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SMALL-VOLUME SOLID-ELECTRODE FLOW-THROUGH ELECTROCHEMICAL CELLS

PRELIMINARY EVALUATION USING PULSE POLAROGRAPHIC TECHNIQUES

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SUMMARY

A preliminary evaluation is given of the use of potentiostatic pulse polarographic techniques for solid-electrode flow-through electrochemical cells as detectors for use in both automated analysis and liquid chromatography. The following advantages are noted over previously reported constant-applied-potential techniques: increased sensitivity, minimal effect of flow-rate on current measurement and a vast increase in electrode stability for the short-term sampling period and for extended routine operation.

INTRODUCTION

This laboratory is responsible for the development of analytical methods for the assay of veterinary drugs used for food-producing animals. The assays include the dosage forms, which typically would be in feed or water, blood levels of the drug during administration and the residue analysis for the drug and its metabolites in the animal tissue. The concentrations involved range from less than 0.1 ppm for tissue residues to more than 100 ppm for blood levels and dosage forms.

The samples involved can be variable in terms of possible interferences and any final assay requires a detection technique to have a reasonable measure of selectivity so as to minimize the separation and isolation procedures needed. The other aspect is that, owing to the number of samples involved during the development and use of a drug, the detection method adopted should be adaptable to an automated analysis system to handle these samples.

Polarography offers the necessary selectivity for the determination of compounds whose oxidation or reduction potentials fall within the potential range of the working electrode material. The adjustment of the applied potential of the working electrode will dictate a response to those compounds whose oxidation or reduction potentials are less than the applied potential with the measured current being proportional to the concentration. The half-wave potential for a given compound in a specified

system is diagnostic for that compound. Polarography has been used successfully in this laboratory for assaying biological samples with a minimum of sample processing. This success prompted the investigation of electrochemical cells for flow applications.

The first use of an electrode in a flowing stream for electroanalysis was reported using a platinum electrode in 1947[1], and the use of a dropping mercury electrode (DME) in a continuous stream was reported by Kemula[2] in 1953. Since that time, there have been reported various DME flow-through cells[3–9] with applications to the determination of inorganic anions[10], metal ions[11–13], nitro compounds[14], amino acids[15] and pesticides[16]. The mercury electrode has a desirable, extensive cathodic range of polarization owing to the large over-potential for the evolution of hydrogen and a constantly renewed fresh electrode surface. The disadvantages of the DME are the current oscillation over the lifetime of the drop with constant applied potential requiring some form of damping, the effect of flow-rate on the drop time, the sensitivity change with flow and the mercury handling problems for the detector.

Solid electrodes characterized by a large cathodic working range can be made of carbon. Joynes and Moggs[17] and Pungor and co-workers[18,19] have reported the use of planer silicon rubber-based carbon electrodes for the determination of Cd^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+} and 2,6-dinitrophenol in a stream.

Tubular platinum electrodes have been utilized by Blaedel *et al.*[20] for flowing streams and have been applied to the determination of inorganic ions[21]; however, when platinum electrodes are operated in a flowing stream with a constant applied potential for organic compound applications, they have a flow-dependent response that decreases with time owing to surface contamination or surface changes.

The above detectors utilize only a very small portion of the available electroactive species for their response, whereas a flow coulometric detector has a large surface area that effectively will reduce or oxidize 100% of the species in the cell. This type of cell has been reported for flow applications with platinum[22], granular glassy carbon[23] and amalgamated nickel surfaces[24] for a number of applications. The coulometric detector is the most sensitive and is flow independent owing to its 100% efficiency; however, it suffers from the deficiency that any surface effect or instability is magnified because of this.

The selectivity of the polarographic method is the primary reason for our interest in a flow-through cell for automated analysis; however, the following criteria would have to be met for an operationally successful cell:

(1) a cathodic as well as anodic potential working range;
(2) response independent of flow-rate;
(3) short- and long-term stability of the electrode suitable for repetitive sampling;
(4) sensitivity comparable with that of a DME;
(5) low noise level;
(6) low volume (less than 2 ml).

The extension of the usefulness of a cell as a detector for liquid chromatography would include all of the above with the further requirements of much lower cell volumes (*i.e.*, less than 30 μl) and higher sensitivity.

The operational problems involved with the previously reported flow-through cells with both DMEs and solid electrodes using constant applied potentials was the

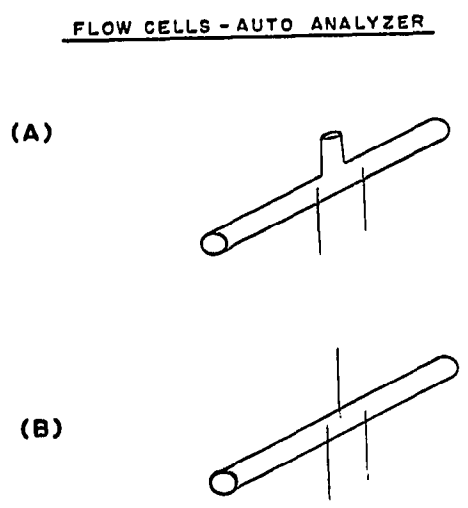


Fig. 1. Flow cells, AutoAnalyzer type.

reason for initiating an evaluation of the use of pulse polarographic techniques to flow-through electrochemical cells.

Barker and Gardner[25,26] initially described two-electrode pulse polarography concepts using a DME, and Parry and Osteryoung[27] reported a potentiostatic three-electrode system in 1964. The three-electrode system was evaluated fully in later work by Parry and co-workers[28,29]. Pulse polarographic techniques primarily use a DME with a drop-knocker to insure a repetitive constant electrode area with the knocker section serving as the starting point for the timing of the subsequent potential pulse and current sampling. The technique of applying a potential pulse to a mercury drop at given repeatable size, and sampling the current at the end of the pulse, results in smooth curve that is free of oscillation with an increase in sensitivity owing to the decreased effect of the charging current. The use of pulse techniques with solid electrodes has been limited, even though Parry and Osteryoung reported in their initial paper the use of a platinum button electrode, and currently wax-impregnated carbon electrodes are used for the differential pulse anodic stripping of trace metals[30,31].

The evaluation of the flow-through electrochemical cells utilized the potentiostatic[32] control of the working electrode–solution surface using a three-electrode system where no current is drawn through the reference electrode. The current is measured using a counter electrode whose potential is controlled to be the same as the reference electrode. The three-electrode system thereby allows the use of high-resistance solutions and the feasibility for operating with organic solvents.

The pulse polarographic approach utilizes a ranged potential pulse near the end of the mercury drop life, with each pulse being slightly larger than the preceding pulse and dependent on the scan rate. The current is sampled in the final portion of the pulse. The potential pulses are stepped from an adjustable initial or base potential at the foot of the polarographic wave or at a potential that would minimize and/or eliminate unwanted reactions at the electrode surface.

The pulse polarographic approach has been initially evaluated for use with the solid electrode materials platinum, carbon and gold in a flow-through cell. The

DME, using pulse polarography, in a flow cell was not included in this evaluation but its application would eliminate some of the previously reported operational problems of DMEs in flow cells. However, the possible problem of the varying drop size as a function of flow-rate through the cell could be a serious drawback.

EXPERIMENTAL

Automated analysis flow-through cell construction

The flow cells designed for automated analysis using a Technicon system (Fig. 1) were constructed of Pyrex glass with 0.025 in. diameter platinum wire fused into the tube with a spacing between the outside electrodes of approximately 1 cm. The cells were made with two sizes of Pyrex tubing, 2 mm I.D. and 3 mm I.D., with either a salt bridge reference electrode connection (tee-tube) (Fig. 1A) or a platinum wire reference electrode connection (Fig. 1B). The estimated internal volumes of the cells were 1 and 2 ml, respectively. Owing to the method of construction, the electrode area could not be determined.

Liquid chromatography flow-through cell construction

The three-pin style (Fig. 2A) utilized a $^1/_2 \times {}^1/_2 \times 1$ in. block of Teflon drilled lengthwise with a 0.070-in. drill. Undersized electrode holes were drilled at right-angles to the passage hole with a 1.5-mm spacing between electrodes. The 0.025-in.

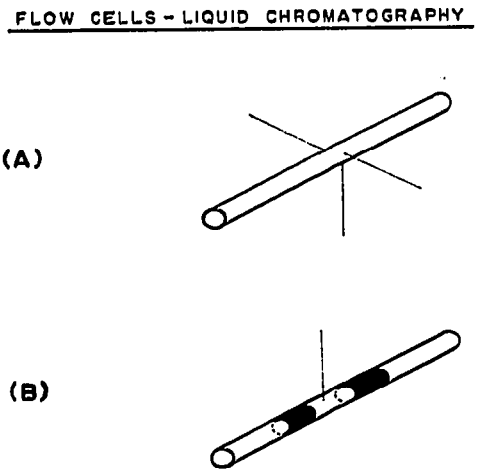


Fig. 2. Flow cells, liquid chromatographic type.

wire (platinum or gold) for the electrode was cut off and ground with grade 400 silicon carbide paper to yield a square end. The electrode was press-fitted into the hole so that it was flush with the inside of the passage hole and sealed with a drop of epoxy resin on the outside. The exposed electrode area was calculated to be 0.32 mm^2 for each pin. The total cell volume was 7.5 μl.

The tubular design (Fig. 2B) was constructed by forming a sandwich with epoxy resin using $^1/_2 \times {}^1/_2 \times {}^3/_4$ in. Teflon end blocks, $^1/_8 \times {}^1/_2 \times 1$ in. carbon

(AGSR grade, Carbon Products, Union Carbide Corp., Chicago, Ill., U.S.A.) plate electrodes and a $^1/_8 \times ^1/_2 \times ^3/_4$ in. Teflon spacer block. The composite stack was then drilled lengthwise using a 0.065-in. drill and the passage hole filled with molten Cerisin wax. The stack with the wax-hardened filled hole was placed under vacuum for 4 h, after which the hole was drilled out using a 0.070-in. drill. The 0.025-in. diameter platinum reference electrode was end-finished and mounted in the center of the spacer block as previously described for the pin electrode cell. The area of the carbon tube electrodes was 18 mm^2 and its volume 8 μl (ref. 3). The total cell volume from outside electrode to outside electrode was 25 μl. The tubing connection to the cells was fixed into place with epoxy resin with $^1/_{16}$ in. O.D. stainless-steel tubing.

Automated analysis set-up

A Technicon AutoAnalyzer sampler I with a Technicon Proportioning pump I (Technicon Instruments, Tarrytown, N.Y., U.S.A.) was used for the automated analysis repetitive sampling studies. The solvent was de-oxygenated with nitrogen and the sampling stream segmented with nitrogen. The segmented stream was debubbled using a standard C-5 Technicon fitting and the appropriate cell pull-through pump tube. The standard sampling rate was 20 samples per hour with a 2:1 sample-to-wash ratio. Standard Technicon connecting tubing, pump tubing and fittings were used to connect the flow-through cells.

A Harvard variable-speed peristaltic pump, Model 500–1200 (Harvard Apparatus, Dover, Mass., U.S.A.) with a Technicon 0.045-in. I.D. pump tube was used to vary the flow-rate of the solvent or test solution through the cell from 0.5 to 5 ml/min.

Liquid chromatography set-up

The solvent was maintained in a heated 500-ml reservoir funnel and pumped using an undamped Milroyal D controlled-volume pump (Milton Roy Co., Jersey City, N.J., U.S.A.) through a 1 m long, $^1/_4$ in. O.D., 3 mm I.D. column packed with Zipax HCP hydrocarbon polymer (DuPont Instruments, Wilmington, Del., U.S.A.). A UV monitor set at 254 nm using a 10-mm path-length cell (Laboratory Data Control (LDC), Riviera Beach, Fla., U.S.A.) was connected to the exit of the column with the electrochemical cell under test directly following the LDC detector. The output of the LDC detector was monitored using a 10-mV span Honeywell Electronik 194 strip-chart recorder (Honeywell, Inc., Minneapolis, Minn., U.S.A.). All interconnecting tubing was $^1/_{16}$ in. O.D. stainless steel. All samples were injected using a 10-μl Hamilton micro-syringe.

Polarographic set-up

A Princeton Applied Research (PAR) Model 147 polarographic analyzer (Princeton Applied Research, Princeton, N.J., U.S.A.) was used for the electrochemical study. The Model 174 has four operating modes: D.C., sampled D.C., pulse and differential pulse. The initial potential is continuously variable from 0 to $\pm$ 5 V and has scan ranges of 0.75, 1.5 or 3.0 V with either polarity. The scan rate can be varied from 0.1 to 500 mV/sec in a 1–2–5 sequence and the scan can be held at a potential or reversed at any point. The output current range is 0.02 μA to 10 mA full scale in a 1–2–5 sequence and there is an output offset adjustable from 0 to 100% scale. The

drop time can be left as natural or set as an interval of 0.5, 1, 2 or 5 sec for a controlled drop time or a pulse interval time for a solid or stationary electrode.

An Omnigraphic 2000 X–Y Recorder (Houston Instrument, Bellaire, Texas, U.S.A.) was used for current–voltage measurements and a Hewlett-Packard Model 7101B strip-chart recorder with a Model 17501A module (Hewlett-Packard, Paramus, N.J., U.S.A.) was used for current–time (flow) measurements.

The supporting electrolyte for all the work was 0.1 *M* H_2SO_4 in methanol–water (1:9) as solvent. The supporting electrolyte was used to prepare the solutions of *p*-aminophenol and *p*-nitrophenol (Eastman Organic Products, Rochester, N.Y., U.S.A.). All peak areas were determined using a Numonics Electronics Graphics Calculator (Numonics Corp., North Wales, Pa., U.S.A.).

RESULTS

The comparative scanning response of the same platinum electrode in the Auto-Analyzer Type Cell A to the same *p*-aminophenol solution under stop-flow conditions is shown in Fig. 3. The output of the pulse polarographic scan in the center has a 20-fold increase over the D.C. polarographic scan at the top with the lower differential pulse polarograms having a 50-fold increase in response. The increases in response are due to the decreased diffusion layer resulting from the short pulse time, thereby giving higher currents for the same bulk concentration. The current sampling at the end of the pulse also achieves a separation of faradaic and capacitive current with the sample containing primarily faradaic current.

The short-term stabilities of the same electrode system for four repetitive scans of the same flowing solution using both the D.C. and pulse polarographic modes are shown in Fig. 4 and 5. The D.C. scans show a decrease in diffusion current in the plateau region with irregularity on the fourth scan. This decrease has to be attributed to the electrode surface, as the scans were made under conditions eliminating a de-

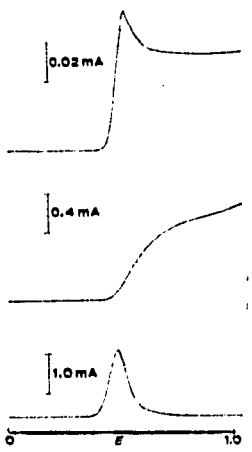


Fig. 3. Comparative polarographic scans. Stop-flow conditions; platinum AutoAnalyzer cell; *p*-aminophenol. Top curve, conventional D.C. polarographic scan; current measured. Middle curve, pulse polarographic scan; current measured. Bottom curve, differential pulse polarographic scan; Δ(current)/Δ(voltage) measured.

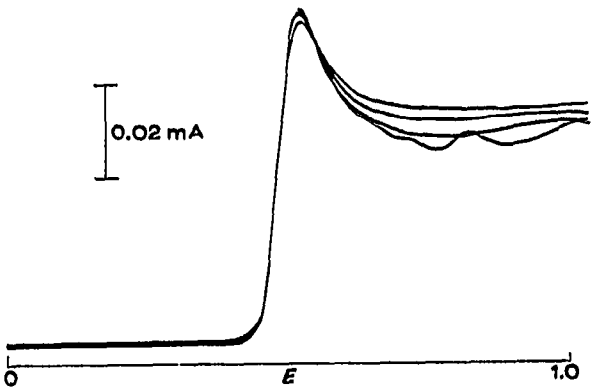


Fig. 4. Four repetitive D.C. polarograms. Platinum AutoAnalyzer cell, 2-ml volume. Top to bottom is the order of repetition. Flow conditions between scans; stop-flow conditions during scans.

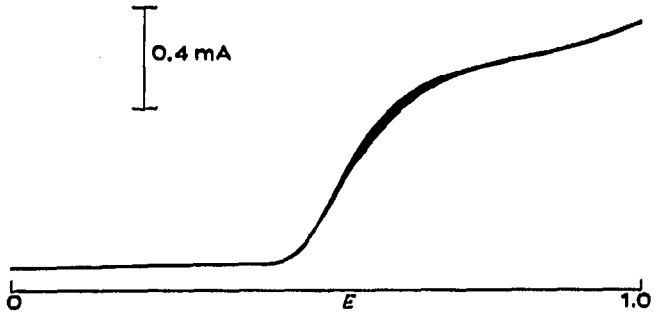


Fig. 5. Four repetitive pulse polarograms. Platinum AutoAnalyzer cell, 2-ml volume. Same flow conditions as in Fig. 4.

pletion effect. The pulse scan shows very good uniformity for the repetitive scans under the same conditions. The uniformity of this response shows the advantage of either ramped or fixed potential pulses with a solid electrode. The potential of the electrode is held at the initial value except for the pulse duration, thereby allowing the substance reacted upon during the pulse to be returned to its original state. Holding the electrode at the initial potential except for the pulse duration ensures that the electrode surface will be in the same state each time the pulse is applied. Three factors are involved in maintaining this stable electrode surface: the potential is held at the initial potential for 90–99% of the time when no reaction will occur, any surface oxidation or adsorption of electrolysis product formed during the pulse can often be removed or "cleaned" from the electrode by the return to the initial potential after the pulse, and, owing to the shortness of the pulse and the very small amount of material involved for each pulse, surface contamination, oxidation or reaction does not occur.

The stability of current measurements on this diffusion plateau is shown in Fig. 6 for repetitive 2-min sampling in the same cell of a *p*-aminophenol solution at +0.84 V *vs.* saturated calomel electrode (SCE) with a Technicon peristaltic pumped

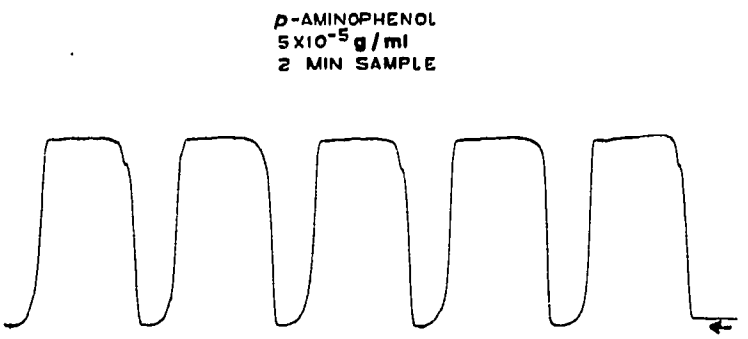


Fig. 6. Repetitive AutoAnalyzer sampling. Twenty samples per hour with 2:1 sample-to-wash ratio. Platinum AutoAnalyzer cell, 2-ml volume. Flow-rate 2.9 ml/min. Pulse mode anodic, 0.84 V *vs.* SCE; response equal to 24.5 μA.

flow of 2.9 ml/min. The output is equivalent to 25 μA (4.9 μA per $1 \cdot 10^{-5}$ g/ml) with peak noise of 0.05 μA (2% of signal). There was no appreciable change in the height of the response for an 8-h run. The same cell with the same conditions operated under constant-applied-potential (D.C.) conditions gave a response of 5 μA with a peak noise of 0.5 μA (10% of signal). The magnitude of the D.C. peak response decreased at the rate of 2% per hour at the sampling rate and concentration. The noise level at the peak response for a $5 \cdot 10^{-4}$ g/ml sample remained at 0.05 μA with an increased signal of 250 μA (0.2% of signal) in the pulse mode operation. The D.C. mode of operation for a $5 \cdot 10^{-4}$ g/ml sample under the same conditions showed a 2.5 μA (5% of signal) noise level for peak response signal of 50 μA.

The above results verify the flow-rate dependence of the current from a solid electrode that is operated with a constant applied potential and the magnitude of this current variation is proportional to the concentration of the reacting species. The same cell, under the same conditions, using a pulse mode operation had a greatly reduced current variation with flow-rate that was independent of the concentration of the reacting species and equal to the current variation obtained with the changes in flow-rate in the carrier electrolyte alone.

The utility of the pulse mode operation was expanded for automated analyzer use by using a tandem cell arrangement for the quantitative current measurement and the qualitative determination of the half-wave potential of the species involved. A cell with a working volume of 2 ml was used to monitor the current at 0.84 V *vs.* SCE as shown in the lower trace in Fig. 7 using the pulse mode. When the current monitoring cell showed a 10% scale deflection, the second cell operated in the differential pulse mode was scanned at 10 mV/sec from +0.3 to +0.6 V *vs.* SCE The described combination will provide the concentration determination via the current measurement of the first cell and a method of monitoring qualitatively the identity of the species involved. The scanning differential pulse techniques are suitable for monitoring the concentration of a plug sample in a flow system. However, the sample plug must be of sufficient volume to allow the necessary time for the required 2 mV/sec analytical scan to take place. Faster scan rates distort and shift the waves, making them unusable for quantitative purposes but adequate for qualitative identification needs.

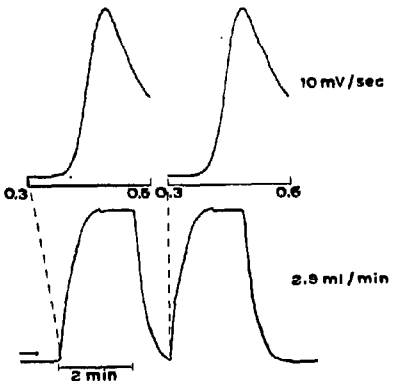
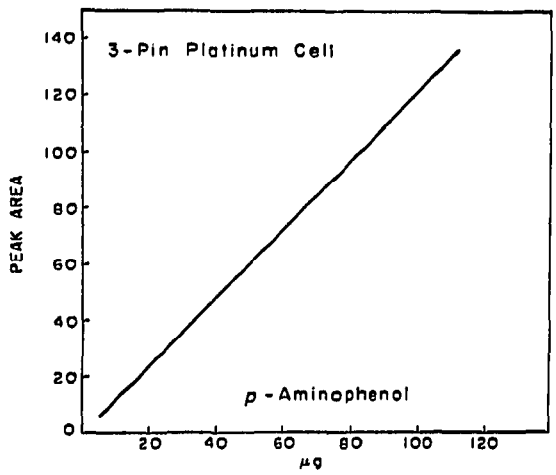


Fig. 7. Tandem detector operation. Repetitive AutoAnalyzer sampling. Bottom trace: platinum AutoAnalyzer cell, 2-ml volume; anodic at 0.84 V *vs.* SCE; current measured. Top trace: platinum AutoAnalyzer cell, 1-ml volume; differential pulse scan, 0.3–0.6 V *vs.* SCE; Δ(current)/Δ(voltage) measured; scan started with 10% of scale on current monitoring cell.

The electrochemical cells built for use with a liquid chromatographic system were evaluated for flow sensitivity, short-term stability, detection limits, concentration range and potential range.

The three-pin platinum cell was evaluated using the described Harvard pump set-up to determine the current variation with change in flow-rate with the supporting electrolyte and $5 \cdot 10^{-5}$ to $5 \cdot 10^{-3}$ g/ml solutions of *p*-aminophenol. The maximum noise level was $3 \cdot 10^{-8}$ A at +0.8 V *vs.* SCE and the maximum flow effect on the current was $5 \cdot 10^{-8}$ per 0.1 ml/min change in flow-rate and is independent of concentration of the reacting species. The constant-applied-potential D.C. operation of this cell, as with the larger cells, showed a 20-fold decrease in current output for the same solution and flow-rate dependence of the signal with the magnitude of the variation being dependent on concentration. This was illustrated by a $5 \cdot 10^{-3}$ g/ml *p*-aminophenol solution in D.C. operation with a current oscillation due to the Harvard pump of 6% of the current output *vs.* a 0.2% maximum fluctuation in the pulse mode. The working potential range of the electrode was 0 to +1.2 V *vs.* SCE in 0.1 *M* H_2SO_4. The detection limit of the cell for *p*-aminophenol was 5 μg or $15 \cdot 10^{-8}$ A and the linear response is shown in Fig. 8. The concentration range tested was $4 \cdot 10^{-6}$ to $5 \cdot 10^{-3}$ g/ml. The relative standard deviation for 10-μl samples equivalent to 100 μg of *p*-aminophenol was 1.4% for the platinum cell *vs.* 0.5% for the LDC detector at a setting of 64. The same 100-μg sample was used to compare the peak area response for the two detectors as a function of flow-rate. A change in flow-rate from 0.67 to 1.3 ml/min resulted in a decrease in area of 28% for the platinum cell *vs.* a 43% decrease in area for the LDC detector at a setting of 64.

The three-pin gold cell was evaluated only with the Harvard pump set-up to determine its current variation with flow-rate in the pulse mode. At −0.8 V *vs.* SCE, the variation was $2 \cdot 10^{-8}$ A per 0.1 ml/min change in flow-rate and was independent of the concentration of *p*-nitrophenol. The working potential range of



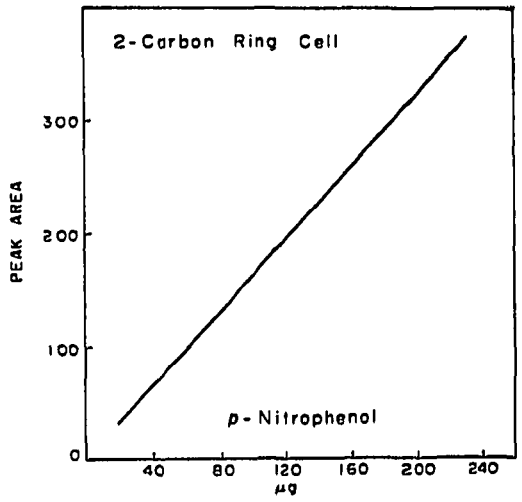


Fig. 8. Calibration graph, three-pin platinum cell. Anodic, 0.84 V *vs.* SCE.

Fig. 9. Calibration graph, two-carbon ring cell. Cathodic, —0.92 V *vs.* SCE.

the electrode in 0.1 *M* H_2SO_4 is —0.8 to +0.6 V *vs.* SCE.

The two-ring wax-impregnated carbon electrode cell with the platinum reference has a working potential range of +1.2 to —1.2 V *vs.* SCE in 0.1 *M* H_2SO_4 supporting electrolytes. The maximum noise level was $1 \cdot 10^{-6}$ A and the current variation was $2 \cdot 10^{-6}$ A per 0.1 ml/min change in flow-rate and independent of the concentration of the reacting species.

The higher current values involved are in agreement with the larger electrode areas and the large residual currents reported for wax-impregnated carbon electrodes[33]. The limit of detection for *p*-nitrophenol is 10 μg or $12 \cdot 10^{-6}$ A and the linear response is shown in Fig. 9. The concentration range tested was $8 \cdot 10^{-6}$ to $5 \cdot 10^{-3}$ g/ml. The relative standard deviation for 3-μl samples representing 60 μg of *p*-nitrophenol was 1.6% for the carbon cell *vs.* 1.5% for the LDC detector at a setting of 64. A 200-μg sample was used to compare the peak area response for the two detectors as a function of flow-rate. A change in flow-rate from 0.67 to 1.6 ml/min resulted in a 30% decrease in peak area for the carbon cell *vs.* a 60% decrease in peak area for the LDC at a setting of 64.

The three-pin platinum cell and the two-ring carbon cell, both operated in the pulse mode, did not show any decrease or modification of response after 1 week of continuous operation.

The cells described were fragile, subject to leaks and had non-reproducible electrode characteristics from cell to cell owing to the construction techniques with epoxy resin used.

DISCUSSION

The preliminary evaluation of the use of potentiostatic pulse polarographic techniques for solid-electrode flow-through electrochemical cells indicate the following advantages over constant-applied-potential techniques:

(A) increased sensitivity (5- to 20-fold);
(B) vastly decreased effect of variation in flow-rate on current measurement
(C) electrode stability for the short-term sampling period and for extended routine operation.

The above advantages, with the decreased noise levels during operation, result from the very limited time the electrode surface is pulsed and the even shorter current sampling time. This short pulse duration eliminates the development of an appreciable diffusion layer at the electrode and the subsequent dependence of the diffusion layer on flow-rate. The increased sensitivity is also a result of the short pulse with the current measured being equivalent to the bulk concentration and not affected appreciably by the development of a diffusion layer.

The primary advantage of the pulse polarographic approach for the solid electrode in a flow-through configuration is the short- and long-term stability of the electrode. The pulse polarographic approach maintains the electrode at a non-interacting potential for 90–99% of the time so that any interaction that could occur during the pulse is potentially "cleaned" from the electrode between the pulses.

The electrode materials, the electrode design and the cells themselves were not optimized for sensitivity or long-term use in this initial study.

The definite advantages of this approach for flow-through applications has encouraged the further development in our laboratory of demountable electrode modules on a rugged single-cell body for automated analysis systems as well as chromatographic systems. The characterization of electrode materials for these modules will center on platinum, gold, glassy carbon and plated surfaces so that the module electrode behavior will be determined prior to cell assembly. This approach is being used so that the future cells will be defined and reproducible both mechanically and electrochemically. The limiting electrical parameters in terms of applicable solvent systems will also be developed to define the operation of the cells.

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REFERENCES

1 O. H. Müller, *J. Amer. Chem. Soc.*, 69 (1947) 2992.
2 W. Kemula, *Rocz. Chem.*, 26 (1952) 281; *C.A.*, 51 (1957) 18479b.
3 L. D. Wilson and R. J. Smith, *Anal. Chem.*, 25 (1953) 218.
4 J. A. Lewis and K. C. Overton, *Analyst (London)*, 79 (1954) 293.
5 R. Tamamushi, S. Momiyama and N. Tanaka, *Anal. Chim. Acta*, 23 (1960) 585.
6 W. J. Blaedel and J. H. Strehl, *Anal. Chem.*, 33 (1961) 1631.
7 W. J. Blaedel and J. H. Strohl, *Anal. Chem.*, 36 (1964) 445.
8 Y. Takemori and M. Honda, *Rev. Polarogr. Jap.*, 16 (1970) 96.
9 E. Scarano, M. G. Bonicelli and M. Forina, *Anal. Chem.*, 42 (1970) 1470.
10 S. Tustanowski, *J. Chromatogr.*, 31 (1967) 266.
11 C. K. Mann, *Anal. Chem.*, 29 (1957) 1385.

12 R. L. Rebertus, R. J. Cappell and G. W. Bond, *Anal. Chem.*, 30 (1958) 1825.
13 W. J. Blaedel and J. W. Todd, *Anal. Chem.*, 30 (1958) 1821.
14 W. Kemula, *Zh. Anal. Khim.*, 22 (1967) 562.
15 W. Blaedel and J. W. Todd, *Anal. Chem.*, 33 (1961) 205.
16 J. G. Koen, J. F. K. Huber, H. Poppe and G. den Boef, *J. Chromatogr. Sci.*, 8 (1970) 192.
17 P. L. Joynes and R. J. Moggs, *J. Chromatogr. Sci.*, 8 (1970) 427.
18 E. Pungor, Zs. Fehér and G. Nagy, *Anal. Chim. Acta*, 51 (1970) 417.
19 G. Nagy, Zs. Fehér and E. Pungor, *Anal. Chim. Acta*, 52 (1970) 47.
20 W. J. Blaedel, C. L. Olson and R. L. Sharma, *Anal. Chem.*, 35 (1963) 2100.
21 W. J. Blaedel and S. L. Boyer, *Anal. Chem.*, 43 (1971) 1538.
22. D. C. Johnson, L. R. Faylor, J. H. LaRochelle and W. S. Wong, *8th A.C.S. Midwest Regional Meeting, November 8–10, 1972, Columbia, Mo.*
23 W. J. Blaedel and J. H. Strohl, *Anal. Chem.*, 36 (1964) 1245.
24 D. K. Roe, *Anal. Chem.*, 36 (1964) 2371.
25 G. C. Barker and A. W. Gardner, *Rep. U.K. At. Energ. Auth.*, AERE-C/R2297, 1958.
26 G. C. Barker and A. W. Gardner, *Z. Anal. Chem.*, 173 (1960) 79.
27 E. P. Parry and R. A. Osteryoung, *Anal. Chem.*, 36 (1964) 1366.
28 E. P. Parry and R. A. Osteryoung, *Anal. Chem.*, 37 (1965) 1634.
29 K. B. Oldham and E. P. Parry, *Anal. Chem.*, 38 (1966) 867.
30 G. D. Christian, *J. Electroanal. Chem.*, 23 (1965) 9.
31 H. Siegerman and G. O'Dom, *Amer. Lab.*, June (1972) 59.
32 A. Hickling, *Trans. Farad. Soc.*, 38 (1942) 27.
33 R. A. Adams, *Electrochemistry at Solid Electrodes*, Marcel Dekker, New York, 1969.