Design of an ion-selective electrode analytical system for monitoring copper in electrochemical reactors

F. C. WALSH

Ecological Engineering Limited, Macclesfield, UK

D. R. GABE

University of Technology, Loughborough, UK

Received 24 April 1980

A flow-through cell using ion-selective electrodes has been designed for continuous on-line monitoring of electrochemical reactors. A full range of design considerations is discussed and the characteristics of the cell investigated. Optimal operating conditions are found, of which solution flow rate and constancy of temperature are particularly important. The cell was also designed to have a rapid response time and minimal 'dead' volume so as to give continuous measurements of gradually changing metal ion concentrations. Performance has been evaluated using laboratory-simulated conditions and pilot-plant operation of the Ecocell, a rotating-cylinder electrode reactor for the electrowinning of copper from dilute solutions (10–1000 ppm).

Nomenclature

C_0 initial metal ion concentration (ppm)
C_t metal ion concentration at time t (ppm)
E potential (V)
$E^{0,1}$ a constant potential (V)
F Faraday constant (= 96498 C)
k apparent rate constant (s^{-1})
r volumetric flow rate $(cm^3 s^{-1})$
R universal gas constant (= 8.314 J K^{-1})
T absolute temperature (K)
t time (s)
V volume of gradient device (cm^3)
τ relaxation time (s)

1. Introduction

For continuous chemical monitoring of flow streams ion-selective electrodes (ISE) offer many attractions and considerable advantages. However, while the last fifteen years have seen very rapid developments in the design of a large range of electrode types selective towards a vast number of ions with varying degrees of selectivity [1–4], relatively little attention has been paid to the novel use of such electrodes. For many simple labora-tory analyses it is sufficient to take a sample, immerse the ion-selective electrode in it, together with a suitable reference electrode and thermo-meter, and after good mixing take a reading of potential. However, this is a batch technique and several advantages may arise from a technique involving a continuous flow of solution; these include increased rates of analyses, convenience and safety, accuracy and precision, mechanical stability of the electrode and improved monitor-ing and control of a continuous process.

In principle, the simplest form of flow cell consists of inserting the electrodes directly into a pipe through which the solution to be monitored is flowing. This is rarely practicable and may even be undesirable because the flow rate may vary and affect the electrode response, it may be of varying ionic strength and pH, interfering ions or solid par-ticles may be present and the electrodes may have to be removed for periodical calibration. Thus a more sophisticated sample 'bleed' system is almost always preferable in which the sample can, if necessary, be conditioned to constant pH and ionic strength and not necessarily returned to the process stream. Furthermore, as the conventional reference electrode may be the least reliable part

of an ISE analytical system a special sampling cell may incorporate several ion-selective electrodes which may be used to detect other specific ions or to establish concentration gradients and ensure that equilibrium potential values are being recorded.

Apart from purpose-built systems, such as those by Technicon (the Autoanalyser) or E.I.L. (model 8000), which are available commercially, many of the flow-through cells described in the literature place the ISE in tight-fitting flow caps with the reference electrode in an overflow position [5] or coupled to the ISE through an agar bridge [6]. The end caps may be made of perspex or PTFE but the fact that they are well-sealed may create pressure differential effects in the flow circuit which may affect liquid junction bridges. By careful design of the end-cap geometry stagnation can be avoided and the volume of solution minimized so that very small wash-out times are involved [5–8]. It is further possible to incorporate a heater and temperature probe [9] or magnetic stirrer bar [10] but the detector cell volume may be increased unacceptably. Electrodes are usually mounted vertically and thus may be susceptible to air bubble contamination especially in systems using gas bubble mixing or dissolution [10, 11]. Such designs have been used in biochemical applications to detect F^-, CN^-, NO_3^-, I^- etc. ions. This study has been directed towards applications in electrochemical engineering involving the removal of metal ions from waste liquors (i.e. at low concentrations) in electrochemical reactors [12–15], which not only enable metal to be recovered but also enable the solution to be acceptable as municipal effluent.

2. Experimental

2.1. Design considerations

Design of the detector cell was considered in the light of previous literature and with the following specific criteria in mind:

(a) The cell should be robust for both laboratory and plant use and provide good mechanical support for the electrodes.

(b) The cell should be transparent.

(c) The cell should be readily dismantled for cleaning and maintenance and easily but securely resealed.

(d) The cell should accommodate all types of commercial and purpose-made electrodes together with a thermometer.

(e) The wash-through characteristics should be good.

(f) Thermostatic control should be possible.

(g) Steady uniform flow should prevail.
Inevitably certain compromises were made in order to keep the design as simple as possible.

2.2. The detector cell

The design was finalized in the form shown in Fig. 1, and consists essentially of two 25 mm thick rectangular sections of perspex, selected for its mechanical and chemical stability, transparency and ease of machining. The electrodes, together with a piece of platinum wire as the solution ground and the thermometer, were mounted vertically through screw-fitting PTFE collars which squeezed down silicone rubber seals located between collars and recesses which were machined into the upper perspex section. This section also carried the PTFE inlet and outlet adaptors. The lower perspex section was grooved to take a silicone rubber 'O' ring seal.

In an early design a rectangular channel 5 mm deep × 12.5 mm wide was machined out of the lower section, but this constituted a high volume (11.25 cm^3) with consequent poor wash-out and response time characteristics due to the low linear flow velocity. The later design reduced the volume to 1.25 cm^3 by making the channel height the constant thickness of the seal, but problems of air bubble entrapment necessarily increased. Such a design facilitated electrode changes without the need for resealing and in addition the rectangular channel gave rise to very steady hydrodynamically controlled flow. Collars of PTFE do not seize in perspex threads (unlike nylon or polypropylene) while only slight pressure was required to seal the electrodes using standard-size rubber 'O' rings. A wide variety of electrode sizes could be accommodated by using different sized seals up to a maximum diameter of 18 mm. The inlet and outlet adaptors were readily removed and accepted a wide range of tube sizes. Stainless steel tie bolts were used to clamp the perspex sections of the cell together, but wing nuts or spring clips may be considered because the seal was so effective.
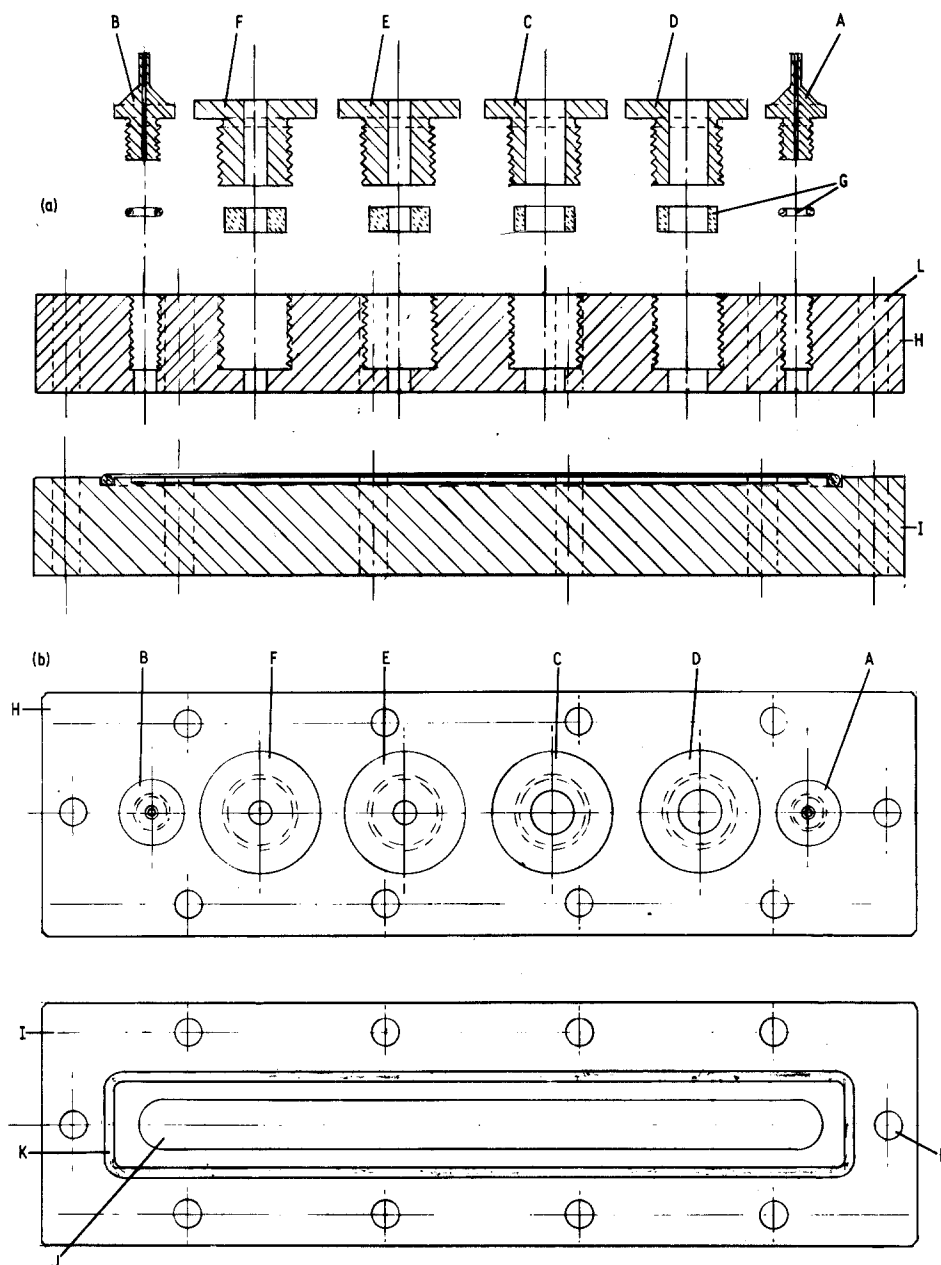
Fig. 1. ISE flow-through detector cell. (a) sectional view; (b) plan view. A, Outlet adaptor; B, inlet adaptor; C, ISE adaptor; D, reference electrode adaptor; E, thermometer adaptor; F, solution ground adaptor; G, 'O' ring seals (silicone rubber); H, upper cell section; I, lower cell section; J, flow channel; K, cell seal (nitrile rubber); L, tie bolt hole.

The cell was found to be very versatile in use because the thermometer could be replaced by a combination pH electrode and a second ISE could be included. The main ISE was normally mounted away from the inlet to minimize any entry length effects and the reference electrode mounted downstream. A double-junction reference electrode was used with a conventional Hg/Hg_2SO_4 element in $1 M$ Na_2SO_4 as the internal solution and $1.5 M$ H_2SO_4 as the outer solution. This minimized liquid junction potentials and removed the liquid junction from the rectangular channel/reference electrode frit interface; a calomel electrode was not used in order to eliminate any possible

chloride contamination which could affect the response of the cupric ISE.

Portex tubing was used for flow connections although silicone rubber was preferred for the peristaltic pump. Tube bores of 2 mm were used in order to decrease the dead volume of the system although a 4 mm bore tube was used at the pump to provide increased flow rates at modest pump speeds thereby reducing tube wear to a negligible level.

2.3. The flow system

The flow diagram is shown schematically in Fig. 2. Calibration was achieved by either the passage of discrete standard solutions, within the appropriate concentration ranges, through the cell or by using a concentration gradient technique to simulate the decaying concentrations for which the cell was required.

The electrical circuitry is shown schematically in Fig. 3, the cupric ISE being connected to the high impedance input and the reference electrode to the low impedance input of a Corning pH/millivoltmeter. This instrument had an expanded 0–100 mV scale enabling readings of potential to be measured to ± 0.05 mV. It could be improved by using a O–IV back-off unit between the output and a Bryans 2800 recorder thus enabling the potential to be monitored and read to ± 0.01 mV if necessary. Both commercial Orion (model 94-29) cupric-ion electrodes and specially prepared electrodes (see Fig. 4) were used, construction details being given in the Appendix.

2.4. Calibration for concentration decay

Because the main application envisaged for the cell was the monitoring of copper ion depletion in the Ecocell [12–15], according to the exponential law

$$C_t = C_0 \exp(-kt) \qquad (1)$$

a concentration decay calibration was considered essential. The concentration gradient device is shown in Fig. 5 and consists of a tall, sealed perspex cylinder equipped with a magnetic stirring bar and of a volume equivalent to the rotating cylinder reactor being monitored (i.e. 1 litre). This was filled initially with the same cupric ion solution as the reactor and 1.5 M H_2SO_4 diluent was pumped in at a fixed rate to overflow as the gradient standard. Initially the pump was a tube fitted to the peristaltic pump used to supply the detector cell; however, as difficulty was experienced in
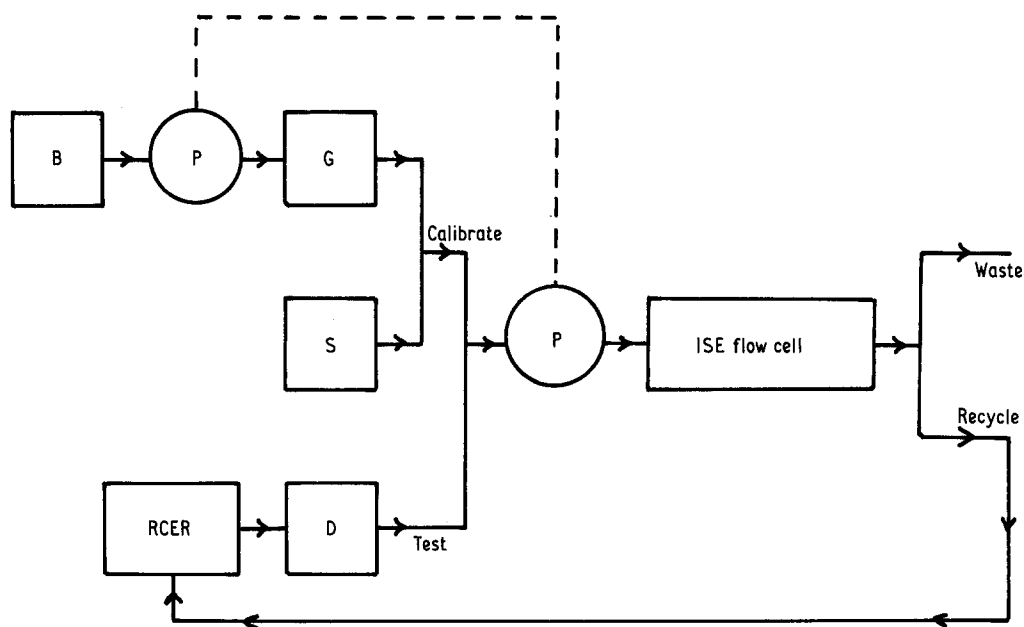

Fig. 2. Schematic flow circuit for experimental ISE flow cell. B, Sulphuric acid support electrolyte; P, peristaltic pump; G, gradient forming device; S, discrete calibration standard; D, drip vessel; RCER, rotating cylinder electrode reactor.
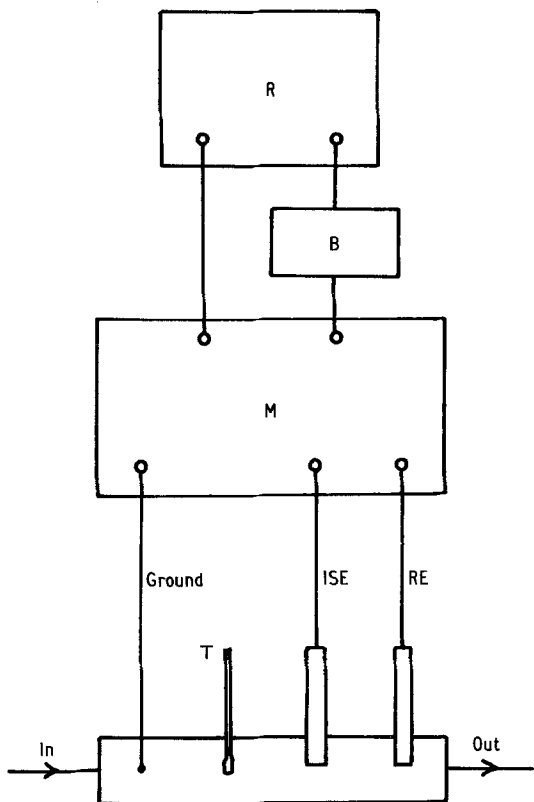
Fig. 3. Electrical connections to ISE flow cell. G, Solution ground; T, thermometer; ISE, ion-selective electrode; RE, reference electrode; R, chart recorder; M, millivoltmeter; B, back-off unit.
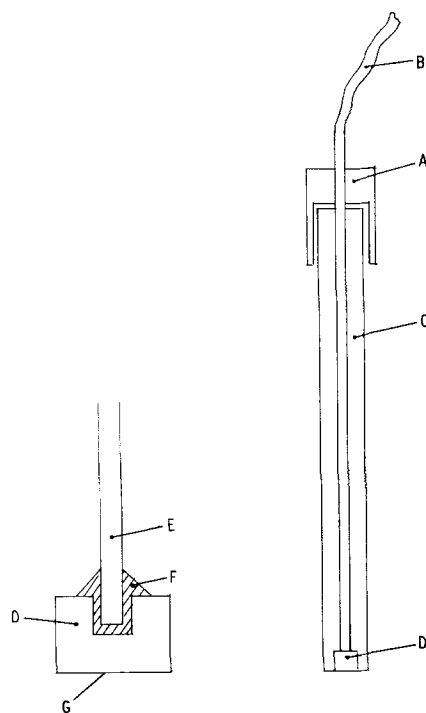

Fig. 4. Construction of the ion-selective electrode. A, Polypropylene press-fit cap; B, shielded cable; C, PTFE body; D, solid-state sulphide pellet membrane; E, silver-plated wire; F, silver-loaded epoxy resin; G, polished membrane face.

obtaining consistently matched flow rates eventually two separate pumps were employed. A two-way valve was used to switch the detector feed from calibrant to sample and used solutions could be passed to waste or recycled in the reactor circuit as deemed appropriate. Typically the flow rate was $1 \, cm^3 s^{-1}$ and the total dead volume in the system $\sim 10 \, cm^3$ resulting in a 10 s delay in the response when solutions were redirected. This is in fact quite negligible in the context of total experimental periods of 1–4 hours and the dead volume is quite small compared with the total reactor volume of 1 litre.

3. Characterization of the ISE cell

3.1. *Calibration*

Calibration of the ion-selective electrode cell was achieved by preparing standard solutions (either discrete standards or a gradient stream) for passage through the cell under optimized flow conditions Calibration curves at 20° C for two commercial 'Orion' electrodes, and the special electrode, are given in Fig. 6. The calibrants were prepared by serial volumetric dilution of a 10^4 ppm cupric standard, itself prepared from AR grade cupric sulphate in 1.5 M sulphuric acid using triply distilled water. Calibrants more dilute than 100 ppm were not stored for any length of time and were used in polypropylene containers and tubes to minimize absorption. It may be seen that all the calibration curves have good linearity in the concentration range studied; i.e. they behave according to

$$E = E^{0,1} + 2.303 \frac{RT}{2F} \log C_{Cu^{2+}} \qquad (2)$$

Although each of the lines has a slope close to the theoretical Nernstian value of 0.0291 V they are displaced parallel to each other; i.e. the E^0 values vary. As an identical reference system was used in each case this means that the standard potentials
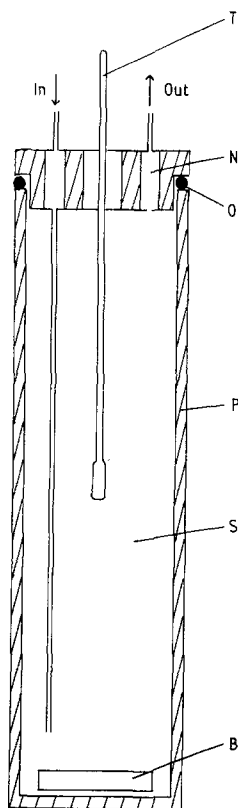
Fig. 5. Experimental vessel for producing the concentration gradient. B, Magnetic stirring bar; N, PTFE adaptor; O, 'O' ring seal; P, perspex cylindrical vessel; S, gradient solution; T, thermometer.

of the three ISE are different. The error margins for ten successive determinations of the calibration curve using the 'Orion B' electrode are shown in Fig. 7, the resulting line being established by least-squares analysis.

When the ISE flow cell was in constant use calibrations were performed before and after experimental runs although the potentials determined at any one concentration were normally reproducible to ± 0.15 mV, equivalent to about $\pm 1\%$. A constant back-off unit was employed to apply corrective potentials to bring the various electrodes to a common calibration when being used for gradient work. Typical concentration decays encountered when using the Ecocell and produced by the gradient technique are shown in Fig. 8. Using an initial concentration of 100 ppm Cu^{2+} the data points were obtained by atomic absorption analysis of negligibly small samples taken at given intervals of time. The concentration decay is of the type

$$\log C = \log C_0 - \frac{1}{2.303} \frac{rt}{V} \qquad (3)$$

such that when $C_0 = 1000$ ppm, $V = 1000$ cm^3 and $r = 1$ cm^3 s^{-1} the slope of the $\log C - t$ curve is 4.34×10^{-4} s^{-1}.

3.2. Response times

In order to characterise the detector cell, and to establish that the response time of the analytical system was low enough for practical use, experimental response times were measured according to the IUPAC recommendation for decade changes in ion concentration in both increasing and decreasing directions [16]. A calibrant of known concentration was flowed through the ISE cell at a steady flow rate, measured volumetrically, until an equilibrium potential was attained (<0.1 mV in 10 min). The pump feed was switched to the second calibrant and the potential was monitored continuously using a recorder. The results of such experiments at various flow rates (0.1 to 2.5 cm^3 s^{-1}) and directions of concentration change are given in Fig. 9. All results are for 20° C and show that:

(a) the response time was substantially lower for increasing, rather than decreasing concentrations;

(b) the response time was lower for higher flow rates;

(c) the response time was lower at higher final concentrations;

(d) the response time was lower for a sub-decadic concentration change;

(e) the response time was less than additive for a multiple decadic change.

The response time is defined as the time required for the electrode potential to reach a value 1 mV away from the final steady-state value after a supposedly instantaneous change. It may be noted that other ways of considering the response time may be adopted; for example, on change of concentration the potential approaches equilibrium in an exponential manner:

$$E_t = E_F + (E_I - E_F) \exp(-t/\tau) \qquad (4)$$

where E is the potential at time t or initially (I) and finally (F) and τ is the relaxation time. Thus a graph of $\ln(E_t - E_F)$ against t will give a slope of $1/\tau$ because
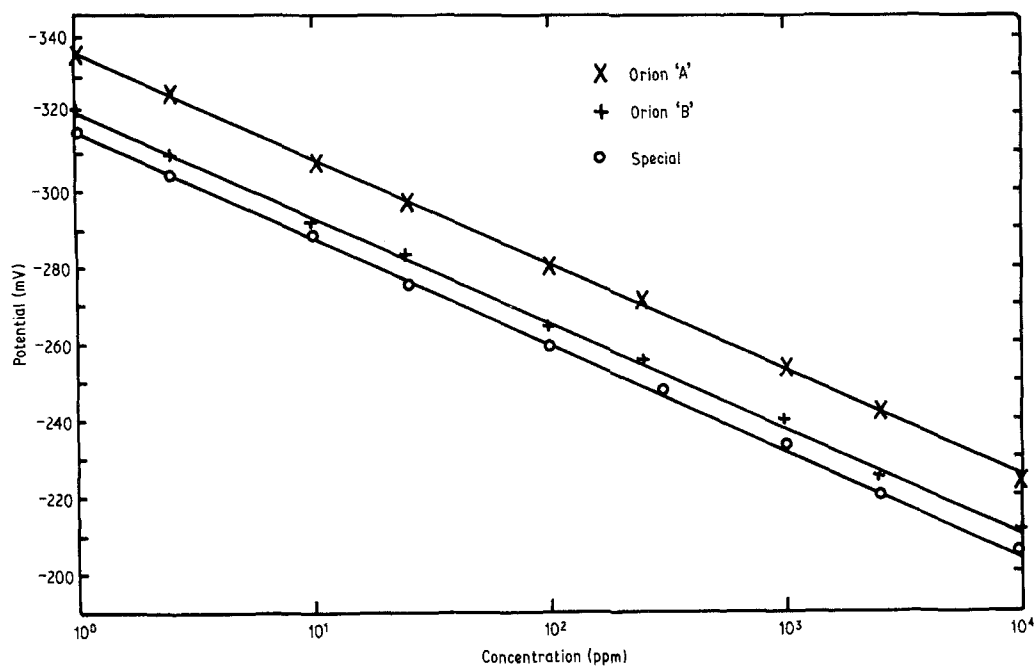
Fig. 6. Calibration curves for Cu^{2+} ISEs.

$$\ln(E_t - E_F) = \ln(E_I - E_F) - t/\tau. \qquad (5)$$

Such behaviour is obeyed in practice (Fig. 10 gives $\tau \simeq 2.67\,s$). Other authors [17, 18] have preferred to interpret response time as the time interval during which the potential changes by $\frac{1}{2}(E_I - E_F)$;

thus $t_{1/2} = 0.7\tau$. Alternatively, the response time may be defined as the interval for the potential to reach 95% of its final equilibrium value [19]; thus $t_{0.95} \simeq \tau$. Comparisons are pointless and each system has its own self-consistency.
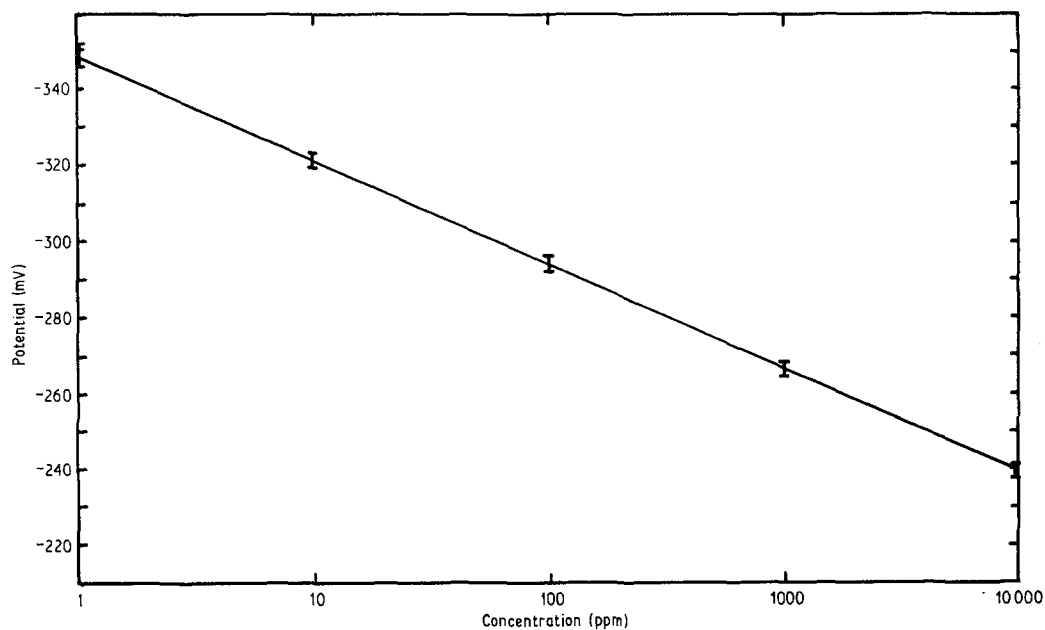

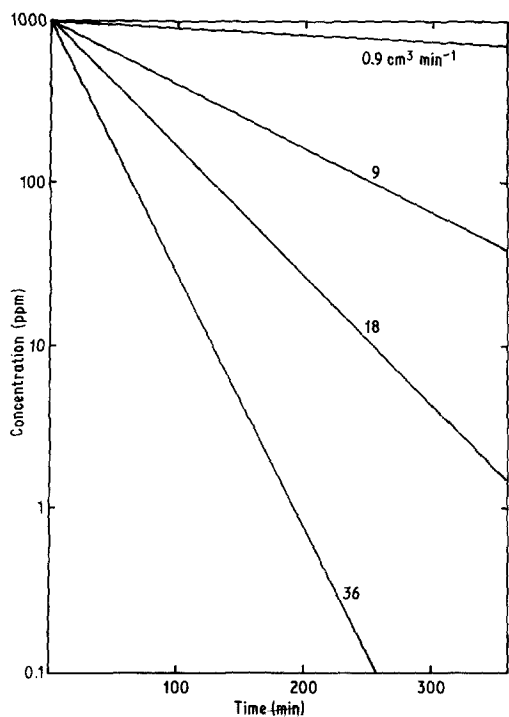Fig. 7. Accumulative variation (10 values) for calibration curves.

Fig. 8. Concentration decay curves using gradient device. Initial concentration of 1000 ppm and various flow rates.

3.3. Drift and noise

Potential drift depended primarily on the copper concentration in solution, flow rate and the state of the reference electrode but rarely exceeded 0.5 mV in 10 hours at 1 ppm concentration level and 60 cm^3 min^{-1} flow, once the electrode was well-conditioned.

Noise was induced by general electrical interference and use of poorly shielded ISE leads. One important source was identified as arising in the peristaltic pump motor due to inconsistency of rotation caused by back-pressure effects in the tube. This could be overcome by using a pulse suppressor between the pump and the cell or using a high-speed motor/small bore tube combination. Electronic suppression was used most effectively; thus for the 10 ppm Cu^{2+} solution a peak-to-peak noise of 0.045 mV at a flow rate of 1 cm^{3}s^{-1} reduced to 0.005 mV with the aid of both a filter and a solution ground (Table 1).

3.4. Temperature

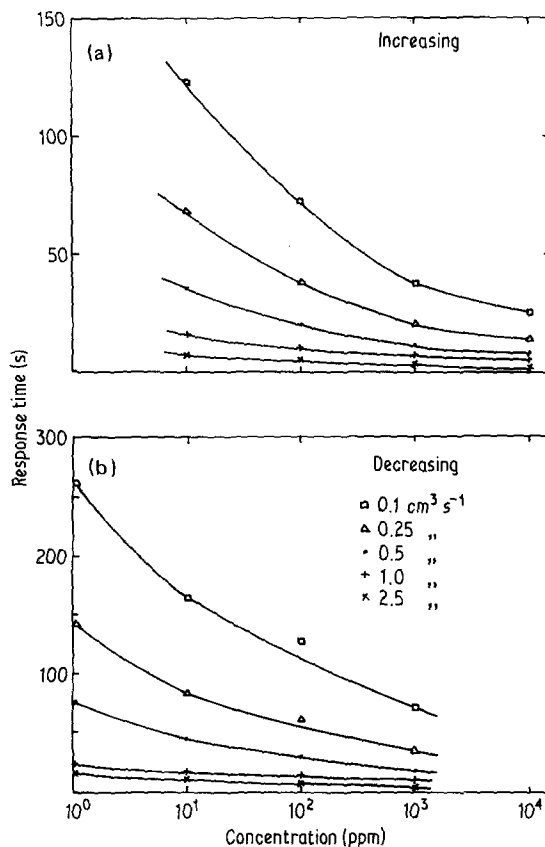Temperatures were controlled to ±0.1° C for pre-

Fig. 9. Effect of final concentration on response time for various flow rates and (a) increasing decadic concentration change; (b) decreasing decadic concentration change.

cise work by immersing the cell in a thermo-statically-controlled water bath at 20° C, and cooling the analytical sample from the prevailing reactor temperature. Because temperature may change the response of the detector cell in several ways (reference electrode potential, ISE response time, Nernstian calibration slope etc.) care must be taken for accurate work: a 10° C change can be equivalent to 1 mV potential change for a divalent ISE.

3.5. Flow rate

The marked effect of flow rate has already been noted (Fig. 9); thus increased flow decreases lag in the system due to dead volume effects. It is clearly desirable that the ISE flow system should have a flat response to flow rate thereby simplifying calibration and eliminating minor effects of varying system geometry. Liquid junction and
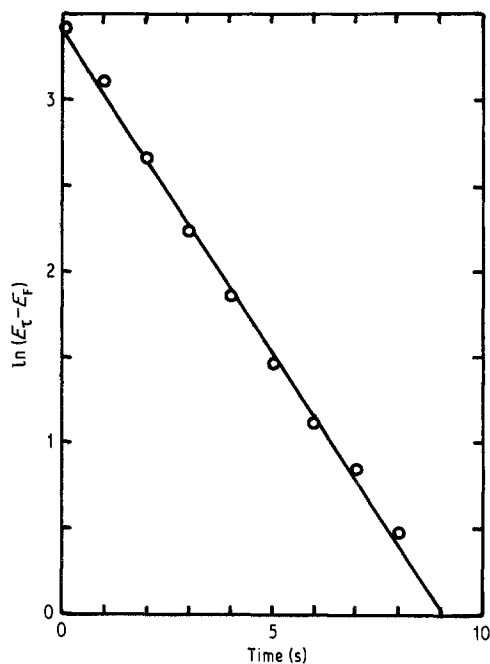
Fig. 10. Determination of relaxation time τ for concentration change of 10^4 to 10^3 ppm at 60 cm^{3}min^{-1} flow rate.

Fig. 11. Effect of flow rate on ISE potential.

membrane diffusion effects must also be considered but can be separately assessed if necessary. The experimental effect of flow rate on potential is shown in Fig. 11 for 10 ppm cupric solution at flow rates in the range 0–15 cm^{3}min^{-1}, corresponding to linear velocities past the membrane of 0–20 cm s^{-1}. The response is virtually linear over this range giving a slope of ~ 0.05 mV cm^{-1} s, with increasing flow rates resulting in a potential shift towards potentials which correspond to a more dilute solution. Electrical interference was eliminated by gravity feeding the solution; thus it can be seen that the potential shows a small, well-defined dependence on flow rate over rather a wide range of linear velocity. A constant flow rate of 60 cm^{3}min^{-1}, equivalent to a linear velocity of
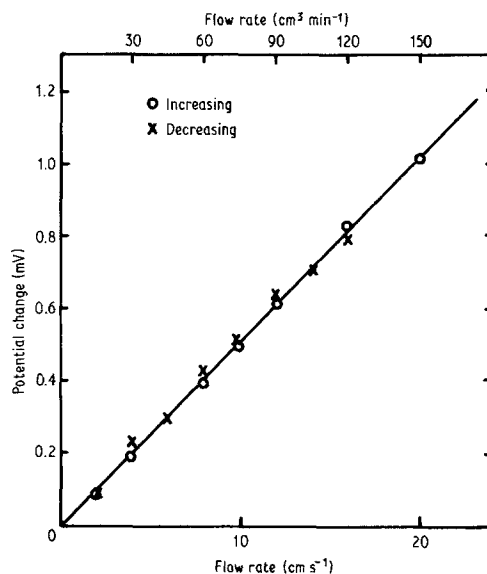
8 cm s^{-1}, was used as a standard condition thereafter.

4. Application of the ISE cell

Once reliability had been achieved, and the major parameters assessed, the ISE cell was tested for on-line viability using a large commercial electrochemical reactor. The application selected was recovery of copper in a 500 A Ecocell and the analytical arrangement was essentially similar to that used in the laboratory assessment.

The catholyte inlet and outlet to the pilot plant were sampled near the reactor and for reasons of convenience relatively long (6 m) lengths of tube had to be used. However, by using narrow bore tubing (1 mm diameter) of equal lengths and a fast flow rate (12 cm^{3}min^{-1}), the 'dead' time w s reduced to a value of ~ 24 s. Calibration was

Table 1. Noise levels determined (10 ppm Cu^{2+} solution)

Mode	Maximum peak-to-peak noise (mV)	
	Flow of 1 cm^{3}s^{-1}	Flow of 0.1 cm^{3}s^{-1}
No ground or filter	0.045	0.080
Filter in	0.035	0.075
Ground in	0.010	0.020
Filter and ground in	0.005	0.010
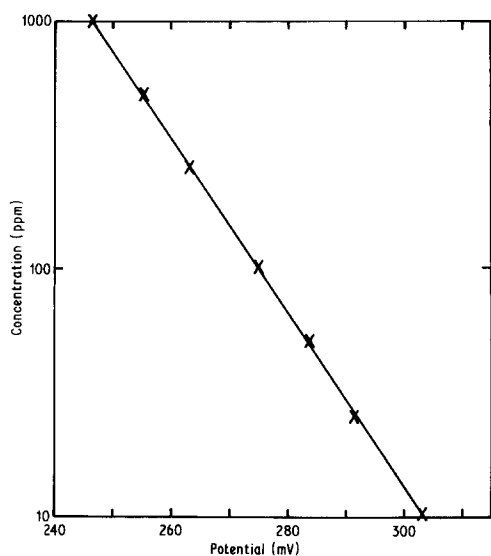
Fig. 12. Calibration curve of ISE in pilot plant operation at 23° C.

Fig. 13. ISE potential measurement to monitor concentra-, tion decay. Atomic absorption analyses marked.

checked by introducing volumetrically prepared standards of Cu^{2+} in 0.5 M H_2SO_4. The detector cell was operated under ambient conditions but the temperature was monitored frequently in order to establish any variability with respect to calibration.

Because the product of the Ecocell is solution-laden with fluidized metal powder, care was taken to ensure that powder did not enter the ISE sample lines by fitting a small filter and sampling in a vertical direction as powder temporarily settled. Electrical interference in the vicinity of the plant also proved troublesome but was effectively eliminated, however, by fitting resistive suppressors across the a.c. mains input to the

instruments and using well-screened high impedence leads. A typical calibration curve for 23° C is given in Fig. 12 and has a measured slope of 28.5 mV/decade. The outlet copper analyses were compared using a standard atomic absorption technique and results are given in Table 2.

The Ecocell was used as a batch reactor to remove copper from a typical waste solution containing 138 ppm Cu^{2+} over a period of 50 min. The data are given in Fig. 13 which show both the continuous recorder trace of potential together with the discrete samples subjected to atomic absorption analysis. It is clear that as a means of monitoring the progress of removal of copper from 138 to 20 ppm the ISE cell has an excellent capability, although if absolute analytical values for residual cupric concentrations are required greater care must be taken to operate the cell under closely controlled conditions.

The precise manner of use of the ISE cell will depend upon the way in which the Ecocell, or any other comparable electrochemical reactor, is employed. Such reactors are frequently used to remove metal from a variety of grades of effluent from levels as high as 2000 ppm down to levels approaching 1 ppm which may be acceptable for drain discharge. Clearly the logarithmic scale relating concentration to potential is a considerable advantage for this large range. In such an application the absolute accuracy of the electrode is not vital because it is the progress of metal removal which is effectively being monitored. In cases where the discharge metal content at about 1 ppm

Table 2. Comparison of ISE and AAS analysis of reactor outlet

Data sample	Analysis value (ppm Cu^{2+})		Difference (%, w.r.t. AAS)
	AAS	ISE	
1	138	128	8.8
2	107	103	3.7
3	68	66	2.9
4	42	40	4.8
5	30	28	6.7
6	22	21	4.5
7	290	285	1.7
8	255	247	3.1

level is to be measured then adequate calibration at that level and solution conditions is obviously necessary.

One of the favoured configurations of the Ecocell is to use it as a 'cascade' cell or a series of simple cells operating on the same drive rotor. The overall efficiency of such an arrangement depends upon controlling conditions precisely within each compartment; such optimization can be achieved by sampling the metal concentration at each stage thereby enabling adjustment of the current or potential to be made for optimal performance. The ISE cell is particularly suited to a control application of this type.

Acknowledgements

Appendix. Construction of a simple ISE for cupric ions

The electrode is illustrated in Fig. 4. The electrode body was machined from PTFE rod. The electrode tip, containing the solid-state membrane, was detachable for ease of maintenance, cleaning and replacement. The electrical lead was similarly detachable, and employed a solid silver contact to the rear of the membrane.

The membrane was produced by compressing an equimolar powdered mixture of silver sulphide and cupric sulphide, the latter being freshly precipitated from solution of cupric ions with H_2S, washed and dried. A machined punch and die of stainless steel was used with spacers to adjust the membrane thickness. The die and punch were lapped and ground to ensure a good fit while the punch was flame hardened to improve wear resistance. Membranes of 6 mm diameter and 4 mm thick pellets were produced using a compaction pressure of $\sim 10^8$ Pa (12 000 psi) at room temperature. When the die surface was well-polished, pellets of good definition were produced which were press-fitted into the PTFE electrode end cap and were then polished to a 6 μm diamond finish. After conditioning in 0.1 M $CuSO_4$ solution for 24 hours they were ready for use.

References

[1] G. J. Moody and J. D. P. Thomas, 'Selective-Ion Sensitive Electrodes', Merrow, Watford (1970).

[2] J. Koryta, 'Ion-Selective Electrodes', Cambridge University Press, Cambridge (1975).

[3] N. Lakshminarayanaiah, 'Membrane Electrodes', Academic Press, London (1976).

[4] P. L. Bailey, 'Analysis with Ion-Selective Electrodes', Heyden, London (1976).

[5] R. A. Llenado and G. A. Rechnitz, *Anal. Chem.* 45 (1973) 826.

[6] B. Fleet and H. Von Storp, *ibid* 43 (1971) 1575.

[7] H. I. Thompson and G. A. Rechnitz, *ibid* 44 (1972) 300.

[8] J. Ruzicka and J. C. Tjell, *Anal. Chem. Acta* 47 (1969) 475.

[9] L. J. Forney and J. F. McCoy, *Analyst* 100 (1975) 157.

[10] P. J. Milham, *ibid* 95 (1970) 758.

[11] A. Hrabeczy-Pall, K. Toth, E. Pungor and F. Vallo, *Anal. Chim. Acta* 77 (1975) 278.

[12] F. S. Holland. *Chem. Ind.* (1978) 453.

[13] F. C. Walsh, N. A. Gardner and D. R. Gabe, *J. Appl. Electrochem.*

[14] F. C. Walsh and D. R. Gabe, *Surf. Tech.* (1981).

[15] F. C. Walsh and D. R. Gable, Work in progress.

[16] Recommendations for nomenclature of ISE. Appendices on provisional nomenclature, symbols, units and standards No. 43. IUPAC Secretariat Office, Oxford (1975).

[17] G. A. Rechnitz and M. R. Kresz, *Anal. Chem.* 38 (1966) 1786.

[18] G. A. Rechnitz, M. R. Kresz and S. B. Zamochnik, *ibid* 38 (1966) 973.

[19] B. Fleet, T. H. Ryan and M. J. Brand, *ibid* 42 (1970) 285.