

1986

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Julian Tyson

University of Massachusetts Amherst

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ANALYTICAL APPLICATIONS OF ABSORPTION SPECTROELECTROCHEMISTRY AT GRAZING INCIDENCE

JULIAN F. TYSON

Department of Chemistry, Loughborough University of Technology, Loughborough, England

(Received 12 July 1985. Accepted 28 August 1985)

Summary—Analytical applications of spectroelectrochemistry are limited by the short path-length, in the absorbing medium, that can be produced with most light-beam/electrode configurations. This disadvantage is overcome for grazing incidence. A cell fitted with glassy-carbon electrodes and used in a conventional spectrophotometer is described and applied to model systems illustrating the use of (a) homogeneous redox reactions, (b) homogeneous redox reaction followed by chemical reaction and (c) electro-deposition followed by stripping into a reagent solution. This last technique is the spectro-electrochemical analogue of anodic-stripping voltammetry.

Although many spectroscopic techniques have been used to monitor species both in the diffusion layer and on the electrode surface (during and after electrolysis), there have been few quantitative analytical applications.¹ The aim of most of such studies has been the elucidation of reaction mechanisms, measurement of rate constants, diffusion coefficients, E^0 and n values, and study of the electrode surface. As candidates for quantitative analytical application, spectroelectrochemical experiments based on the absorption of light by species in the diffusion layer after imposition of a potential step are the most interesting, because the equations which relate the absorbance to various parameters of the system are analogous to the Beer-Lambert equation for conventional solution spectrophotometry. These experiments include total internal reflection at an optically transparent electrode (OTE)² and normal transmission at an OTE.³ The limitations of the former technique are set by the path-length in the absorbing medium, which in turn depends on the extent to which the totally internally reflected beam passes into the solution at the other side of the electrode interface. The latter technique is limited by the time taken for the "equivalent path-length" to reach high enough values, the basic equation being

$$A = \epsilon_R 2 \left(\frac{D_o t}{\pi} \right)^{1/2} C_o^b \quad (1)$$

where A is the absorbance, ϵ_R the molar absorptivity of the reduced species, D_o the diffusion coefficient of the oxidized species, t time and C_o^b the bulk concentration of the oxidized species. This form of the equation is for the reaction $O + ne \rightarrow R$, namely a homogeneous reduction at the electrode surface. The "equivalent path-length" is $2(D_o t/\pi)^{1/2}$ and thus for a given system with constant ϵ_R , C_o^b and D_o , the absorbance increases with the square root of the time.

For a hypothetical value of 10^{-5} cm²/sec for D_o , the change in equivalent path-length (cm) with time is given in Fig. 1. It can be seen that the path-length (and hence absorbance) increases only very slowly with time. It can readily be calculated from equation (1) that it will take something approaching 22 hr for the equivalent path-length to become 1 cm.

If the light-beam is passed at grazing incidence over the surface of the electrode the equation (1) is modified⁴ to

(2)

where b is the length of electrode surface traversed by the light-beam, h the width of the beam and the other symbols have the same meaning as before. The "equivalent path-length" in this equation is $2(D_o t/\pi)^{1/2}(b/h)$ and is shown as a function of time in Fig. 1 for values of b and h of 1 and 0.05 cm respectively. It can readily be seen that potentially useful "path-lengths" are obtained in only a few minutes.

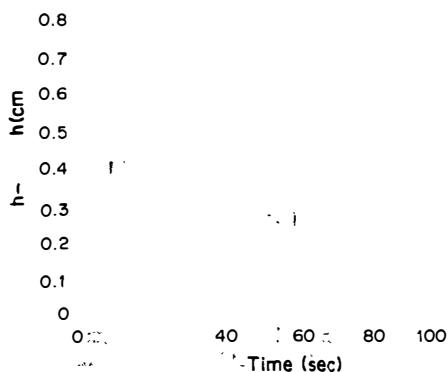


Fig. 1. Variations of "equivalent path-length" with time, for a hypothetical compound with a diffusion coefficient of 10^{-5} cm²/sec, with absorbance measured normal to (curve A) and parallel to (curve B) the electrode surface.

The quantitative analytical basis of the technique is also seen from equation (2). The absorbance is directly proportional to concentration at a given time, and furthermore, the slope of the A vs. $t^{1/2}$ plot is also proportional to concentration. The "equivalent path-length" model predicts that the absorbance will reach a maximum value when $2(D_0 t/\pi)^{1/2} = h$. For the values used here, the time for this to occur is 196 sec.

In recent years there has been an increase in the use of the parallel or near-parallel absorption method (see, for example, references 5–10) and other methods of increasing the sensitivity of the measurement, such as use of a circulating, long optical-path, thin-layer cell.¹¹

In this paper, two methods using grazing incidence and a glassy carbon electrode are reported. In the first, homogeneous reactions are used, in which the determinand species undergoes a spectral change on oxidation or reduction at the electrode surface. The possibility of producing a spectral change by a chemical reaction subsequent to the electrode reaction was also investigated. In the second method, a spectroelectrochemical analogue of anodic-stripping voltammetry is used, in which the metal to be determined is electro-deposited on the electrode surface and then stripped off into a solution of a spectrophotometric reagent.

EXPERIMENTAL

Reagents

Metal-ion solutions were prepared from analytical-reagent grade salts. Spectrophotometric and other reagent solutions were prepared from the solid reagents. All solutions were prepared with triply distilled water.

Apparatus

The cell-holder of a Pye Unicam SP600 Series 2 spectrophotometer was modified to accept a cell with two glassy-carbon plate electrodes (see Fig. 2). Slits (approximately 1 mm wide) mounted in front of and behind the cell

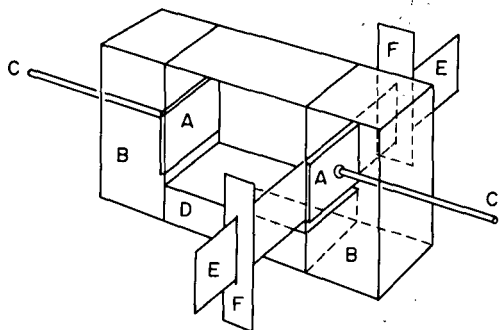


Fig. 2. Sketch of the spectroelectrochemical cell. The glassy-carbon electrodes, A (10×20 mm), are mounted in resin blocks, B, and connected to the external circuit by copper wires, C, joined to their backs with silver-loaded epoxy resin. The blocks are secured to a Teflon base, D, with the electrodes about 20 mm apart. The cell windows are microscope slides cut to size and glued in place. The path and dimensions of the light-beam, E, are defined by the slits, F, mounted either side of the cell assembly.

defined the light-beam and the cell was positioned by horizontal adjustment with a worm gear drive. The cell was equipped with a variety of inlets and outlets so that sample solutions *etc.* could be pumped in and out, the solution deoxygenated with oxygen-free nitrogen and a nitrogen atmosphere maintained. The spectrometer output was converted into absorbance by an SP45 unit and monitored with an $X-t$ recorder. The electrode potential was controlled by means of a manual polarograph (Southern Analytical A1650) or a potentiostat (Princeton Applied Research 174).

Procedures

The general procedure for the homogeneous reactions was to transfer the solution (in background electrolyte) to the cell, deoxygenate it, set zero and 100% transmission, start the chart recorder and apply a potential step (typically 2 V vs. the counter-electrode). For the anodic-stripping mode, after a suitable deposition time, the solution was replaced by one containing the spectrophotometric reagent (dissolved in background electrolyte), the absorbance scale was set, the chart recorder started, and a potential step applied.

RESULTS AND DISCUSSION

Homogeneous reactions

Various species were investigated, including ferroin, ferrocyanide, phosphomolybdate, methyl viologen (1,1'-dimethyl-4,4'-bipyridinium), permanganate, dichromate and iodide. The oxidation of iodide was monitored by means of the absorbance of the iodine produced or that of the blue starch-iodine compound. For all the species examined, the plots of A vs. $t^{1/2}$ had a linear region (as shown in Fig. 3), the slope of which showed a high correlation with concentration. A similar correlation between the maximum absorbance obtained and concentration was also observed. As examples, the results for phosphomolybdate and the iodide-starch system are given in Table 1.

Anodic-stripping

The following combinations of metal and spectrophotometric reagent were investigated: (a) copper and Pyrocatechol Violet (PCV), murexide, or pyridyl

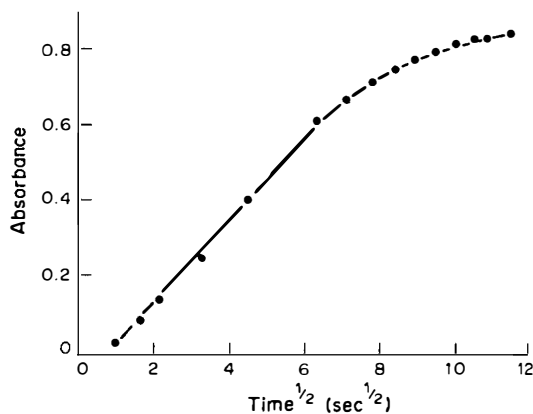


Fig. 3. Plot of absorbance (at 720 nm) against $t^{1/2}$ for phosphomolybdenum blue ($8 \times 10^{-4} M$). The applied potential was -2.0 V.

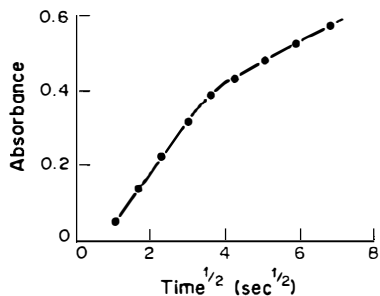


Fig. 4. Plot of absorbance (at 630 nm) against time^{1/2} for the anodic redissolution of copper (at +2.0 V) into a solution of Pyrocatechol Violet.

azo resorcinol (PAR), (b) zinc and zincon or PCV, (c) cadmium and murexide or PCV, (d) silver and 1,10-phenanthroline plus tetrabromofluorescein. All these systems exhibited a linear portion in the plot of A vs. $t^{1/2}$ (see Fig. 4 for example), with a slope strongly correlated with concentration; the maximum absorbance was also correlated with concentration. Results for the copper-PVC system are given in Table 1. The best performance in terms of sensitivity and detection limit was obtained for silver, with a $3 \times 10^{-7}M$ concentration (0.03 $\mu\text{g/ml}$) being detectable after a deposition time of 15 min.

It is interesting that the linear A vs. $t^{1/2}$ relationship is obtained for systems which might be expected to be far removed from the simple case of semi-infinite linear diffusion. This shows that in the systems so far chosen for investigation, the reaction kinetics are fast compared with the diffusion-controlled movement of species in solution. The homogeneous reactions show that the electrode acts as a solid redox reagent in the system and eliminates the thermodynamic and kinetic problems that are sometimes associated with the use of conventional redox reagents. The chemistry of the molybdenum heteropoly acid species provides a good example of the difficulties that can beset a spectrophotometric procedure. At least six different reducing agents have been recommended for the production of phosphomolybdenum blue and the product of the reaction may be either the α or the β form, depending on the reaction conditions and order of addition of reagents.^{12,13} Often, as well as specifying the order of addition of reagents, a conventional procedure will specify a time period during which the absorbance should be measured. The use of the slope of the A vs.

$t^{1/2}$ plot as the quantitative parameter means that solutions more concentrated than those that can be handled by the conventional procedure can be measured without predilution. Both modes of operation can provide procedures for given analytes, as selectivity can be introduced by control of the electrode potential at the various stages, by use of masking agents, and by use of consecutive chemical reactions following the electrochemistry. At present the methods are slow and have not demonstrated any dramatic improvement in sensitivity or detection limits (this is not expected for homogeneous systems), but in principle the anodic-stripping mode could rival its voltammetric analogue, as it is not limited by the problem of distinguishing between faradaic and non-faradaic processes. It can be seen from equation (2) that the speed of the technique could be improved by reducing h , the width of the beam defined by the slits. With a conventional solution spectrophotometer, there is a limit to the reduction in beam-width that can be achieved before an unacceptable lowering of the signal to noise ratio occurs. This difficulty could be overcome by use of a laser as light-source, and the use of a slit-width as narrow as 3 μm with such a source and consequent improvement in the rise time have been reported.⁵ The electrode material, glassy carbon, appears more suitable than platinum, which was used in previous studies¹⁴ and produced OH^- in the diffusion layer on reduction after an anodic pretreatment. No special cleaning of the electrodes has been found necessary and their efficiency has been maintained for several months.

CONCLUSIONS

The results of these preliminary investigations show that spectroelectrochemistry at a glassy-carbon electrode with use of the grazing-incidence configuration has considerable promise as a quantitative analytical technique, particularly when coupled with potential-step electrochemistry. The two modes described here, homogeneous reaction and anodic stripping, have both been shown to have features capable of exploitation for achieving selective and sensitive analytical determinations. It is expected that some improvement on these preliminary results would be obtained with a better quality spectrophotometer, but a purpose-built instrument (incorporating a tunable laser source) would be ex-

Table 1. Least-squares linear regression analysis of calibration data [A_{max} is maximum absorbance on absorbance-time plot, m is slope of absorbance-time^{1/2} plot ($\text{sec}^{-1/2}$), C is concentration (M), n is number of data points, and r is Pearson's correlation coefficient]

System	A_{max} vs. C				m vs. C			
	n	slope, $l./\text{mole}$	intercept	r	n	slope, $l.\text{mole}^{-1}.\text{sec}^{-1/2}$	intercept	r
Phosphomolybdenum blue	10	8.1×10^3	0.004	0.996	9	1.1×10^3	0.014	0.999
Iodide-starch	9	8.5×10^3	-0.35	0.998	8	2.5×10^3	-0.10	0.988
Copper-Pyrocatechol Violet	7	4.6×10^2	-0.018	0.983	7	1.6×10^2	-0.003	0.993

pensive, and one of the attractive features of the technique in its present form is that it forms the basis of a low-cost accessory for an existing conventional spectrophotometer. It is expected that the analytical capability of the technique could be extended by use of fluorescence and chemiluminescence measurement.

Acknowledgement—Assistance from J. R. Erone, A. S. Khulumula and P. J. Weir with aspects of the experimental work is gratefully acknowledged.

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Dedication—As one who had the good fortune to be first made aware of the fascination of the application of chemical principles to the solving of analytical problems by Bob Chalmers, it is indeed a pleasure to have a small part in this tribute to him. In all aspects of his career as a professional analytical chemist, he sets examples of the highest standards and, in making this contribution, I am pleased to acknowledge that much of the enjoyment derived from the challenge of trying to emulate his example is due to his valued guidance, encouragement and friendship.