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Electrochemical flow measurements in environmental analysis

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Abstract - The field of electrochemical detection in flowing liquids is briefly surveyed, with emphasis on ion-selective electrode potentiometry, polarography, voltammetry and coulometry. The main requirements on the measuring system, the operational parameters of electrochemical detectors and the principal advantages and drawbacks of electrochemical detection are discussed. Special attention is paid to the selection of the electrode material, the cell geometry and the effective volume and also the measuring method used. The performance of typical detectors is compared with the theoretically predicted values. Various construction types of detector cell for flow injection analysis and high-performance liquid chromatography and typical applications to environmentally important compounds are described, with special reference to the authors original works.

INTRODUCTION

Measurements in flowing liquids are becoming progressively more important in all branches of analytical chemistry, including environmental analysis. These involve not only continuous monitoring of substances in e.g. natural waters, waste waters, process streams, etc., but also laboratory analyses of discrete samples using the methods of continuous flow analysis (CFA), flow injection analysis (FIA) and especially high-performance liquid chromatography (HPLC). Analyses in flow systems generally permit an increase in the sample throughput, save manual work and lend themselves readily to extensive automation. As a large proportion of analyses involves determinations of traces of substances in complex matrices (this is especially important in environmental and clinical analysis), the methods employed must simultaneously be highly sensitive, reproducible and selective.

Electrochemical methods of analysis in flowing liquids have traditionally been used in process stream monitoring and recently have also found increasing application in the methods of CFA, FIA and especially HPLC. Of the many available electrochemical methods, only a few are important in analytical practice. Low-frequency conductometry and high-frequency impedance measurements have limited application and will not be discussed here. We will be concerned with the most important methods, based on charge-transfer reactions at an electrode - solution interface, namely, ion-selective electrode (ISE) potentiometry, polarography, voltammetry and coulometry.

These electrochemical methods are not as universal as, say, spectrometric methods, but for certain important groups of substances they exhibit unrivalled sensitivity, combined with good precision and accuracy. A great advantage is selectivity of the measurement, which simplifies the sample pretreatment and facilitates identification and quantitation of analytes in complex matrices, typical examples of which are environmental samples. All these advantages are fully utilized in HPLC, where the high sensitivity and selectivity of electrochemistry is combined with highly efficient separation - in fact, this is probably the most important recent application of electrochemistry to analytical chemistry.

On the other hand, most electroanalytical methods suffer from a serious drawback, namely, poor reproducibility of the sensor surface activity, as a result of interactions with the test solution. To overcome this problem, knowledge of the principles of electrochemistry and a certain amount of experience are required; this often compares unfavourably with, e.g., simple spectrometric methods and causes electroanalytical methods to be less popular in analytical laboratories than they deserve to be.

Below, certain aspects of electrochemical detection in FIA and HPLC are discussed on the basis of our own original work; only a few papers by other authors are cited where appropriate. For more complete treatment of this extensive field and a literature survey, the reader is referred elsewhere (refs. 1-7). The performance of any detector in a liquid stream is evaluated in terms of several parameters, such as the sensitivity, selectivity, linear dynamic range, precision and accuracy of measurement, signal-to-noise ratio and the detection limit. The dynamic properties, long-term response stability and the effective volume and geometry of the cell are especially important, to avoid distortion of analyte zones in the liquid stream in CFA, FIA and HPLC. The detectors are evaluated below on the basis of these parameters.

POTENTIOMETRY WITH ION-SELECTIVE ELECTRODES (ISEs)

This is an attractive method because of the extreme simplicity of the apparatus and the measuring technique. Two other features are ambiguous: The fact that ISE's respond to the activities of analytes is advantageous in e.g. speciation studies in the environment and in some clinical analyses, but complicates the determination of total analytical concentrations of substances. The very high selectivity of the measurement is advantageous in CFA and FIA, but limits the applicability of HPLC detection. The greatest drawback for any flow measurement is a slow response of most ISE's, especially at low analyte concentrations. Problems also arise from the high impedance of most cells containing ISE's, especially when the signal is to be transmitted over long distances (e.g. in environmental monitoring).

We have recently studied the properties of a cell with an ISE under FIA conditions (ref. 8). A planar cell was used (Fig. 1) whose volume could be adjusted by using appropriate spacers to 25, 100 and 1500 µl, thus representing typical cells for FIA (25 and 100 µl) and for process stream and environmental monitoring (1500 µl). Laminar flow could be assumed in the connecting tubing, which was 1 mm in internal diameter. A cyanide-selective ISE, characterized by a fast response, was used and some measurements were carried out with a calcium-selective ISE and an ammonia gas probe that exhibit slow responses.

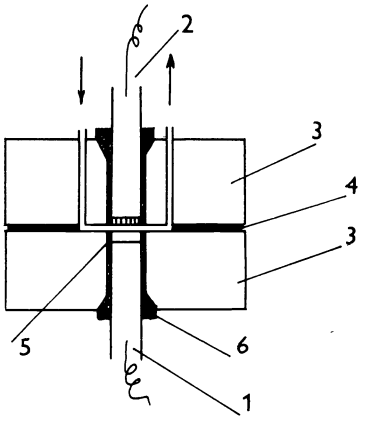

Fig. 1. Thin-layer cell with an ISE. 1 - ISE, 2 - reference electrode, 3 - cell body, 4 - spacer, 5 - rubber seal, 6 - fixing screw

The response generally consists of peaks with pronounced tailing, indicating that convection is the predominant factor in the control of the analyte zone dispersion and thus the Taylor model (ref. 9) is generally inapplicable. As can be expected, the importance of convective dispersion increases with increasing cell volume. The experimental widths of the response curves are always greater than the theoretical values calculated from the relationships derived by Vanderslice et al. (ref. 10), chiefly because the theoretical treatments neglect the contribution of the sensor itself to response curve broadening and consider only the dispersion in the tubing. Diffusional dispersion gradually becomes more important as the cell volume decreases. Thus, at cell volumes below 100 µl, the response curve width is independent of the sample concentration, while there is a pronounced increase in the width with increasing concentration in the 1500 µl cell.

The response curve tailing sharply increases when the flow rate decreases below a certain value, which equals ca. 3, 6 and 12 ml.min^{-1} for cell volumes of 25, 100 and 1500 µl, respectively. The response rates, expressed in terms of the time constants (the time from the beginning of the response change to the attainment of 63.2% of the maximum response), are given in Table 1, together with the corresponding response volumes, V_{resp}, calculated by

TABLE 1. Time constants (T_k) and response volumes (V_{resp}) in dependence on the liquid flow rate.

Flow rate (µl/s)	Detector cell volume					
	1500 µl		100 µl		25 µl	
	T_k (s)	V_{resp} (µl)	T_k (s)	V_{resp} (µl)	T_k (s)	V_{resp} (µl)
1.5	135.0	200	75.0	110	75.0	110
3.0	75.0	225	50.0	150	47.5	140
6.0	40.0	240	25.0	150	25.0	150
12.0	21.6	260	15.0	180	15.0	180
22.0	12.5	275	7.5	165	6.0	130
47.0	9.0	420	5.0	235	2.5	120
92.0	5.0	460	4.0	360	2.0	180
180.0	4.0	720	2.5	450	1.5	270

multiplying the time constant by the volume flow rate. A response volume equal to the geometric volume of the cell indicates that the cell functions as an ideal mixer; response volumes greater than the geometric volume indicate that diffusion plays a role in the signal control. It can be seen that, at low flow rates, the response times of detector cells with volumes of up to 100 µl are similar, while the cell with a volume of 1500 µl exhibits a substantially slower response. However, with increasing flow rate, the response times of all the cells gradually become similar. The response volumes of the smaller cells (25 and 100 µl) are larger than the geometric volume, indicating participation of diffusion in the cell. On the other hand, the response volume of the 1500 µl cell is substantially smaller than the geometric volume; this demonstrates that the effective volume of the cell is smaller than the geometric volume, i.e. that only part of the analyte reaches the sensor during the residence time in the cell. The response volumes increase with increasing flow rate above a certain value, equal to ca. 25, 47 and 91 $\mu l.s^{-1}$ for detector volumes of 1500, 100 and 25 µl, respectively. This increase reflects not only the increasing importance of diffusion in the detector signal control with increasing flow rate, but probably also the effect of the limited response rate of the sensor itself. It can generally be concluded that higher flow rates should be used when the detector cell volume is large.

The length of the inlet tubing required for the stabilization of the analyte concentration profile can be assessed from the dependence of the signal magnitude on the detector volume. With a tubing length typical for FIA measurements (30 cm), the calibration curves differ for different cell volumes and this difference disappears on increasing the inlet tubing length to 100 cm. Consequently, FIA measurements are sometimes carried out in practice with an unstabilized concentration profile.

As could be expected, the response curve width generally decreases with increasing flow rate. The peak height is virtually independent of the flow rate for small cell volumes, while it increases with decreasing flow rate for the large cell. However, this increase is not sufficiently high to counterweigh the advantage of a faster response at high flow rates. The experiments with the calcium ISE and the ammonia gas probe yielded very poor sensitivity and a very sluggish response.

The problem of the high impedance of cells with ISE's, causing a high level of noise and a poor precision of the measurement, can be removed by placing suitable electronic circuitry directly in the body of the ISE, digitizing the signal and transmitting it using an optical link (ref. 11). An example of such a circuit is given in Fig. 2. The response then exhibits virtually no noise, excellent precision and can readily be transmitted over long distances.

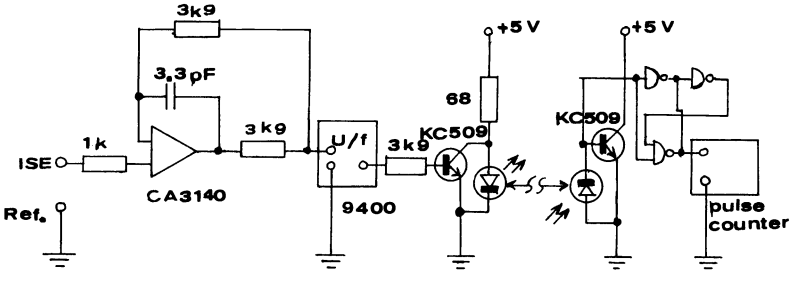

Fig. 2. Transmission of a low-impedance, digitized signal by an optical link

POLAROGRAPHY, VOLTAMMETRY AND COULOMETRY

It is appropriate to discuss these three methods together, as polarography and voltammetry differ only in the working electrode material and the experimental conditions alone determine whether the detection cell operates amperometrically or coulometrically. In designing and operating such a detector, three principal aspects must be considered:
(a) The working electrode material must be selected and the working electrode constructed so that the accessible potential range suffices for the given purpose, the residual current and noise are sufficiently small and constant, the surface activity of the working electrode is reproducible and the analyte electrode reaction has favourable kinetic and thermodynamic parameters.
(b) The cell geometry must allow for the smallest possible effective volume, to suppress the analyte zone broadening and distortion, and the hydrodynamic conditions must be favourable.
(c) The measuring technique must be sensitive, reproducible, sufficiently selective and the signal should be easy to handle.

Working electrode material

The properties of common working electrode materials, i.e. mercury, various forms of carbon and noble metals, have been extensively studied and need not be discussed here. However, it is worthwhile to point out the advantages of microelectrodes and microelectrode arrays (Fig. 3). It has been found (ref. 12) that the best signal-to-noise ratios are obtained on carbon paste electrodes, mainly because these electrodes behave as microelectrode arrays. It has recently been shown (refs. 13-15) that the main advantages of microelectrodes include rapid mass transport toward the electrode permitting high measuring sensitivity, very rapid relaxation permitting steady-state measurements at high potential-scan rates and very low ohmic drop values, enabling measurement in solutions with high resistances (i.e. virtually in the absence of a base electrolyte). In addition, the signal-to-noise ratio is further enhanced in flow measurements by the edge effect (the effect of lateral diffusion). Further, in flow measurements with microelectrode arrays, the diffusion layer is partially replenished with the analyte during the passage of the solution over the insulator separating the individual microelectrodes. Therefore, microelectrodes and microelectrode arrays exhibit not only a high signal-to-noise ratio, but also a suppressed dependence of the signal on the liquid flow rate, permit measurement in very poorly conductive media and allow pulse measurements without a large increase in the background current.

The main disadvantages of classical carbon paste electrodes are poor mechanical stability, difficulties in making the electrode surface smooth and bleeding of the diluent. These problems are solved by using composite electrode materials, in which carbon particles are dispersed in a suitable porous polymer. We have obtained good results (ref. 16) using mixtures of graphite powder with polyvinyl chloride (a carbon-to-PVC ratio of 17 : 1) and with a chloroprene rubber - alkylphenol resin (a carbon-to-resin ratio of 1.2 : 1). Excellent results have been obtained using an array of carbon fibre microelectrodes (ref. 17); the detector cell is described below.

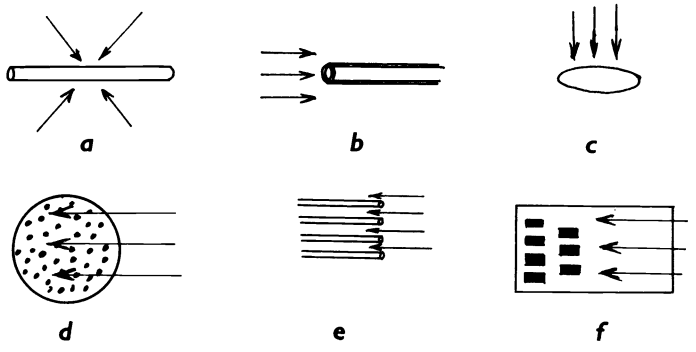

Fig. 3. Microelectrodes (a to c) and microelectrode arrays (d to f). a - fibre, b - insulator-coated fibre, c - microdisk, d - composite electrode, e - fibre array, f - array produced by a lithographic technique

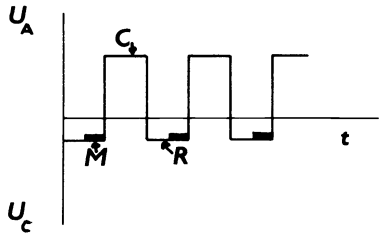

Fig. 4. Electrode polarization by alternate measuring and cleaning pulses
M - measuring interval, C - cleaning interval, R - relaxation interval

It is difficult to maintain the surface of solid electrodes in a reproducible, active state; this subject has been treated extensively in the literature and the techniques involve mechanical polishing, as well as chemical and electrochemical procedures. We have found (ref. 18) that passivation effects in flow measurements can often be suppressed by polarizing the electrode alternately by measuring and cleaning pulses at a low frequency (units of Hz), with current sampling to suppress the charging current effect (Fig. 4). The method was later developed (ref. 19) and more complex waveforms were used. Passivation effects are substantially less serious with microelectrodes; a carbon fibre detector (ref. 17) could be used for more than one year without any cleaning or activation procedure.

Chemically modified electrodes seem very promising for the future (ref. 20). So far, however, practical use of these electrodes in flow measurements is hindered by their poor mechanical strength and poor long-term stability.

Cell design

It is very difficult to simultaneously make the effective cell volume sufficiently small (especially for microbore and capillary column HPLC) and to ensure optimal electrochemical conditions. Small cells with capillary liquid pathways generally have a very high electrical resistance and thus the distance between the electrodes should be as small as possible to minimize the uncompensated ohmic drop (Fig. 5a). To ensure uniform polarization of the working electrode, the working and counter electrodes should be placed opposite one another (Fig. 5b), but then the counter electrode reaction products can cause interference at the working electrode (this position is sometimes useful in dual working electrode cells). Therefore, the most common position of the counter electrode is downstream from the working electrode, as close to it as possible (Fig. 5c), even if the working electrode is nonuniformly polarized. It must always be borne in mind that the conditions in flow-through microcells are very different from those in batch experiments in macrocells; therefore, the measuring conditions should always be optimized on the basis of polarization curves obtained in the microcell under the actual flow conditions and not on the basis of measurements in macroscopic cells.

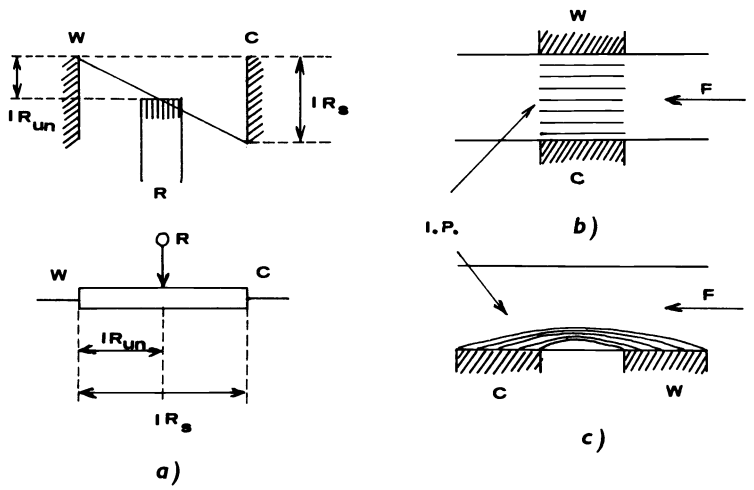

Fig. 5. Uncompensated IR drop and potential distribution at the electrodes. a - origin of an uncompensated IR drop, b - uniform polarization of the working electrode, c - nonuniform polarization of the working electrode. W, C, R - working, counter, reference electrode, respectively, IR_s - ohmic drop in solution, IR_{un} - uncompensated IR drop, I.P. - isopotential planes

Examples of the cells that meet the above requirements reasonably well are given in Fig. 6 - the tubular system (ref. 21) and in Fig. 7 - the thin-layer/wall-jet system (refs. 16,22). A disadvantage is that the performance of these cells strongly depends on the precision of the cell fabrication and on the quality of polishing of the cell walls. This problem can be circumvented by using a macroscopic cell with macroscopic reference and counter electrodes and making only the cell effective volume small. Examples are a polarographic cell in Fig. 8 (ref. 23) that is a modification of the cell manufactured by Princeton Applied Research, USA, and a cell with carbon fibre microelectrodes in Fig. 9 (ref. 17). The latter cell exhibits especially good performance and its effective volume can be varied by varying the fibre length.

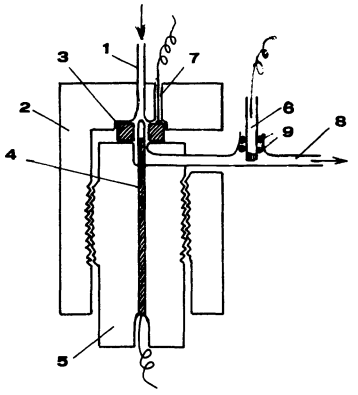

Fig. 6. Tubular detector. 1 - Inlet, 2 - PTFE detector body, outer part, 3 - platinum tubular working electrode, 4 - platinum cylindrical counter electrode with a PTFE insulating cap, 5 - PTFE detector body, inner part, 6 - reference electrode, 7 - channel for the lead to the working electrode, 8 - glass tube to waste, 9 - PTFE O-rings

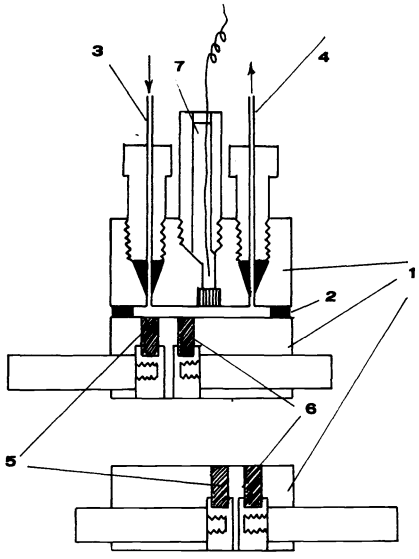

Fig. 7. Thin-layer/wall-jet detector. 1 - PTFE blocks, 2 - PTFE spacer, 3 - inlet, 4 - outlet, 5 - working electrode, 6 - counter electrode, 7 - reference electrode. The thin-layer detector is changed into the wall-jet detector by turning the bottom part of the cell by 180°

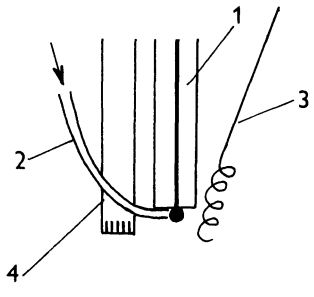

Fig. 8. Polarographic detector. 1 - DME, 2 - PTFE capillary, 3 - counter electrode, 4 - reference electrode

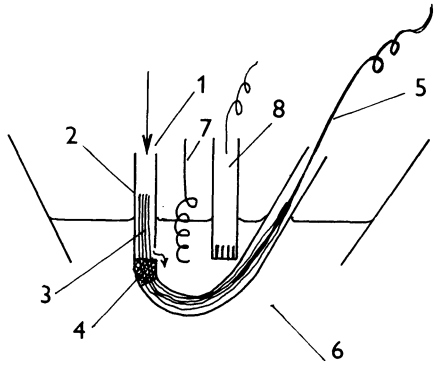

Fig. 9. Detector with a carbon fibre microelectrode array. 1 - Inlet, 2 - PTFE capillary, 3 - carbon fibres, 4 - silicone rubber seal, 5 - lead to the working electrode, 6 - base electrolyte, 7 - counter electrode, 8 - reference electrode

TABLE 2. Operational parameters of some polarographic and voltammetric detectors

Detector type/ working electrode	Detection limit (ng)	Lin.dynamic range (ng)	Calibr. curve slope (nA/ng)	corr. coeff.	Time const. (s)	Response volume (µl)	Geometric volume (µl)
Polarogr./ HMDE	15[a]	100-30000	0.99	1.000	2.2[b]	36.7	8
Polarogr./ conical HMDE	3[a]	10-30000	0.53	0.999	2.3[b]	38.3	8
Polarogr./ conical HMDE[c]	3[a]	10-25000	0.27	1.000	0.6[b]	10.0	8
Polarogr./ HMDE - PAR	6[d]	-	6.2	0.997	3.7[e]	18.5	-
Tubular/ Pt	0.3[f]	0.3-2500	1.3	0.998	1.7[e]	8.5	2.3
Thin-layer/ glassy C	0.5-1.0[f]	1.0-5000	2.6	0.999	0.8[e]	3.8	0.7
Thin-layer/ C paste(nujol)	0.5-1.0[f]	1.0-5000	1.2	0.997	1.7[e]	8.5	0.7
Wall-jet/ glassy C	0.3[f]	0.3-3000	2.3	0.998	1.0[e]	5.0	0.4
Wall-jet/ C paste(nujol)	0.03[f]	0.03-3000	2.3	0.958	0.9[e]	4.3	0.4
Wall-jet/ C composite	0.1[f]	0.1-3000	3.0	0.999	-	-	0.4
Carbon fibre/ glassy C	0.003[g]	0.003-50	3.7	0.997	0.2[e]	1.0	0.4

a - nitrobenzene; b - flow rate, 1 ml/min; c - wall-jet system; d - picric acid; e - flow rate, 0.3 ml/min; f - adrenaline; g - benzidine. Amperometric measurement at a constant potential corresponding to the analyte limiting current.

The operational parameters of the above detectors are summarized in Table 2; for the sake of comparison, the data on classical polarographic cells with small dropping mercury electrodes were taken from ref. 24. As can be seen from Fig. 10 (ref. 12), voltammetric detectors are generally somewhat less sensitive than could be expected from the hydrodynamic electrochemical theory, mainly because of electrode passivation effects. Other factors that may cause deviations of the cell behaviour from theory involve uncertainty in the numerical values substituted into the equations, deviations from laminar flow if laminar flow is assumed by the theory and the effect of the very small working space (often smaller than the hydrodynamic boundary layer volume).

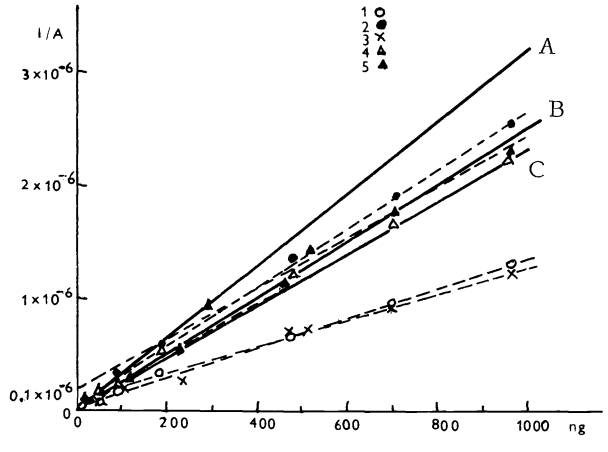

Fig. 10. Experimental and theoretical calibration curves. A, B, C - theoretical curves for the thin-layer, wall-jet and tubular system, respectively; 1 - tubular (Pt), 2 - thin-layer (glassy C), 3 - thin-layer (C paste), 4 - wall-jet (glassy C), 5 - wall-jet (C paste). Adrenaline, aqueous citrate-phosphate buffer, +0.8 V (Ag/AgCl), 0.3 ml/min

Measuring techniques

The simplest and commonest technique is d.c. amperometry which may be combined with low-frequency cleaning potential pulses (ref. 18). Pulse voltammetric techniques have repeatedly been introduced in an attempt to improve the sensitivity and selectivity of measurements and to suppress the signal dependence on the liquid flow rate and electrode passivation. However, the sensitivity and the detection limit are usually poorer in pulse measurements (refs. 21,23), especially when working with solid electrodes, because the noise is high. The signal dependence on the liquid flow rate is decreased in pulse measurements only when the flow rate is low. The selectivity of measurement is improved, but the electrode potential must be adjusted exactly to the value corresponding to the peak of the pulse-voltammetric curve. Microelectrodes seem to be very promising for pulse measurements (see above); they are also useful for rapid potential scan measurements (ref. 25).

Under the conditions discussed above, all the detectors operate amperometrically, with a maximum conversion of units of per cent (ref. 17). However, at sufficiently low liquid flow rates (units to tens of microlitres per minute, typical of microbore column HPLC) they may yield a coulometric response, with all the advantages of this technique.

Application range

In applying electrolytic detectors, their sensitivity to certain classes of compounds can be utilized; in many cases, their selectivity is useful, and identification and quantitation of substances in complex mixtures can be facilitated by combining electrochemical and photometric (or other) detectors in series. The sensitivity of voltammetric detectors, compared with photometric detection, is illustrated for some environmentally important substances in Table 3 (refs. 26-28).

TABLE 3. Detection limits for some environmentally important substances

Substance	Detection limit (ng)	
	Photometry	Voltammetry
Aromatic amines (280 nm, +0.9 V)		
4,4′-diaminobiphenyl (benzidine)	3.0	0.003
3,3′-dimethoxybenzidine (o-dianisidine)	4.0	0.05
3,3′-dichlorobenzidine	16.0	0.45
3,3′-diaminobenzidine	3.0	0.05
3,3′-dimethylbenzidine (o-tolidine)	4.0	0.03
4-aminobiphenyl	10.0	1.1
4-nitrobiphenyl	12.0	-
1-naphthylamine	11.4	1.4
2-naphthylamine	11.4	9.0
2,5-diaminotoluene	12.2	0.06
4,4′-methylenebis-(o-chloroaniline)	5.0	4.6
Biphenols (254 and 280 nm, +1.2 V)		
2-hydroxybiphenyl	0.5	0.2
3-hydroxybiphenyl	0.9	0.7
4-hydroxybiphenyl	0.9	0.2
2,2′-dihydroxybiphenyl	0.2	0.1
4,4′-dihydroxybiphenyl	0.6	0.1
2,5-dihydroxybiphenyl	0.2	0.1
3,4-dihydroxybiphenyl	4.0	2.3
2,2-bis(4-hydroxyphenyl)propane	0.4	0.2
Azobenzenes (410 nm, +0.8 V)		
4-amino-4′-hydroxyazobenzene	0.08	0.02
4-methylamino-4′-hydroxyazobenzene	0.1	0.03
4-dimethylamino-4′-hydroxyazobenzene	0.06	0.03
dimethylamino azobenzene	0.04	2.20
azobenzene	0.30	2.70
4-dimethylamino-4′-aminoazobenzene	0.07	0.02
4-dimethylamino-4′-fluoroazobenzene	0.09	2.50

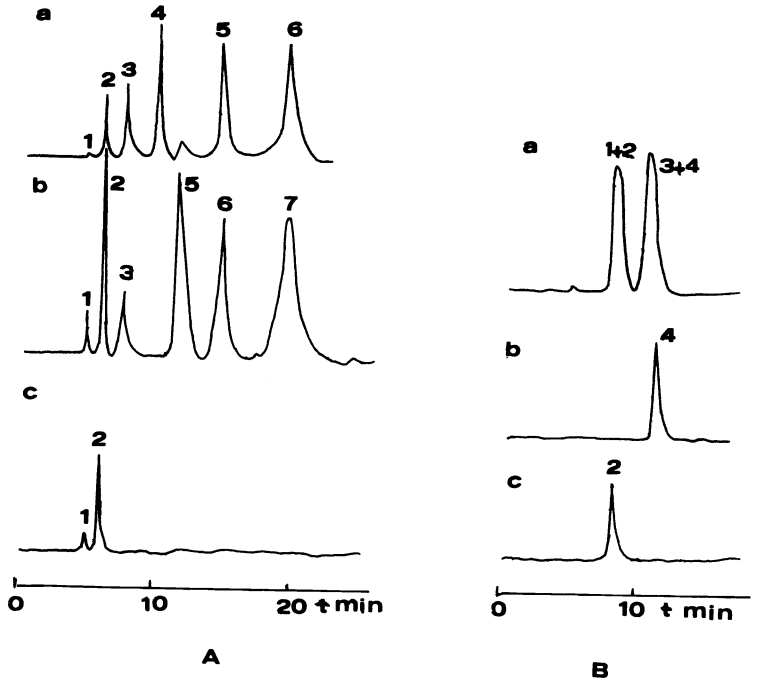

Fig. 11. (A) Separation of several pyrimidine derivatives. a - UV photometric detection at 254 nm; b - voltammetric detection, +1.4 V (Ag/AgCl); c - voltammetric detection, +0.8 V (Ag/AgCl). 1 - hold-up time; 2 - 2,4,5-triamino-6-hydroxypyrimidine; 3 - 2-amino-4,6-dihydroxypyrimidine; 4 - uracil; 5 - 4,5,6-triaminopyrimidine; 6 - 6-amino-4-hydroxy-2-mercaptopyrimidine; 7 - 4-mercaptouracil.
(B) Chromatograms of cytosine (1), 6-azacytosine (2), uracil (3) and 6-aminouracil (4). a - UV photometric detection at 254 nm; b - voltammetric detection at +1.4 V (Ag/AgCl); c - polarographic detection at -1.0 V (Ag/AgCl)

The importance of the selectivity of the measurement and of combination of several detectors in series is demonstrated in Fig. 11 (ref. 29): In the HPLC determination of pyrimidine derivatives, a UV spectrometric, a voltammetric and a polarographic detector were used in series. All the derivatives are detected photometrically, while the voltammetric detector responds only to the derivatives containing oxidizable substituents (e.g. amino and mercapto) and the polarographic detector responds to the derivatives containing reducible groups (e.g. nitro and aza). The selectivity can further be improved by variation of the working electrode potential (Fig. 11A). An example of resolution of substances poorly resolved in the HPLC column is given in Fig. 11B.

Electrochemical detection can conveniently be combined with chemical reactions. For example, a simple thin-layer cell containing a Clark oxygen sensor with an enzyme immobilized on the sensor membrane (ref. 30) enables FIA determinations of e.g. glucose with glucose oxidase and phenols with tyrosinase. The determinations are sensitive (detection limits of units to tens of nanograms), selective, simple and the sample throughput is 20 to 60 samples per hour. Another possibility is the use of a copper electrode, polarized anodically, to detect substances that rapidly form stable complexes with cupric ions (ref. 31). This technique permits sensitive and selective detection of a great many substances (ref. 32).

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