ADSORPTIVE STRIPPING VOLTAMMETRY

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Abstract

After the impact produced by the introduction of anodic (and cathodic) stripping voltammetry as a very convenient method for the analysis of ultratrace compounds, specially metal ions, alternative methods for the pre-concentration step were investigated to extend the field of application of the stripping techniques to non-electroactive species. In adsorptive stripping voltammetry, species with some tendency to be adsorbed at electrode surfaces can be pre-concentrated in this way and then stripped just as in anodic or cathodic stripping voltammetry.

This lecture is sarted with a general view of the methods used in the pre-concentration step of stripping voltammatric methods. Afterwards, focus is moved to adsorptive stripping voltammetry: first, some simple theoretical aspects are considered, related with the steps of adsorption and stripping; then, a reference is made to instrumentation, methodology and elimination of interferences; finally, examples of the use of the technique are presented.

Resumo

Depois do impacto causado pela introdução da voltametria de redissolução anódica (e catódica) como um método de análise de ultravestígios de muitos compostos, designadamente iões metálicos, começaram a surgir métodos alternativos de acumulação, que permitiram alargar a espécies não electroactivas o campo de aplicação das técnicas de redissolução. Na voltametria de redissolução com adsorção, as espécies que tenham alguma tendência para serem adsorvidas à superfície de eléctrodos são acumuladas desse modo e depois desalojadas por um processo idêntico ao utilizado na voltametria de redissolução anódica ou catódica.

Esta lição começa com a apresentação geral dos métodos de pré-concentração utilizados nas técnicas voltamétricas de redissolução. Segue-se a abordagem da voltametria de redissolução com adsorção: primeiro, referem-se alguns aspectos simples ligados às fases de adsorção e de redissolução; depois, tecem-se algumas considerações sobre a instrumentação, a metodologia e a eliminação de interferências; por fim, são dados alguns exemplos de aplicação da técnica.

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I. INTRODUCTION(1,2)

1. USE OF PRECONCENTRATION IN QUANTITATIVE ANALYSIS

Among the most important tasks of modern analytical chemistry is the quantitation of trace and ultratrace components in complex samples of environmental,industrial or biological origin.

In the analysis of very dilute samples,it is often necessary to employ some type of preconcentration step prior to the actual quantitation(simultaneously it can serve to isolate the analyte from the complex matrix).

2. PRECONCENTRATION IN ELECTROCHEMISTRY

2.1. Preconcentration involving a faradaic process

In the content of electrochemistry,preconcentration is usually accomplished by electrolytic deposition.The most common method using this preconcentration process is stripping voltammetry,which incorporates two main versions:anodic stripping voltammetry(ASV) and cathodic stripping voltammetry(CSV).

ASV was the first method to be developed and is still the more popular.This is a consequence of its ability to analyse traces of several heavy metal ions using a hanging mercury drop electrode(HMDE) or a mercury film electrode(MFE).Preconcentration is performed by reduction of the metal ion at a potential selected in the diffusion current region for a length of time depending on the solution concentration and under controlled stirring.After a rest period,the potential is scanned towards less negative values in order to oxidize the amalgamated metal,which is released.

CSV has been used to determine several organic compounds or anions such as halides,sulphide,selenide and some oxyanions that form insoluble salts with the oxidized electrode,usually a mercury or a silver electrode.The application of a relatively positive deposition potential results in the formation of an insoluble film on the electrode surface.The stripping step occurs during a negative potential scan,corresponding to the reduction of the cation at the electrode.

Numerous important analytes are not accessible to conventional stripping measurements because of the electrolytic nature of the preconcentration step and this is a limitation to ASV and CSV;nevertheless,in view of the inherent sensitivity afforded by analyte accumulation prior to voltammetric measurements,intense activity has been devoted to the development of alternative methods for the preconcentration step that do not include any faradaic process.

2.2. Nonelectrolytic preconcentration

The area of voltammetry following nonelectrolytic preconcentration is a fascinating field of research.The two major non faradaic routes for effective preconcentration include accumulation at ordinary electrodes and specific reactions at chemically modified electrodes.Only the former will be considered here,as the first step of adsorptive stripping voltammetry.

Numerous organic derivatives exhibit adsorption phenomena which are generally considered to have adverse effects on voltammetric measurements.In adsorptive stripping voltammetry(AdSV) however,this adsorption process is purposely used as a preconcentration step.As a result,a wide variety of substances possessing surface-active properties are easily measurable at the subnanomolar concentration level.

The principle of the method can be compared to that of anodic or cathodic stripping(Figure 1),except that no charge is transferred during the preconcentration step.Accumulation of the compound at the electrode surface is performed at open circuit or by applying a suitable potential at which no electrochemical reaction occurs.After an equilibration time,the potential is scanned anodically(AdASV) or cathodically(AdCSV),depending on the redox properties of the compound;in some cases of electroinactive derivatives,a tensammetric peak can be recorded.

In a simplified way,it is possible to say that both adsorptive and electrolytic methods are performed in two steps,deposition and stripping,separated by a rest period,for equilibration,as it is schematically depicted in Figure 1 and in Table 1.

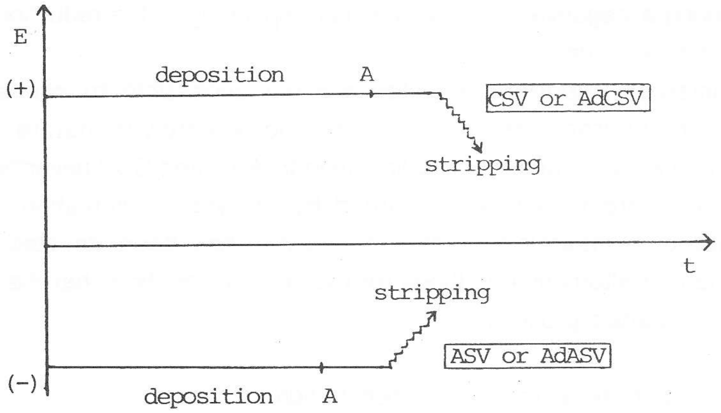


Figure 1. Time dependence of potential in stripping voltammetric methods. A - stirring is stopped.

Table 1. Stripping voltammetric methods

Technique	Methodology
ASV	$M^{n+}_{(aq.)} + Hg + ne \underset{\text{stripping}}{\overset{\text{deposition}}{\rightleftarrows}} M\,(Hg)$
CSV	$2Cl^- + 2Hg \underset{\text{stripping}}{\overset{\text{deposition}}{\rightleftarrows}} Hg_2Cl_{2(s)} + 2e$
AdSV	Analyte (solution) $\overset{\text{deposition}}{\rightleftarrows}$ Analyte (adsorbed) ① ① $\xrightarrow{\text{stripping}}$ $\left\{\begin{array}{l}\text{Reduction (AdCSV)}\\ \text{Oxidation (AdASV)}\\ \text{Tensammetric dessorption}\end{array}\right.$

II. ADSORPTIVE STRIPPING VOLTAMMETRY(AdSV)

1. THEORY(1,3,4)

Generally,when developing a quantitative method for the analysis of species in solution it is very convenient if a linear relationship can be established between the concentration of the analyte in the bulk of the solution and the instrumental response.

In the case of adsorptive stripping voltammetry,in which the current intensity produced during the stripping of material from the electrode is the variable measured,the possibility of obtaining a linear calibration will depend simultaneously on the process of adsorption of the analyte(deposition step) and on the form of the scanning potential used top produce the voltammetric response,assuming that there are no kinetic problems.

As we will see,conditions can be established for the existence of linear relationships between the bulk concentration of the analyte and its concentration after deposition and between this and the current intensity produced during the stripping step.Consequently a voltammetric response directly proportional to the bulk concentration of the analyte can be obtained.

1.1. The adsorption step

The action of interfacial forces at the boundary between two phases leads to the formation of an interface with a thickness usually comparable to molecular dimensions.If these interfacial forces lead to an increase in the concentration of some substance at the interface compared to the concentration in solution,then this substance is adsorbed on the surface of the other phase.

In electrochemistry,adsorption generally means the attachment of molecules or ions to the surface of electrodes.Our discussion will be limited to specific adsorption,which takes place in the compact double layer(unlike non-specific adsorption,which includes long-range electrostatic forces).

Adsorption equilibrium is established between the concentration in the solution and that on the surface of the electrode.At a given temperature,the amount of substance adsorbed is dependent on its concentration in solution and on the adsorption coefficient,a parameter that measures the interaction between the adsorbed species and the surface.

The velocity of formation of the adsorbed layer is affected both by the rate of the actual adsorption of the substance from the solution layer in direct contact with the electrode and also by the rate of transport of the substance from the bulk of the solution to the electrode surface.The slower of these two processes then becomes the rate-controlling step in the formation of the adsorbate.

In a simple way,adsorption of a solute can be visualized as a displacement process in which molecules or ions of solvent are replaced at the electrode surface by molecules or ions of solute.The extent of adsorption is often related to the solubility of the reactant in the solvent concerned.Smaller solubilities tend to promote strong adsorption.Besides the hydrophobicity of adsorbate,other driving forces can lead to adsorption at electrode surfaces,such as electrostatic attraction between an ionic adsorbate and a charged electrode,field-dipole interaction between the electrode double-layer and functional groups of organic reactants,or chemisorption of certain electron or atomic groups on metallic electrode surfaces.

Equilibrium relationships between concentration of adsorbate on the surface and in the bulk of the solution are known as adsorption isotherms.The relationship most frequently used is the Langmuir isotherm,which assumes that there are no interactions between adsorbed species on the electrode surface,with the maximum surface coverage being a complete layer,generally a monolayer.The Langmuir isotherm can be expressed by:

$$\tau = \tau_m \left(\frac{BC}{1+BC} \right) \quad \text{,with}$$

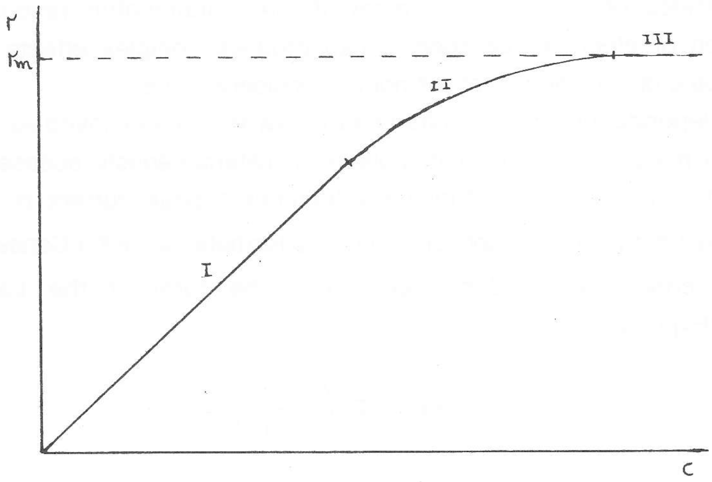
τ - surface concentration of adsorbate.

τ_m - surface concentration corresponding to a monolayer.

C - bulk concentration of adsorbate.

B - adsorption coefficient(depending on the interaction between the adsorbed species and the surface).

The Langmuir isotherm can be represented graphically as follows:



At low bulk concentrations of adsorbate($BC<<1$) its surface concentration, τ, is directly proportional to the bulk concentration(section I).This linearity is lost with increasing bulk concentration,as surface coverage becomes appreciable(section II).Finally,when full coverage is attained ($BC>>1$) surface concentration of adsorbate reaches the maximum value τ_m and becomes independent of the bulk concentration of adsorbate(section III).

<u>section I</u> : $BC<<1$ ===> $\tau = \tau_m BC = KC$ (low coverage).

<u>section II</u> : τ is not directly proportional to C (intermediate coverage).

<u>section III</u> : $BC>>1$ ===> $\tau = \tau_m$,independent of C (full coverage).

Obviously,when using adsorption as a preconcentration step for a quantitative method of analysis it is convenient that the situation depicted in section A is fulfilled.

1.2. The voltammetric response

Besides possible enhancement of the voltammetric response,the adsorption of electroactive species can produce complex effects on the voltammetric observations,that will not be considered here.

Independently of the voltammetric waveform employed,as all the adsorbed material,being in a monolayer,is instantaneously accessible for reduction or oxidation,the stripping voltammetric peak current is directly proportional to the surface concentration of adsorbate($i_p = K\tau$).Consequently its bulk concentration dependence has the form of the Langmuir isotherm(Figure 2) :

$$i_p = K\tau = K\tau_m \left(\frac{BC}{1+BC} \right)$$

At low analyte levels(10^{-7} - 10^{-10} M),for which the method is usually applied,a linear adsorption isotherm is obeyed,with the slope of the resulting linear calibration plots proportional to τ_m B :

$$BC<<1 ===> i_p = K\,\tau_m\,BC.$$

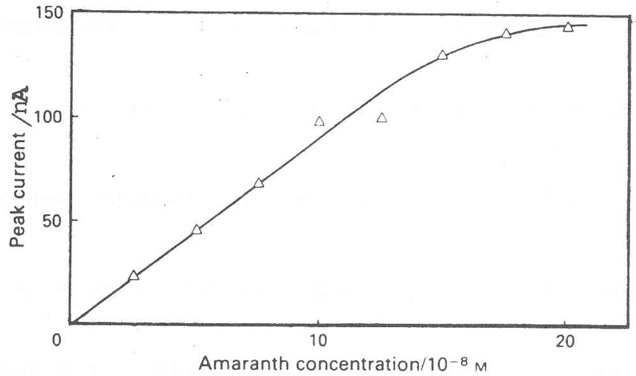


Figure 2. DPP calibration curve for amaranth in pH 10 buffer.Accum. pot. = -40 mV;accum. time = 3 min.

The most popular waveform used for the potential scan is that employing the differential-pulse modulation,probably as it is available on all commercial equipment.This type of scan is adequate for anodic stripping voltammetry where the metal diffuses out of the mercury drop,limiting the rate at which scans can be carried out. In adsorptive stripping, as all the material is present in a monomolecular layer, the reduction current is independent of the diffusion of the reactant and relates directly to the scan rate. An increase in sensitivity can therefore be obtained if higher scan rates are employed, as can be seen with peak 2 in Figure 3(5). Nevertheless the form of the potential scan employed in differential-pulse voltammetry is not compatible with very high scan rates, suggesting that other potential modulations less restrictive on this particular point can be advantageously used in connection with adsorptive preconcentration.

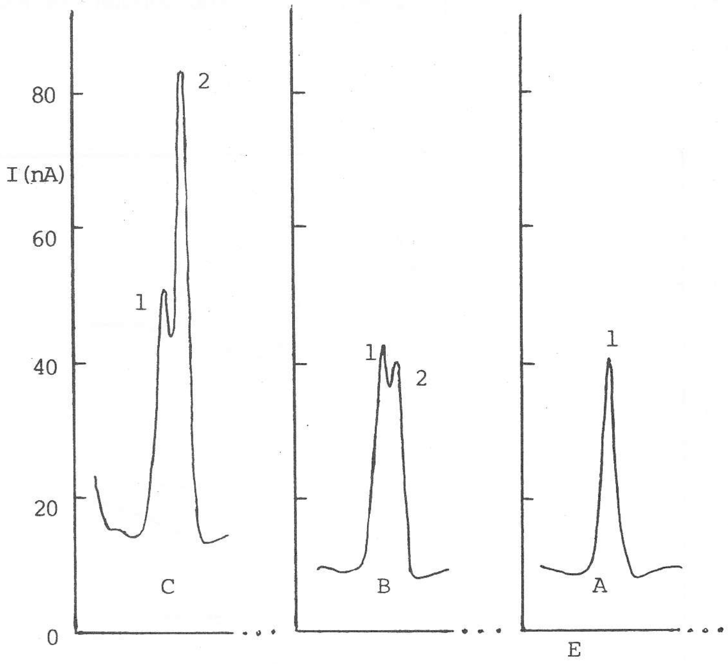


Figure 3. DPP determination of a mixture of D & C Red 6 (peak 1) and D & C Red 8 (peak 2). A - t_{step} = 5 s (scan rate = 2 mV/s); B - t_{step} = 1 s (scan rate = 10 mV/s); C - t_{step} = 0.2 s (scan rate = 50 mV/s). E_{set} = -350 mV; E_{end} = -900 mV.

As a consequence,a more recent technique,square wave voltammetry,is becoming more popular,as it can be carried out at very high frequencies by reducing the width of the potential step.Van den Berg found that the peak current obtained using adsorptive cathodic stripping voltammetry(AdCSV) for copper in sea water is greatly enhanced as a result of increasing the frequency of the square-wave modulation(Figure 4).This increase was achieved by shortening the potential step -width;the current was therefore measured earlier after the onset of each potential step and this increased the contribution of the faradaic current but also that of the capacitance currents.The background current of each scan can therefore be seen to rise,but the peak height rises more rapidly and the background current can be subtracted as it is comparatively smooth and constant during a scan anyway.

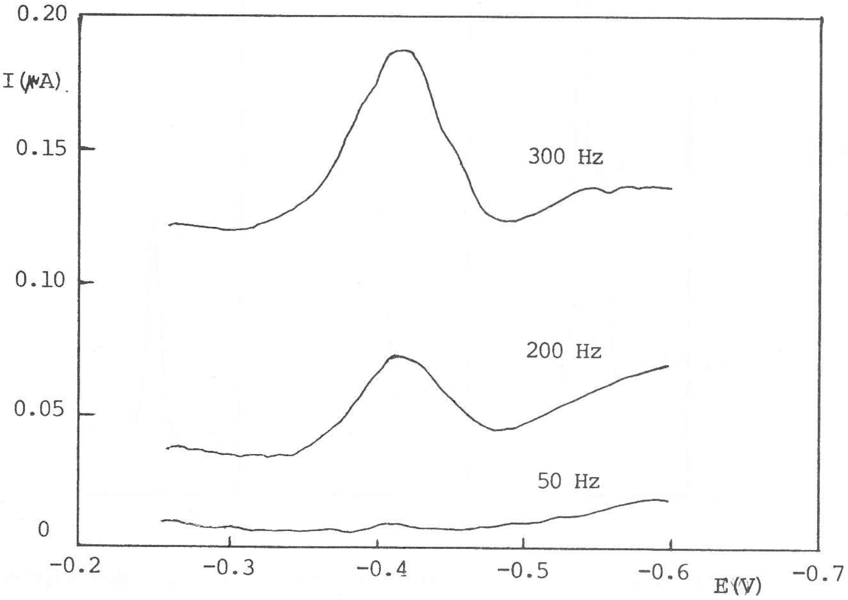


Figure 4. Effect of increasing the square-wave frequency on the peak current for 2 nM Cu in sea water.

2. INSTRUMENTATION (3)

The instrumentation used in AdSV is the same as for ASV or CSV and a commercially available polarograph can be used.However,a computerized instrument with automatic timing of the successive operations is useful for this purpose.

AdSV can be performed with any electrode used in direct voltammetry,provided that a reproducible and constant surface area can be ensured during a series of measurements.When the adsorbed layer is to be reduced,the HMDE remains the best choice since the drop is renewed after each scan with high reproducibility when an automatic stand is used.Oxidation processes require a metallic or carbon solid electrode.Platinum and glassy carbon electrodes have been proposed as well as carbon paste electrodes,the surface of the latter being more easily renewed by removing the surface layer of the paste.Reproducibility is however not as good as that of the HMDE which also gives lower detection limits.It should be noted when using a carbon paste electrode that the compound can be accumulated not only as a result of adsorption but also by dissolution in the pasting liquid of the carbon paste.In some applications the proper choice of the pasting liquid may lead to higher selectivity.

3. METHODOLOGY (6)

In order to decide if adsorptive stripping voltammetry should be used,a direct voltammogram of a solution 10^{-7} - 10^{-8} M in the compound should be recorded.This should be repeated after imposing the initial potential during a short period (1 or 2 minutes) under stirring conditions.A comparison of the curves will immediately show a substantial increase of the peak current if the compound has been accumulated at the electrode surface(Figure 5).

To achieve maximum sensitivity,optimum conditions should be utilized.The adsorption process depends on many variables such as solvent,nature and concentration of the supporting electrolyte,pH,mass transport,temperature and deposition potential.Adsorptive stripping procedures generally utilize aqueous solutions since most neutral organic analytes are adsorbed as a result of hydrophobic forces.With aqueous solutions,the analyte concentration remains sufficiently low to avoid solubility problems.The influence of pH should be investigated since adsorption processes strongly depend on this parameter.Significant enhancement of the peak can result from the selection of the optimal pH value as can be seen in Figure 6.The choice of the supporting electrolyte is also of great importance since it can affect the intensity and the shape of the peak.In some cases where a buffer is not required it is more convenient to use a simple supporting electrolyte known to be non-adsorbed,as sodium perchlorate or dilute acids or bases.As the AdSV peak height often increases up to 7% on an increase in the solution temperature by one degree Celsius(depending on the substance studied),the temperature control must be imposed when doing quantitative work.

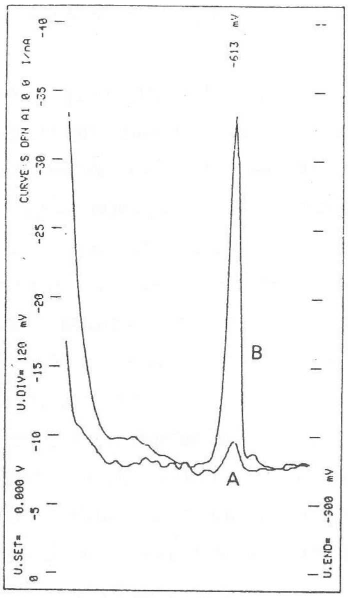


Fig. 5. Differential-pulse adsorptive stripping voltammograms for amaranth (3×10^{-8} M) in pH 10 buffer. Accumulation time: A, 0; and B, 3 min.

Several operating parameters are also top be investigated. The accumulation should proceed at the potential of maximum adsorption. For neutral molecules, a potential corresponding to the electrocapillary zero value is generally favourable and an open-circuit accumulation may be performed. However, when the charged or neutral character of the molecules is not known, it is often better to record several voltammograms after the accumulation has been performed at different potentials(Figure 7). The change of the peak height as a function of the deposition potential will indicate the optimum value. However, this choice may be subject to a compromise if interfering compounds are present in the sample.

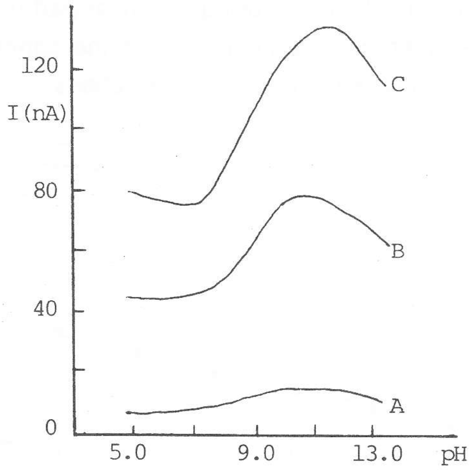


Figure 6. Influence of pH on the AdSV(DPP) of 20 p.p.b. of aniline, after derivatization(diazotization and coupling with α- naftol). Acc. time(min): A-0; B-1; C-2.

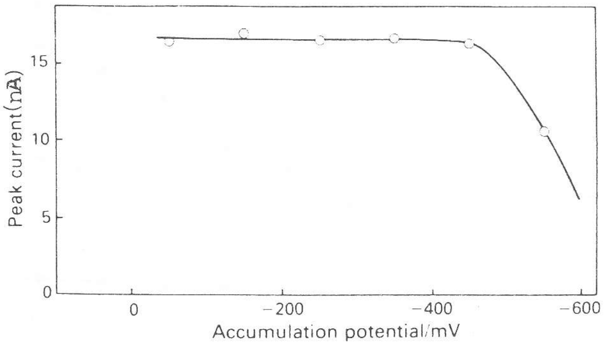


Fig. 7. Effect of accumulation potential on the differential-pulse adsorptive stripping peak height for a 3×10^{-8} M amaranth solution in pH 10 buffer. Accumulation time, 2 min; peak potential, −620 mV

The relationship between the amount of accumulated compound and the deposition time should be linear,indicating a constant adsorption rate.This increase will reach a maximum value rapidly at a rate depending on the solution concentration and on the degree of saturation of the electrode surface(Figure 8)

Linearity between the peak height and the concentration is generally observed between 10 $^{-7}$ and 10^{-9} M but ,depending on the adsorption properties of the compound,this range can be extended from 10 $^{-6}$ to 10 $^{-10}$ M with detection limits of about 10^{-11} M.At high concentrations,the curve deviates from linearity due to the saturation of the electrode surface.Since analytical measurements must be made using the linear part of the curve,such concentrations will be determined after dilution of the sample or by using shorter accumulation times(Figure 9) or unstirred solutions.

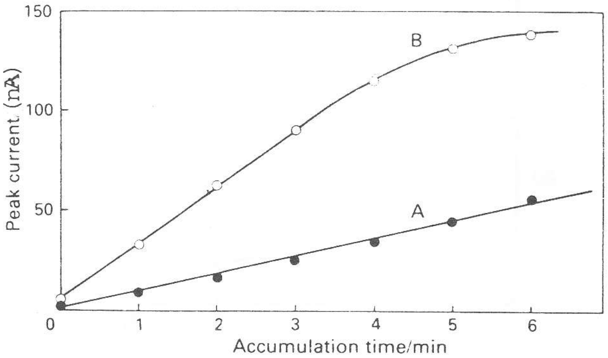


Fig. 8. Effect of accumulation time on the differential-pulse adsorptive stripping peak height for amaranth solutions in pH 10 buffer. Accumulation potential, −400 mV; peak potential, −620 mV. Amaranth concentration: A, 3 × 10^{-8}; and B, 10 × 10^{-8} M

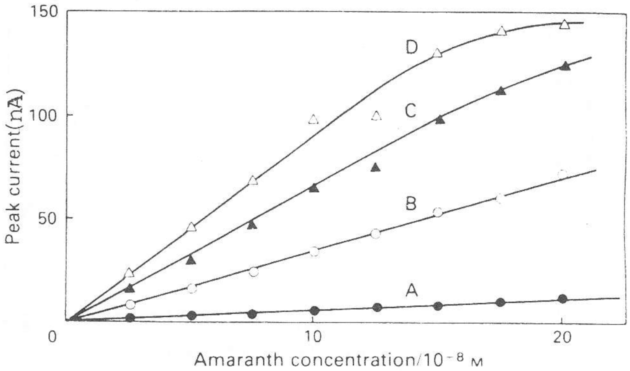


Fig. 9. Calibration graphs at different accumulation times for amaranth solutions in pH 10 buffer. Accumulation potential, −400 mV. Accumulation time: A, 0; B, 1; C, 2; and D, 3 min

4. ELIMINATION OF INTERFERENCES

Several interferences may occur,mainly when complex or biological samples are analysed.They result from the presence of other surface-active species in the sample solution.These species can affect the accumulation via a competitive coverage of the electrode surface,resulting in depletion of the stripping peak.The problem can be minimized by various approaches.Small reductions in the magnitude of the peak can be corrected by using the standard addition method,shorter accumulation times or by a proper choice of the accumulation potential.More severe peak depressions require a preliminary chromatographic separation of the interfering surfactants.

A different kind of interference is possible in the determination of trace metals,for instance in natural waters,and is due to complexation of the metal ions by organic complexing material present.Only a reactive("labile") fraction is determined in such cases if the AdCSV analysis is carried out without some pretreatment to destroy the organic complexing material.A convenient way of eliminating organic material is by UV irradiation of the sample prior to the voltammetric analysis,with suitable precautions to prevent losses of the analyte due to adsorption on the vessel walls,precipitation or formation of volatile compounds.

5. APPLICATIONS

More than 200 organic compounds including a large number of pharmaceutical or biological substances and metal ions complexated with an organic ligand have been submitted to adsorptive stripping voltammetry.Two particular references will be considered here,one to the adsorptive cathodic stripping voltammetry(AdCSV) of trace metals and the other to a study undertaken in our laboratory of determination of aromatic amines by AdSV following a derivatization step.

5.1. Adsorptive cathodic stripping voltammetry(AdCSV) of trace metals(4).

The preconcentration step in anodic stripping voltammetry(ASV) of metals is by plating of the analyte(metal ions) onto a mercury electrode.Prerequisites of plating are that the metal is soluble in mercury(otherwise the reoxidation step is electrochemically irreversible) and the reduction potential is more negative than that of mercury and more positive than that of hydrogen ions or any major reducible ion in the electrolyte(otherwise the reoxidation current is masked by that of hydrogen or by that of the major reducible ion).The preconcentration step in ASV is at the same time very effective and limiting : amalgam-forming elements are collected efficiently,whereas elements that do not form a soluble amalgam with mercury or are reduced to the metallic state at very negative potentials cannot be determined.

Many more metals and also metalloids,non-metallic and organic compounds can be determined by voltammetry if an alternative adsorptive deposition step is used,which does not utilize plating to the metallic state.There are two main advantages related to adsorptive deposition.First,any oxidation state can be collected rather than only the metallic state.This aspect of AdCSV has opened up the technique of electroanalysis to any element with a reduction potential(any reduction potential,not just that to the metallic state) falling within the stability range of mercury and hydrogen.The second advantage is that the material is collected as a monomolecular layer on the electrode surface,all of it being instantaneously accessible to reduction(or oxidation); therefore,the reduction current is independent of diffusion of the reactive species and very fast potential scanning techniques can be employed,producing larger currents.

Generally,the adsorbed material is a complex of the metal ion and the voltammetric response is due to the reduction of the metal ion in the adsorbed complex.Sometimes reduction of the ligand is used instead.Nevertheless,reduction of the metal ion is preferable to ligand reduction as the reduction peak potential is specific to the metal which minimizes interferences by other metals.Further,the sensitivity of methods employing ligand reduction tends to be lowered by adsorption and reduction of the free ligand in addition to that of the chelate.However,reduction of the ligand is convenient if the metal ion is reduced only at very negative potentials,such as Th and some of the rare earths.

5.2. Determination after derivatization

The use of derivatization reactions in analytical chemistry to improve the characteristics of determinands is well known.The possibility of using derivatization reactions prior to making determinations by adsorptive stripping voltammetry has extended the advantages of this technique to a range of electroinactive or poorly adsorbed compounds(7).The determination of aniline,undertaken in our laboratory is an example.

Several methods for the determination of aromatic amines in a variety of matrices already exist.A method frequently employed involves diazotization of the amine and coupling followed by spectrophotometric examination of the intensely coloured product,an azo dye(8).And as the determination of azo dyes using adsorptive stripping voltammetry has been reported already(6),a method for the determination of aromatic amines was developed,based on their conversion into azo derivatives,which were assayed using AdSV.As we can see in Figure 10,the use of accumulation periods of several minutes allows the determination of very low concentrations of aniline.

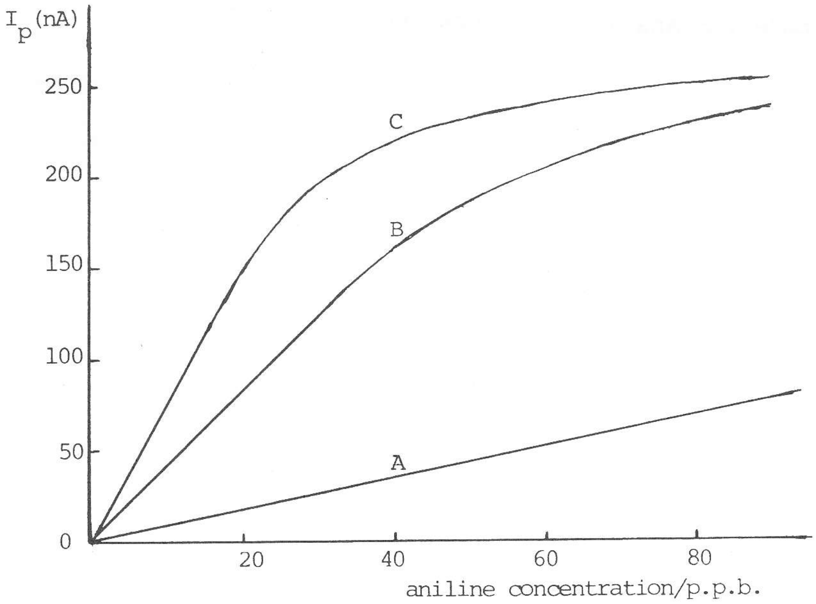


Figure 10. Calibration curves for aniline(after derivatization) using AdSV(DPP).Scan rate = 10 mV/s; t_{drop} = 1s; $E_{acc.}$ = -240 mV; pH = 10; acc. time(min):A-0,B-1,C-2.

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