THE APPLICATION OF STRIPPING PROCESSES IN VOLTAMMETRY

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ABSTRACT

The use of the hanging mercury drop electrode in conjunction with pre-electrolysis and chronovoltammetric stripping has found wide application for the determination of trace amounts of certain ions which form amalgams or insoluble salts with mercury. When the concentrations of the trace elements to be determined are of the order of 10^{-6} M, the influence of the double-layer capacity on the stripping curve is negligible. However, the double-layer capacity is important when the concentrations are of the order 10^{-8} to 10^{-9} M, and at such concentrations, the presence of impurities or surface-active substances in the base electrolyte can be of vital importance.

Some years ago, a two-electrode subtractive method of overcoming these effects was described[6]. An improved chronovoltammetric procedure will be discussed; this involves a variable time of pre-electrolysis and the addition of variable amounts of standard solutions. The new method gives more precise and reproducible results without the preparation of a complete calibration curve. Numerous examples are given to illustrate the proposed method.

INTRODUCTION

A predominant feature of modern analytical chemistry is the great importance of the determination of trace amounts of inorganic and organic substances. Electrochemical techniques of various types have been widely applied for such analysis but the polarographic method, proposed nearly fifty years ago by J. Heyrovsky, is undoubtedly the most important and has found extensive applications in trace analysis for inorganic and organic species present in solutions.

Polarography in its conventional form has allowed many very important achievements, yet it has a considerable limitation in that concentrations below about 10^{-5} mol/l cannot be determined. The diffusion current, i_d, that flows in a polarographic circuit when a sufficient concentration of background electrolyte is present in the test solution, is composed of two components: the electrolysis current, i_e, and the capacity (condenser) current, i_c. Thus

$$i_d = i_e + i_c$$

The concentration of the test substance is determined by measuring the height of the polarographic wave which depends on both these currents, but only the electrolysis current component is proportional to the concentration of the required substance. The magnitude of the capacity current, i_c, which is caused by charging the double layer of the continuously dropping mercury electrode, forms a serious barrier to the determination of concentrations lower than about 10^{-5} mol/l, for when the analysed solutions are very dilute, the capacity current can become many times greater than the electrolytic (Faradaic) current—the required component of interest—which is controlled by diffusion of the species to be determined. Accordingly, it becomes impossible to calculate the required concentration from the wave heights with the necessary degree of accuracy, unless the contribution of the capacity current is known precisely.

NEWER POLAROGRAPHIC TECHNIQUES

Several modifications of the basic polarographic method have been proposed to overcome the above-mentioned limitations[1]. For example, voltage-sweep chronoamperometry at stationary electrodes (hanging mercury drop electrodes) provides a certain improvement in sensitivity so that concentrations below 10^{-6} mol/l can be determined with reasonable accuracy. This method does, however, possess the disadvantage that, in many cases, the simultaneous determination of several ions can be rather difficult; the precise measurement of the reduction peak of an ion reduced at a certain potential may be impossible because the reduction of ions at more positive potentials has not reached a steady state.

Stripping voltammetry

Another possibility is to use voltammetry with a rotated electrode or a

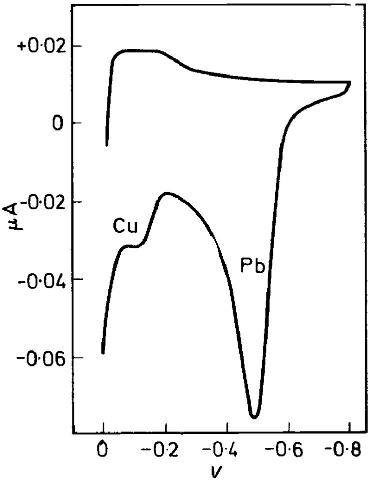

Figure 1. Current–voltage curves for a solution of 1 × 10^{-7} M lead and traces of copper in 0·1M lithium carbonate. Upper part recorded from 0·0 to −0·8V; lower part recorded in the reverse direction after electrolysis for 6 min at −0·8V at HMDE.

stationary electrode in stirred solution[1]. Such techniques provide higher diffusion currents than conventional polarography and so a better sensitivity, but the limiting concentrations still seem to be of the order of 10^{-7} mol/l.

Some years ago, another means of combating the sensitivity limitations of conventional polarography was proposed by Kemula and Kublik[1,2]. This method is based on preliminary concentration by electrolysis at a hanging mercury drop electrode (HMDE) followed by stripping of the required component. In the preliminary cathode process, the required component is reduced to a form that will dissolve in mercury or form a slightly soluble or adsorbed film at the surface of the mercury drop. In the subsequent anodic process, this concentrated component is dissolved or oxidized during the decrease in the applied voltage. *Figure 1* indicates the basic principle of the technique; after the concentrating electrolysis, the concentrations of the elements of interest in the electrode have increased to such an extent that the anodic waves on the current–voltage curve are very clearly marked. The general idea is of long standing, having been suggested in 1931 by Zbinden[3], who used a platinum electrode and coulometric measurement, but for practical purposes, the method remained a curiosity until the introduction of the specially prepared HMDE of simple construction. The method developed has made it possible to increase the sensitivity of the voltammetric technique many times, although only a conventional polarograph is used in conjunction with the HMDE, instead of the dropping mercury electrode. The total amount of ions deposited depends on the concentrations of the ions in the test solution, provided that experimental conditions are kept constant.

With relatively simple apparatus, the optimal results are obtained when the preliminary electrolytic deposition is done during vigorous stirring of the solution and then the accumulated substances are stripped in an unstirred solution. The method possesses the great advantage, compared to other concentration techniques, that all operations are carried out in the same solution in the same vessel and that no impurities can be introduced by reagents other than the background electrolyte.

Methods of stripping

Various modes of stripping have been studied[1]. Anodic stripping chronoamperometry involves the recording of current–time curves at constant potential, the current being measured, whereas in constant potential stripping coulometry, integration of the current–time curve allows the measurement of the number of coulombs involved. However, both these procedures are rather inconvenient. Another seldom used method is stripping chronopotentiometry[4], in which oxidation at constant current is followed by recording of the potential–time curves. The most commonly applied method is voltage-sweep stripping chronoamperometry[1]; in this method, current–voltage curves are recorded at linearly changing applied potential, the heights of the anodic current peaks being recorded. An advantage of this technique is that a conventional polarograph can be employed without extensive modifications; moreover, the amount of theoretical background work that has been done allows greater reliability of application.

To prevent the effect of mutual influence and superimposition of two peaks of close potentials on the accuracy of the determination, the total charge that flows during the anodic stripping can be measured. A new chronopotentiometric method in which the changes of potential with time are followed during the stripping process in a circuit containing a large resistor (more than $10^7\ \Omega$ so that the stripping process is comparatively slow) either without or with controlled current has been recommended[5]. From the plots of voltage (measured by a dynamic voltmeter) against time, the transition (stripping) time (τ) is determined and the quantity of electricity (in microcoulombs) is calculated by multiplication of the transition time by stripping current. The newest direct microcoulometric method[6] is discussed further below.

Application of these methods allows the determination of various ions in concentrations down to the order of 10^{-10} mol/l.

The role of double layer capacity

When trace amounts of ions have to be evaluated by the above techniques, so that high sensitivities of the secondary equipment become essential, the double layer capacity of the stationary hanging mercury drop electrode plays an increasingly important rôle as the sensitivity increases. Depending on the rate of change of the potential, the differential capacity of the mercury electrode also changes.

Calculation of the analytical results is made still more difficult by the fact that the double layer capacity of mercury is also strongly dependent on the varying applied potential, the nature and concentration of the background electrolyte, the presence of surfactants, etc.

A simple method of recording the values of the double layer capacity in any sample solution, which is useful for the evaluation of the base line of the reduction current, has been described[7] quite recently, but the procedure is time-consuming.

Standard addition methods

At the present time, few problems are involved in maintaining constant the properties of the recording equipment and of the electrolysis vessel with the HMDE. Much greater difficulties are to be found in keeping constant other parameters that influence the results of a stripping analysis, such as the purity of the background electrolyte, the nature and quantity of surfactants present, etc.

In order to avoid the preparation of calibration graphs in conventional polarography, the standard addition method is very often applied. Known quantities of a certain component or components are added, the final wave-heights are recorded and the results are calculated on the assumption of straightforward additivity. An essential part of this method is the repeated deaeration of the sample solution; the dilution of the analysed sample must also be calculated.

Both these inconveniences can be obviated by using an electrolysis vessel with a 'sluice'[8, 9] By this modification it is possible to introduce a sample which contains a known amount of one of the sample components, while all the other

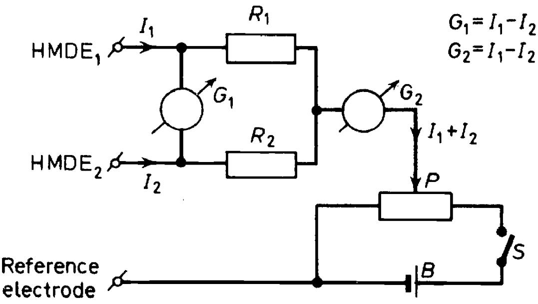

Figure 2. The circuit for differential (subtractive) recording of metals deposited by pre-electrolysis on two separate HMD electrodes. R_1, R_2 resistors; G_1 high input resistance galvanometer; G_2 high sensitivity recording galvanometer; P potentiometer; B battery; S switch.

parameters, including the volume of the sample solution, are kept constant.

The simple comparative procedure makes it possible to determine the unknown concentration of the required species in a sample solution quite easily without the previous preparation of a calibration curve or repeated deaeration; all that is necessary is a straightforward comparison of the heights of the stripping peaks or the lengths of the stripping steps[7]. However, the results obtained by this prodecure were still not satisfactory for extremely dilute solutions where the double layer capacity becomes of vital importance.

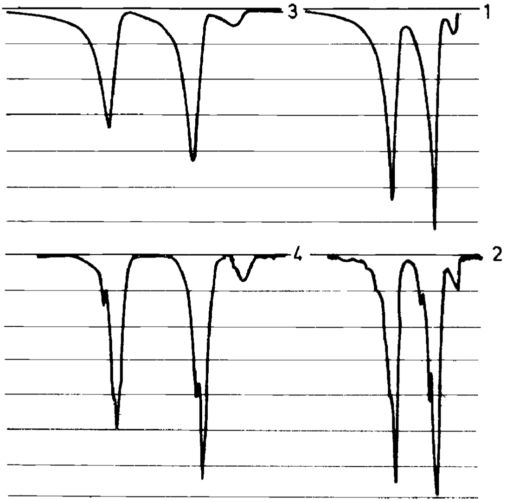

Figure 3. I_1—I_2 curves recorded with different rates of potential change (curves 1 and 3) and in unstirred (curves 1 and 3) and stirred (curves 2 and 4) solution. The solution contained 10^{-6} M copper(II) and lead(II) and 10^{-7} M cadmium(II) in 0·1 M potassium nitrate + 10^{-4} M nitric acid. Stripping rate 0·8 V/min (curves 1 and 2) and 0·4 V/min (curves 3 and 4).

EVALUATION OF VERY LOW CONCENTRATIONS

Thorough investigations[5] have shown that the double layer capacity of the HMDE has a great influence on the precision of the stripping curves obtained when only small traces of metallic impurities have to be evaluated, and high recording sensitivities become necessary.

In order to combat this difficulty, two approaches are possible. The first possibility is to decrease severely the rate of recording, but for the same sensitivity of the recording equipment, this method entails a very considerable decrease in the heights of the peaks measured. The other approach is to apply a differential (subtractive) method which makes it possible to subtract the values of the heights of the peaks recorded under identical conditions from the same starting point but after different times for the preliminary electrolytic deposition.

Characteristics of the subtractive method

On the assumption that the effects of surfactants and other substances, e.g. oxygen present in the sample solution, are identical in all cases, the subtractive method should yield results depending only on the quantities of metal deposited, which in turn depend only on the times of pre-electrolysis as recorded on the two curves, the values of the double layer capacity cancelling each other out.

The main difficulty in the practical application of this method is in maintaining identical conditions of deposition and stripping on two identical working electrodes immersed in the solution to be analysed. However, measurements performed under appropriate conditions have given very satisfactory results[5]. The three-electrode circuit used in this work is shown in *Figure 2*. With this instrumentation, the effects of different parameters on the dissolution rate of the accumulated metals, i.e. on the heights of the peaks, have been studied; such parameters include variations in the rate of change of applied potential, alterations in the stirring. etc.

It has been shown that the direct recording of the differences in the amounts of metals deposited during different pre-electrolysis times does in fact make it possible to ignore the effects of those impurities that are not accumulated on both electrodes during the deposition of the required ions on mercury. *Figure 3* shows the curves obtained for different rates of potential change and in stirred and unstirred solutions, which confirm the initial assumptions made in the development of the method.

Characteristics of constant current-constant resistance methods

The chronopotentiometric method with a constant current and large resistance[5] described above is also preferable to other possibilities when small amounts of certain metals have to be evaluated in the presence of large amounts of other metals.

Laws governing the stripping process

A theoretical study[10] of the laws governing the stripping process when

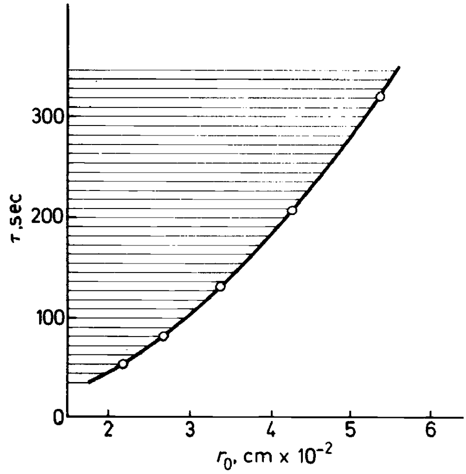

Figure 4. The range of applicability of the equation $(i \cdot \tau)_{\max}$ = const.

essentially complete oxidation of the accumulated metals from the HMDE occurs, has shown that, for the working conditions used, the chronopotentiometric stripping process from the hanging mercury drop electrode can be characterised by the following equation:

$$(i\tau)_{\max} = nFAC^{\circ} \cdot r_0/3$$

where i = stripping time,
τ = transition time,
A = surface area of the electrode,
C° = initial concentration of the ion of interest,
r_0 = radius of the HMDE

and n and F have their usual significance.

Figure 4 shows that the value of $(i\tau)_{\max}$ is constant only when the intensity of the current for stripping does not exceed a certain value. It is therefore evident that well-defined conditions of recording must be maintained in order to obtain precise results. This is in accordance with the experimental evidence found in earlier work.

Method involving measurement of total charge

Measurement of the total electrical charge accompanying the stripping process under constant potential conditions[7], rather than the peak heights or the dissolution times of the accumulated metals, has certain advantages. Such charge measurements yield results that are more independent of stripping conditions. However, the amount of metallic ions deposited from very dilute solutions on the HMDE are so small that no commercially available coulometer is suitable for the measurement. Accordingly, a digital electronic integrator (a Polaroquanter) has been constructed; with this instrument it is possible to measure the very small charges accompanying the stripping processes with sufficient accuracy and precision for determination of the amounts of the metals accumulated during the preliminary electrolysis.

These investigations showed that the charges measured during the stripping process for very low concentrations of ions, are much smaller than the charge of the double layer capacity of the HMDE. Accordingly, it seems advisable to use a subtractive method for all types of investigation, chronovoltammetric, chronopotentiometric or coulometric, when charges accompanying stripping processes are measured for the analytical determination of very low concentrations.

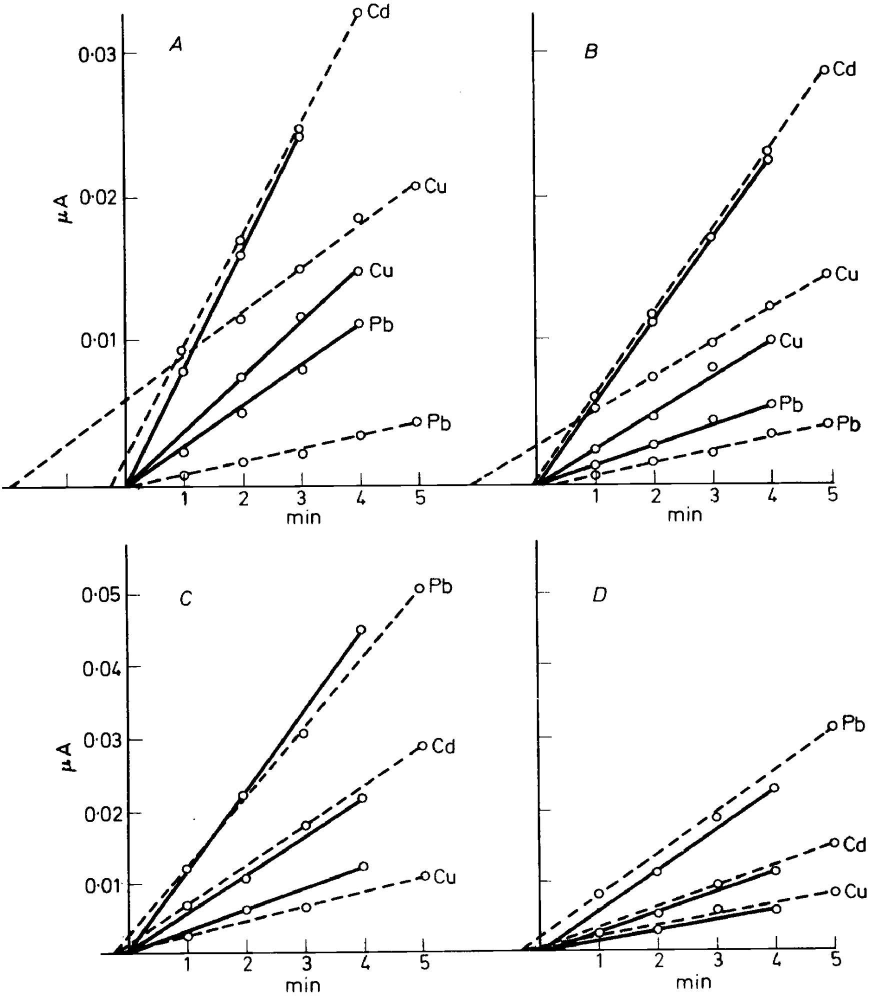

Figure 5. The results of chronovoltammetric stripping for differential deposition times of 10^{-7} M (graphs *A* and *B*) and 10^{-8} M (graphs *C* and *D*) solutions of copper, lead and cadmium in 0·1 M potassium nitrate. Stripping rate 0·8 V/min, for *A* and *C* and 0·4 V/min for *B* and *D*. Continuous lines indicate subtracted results; dotted lines indicate recorded values.

Simplified single-electrode subtractive method

A comparative stripping study has been done for the chronovoltammetric and chronopotentiometric technique with a constant dissolution current under different conditions, a simplified single-electrode subtractive procedure being employed. With this mode of operation, the effects of double-layer capacity and surfactants are not significant, and calibration curves passing through the origin are readily obtained. This can be judged from *Figure 5* which shows the effect of the stripping current on the deposition time.

This modification obviates the need for an electrolytic cell with two hanging mercury drop electrodes, and for a complicated two-channel electronic amplifier, etc. In order to achieve the optimal results under any selected experimental conditions, a simple electrolysis cell with one HMDE is all that is necessary; however, the temperature, drop size, rate and nature of stirring and other possibly variable conditions must be kept constant during the series of experiments in which deposition times are varied systematically for otherwise identical deposition and stripping processes. After the addition of known amounts of solutions containing appropriate concentrations of the relevant ionic species by means of a 'sluice' arrangement[8], it is advisable to repeat exactly the same sequence of pre-electrolysis and stripping. Experience has shown that for the best precision, a second known amount of the standard solution should be added from the 'sluice', and the pre-electrolysis and stripping sequence should be repeated for a third time.

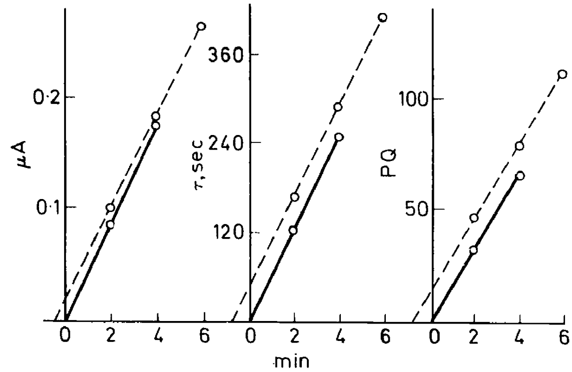

Figure 6. The evaluation of 5 × 10^{-7} M copper(II) in 0·1 M potassium nitrate + 10^{-4} M nitric acid solutions by chronovoltammetry, chronopotentiometry and microcoulometry. Continuous lines indicate subtracted results; dotted lines indicate recorded values.

The results of a comparative study of the chronovoltammetric, chronopotentiometric and microcoulometric methods are shown in *Figures 6* and *7* for 5 × 10^{-7} M solutions of lead(II) and copper(II). From this type of result, it is possible[9] to prepare a graph from which the unknown concentration of the ion of interest can be evaluated without any preliminary special checking of the electrolysis and recording instrumentation; the only prerequisite is an exact knowledge of the concentrations of the amounts of solutions added by means of

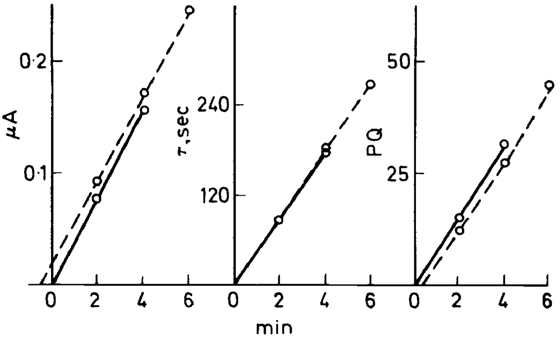

Figure 7. The evaluation of 5 × 10^{-7} M lead(II) in 0·1 M potassium nitrate and 10^{-4} M nitric acid solutions by chronovoltammetry, chronopotentiometry and microcoulometry. Continuous lines indicate subtracted results; dotted lines indicate recorded values.

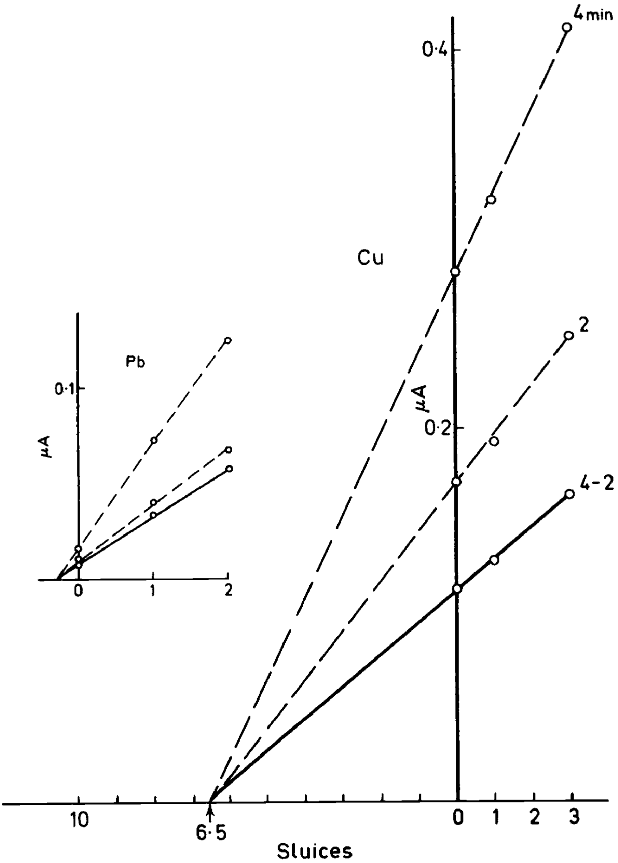

Figure 8. The evaluation of copper and lead in water. Continuous lines indicate the final subtractive result, and dotted lines indicate original measurements. One 'sluice' addition corresponds to 8 × 10^{-8} M copper(II) or lead(II).

the 'sluice'. Examples of such analyses for water samples are shown in *Figure 8*; for these results, one and three sluices were added, and deposition times of two and four minutes were used before the final stripping processes. Evaluation of the graphs leads to 4·8 × 10^{-8} M lead(II) and 1·1 × 10^{-6} M copper(II) as the original concentrations of the two metals in water.

The above method is basically a double differential method: differences in the deposition times and in the concentrations of the species added are measured, the results being obtained with a single cell and HMDE under constant experimental conditions. Although the procedure described is perhaps a little tedious, it does readily allow the interpretation of any unexpected influence of, for example, surfactants on the double layer capacity. Such effects can appear very similar to a copper peak, as is shown in *Figure 9* where both the stripping curves and the cyclic recording indicate an unexpected peak height for copper in the solution. Only the proposed method makes it possible to establish that the error is caused by a large capacitative effect on the mercury double layer which is similar to the dissolution potential of copper from mercury.

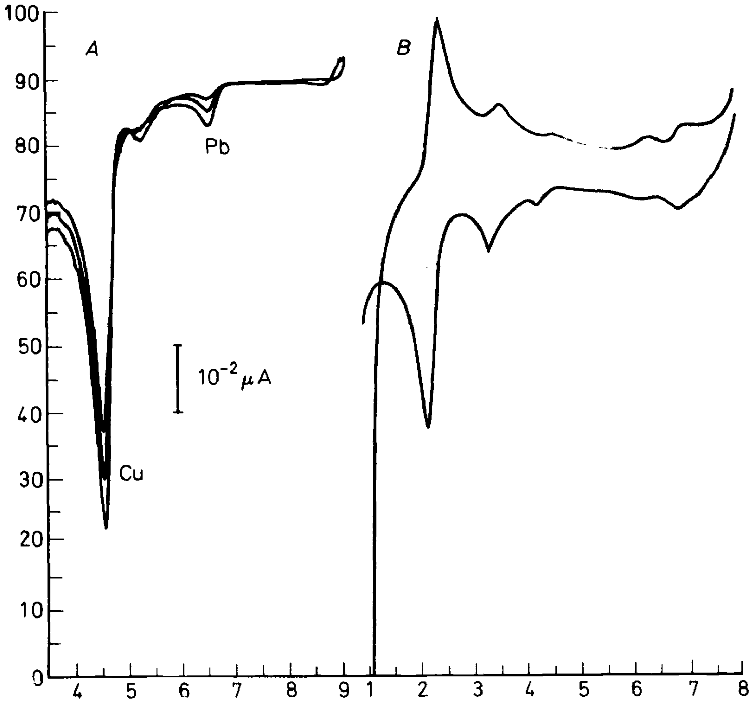

Figure 9. The influence of the surfactant on the stripping peaks of lead and copper in an aqueous 1M potassium nitrate solution. *A*, stripping curves. *B*, cyclic recording.

The comparison of results given in *Figure 6* shows that all these methods, chronovoltammetric, chronopotentiometric and coulometric, yield the same results only when the double differential procedure is employed. Further applications of this new method should allow the elucidation of discrepancies caused by traces of surfactants, the adsorption of ions in container walls, and other phenomena. Detailed studies of these possibilities are in progress.

CONCLUSIONS

The modified techniques that have been described recently allow concentrations as low as 10^{-8} M of certain ions to be analysed with very reasonable accuracy and precision. Comparisons of the chronovoltammetric, chronopotentiometric and coulometric methods for the evaluation of stripping techniques have shown that the most reliable results can be achieved when several deposition times are used together with a modified 'sluice' method of standard addition. The differential procedures involved make it possible to achieve highly sensitive and precise analyses with relatively simple instrumentation.

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