this case [7]. This possibility should be born in mind by workers developing AdSV methods for organics.

Our first paper on AdSV was with the permitted synthetic food colouring matters [8], which make good test substances. Use of an HMDE modified by the addition of phosphonium compounds, which shifts reduction potentials and can enhance or reduce peak currents, allowed the partial identification of some food colours, such as tartrazine, at levels below which they can be seen visibly. AdSV was applied to real samples, viz. tablet coatings and lipsticks, with sample pretreatment methods in the latter case.

Kubiak and Wang [9] removed the non-ionic surfactant, Triton X-100, from organic determinands in aqueous solution by adsorbing it onto fumed silica.

A study of the copper complexes of imidazole was made early in our investigations of the AdSV of peptides and related substances [10]. Two distinct peaks are obtained, and the interconversion of the complexes responsible can be observed by carrying out repeated cyclic voltammetric scans on the adsorbed species. The second peak is most probably the reduction of the highest mononuclear copper(II)-imidazole complex. The first peak could well be due to the reduction of a copper(I) polymeric complex. Previously, preliminary studies on the AdSV of copper complexes of histidine-containing peptides were reported [11]. Further studies have shown that, in determining ggh and ghg by AdSV it is the copper(I) complex that is accumulated. In carrying out cyclic voltammetry in the presence of excess peptide, two peaks are obtained in each cases. In the case of ggh a peak due to reduction of the copper(I) complex occurs at a less negative potential than that due to reduction of the copper(II) complex [12], whereas for ghg the copper(II) complex is the more easily reduced (to be published).

Preliminary studies of the use of polyaminoacid films on an HMDE were also reported [11], in particular the difference in the accumulation mechanism of copper hexacyanoferrate(III) at bare and poly-L-lysine-modified HMDEs [13]. Poly-L-lysine might be expected to act as an anion exchanger, and there is evidence that this is the case. However, as a result of our selection of other reducible anions for study, several anti-asthma and other drugs (including sodium cromoglycate [14] and Nedocromyl (to be published)) have been shown to be determinable by AdSV at bare HMDEs. We hope to be able to report shortly on the application of polyaminoacid-modified solid electrodes for sensor use.

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SEPARAÇÃO E DETERMINAÇÃO POLAROGRÁFICA DE ÁCIDO SULFANÍLICO E TARTARAZINA

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The determination of sulfanilic acid in the colouring matter tartrazine was undertaken. Sulfanilic acid is determined by differential pulse polarography after derivatisation to an azo compound (diazotisation /coupling procedure). Being an azo compound too, tartrazine will interfere in the polarographic determination of derivatized sulfanilic acid. To solve this problem two approaches were tried successfully: a chromatographic separation and a masking procedure for tartrazine. Separation was achieved in a column packed with Amberlite XAD-2. Addition of gelatine caused the elimination of polarographic peak of tartrazine, allowing the determination of derivatized sulfanilic acid without need of a separation procedure.

A importância atribuída aos métodos de determinação de aminas aromáticas primárias está intimamente relacionada com o reconhecimento da toxicidade desses produtos (envenenamento por absorção percutânea e efeitos cancerígenos). Por outro lado, grande número de corantes sintéticos usados em alimentos pertencem à classe dos corantes azóicos, cuja síntese é efectuada precisamente a partir de aminas aromáticas primárias. Atendendo a tudo isto, é evidente o interesse na determinação dessas aminas nos correspondentes corantes sintéticos.

No seguimento do estudo efectuado por J. A. Rodrigues e A. A. Barros (1), sobre a determinação de anilina no corante azóico D&C Red Nº 33 (uma amina pouco solúvel em água num corante hidrossolúvel), procurou-se avançar para um caso mais comum de quer a amina quer o corante terem solubilidades semelhantes em solução aquosa, situação em que não é aplicável o processo de extracção com solventes utilizado nesse trabalho referido. Assim, decidiu-se proceder ao estudo da determinação do ácido sulfanílico na tartarazina (FD&C Yellow Nº 5), corante azóico sintetizado a partir do referido ácido. Refira-se que a tartarazina, identificada em termos de legislação da Comunidade Europeia como o aditivo E102, é um dos corantes sintéticos mais utilizado em alimentos, sendo o mais importante dentro do grupo dos amarelos.

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