*Journal of Chromatography*, 208 (1981) 269–278
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,564

# COMPARISON OF SEVERAL VOLTAMMETRIC DETECTORS FOR HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY*

KAREL ŠTULÍK* and VĚRA PACÁKOVÁ
*Department of Analytical Chemistry, Faculty of Sciences, Charles University, Albertov 2030, 128 40 Prague 2 (Czechoslovakia)*

## SUMMARY

The performance of several voltammetric detectors, namely, a tubular detector with a platinum working electrode and thin-layer and wall-jet detectors with glassy carbon and graphite paste, was compared using d.c. and differential pulse polarization and adrenaline as the test substance. The parameters studied were the residual current, the accessible potential range, the detection limit, sensitivity, reproducibility, the time constant, the response volume and the dependence of the signal on the eluate flow-rate. The theoretical detector response was calculated and compared with the experimental values.

## INTRODUCTION

The recent great progress in high-performance liquid chromatography (HPLC) has stimulated development of many new detectors. Among them, an important rôle is played by electrochemical detectors that exhibit a high sensitivity, good reproducibility and a wide linear dynamic range for certain groups of substances[1–3]. Of electrochemical detectors, voltammetric ones have found by far the widest use. Detectors employing dropping mercury electrodes have the advantage that the electrode surface is periodically renewed and they exhibit a large negative potential range. However, a serious drawback lies in the construction of a reliable dropping electrode in a sufficiently small working space. This disadvantage is removed by using stationary mercury electrodes, but these no longer have the advantage of electrode surface renewal and are prone to adsorption and passivity effects. A common drawback of mercury electrodes is the limited anodic potential range and thus various solid electrodes must be used to monitor substances that are anodically oxidized. The materials used are most often various forms of carbon and less often platinum. The hydrodynamic systems employed are generally based on the thin-layer and wall-jet principles and less frequently on other systems, *e.g.*, tubular.

The performance of several detectors with dropping mercury electrodes has

* Presented at the *6th International Symposium "Advances and Application of Chromatography in Industry", Bratislava, September 16–19, 1980.*

0021-9673/81/0000–0000/$02 50 

been compared[4] with a commercial wall-jet detector Detektorzelle EA 1096 (Metrohm, Herisau, Switzerland) and with a UV detector; wall-jet detectors with glassy carbon, graphite paste and mercury electrodes were compared[5] with the EDT Research[6] and Bioanalytical Systems[7] commercial detectors. The parameters of the EDT Research detector were compared[8] with those of UV and fluorescence detectors. The function of detectors with various carbon electrodes[9,10] and with a dropping mercury electrode[11] has recently been studied.

In the present work, the performance of voltammetric detectors of our own construction based on tubular, thin-layer and wall-jet hydrodynamic systems and employing platinum, glassy carbon and graphite paste working electrodes is compared.

## EXPERIMENTAL

The tubular detector with a platinum working electrode has been described elsewhere[12]. The thin-layer and wall-jet detectors with glassy carbon and graphite paste working electrodes are constructed as a single unit (see Fig. 1). The detectors

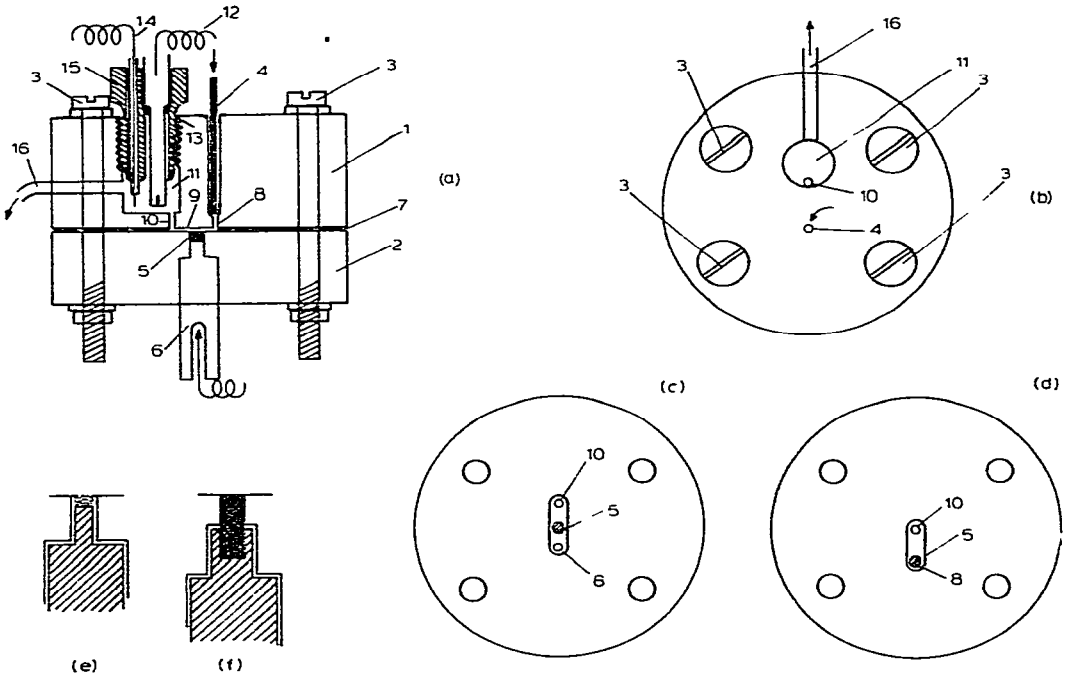


Fig. 1. Construction of the thin-layer and wall-jet detectors. a, Side view; b, top view; c, the 0.05-mm PTFE spacer in the thin-layer detectors, showing the positions of the working electrode, inlet and outlet; d, as c for the wall-jet detectors; e, expanded view of the graphite paste electrode; f, expanded view of the glassy carbon electrode 1 = PTFE body (7 cm in diameter, 3 cm high), upper part; 2 = PTFE body (7 cm in diameter, 2 cm high), lower part; 3 = plastic screws; 4 = inlet (stainless-steel capillary, 0.23 mm I.D.); 5 = working electrode (3 mm in diameter); 6 = brass contact; 7 = PTFE spacer (0.05 mm thick); 8 = inlet PTFE capillary (0 2 mm); 9 = working space; 10 = outlet (0.5 mm); 11 = reference and auxiliary electrode space; 12 = SCE; 13 = PTFE O-ring; 14 = platinum wire auxiliary electrode; 15 = plastic screw; 16 = outlet from the detector.

consist of two cylindrical PTFE parts that are tightly screwed together and separated by a thin PTFE spacer. The upper part contains the eluate inlet, the compartment for a reference and an auxiliary electrode and an outlet. The lower part contains the working electrode; in the thin-layer detectors, the electrode is located 2 mm from the inlet (Fig. 1c), whereas in the wall-jet detectors the inlet is directed to the centre of the working electrode (Fig. 1d). The hole cut in the 0.05-mm PTFE spacer defines the working space of the detectors. The bases of the PTFE cylinders that are pressed to the PTFE spacer are polished to a mirror-like finish with metallographic papers (SIA, Chur, Switzerland) and damp velvet. The SCE (saturated calomel electrode) reference and platinum wire auxiliary electrodes are fixed in a plastic screw and screwed into the reference compartment (Fig. 1a).

The glassy carbon working electrodes (Tokai Electrode Mfg. Co, Nagoya, Japan), 3 mm in diameter, are fixed in a brass contact, pressed into the PTFE body at a temperature of 200°C (Fig. 1f) and polished to a mirror-like finish as above. Graphite paste electrodes were prepared from finely pulverized spectral graphite (Kablo, Topolčany, Czechoslovakia) by mixing it with α-bromonaphthalene (p.a.) or Nujol (Lachema, Brno, Czechoslovakia) to form a thick, smooth paste. The paste was placed in a depression in the PTFE block over a brass contact (Fig. 1e) and its surface was smoothed with a glazed paper card. Details of the detectors are given in Table I.

The measurements were performed with Pye Unicam LC-XP liquid chromatograph, LP-7e and PA-3 polarographs (Laboratorni, Přístroje, Prague, Czechoslovakia) and a Varian-Techtron line recorder. The samples were injected either directly into the detector through a short stainless-steel capillary (0.23 mm I.D.) or through a Partisil 10 ODS (10 μm) column (250 × 4.6 mm) (Pye Unicam, Cambridge, Great Britain). A 20-μl sampling loop was used for sample injections, as it has been shown[13] that two to three times better sampling precision is attained than when using a syringe.

TABLE I
DETAILS OF THE DETECTORS

| *Detector* | | *Working electrode* | *Electrode surface area* ($mm^2$) | *Geometrical volume* (μl) |
|---|---|---|---|---|
| *No.* | *Type* | | | |
| 1 | Tubular | Platinum | 12 57 | 2 26 |
| 2 | Thin-layer | Glassy C | 7.07 | 0 65 |
| 3 | Thin-layer | Carbon paste | 7.07 | 0 65 |
| 4 | Wall-jet | Glassy C | 7.07 | 0 35 |
| 5 | Wall-jet | Carbon paste | 7.07 | 0.35 |

Adrenaline hydrogen tartrate (MW 333.3; Fluka, Buchs, Switzerland) was used as the test substance. A citrate–phosphate aqueous buffer[14] (300 ml of 0.1 *M* citric acid and 160 ml of 0.1 *M* $Na_2HPO_4$, pH 4.7) was used as the mobile phase. Before use it was deaerated by purified nitrogen and degassed *in vacuo*. A $10^{-3}$ *M* adrenaline stock solution was prepared in the buffer solution and diluted immediately before measurement.

The measurements were carried out at laboratory temperature, at +0.8 V (SCE) and all current values were scaled to the electrode surface area of 7.07 $mm^2$.

## RESULTS AND DISCUSSION

The results are summarized in Table II and Fig. 2.

*Accessible potential range*

All the electrode materials have similar anodic potential limits (for a current of 1 $\mu$A) [about +1.2 V (SCE) at the buffer pH of about 4.5], except for graphite paste in the wall-jet detector which has a somewhat lower value. The negative potential limit is lowest with the platinum electrode, and the most negative for the graphite paste electrode. From this point of view, the graphite paste is undoubtedly the most suitable electrode material.

*Residual current and noise*

In this respect, graphite paste is by far the best electrode material, as its residual current is more than an order of magnitude lower than with glassy carbon and platinum and exhibits a very low and regular noise. The residual current and noise level with platinum and glassy carbon strongly depend on the quality of the electrode surface polishing. Glassy carbon is especially sensitive to polishing and is easily damaged by passage of high currents. An improvement in the reproducibility of the residual current magnitude and noise level was reported after impregnation of glassy carbon with ceresine wax[15]. The noise with the platinum electrode is regular and increases uniformly with increasing sensitivity of measurement; that with glassy carbon is low and increases suddenly when currents below *ca.* $10^{-7}$ A are measured.

On the other hand, platinum and glassy carbon electrodes, when polished well, yield reproducible values for a long time (about one month in the absence of surfactants) and virtually the same absolute current values are obtained after repolishing. Graphite paste electrodes require frequent replacement (every day for those containing $\alpha$-bromonaphthalene, at least once a week for those with Nujol) as their response deteriorates quickly (the residual current increases and the measuring sensitivity decreases). This is apparently caused by bleeding of the diluent from the paste, leading to roughening of the electrode surface, and by mechanical damage to the electrode at high flow-rates, especially in the wall-jet system. Graphite paste electrodes cannot be used in non-aqueous media that dissolve the paste diluent. After replacement of the paste, recalibration must always be carried out, as the absolute current values are not reproducible.

The current value stabilizes almost instantaneously after adjustment of the potential at a graphite paste electrode, whereas at glassy carbon and platinum electrodes it drifts for tens of seconds or even several minutes. No drift of current after initial stabilization, as is sometimes reported[8], was observed. In the presence of strongly adsorbing substances (*e.g.*, phenols), the activity of all electrodes decreases rapidly.

Thus it can be concluded that for most measurements graphite paste electrodes are most suitable. Glassy carbon and platinum electrodes are useful for measurements in non-aqueous and mixed media and under conditions when the paste would be mechanically damaged (*e.g.*, high flow-rates).

*Detection limit*

The detection limit was calculated as twice the standard deviation of the noise. It is generally lower for wall-jet than for thin-layer systems and the lowest detection limit is obtained for graphite paste in the wall-jet system. The detection limit obtained with the tubular system lies between that of the thin-layer systems and the graphite paste wall-jet detector.

*Linear dynamic range and parameters of the calibration curves*

All the detectors exhibit a broad linear dynamic range, whose upper limit is dependent virtually only on the properties of the electronic circuitry. The calibration curves, obtained by the least squares method, exhibit good linearity (see the correlation coefficients of the regression straight lines in Table II), except for detector 5, where the linearity is poorer for larger injected amounts. The detectors with glassy carbon electrodes generally exhibit a higher sensitivity than graphite paste and platinum electrodes (see the slopes in Table II). All the calibration curves have a positive intercept (see Table II), which is apparently caused by adsorption of adrenaline over the whole measuring system. After several injections of adrenaline, a peak is obtained even when pure mobile phase is injected, which decreases and finally disappears on repeated injections of the mobile phase.

*Time constants and response volumes*

The time constants of the detectors were determined for a flow-rate of 0.3 ml $min^{-1}$ as the time required for attaining a current $I = 0.632\ I_{max}$ in a step change in the adrenaline concentration (see ref. 4). The response volumes were then calculated as the products of the time constants and the flow-rate. The time constants are not very different and the response volumes are somewhat greater than the geometrical volumes of the cells, indicating that diffusion plays a rôle in the overall hydrodynamics of the systems.

*Reproducibility of measurement*

The reproducibility of peak heights, half-widths and areas strongly depends on the state of the electrode surface and is similar for all the detectors. Typical values of the relative standard deviations for these values are 1% for amounts greater than 500 ng adrenaline, 3% between 100 and 500 ng, 5% for 20–100 ng and about 10% for lower amounts.

*Differential pulse polarization (DPP) measurements*

The performance of the detectors was also tested using differential pulse polarization of the electrodes. As already shown in our previous paper[12], differential pulse measurement has the same sensitivity as d.c. measurements, the residual current and noise are somewhat higher and the reproducibility of peak height is somewhat poorer. Therefore, it seems that there is no advantage in using DPP with detectors containing solid electrodes, except for an improvement in the selectivity over d.c. measurement[16].

*Response dependence on the spacer thickness*

Tests of the dependence of the detector response on the spacer thickness gave

TABLE II

OPERATING PARAMETERS OF THE DETECTORS TESTED

Adrenaline; citrate-phosphate buffer, flow-rate 0.3 ml $min^{-1}$; +0.8 V (SCE). The current values are scaled to an electrode surface area of 7.07 $mm^2$.

| *Detector* | | *Potential range (V)* | *Residual current (A)* | *Detection limit (ng)* | *Linear dynamic range (ng)* | *Parameters of calibration curves* | | | *Time constant (sec)* | *Response volume (µl)* |
|---|---|---|---|---|---|---|---|---|---|---|
| *No.* | *Type* | | | | | *Slope ($A\ \mu g^{-1}$)* | *Intercept (A)* | *Corr. coeff.* | | |
| 1 | Tubular (Pt) | −0.5 to +1.2 | $3\ 10^{-6}$–$1\cdot10^{-5}$ | 0.3 | 0.3–2500 | $1.3\cdot10^{-6}$ | $4.1\cdot10^{-8}$ | 0.998 | 1.7 | 8.5 |
| 2 | Thin-layer (glassy C) | −0.8 to +1.2 | $2.4\ 10^{-6}$–$5.6\cdot10^{-6}$ | 0.5–1.0 | 1–5000 | $2.6\cdot10^{-6}$ | $8.6\ 10^{-8}$ | 0.999 | 0.75 | 3.75 |
| 3 | Thin-layer (paste) | −1.5 to +1.2 | $1\cdot10^{-7}$–$2\cdot10^{-7}$ | 0.5–1.0 | 1–5000 | $1.17\cdot10^{-6}$ | $1.13\ 10^{-7}$ | 0.997 | 1.7 | 8.5 |
| 4 | Wall-jet (glassy C) | −0.8 to +1.2 | $1\cdot10^{-5}$ | 0.3 | 0.3–3000 | $2.3\cdot10^{-6}$ | $5.6\cdot10^{-8}$ | 0.998 | 1 | 5 |
| 5 | Wall-jet (paste) | −1.8 to +1.0 | $1.8\cdot10^{-7}$ | 0.03–0.1 | 0.03–3000 | $2.25\cdot10^{-6}$ | $2.1\cdot10^{-7}$ | 0.958 | 0.9 | 4.3 |

results similar to those reported previously[17]. On decreasing the spacer thickness, the linear flow-rate increases with consequent increase in the sensitivity; however, the noise also increases, so that the detection limit remains unchanged. The noise value is dependent chiefly on the quality of polishing of the walls of the cell; the better polished they are, the thinner the cell can be and the lower is the detection limit.

With decreasing thickness of the cell the electric impedance increases, which places greater demands on the potentiostat used. With a cell thickness of 0.05 mm, a typical value of the electric resistance between the working and reference electrodes is $10^4$ Ω.

*Response dependence on the flow-rate*

The dependences of the peak height and half-width on the flow-rate are given in Fig. 2. There are no deviations from the theoretical assumptions and no significant differences among the detectors tested. For a comparison with the theoretical dependences see below.

*Comparison of the detector performance with theoretical assumptions*

The theory of thin-layer detectors is based on the relationship derived by

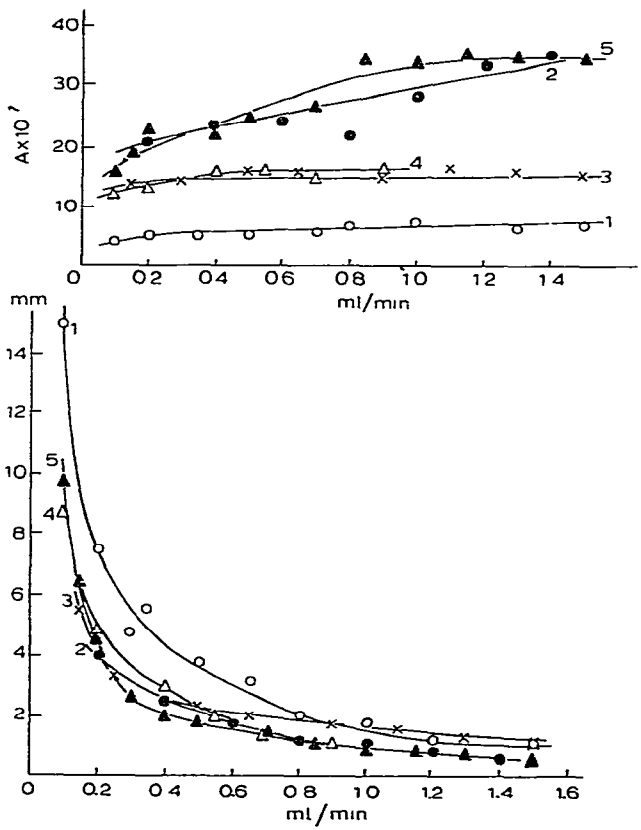


Fig. 2. Dependence of the peak height (a) and half-width (b) on the flow-rate Curves 1–5 are for detectors 1–5, respectively (see Table I). Sample 560 ng adrenaline; +0.8 V; chart rate 3 1/3 cm $min^{-1}$.

Levich[18] for the limiting current at a planar electrode immersed in a medium with laminar flow

$$I_l = 0.68\, nFD^{2/3} bl^{1/2} u^{1/2} \nu^{-1/6} c^0 \qquad (1)$$

where the symbols have their usual significance; $b$ and $l$ are the dimensions of the plate, perpendicular to and parallel with the flow, respectively. As shown in our previous paper[12], the tubular detector described behaves similarly to thin-layer detectors, because the gap between the working and auxiliary electrodes is so thin that the curvature of the electrode surface can be neglected.

For the limiting current at wall-jet electrodes, the relationship

$$I_l = (1.60 \times k)\, nFD^{2/3} \nu^{-5/12} V^{3/4} a^{-1/2} r^{3/4} c^0 \qquad (2)$$

was derived by Matsuda[19,20], in which volume flow-rate, $V$, appears instead of linear flow-rate, $u$, $a$ is the diameter of the jet, $r$ is the radius of the working disk electrode and $k$ is an empirical constant.

Using eqns. 1 and 2, theoretical maximum currents were calculated for the given detectors and the system studied. As the diffusion coefficient of adrenaline could not be found in the literature, the value $D = 0.8 \times 10^{-5}$ cm$^2$ sec$^{-1}$ was selected[21] (the diffusion coefficient of resorcinol, which is structurally the most similar to adrenaline among the substances for which diffusion coefficients were available). In the electrochemical oxidation of adrenaline two electrons are exchanged[22], *i.e.*, $n = 2$. The kinematic viscosity of the buffer solution is $\nu = 0.0104$ St. The value of the

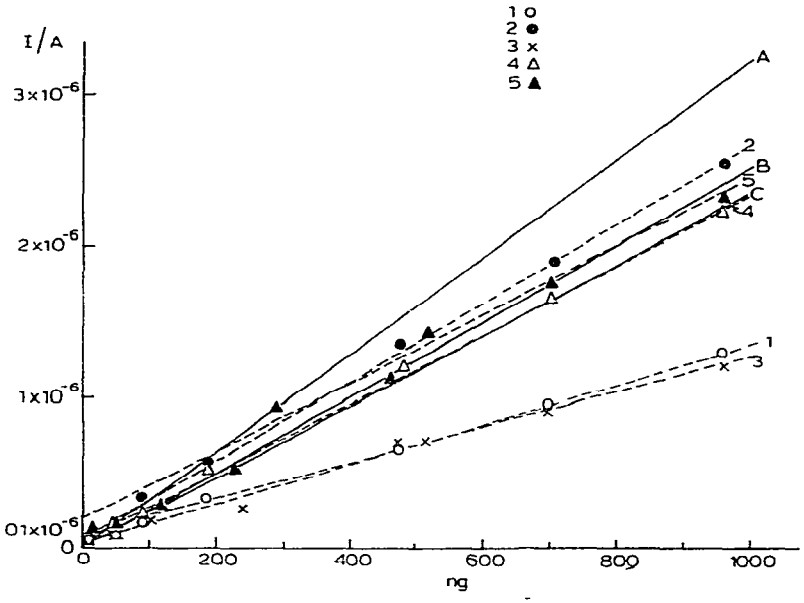


Fig. 3. Experimental and theoretical calibration curves· 1–5, detectors 1–5 (see Table I); A, theoretical curve for the thin-layer detectors, B, theoretical curve for the wall-jet detectors; C, theoretical curves for the tubular detector. Conditions: +0 8 V (SCE); flow-rate 0.3 ml min$^{-1}$. The experimental curves were not corrected for the peak caused by adsorption of adrenaline (see text).

empirical constant $k$ in eqn. 2 was taken from ref. 20 ($k = 0.86$) where it was determined with hexacyanoferrate(III) and a gold electrode. The charge-transfer reaction of adrenaline is reversible ($k' = 0.27\ sec^{-1}$ at pH 4.5)[22]. The concentrations of adrenaline in the eluate at the peak maximum were calculated and substituted into eqns. 1 and 2.

The theoretical calibration curves are given in Fig. 3, together with the experimental curves. Fig. 4 depicts the dependences of $I_{max}$ on $\sqrt{u}$ for all the detectors and of log $I_{max}$ on log $V$ for the wall-jet detectors. It can be seen that the theory predicts a somewhat higher sensitivity for thin-layer detectors than for wall-jet detectors. The tubular detector has a greater internal volume than the other detectors and thus its theoretical sensitivity is lowest.

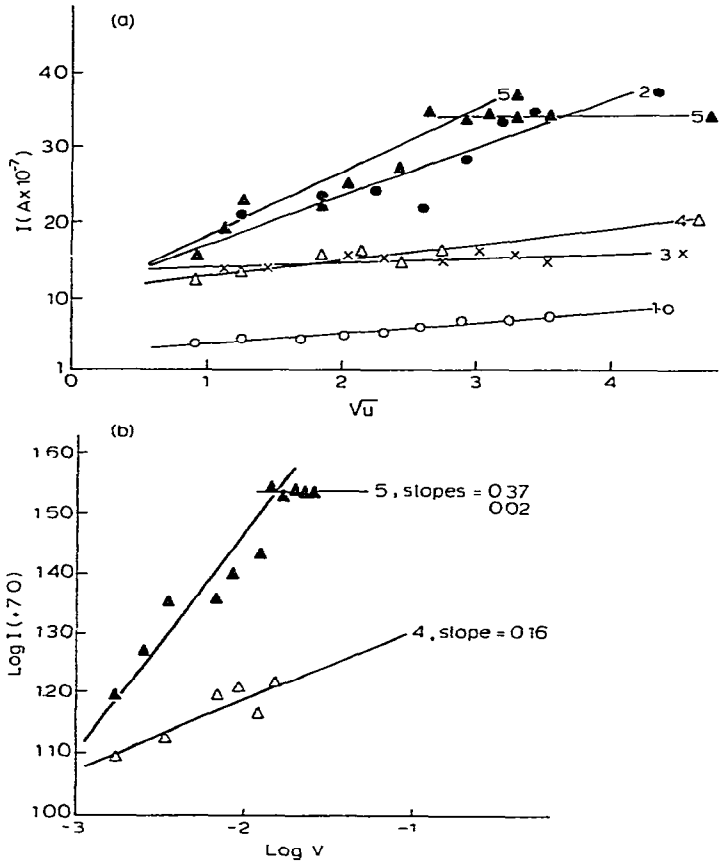


Fig. 4 Dependence of $I_{max}$ on $\sqrt{u}$ (a) and of log $I_{max}$ on log $V$ (b) Curves 1–5, detectors 1–5 (Table I) Conditions +0 8 V (SCE); 506 ng adrenaline injected

The detectors tested exhibit somewhat lower sensitivities than predicted. This is probably caused by several factors: (a) uncertainty in the values substituted into eqns. 1 and 2 (chiefly in $D$, and $k$ in eqn. 2); (b) the specific effects of the electrode material (chiefly the lower sensitivity with graphite paste compared with glassy carbon); (c) the

effect of adsorption on the electrode surface, leading to its passivity; (d) deviations from laminar flow with thin-layer systems; (e) the effect of a very small working space (*i.e* , the assumption that the thickness of the hydrodynamic boundary layer is negligible compared with the cell dimensions is invalid). The contribution from effects (d) and (e) will certainly strongly depend on the quality of electrode surface polishing and on the precision of the detector construction. The wall-jet detectors exhibit a better agreement with the theory, because the turbulent flow, also assumed by the theory, is apparently the predominant parameter.

The dependence of $I_{max}$ on $\sqrt{u}$ is linear as predicted by the theory; however, sometimes a relatively large scatter of the individual points is observed, as a result of differences in the state of the electrode surface when the dependence is constructed from the results of several separate measurements.

The experimental slopes of the log $I_{max}$ *vs.* log $V$ dependence for the wall-jet detectors are substantially less than 3/4. This is most probably caused by the mode of construction of the given detector, which does not permit free flow of the eluate radially in all directions along the electrode surface, as the spacer directs the flow in one direction, toward the outlet from the working space. The break in this dependence for the wall-jet detector with a graphite paste electrode is apparently caused by mechanical damage to the electrode at high flow-rates.

REFERENCES

1 P T Kissinger, *Anal. Chem* , 49 (1977) 447A
2 K Štulík and V Pacakova, *Chem Listy*, 73 (1979) 795.
3 K. Brunt, *Pharm. Weekbl.*, 113 (1978) 689
4 H B Hanekamp, P Bos, U. A Th Brinkman and R W Frei, *Z. Anal. Chem* , 297 (1979) 404
5 W Lund, M. Hannisdal and T. Greibrokk, *J. Chromatogr.*, 173 (1979) 249.
6 B Fleet and C J. Little, *J. Chromatogr. Sci* , 12 (1974) 747.
7 P. T. Kissinger, C. Refshauge, R. Dreiling and R. N. Adams, *Anal. Lett.*, 6 (1973) 465.
8 F. Vandermark and T. H. Ryan, *Chromatogr. Newsletter*, 6 (1978) 20.
9 R. M. Wightman, E C Paik, S. Borman, M A. Dayton, *Anal. Chem.*, 50 (1978) 1410
10 D. N. Armentrout, J. B. McLean and M W. Long, *Anal. Chem.*, 51 (1979) 1039.
11 H B Hanekamp, P. Bos and W. Frei, *J Chromatogr.*, 186 (1979) 489.
12 K. Štulík and V. Pacaková, *J. Chromatogr.*, 192 (1980) 135.
13 C. L. Blank, *J Chromatogr.*, 117 (1976) 35
14 R. M. Riggin and P. T. Kissinger, *Anal. Chem.*, 49 (1977) 2109
15 B. R. Hepler, S. G. Weber and W. C. Purdy, *Anal. Chim. Acta*, 102 (1978) 41
16 W J. Mayer and M. S. Greenberg, *J. Chromatogr. Sci.*, 17 (1979) 614.
17 K. Brunt and C. H. P. Bruins, *J. Chromatogr* , 172 (1979) 37.
18 V. G. Levich, *Discuss. Faraday Soc.*, 1 (1947) 37
19 H. Matsuda, *J Electroanal. Chem. Interfacial Electrochem* , 15 (1967) 109
20 J. Yamada and H. Matsuda, *J. Electroanal. Chem. Interfacial Electrochem.*, 44 (1973) 189.
21 D'Ans-Lax, *Taschenbuch für Chemiker und Physiker*, Vol. I, Springer, Berlin, 3rd ed , 1967.
22 L. Meites and P. Zuman, *Electrochemical Data*, Part 1, Vol. A, Wiley, New York, 1974.