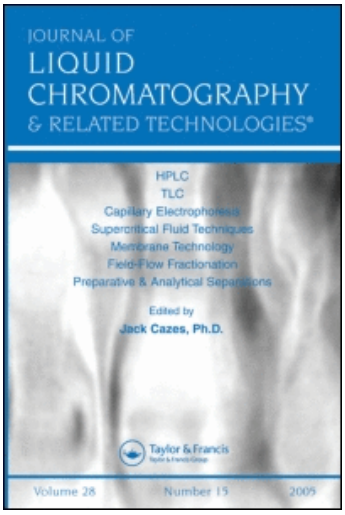

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NOISE AND DRIFT PHENOMENA IN AMPEROMETRIC AND COULOMETRIC DETECTORS FOR HPLC AND FIA

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ABSTRACT

Noise and drift phenomena in electrochemical detectors with solid electrodes are discussed.A relationship between the capacity of the working electrode and the noise of the detector is demonstrated in three different ways,using direct correlation of noise with capacity,time correlation functions and electrical simulation of the cell properties.Conclusions are drawn with respect to the prospects of various measures to improve the detection limit.

INTRODUCTION

As small electrical currents,down to picoamperes,corresponding to picocoulombs during a time constant of 1 second,can be readily measured electronically,the detection limit of electrochemical devices could be expected,from that point of view,to be in the range of 10^{-17} mole (1). However,detection limits in or below the picogram range,roughly 10^{-14} mole,still form an exception in routine analysis.As many analytical investigations nowadays aim at the quantita-

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tive determination of analytes at extremely low concentrations it is worthwhile to improve the performance of detectors in this respect.

As a first step the investigation of the various sources of noise and drift may be helpful,in order to indicate those measures which could lead to substantial improvement.An inventory of these sources is as follows.

Causes of drift may be:

1. The stabilisation processes taking place at the working electrode (2-5),
2. Gradual fluctuations in temperature (6) and air humidity,
3. Electrode contamination (7),
4. Gradual changes in the composition of the background electrolyte (carrier,mobile phase), e.g. due to the dissolution of oxygen or metals somewhere in the system (2,8,9).

Noise may originate from various sources:

1. The detector cell and the electronic equipment,
2. Power frequency pick up,
3. Electrical pulses,produced by other instruments,received via the power cord or otherwise,
4. Electrostatic influences often exerted by the operator.

In this paper some work on the characterisation of some of these phenomena is reported.Special attention is given to the generally observed proportionality of base line noise with electrode area.Such a dependence is not probable under all circumstances.An electrode may be considered as consisting of several parts;e.g. two parallel electrodes in the same liquid layer are in principle not different from one wide electrode of the same total area.The noise component in the total current of the two separate electrodes is $\sqrt{2}$ times larger than that of a single electrode,when the two behave independently,i.e. when there is no correlation between the two signals. Rather than addition of standard deviations an addition of variances has to be applied in such a case.

On the other hand,with full correlation between the two electrodes a summation of amplitudes,that is of standard deviations,has to be expected.In that case a two times larger noise for the two

times larger area is found in the given example.Thus,depending on conditions a proportionality of noise with area or with the square root of the area may be found.

Some kinds of noise may lead to correlation between the various parts of an electrode surface.Examples are the contributions due to fluctuations in the concentration of an electroactive substance in the carrier stream,temperature fluctuations,etc..However,when detection limits are approached and proper operating conditions are chosen so as to avoid large background signals and thermal instability,the noise contribution of the electrode itself is likely to be the predominant contribution.On first consideration an independent behaviour,uncorrelated noise,would be expected for distinct electrode sections.This would lead to a square root dependence of noise on area.Nevertheless,in general a direct proportionality is observed.An important objective of this work is to clarify these matters,with the idea that a good understanding of the origin of noise may indicate ways to further improvement.

THEORETICAL

It is assumed that it is possible to exclude all external effects by sufficient isolation of the whole system from electrical,thermal and other influences.When also the working electrode has stabilised sufficiently,we can restrict ourselves only to the voltage and current noise sources present in the system itself.What follows is an analysis of the effect of various noise sources on the output voltage,which is a representation of the current flowing through the working electrode.A schematic circuit,as given in fig.1,allows such calculations,which are carried out with the usual electric circuit laws, e.g. using complex alternating current formalism.

The following assumptions are made:

1. The various noise sources are independent;the variances caused by them are additive.
2. No current flows through the reference electrode so the impedance of the latter can be neglected.The potential applied by the

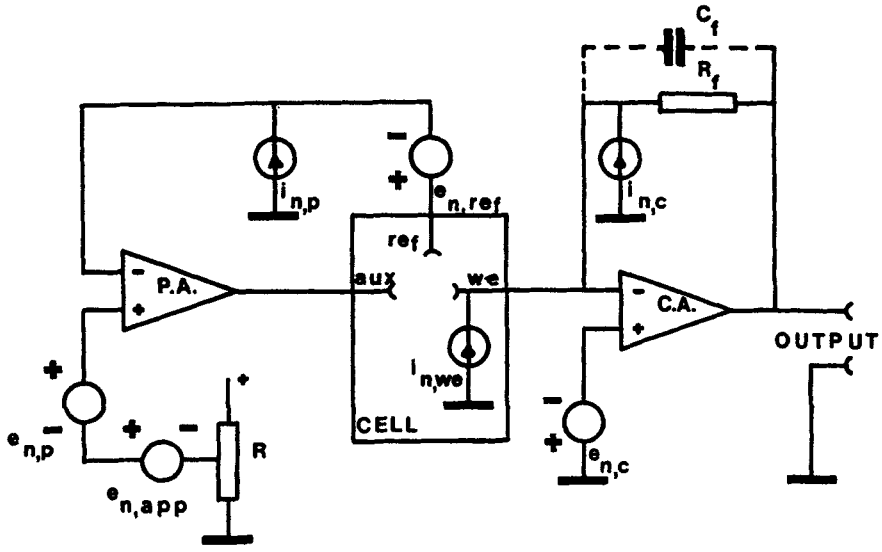

FIGURE 1 Simplified representation of the cell and the electronic circuits of the potentiostat and current amplifier.Cell: we: working electrode; ref:reference electrode; aux:auxiliary electrode.Potentiostat amplifier circuit: P.A.:potentiostat amplifier; R:potentiometer for adjustment of cell potential.Current amplifier circuit: C.A.: current amplifier; R_f:feedback resistor; C_f: feedback capacitor for low pass filtering. Current noise sources:$i_{n,p}$, $i_{n,we}$ and $i_{n,c}$ generated by the potentiostat amplifier,the working electrode and the current amplifier respectively.Voltage noise sources: $e_{n,app}$, $e_{n,p}$, $e_{n,ref}$ and $e_{n,c}$ generated by the potential source,the potentiostat amplifier ,the reference electrode and the current amplifier respectively.

potentiostat ,which is the potential difference between reference and working electrode,therefore accurately represents the potential difference between working electrode and liquid.

3. No large potential differences occur in the liquid.
4. For small voltage and current fluctuations for which the system can be considered as linear,the impedances are located at or quite near to the electrodes.This assumption is based on the observation (see Results and Discussion) that measured cell resistances are much larger than those calculated from the specific resistance of the carrier.

5. The linear system behaves ideally in the sense that deviations due to finite open loop gain of the amplifiers can be neglected at the frequencies of interest.

The current and voltage noise generated by each part of the system are accounted for by insertion of parallel or series sources in the system respectively,as is shown in fig.1.This is a standard method in the noise analysis of electronic circuits.The sources will be described alternatively as a function of time or frequency: $i_{n,k}(t)$ and $e_{n,k}(t)$ or $i_{n,k}(\omega)$ and $e_{n,k}(\omega)$ in which i is currrent, e is voltage,n refers to the noise component,k identifies the element generating the noise (electrode or amplifier),t is time and ω is angular frequency.The various noise sources given in fig.1 will now be discussed.

a) The potentiostat amplifier and the current amplifier

These contribute voltage noise,$e_{n,p}$ and $e_{n,c}$,respectively and current noise $i_{n,p}$ and $i_{n,c}$ respectively.However,the reference electrode was assumed to have a low impedance and $i_{n,p}$ can be neglected because it is short-circuited.

b) The working electrode

Its voltage noise will be neglected,because it cannot be distinguished from the current noise in potentiostatic operation. The working electrode contributes current noise, $i_{n,we}$, e.g. due to chemical processes taking place at its surface.

c) The reference electrode

This contributes voltage noise,$e_{n,ref}$, e.g. due to fluctuations in the temperature,the chemical equilibrium of the half raction $AgCl + e^- \rightleftarrows Ag\downarrow + Cl^-$, etc..The current noise of this element will be neglected as the impedance of the electrode was assumed to be very low.

d) The auxiliary electrode

Both voltage and current noise of this electrode will be neglected because these effects are eliminated by the potentiostat amplifier.

The potential difference between the working electrode and the liquid is:

$$\Delta E = E_{app} + e_{n,p} + e_{n,ref} + e_{n,c} \quad (1)$$

where ΔE is the potential difference and E_{app} is the applied potential. As E_{app} may also display noise of magnitude $e_{n,app}$, due to insufficient stabilisation of E_{app}, the fluctuations in E will amount to :

$$e_{n,tot} = e_{n,p} + e_{n,ref} + e_{n,c} + e_{n,app} \quad (2)$$

The varying potential difference between the working electrode and the liquid leads to fluctuations in the current through the working electrode, the magnitude of which depends on the impedance of this electrode.

Baseline noise is especially important when very low concentrations are to be measured. When also sufficient precautions are taken to prevent the presence of electroactive contaminations in the carrier the current is small; the slope in the voltammogram is also small and the resistive part of the conduction can be neglected. Under these conditions the electrode behaves as a pure capacitor, which is of the order (see Experimental) of a few hundreds $\mu F/cm^2$. This means that a capacitive current, i_C, results:

$$i_C = C_{we} \frac{d}{dt} (e_{n,tot}) \quad (3)$$

The output voltage of the current amplifier will contain a noise component, $e_{n,out}$, which can be calculated to be:

$$e_{n,out} = R_f\{C_{we} \frac{d}{dt}(e_{n,tot}(t) + i_{n,we}(t) + i_{n,c}(t)\} + e_{n,c}(t) \quad (4)$$

where R_f is the value of the feedback resistor in the current amplifier circuit.

The last term in eqn (4) can be made negligible by choosing a large value for R_f. Insertion of a value of 100-400 $\mu F/cm^2$ for the capacity and a few μV for $e_{n,tot}$ suggests that the first term of eqn (4) may be responsible for a substantial part of the noise observed at the detector output. High frequency noise contained in $e_{n,tot}$ is especially amplified because of the derivative in eqn (4). In all electrochemical detectors this effect is diminished by the

application of low pass filtering with a feedback capacitor C_f (see fig.1),or by means of filtering in subsequent amplifier stages.

The effect of such measures is more easily represented in the frequency domain.For filtering with C_f it follows:

$$e_{n,out}(\omega) = \left(\frac{1}{R_f} + j\omega C_f \right)^{-1} \{ j\omega C_{we} e_{n,tot}(\omega) + i_{n,we}(\omega) + i_{n,c}(\omega) \} \quad (5)$$

where $j^2 = -1$. The total variance in the output voltage, $\sigma^2_{V,out}$, which is the mean square value of $e_{n,out}$ can be found from equations such as (5) by applying Parseval's theorem (10).This leads to an integration in the frequency domain and the noise power spectra of the contributions in eqn (5) should be known.However, without performing this task in all detail we can derive in this way that:

$$\sigma^2_{V,out} = c_1 C_{we}^2 \overline{e^2_{n,tot}} + c_2 \overline{i^2_{n,we}} + c_3 \overline{i^2_{n,c}} \quad (6)$$

where c_1 , c_2 and c_3 depend on the spectral characteristics of noises and filters and the upper bars refer to mean (square) values.

It can be seen from eqn (6) that the capacity of the electrochemical double layer of the working electrode,C_{we}, which we shall indicate as "cell capacity" ,is at least partly determining the noise at the detector output.By mounting various electrodes having different values for the cell capacity and measuring the resulting noise at the output,relation (6) can be verified experimentally. The cell capacity can be estimated e.g. by measuring the charging current resulting from a small potential step E' applied via the potentiostat.The capacity is:

$$C_{we} = \frac{1}{E'} \int_0^t i(t)\, dt \quad (7)$$

Our interpretation of the cell capacity obtained in this way is that it resides mainly in the interface between solution and working electrode.It may be partly associated with redox and adsorption desorption phenomena,and its interpretation as the capacity of the double layer may therefore be questioned.However,for the present discussion this is not of great concern provided the cell response

is the same, on the time scale used, as that of a real capacitor of a suitable value (which might be bigger than the capacity of the interface due to the phenomena referred to). The effect on the output noise would be still described by eqns (5) and (6), with insertion of the effective value for C_{we}, measured by the experiment indicated. As is reported under Results and Discussion, the current response in this experiment was as fast as could be observable under the experimental conditions. We therefore believe that the modelling of a probably complicated set of phenomena by one capacitor is adequate for our purpose as a first approximation.

From eqn (4), it can be seen that a relationship should exist between the instantaneous values of the noise voltage at the output, $e_{n,out}$, and the potentials of working and reference electrodes. Such relationships can be studied (11) by measuring the auto- and crosscovariance functions between the potentials at the electrode terminals on the one hand and the output signal on the other hand.

The expression for a autocovariance function ϕ_{xx} of a signal x is :

$$\phi_{xx}(\tau) = \lim_{T\to\infty} \frac{1}{T} \int_0^T x(t)\, x(t+\tau)\, dt \qquad (8)$$

in which T is the measuring time and τ is the time delay. For $\tau = 0$ the autocovariance function is equal to the variance (12).

The expression for the crosscovariance function ϕ_{xy} of two signals x and y is:

$$\phi_{xy}(\tau) = \lim_{T\to\infty} \frac{1}{T} \int_0^T x(t)\, y(t+\tau)\, dt \qquad (9)$$

A correlation coefficient, $\rho(\tau)$, can be defined:

$$\rho(\tau) = \phi_{xy} \{ \phi_{xx}(0)\ \phi_{yy}(0) \}^{-\frac{1}{2}} = \phi_{xy} / \sigma_x \sigma_y \qquad (10)$$

For all τ it holds:

$$\rho(\tau) \leq 1 \qquad (11)$$

If the equality applies, $\rho(\tau) = \pm 1$ for some value of τ, both signals x and y are completely correlated; the one is a time shifted

version of the other. If $\rho(\tau) = 0$ for all τ both signals are completely uncorrelated. This means that there is either no relationship at all, or such relation is strongly non-linear. Intermediate values indicate a partial correlation, in combination with other, uncorrelated influences.

EXPERIMENTAL

A coulometric detector (775 LP, Kipp Analytica, Emmen, Holland) and an amperometric detector (LC-4A, Bioanalytical Systems, West Lafayette, Indiana, USA) were used. Both electrochemical cells were operated with the supplied potentiostat and amplifier electronics. The smallest time constants were used, 0.1 and 0.5 seconds for the coulometric and amperometric detector respectively. The design of the cells and the electronic circuits have been described elsewhere (2,13), although some alterations in both systems have been applied since then.

In order to minimize power frequency pick up as much as possible, the systems were built up step by step. After the addition of each successive component, the output signal was examined with an oscilloscope, paying special attention to power frequency, 50 Hz in our case. First the electronics were examined, next the cell was connected, and then the solvent delivery system was connected to the cell. The last step, especially the connection of the metal parts, appeared to be the most important cause of power frequency pick up. Solvent was delivered by a hydrostatic syphoning system consisting of two glass solvent containers, connected via 1/16'' teflon^R tubing, 0.5 mm i.d. A stainless steel stopcock, two low dead volume unions positioned directly at the inlet and outlet of the cell and a restrictor, 10 m teflon^R tubing, 0.25 mm i.d., connected with a union at the outlet of the cell completed the system.

The solvent delivery system was completely shielded electrically by means of metal tubing and aluminium foil. The cell with the unions and the stopcock were placed under a dewar vessel, serving the dual purpose of faradaic cage and thermal insulation. Sudden fluctuations

in air humidity could also be avoided in this way.All metal shielding parts were connected to a single grounding point at the grounding strip of the power connection.These precautions reduced the 50 Hz component in the output significantly.Additional reduction was obtained by connecting the unions near the cells via a capacitor of 500 μF to ground.This of course can only be applied in the case of potentiostatic operation.

After the system proper had been installed in this way,measuring instruments needed for this work were connected,avoiding ground loops as much as possible and carefully observing the effect of each addition on the signal.Residual power frequency pick up could be eliminated by using passive custom made 5o Hz filters.

For the analysis of signal fluctuations at various points in the system the following instruments were used:
Correlator:Hewlett Packard,model 3721 A,West Lothian,U.K.
Oscilloscopes:Advance Instruments,model OS 1000 and OS 1000A, Hinault,U.K.
Preamplifier:Princeton Applied Research,model 113,Princeton,N.J., USA.
DC Amplifiers:Knick,model A3,Berlin,G.F.R. and Philips,model PM 5170 Eindhoven,Holland.
Recorder:Siemens,model Kompensograph III,Karlsruhe,G.F.R.
Precision voltage source:Knick,model S 16,Berlin,G.F.R.
The time integral of charging currents could be measured with an integrator,Autolab System I,Spectra Physics,Santa Clara,Cal,USA.
Cell impedances were measured with a conductivity bridge,Philips , model RR 9500,Eindhoven,Holland.

Potassium chloride (Suprapure^{R},Merck,Darmstadt,G.F.R.) and glacial acetic acid (Baker Chemicals b.v.,Deventer,Holland) were used to prepare the solvent, 0.1 M in acetic acid and 0.01 M in potassium chloride.The pH was 2.75.The solutions were prepared in double distilled water and filtered through 0.8 μm Millipore^{R} filters before use.

RESULTS AND DISCUSSION

Drift due to environmental influences

During our work we confirmed the observation by Fenn (6) that temperature changes near the cell induce drift.In electrochemical detectors both silver-silver chloride (2,3,6,13,14) and calomel electrodes (6,8,15,16) are used as a reference electrode.The temperature coefficients of their potentials are -1 mV/^{o}C (17) and -0.3 mV/^{o}C (18) respectively.Apart from the direct effect via the working electrode,the reference electrode may therefore also be involved in the temperature sensitivity.With the coulometric detector,we found that air humidity changes also cause drift.We could trace this to conduction between the electrodes at the outside of the cell.The long term stability was improved when the cell was placed underneath the dewar vessel.

Stabilisation drift

Stabilisation drift was observed after applying the potential to the cell and after potential changes.It was already reported by Kissinger et al. that especially for a freshly mounted working electrode the stabilisation process takes several hours (3-5). Accepting a drift of 1 % full scale per minute we found that at a full scale sensitivity of 100 nA for the coulometric detector and of 0.5 nA for the amperometric detector this process took three hours.An electrode which has been in use for some days stabilises faster after switching on the potential and eventually one half hour is sufficient.The procedure of injecting a standard a few times as suggested in the Bioanalytical Systems operations and service manual did not influence the stabilisation time noticeably.This problem has not yet been solved.

Drift due to electrode deactivation

In a previous paper (7) we discussed the decrease of the response of the working electrode after deactivation.This time-dependent be-

haviour also applies to the electrochemical reactions of the background electrolyte which are responsible for the background current. We observed that repeated injection of a deactivating agent or the addition of the latter (7) to the background electrolyte resulted in a continuous decrease of the background current.The electrochemical method for restoring the electrode activity proposed in ref.(7) can partially abate deactivation problems.

Power frequency pick up

With the precautions as described under Experimental power frequency pick up usually was not a problem as long as the signals were displayed on a strip chart recorder.This is in accordance with the strong rejection of mains frequency signals by most recorders of good quality.In a few cases we observed that the amperometric detector was in an overload mode at sensitivities of 5 nA/V or lower,while the absolute value of the background current certainly could not be out of range.In such cases overload was caused by power frequency signals.For the experiments to be described it was essential to reduce these interferences further,because very high total amplification were needed and overload of later stages otherwise would occur.The amplitudes at 5o Hz measured at the output with the precautions described ranged from 1.3×10^{-1} to 10^{-2} nA for the amperometric detector and from 20 to 1.5 nA for the coulometric detector.In some case it was necessary to insert the 50 Hz filters.

Capacity and output noise

The cell capacity was measured as described under Theoretical.Potential steps between 5 and 50 mV were applied after stabilisation at 400 mV.Usually the integrator terminated integration after 2-5 seconds.With the same electrode the peak-to-peak noise was measured from the trace on the recorder.

In fig.2 these values are plotted.The following electrode materials have been used:

Au I and Au II: polished gold electrodes

Pt I and Pt II: polished platinum electrodes

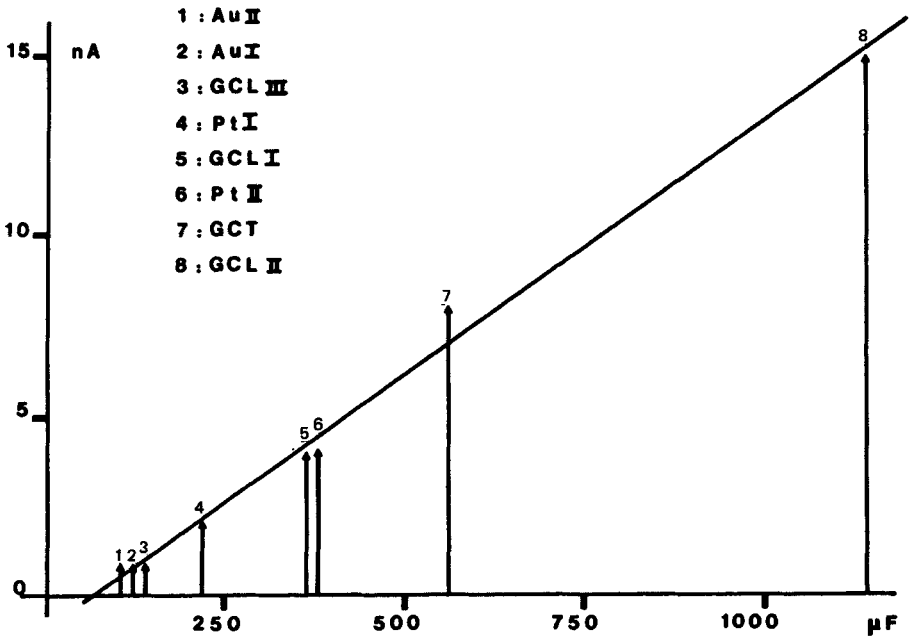

FIGURE 2 Relationship between the peak-to-peak noise and the cell capacity for different electrode materials. Coulometric detector equipment; surface area of the electrodes 3 cm^2.

GCL I and GCL II: polished glassy carbon electrodes, material from Le Carbone Lorraine, grade V 25 (ref.17)

GCT : polished glassy carbon electrode, material from Tokay Man.Co., grade GC 10 (ref.17)

GCL II: scoured glassy carbon electrode, material from Le carbone Lorraine, grade GC 25 (ref.17)

The relationship between the output noise and the capacity appears to be linear. It should be noted that in this experiment the surface areas of the electrodes were the same, equal to 3 cm^2. The differences in capacity are therefore related to differences in geometrical or chemical structures of the surfaces. Therefore we believe that the increase of noise levels observed for the high capacities in fig.2 is intrinsically related to the high capacity, also because a nearly perfect linear relation is observed. Also, an alternative

explanation,assuming that the noise is predominantly of faradaic nature would require to assume that the activity of the electrode or the noise generation in a faradaic process would be proportional to capacity.

As can be seen from fig.2,the rougher surface of the GCL II electrode leads to a considerably higher capacity and noise level,indicating the importance of proper electrode preparation procedures. Microscopically it can be observed that the surface of glassy carbon contains many pores,leading to enlargement of the electrode surface exposed to the liquid.This may explain why this material in general yields higher noise levels than do gold and platinum, which have a smoother surface.Although carbon paste was not included in this study we generally observe smaller noise levels with this material as well.

The relationship between the geometric surface area,cell capacity and noise level was studied also by using spacers of varying slit areas.This yielded the result that these three parameters are in proportion for a given electrode material.Contrary to the experiment of fig.2 this does not allow to distinguish between capacitive and faradaic sources of noise.

Auto- and crosscorrelation measurements

In order to corroborate further the results obtained,auto- and crosscorrelation functions were measured.In our opinion this would give more direct evidence of the contribution of voltage noise via the cell capacity ,because such measurements show the correlation between two parameters in the most direct way.

As the correlator needs relatively high input levels,each voltage to be studied was amplified by two amplifiers in series.The signal was also visualised on an oscilloscope in order to ascertain that random noise was predominant.

For the coulometric detector the results for the autocorrelation functions are presented in fig.3.For $\tau = 0$ the characteristic values are:

σ_V = 1.6 μV for the working electrode connection,

σ_V = 7.0 μV for the auxiliary electrode connection,

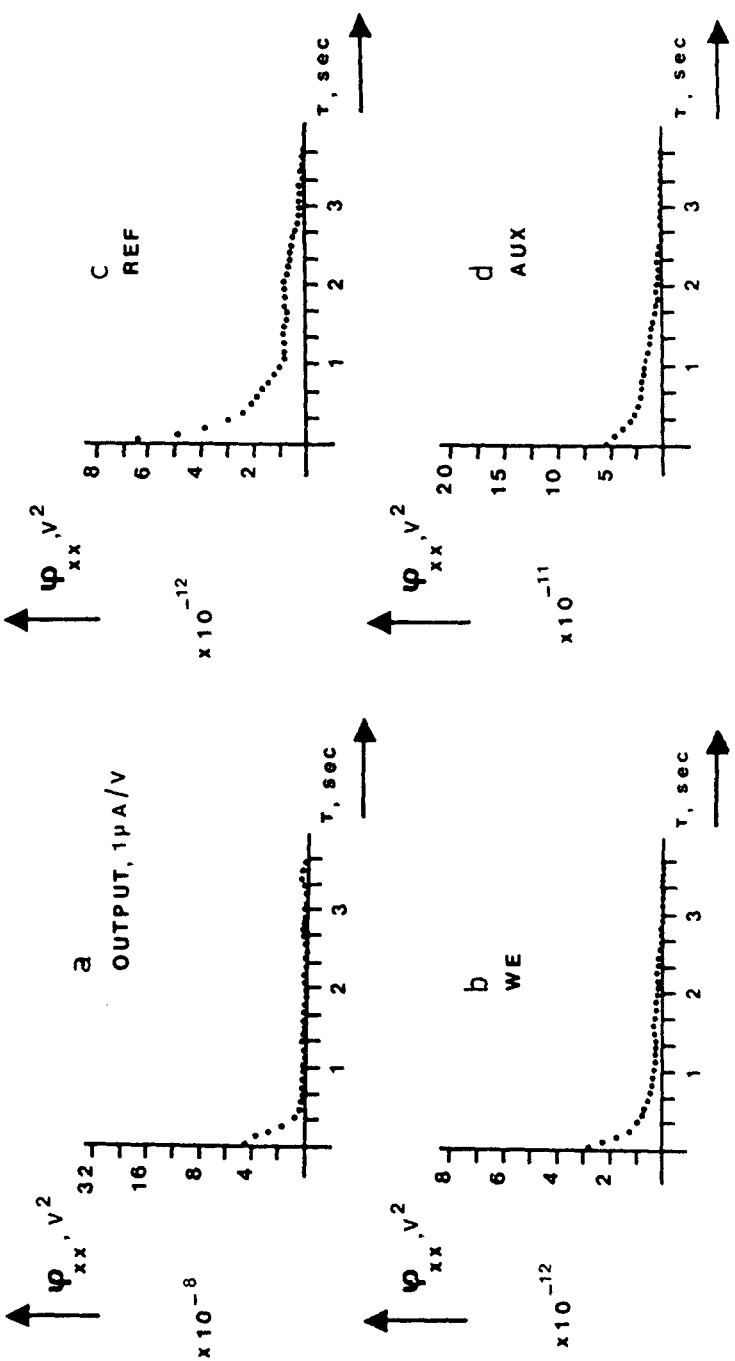

FIGURE 3 a,b,c,d Autocovariance functions measured on various terminals of the coulometric detector: a at the detector output,b at the working electrode,c at the reference electrode and d at the auxiliary electrode.

σ_v = 2.3 μV for the reference electrode connection and

σ_i = 0.2 nA for the detector output.

Note that,contrary to what has been done in eqns(4-6) , the detector output parameter is expressed in current units.This was done in order to avoid confusion due to varying attenuator settings.

The crosscovariance functions of the signals measured at the same connections of the electrodes,with the output of the detector are shown in fig.4.These curves have the shape of a peak,rather than that of the first derivative of a peak,with positive and negative excursions,as would be expected from the derivative operator in eqn (4). However,this operator cancels with integrating operations on the signal in the subsequent parts of the measuring chain,such as the low pass filters in the detector electronics and in the additional amplifiers used in our experiments.In the maximum of the crosscovariance functions we found the following values for ϕ and ρ:

working electrode-output $\phi_{max} = 2\times10^{-16}$ VA ; $\rho_{max} = 0.63$

auxil.electrode - output $\phi_{max} = 1\times10^{-15}$ VA ; $\rho_{max} = 0.07$

refer. electrode -output $\phi_{max} = 2.7\times10^{-16}$ VA;$\rho_{max} = 0.59$

These values indicate that the voltage noise at the electrode connections contributes significantly to the current noise observed at the output.The contribution from the auxiliary electrode appears to be an order of magnitude smaller than that of the other ones,which is not surprising because the circuit point is within a electronic feedback loop.

Similar measurements were carried out with the amperometric detector.With the amplifiers available it was impossible to measure the autocovariance functions at the working and auxiliary electrode connections;the fluctuations were too small compared to the noise of the best amplifier available (PAR 113).For $\tau = 0$ the standard deviations were less than 0.1 μV. The noise of the current amplifier (measurable with disconnected working electrode), $\overline{i^2}_{n,c}$, (see eqn(6)) and that of the potential source, $\overline{e^2}_{app}$, were also small compared with the other signals.From the autocovariance functions measured

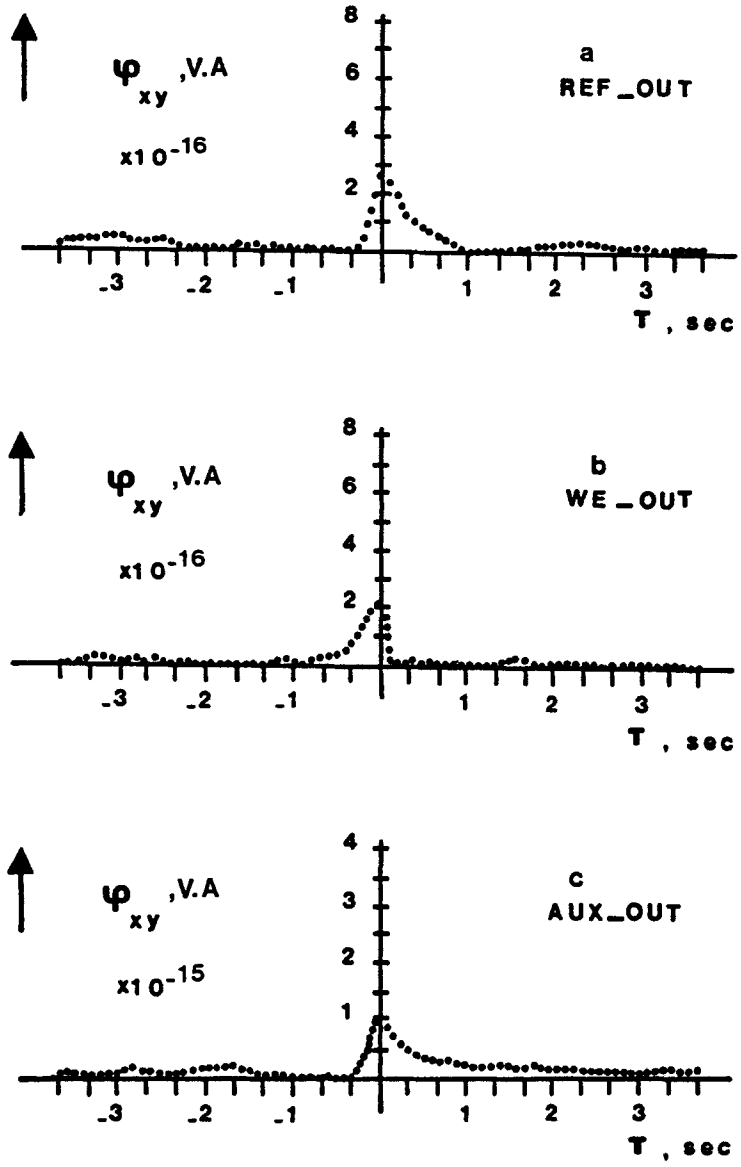

FIGURE 4 a,b,c Crosscovariance functions measured between the detector output of the coulometric detector and the signals present at a the reference electrode,b the working electrode and c the auxiliary electrode.At the right hand side of the curves the detector output signal is delayed.

at the reference electrode connection and the detector output we found, for $\tau = 0$, that $\sigma_V = 9\ \mu V$ and $\sigma_i = 2.2\times10^{-11}$ A respectively. The crosscovariance function of these two signals had a maximum value of 2.3×10^{-16} VA. Therefore the correlation coefficient according to eqn(10), ρ, is close to unity. This indicates that the voltage noise present at the reference electrode connection has a significant effect on the noise in the output signal. A correlation coefficient unity means that the reference elctrode signal is virtually completely responsible for the noise.

According to these results eqn(6) may be considerably simplified for the amperometric detector. The voltage noise factor $\overline{e^2_{n,tot}}$ is virtually equal to the contribution of the reference electrode, $\overline{e^2_{n,ref}}$, because the other contributions were too small to be measured, and the current contributions in eqn(6) can also be neglected; the amplifier noise, $\overline{i^2_{n,c}}$, was measured to be small and the working electrode contribution, $\overline{i^2_{n,we}}$, is probably also small because the nearly complete correlation found in the crosscorrelation experiment. Therefore eqn(6) becomes:

$$\sigma^2_{V,out} = c_1 C^2_{we} \overline{e^2_{n,ref}} \qquad (12)$$

or in current units and taking the square root:

$$\sigma_{i,out} = c_1' C_{we} (\overline{e^2_{n,ref}})^{\frac{1}{2}} = c_1' (\overline{e^2_{n,ref}})^{\frac{1}{2}} C'_{we} A_{el} \qquad (13)$$

$$= \beta A_{el}$$

in which c_1' replaces c_1 when the output is expressed in current units, C'_{we} is the capacity per unit area of the working electrode material under the chosen conditions, A_{el} is the electrode area and β summarizes the proportionality between electrode area and noise and is a constant for a particular combination of electrode material, voltage noise level and filter settings.

Equation (13) is also useful for more complicated cases, such as that of the coulometric detector used in this work, be it that other voltage noise sources may also contribute to β.

Electrical simulation of the cell properties

As an additional check on the validity of the approach taken in this work we wanted to ascertain that a system which accurately conforms to the adopted model for the cell and amplifiers would respond as can be expected on the basis of this model.We therefore simulated the electrical properties of the cell,incorporating the observed values of the cell capacity and the cell resistances in the simulation (19).With this some of the experiments described above were repeated.

The cell resistances were measured on the real cells using a frequency of 1000 Hz on the conductivity bridge.We assumed that at this frequency the cell capacity will not give a significant contribution to the observed impedances.The results are given in table 1. In a simulation these values can be duplicated by means of a network consisting of resistors,for which we took a triangular one. The cell capacity was introduced in the simulation by insertion of a capacitor in series at the working electrode terminal.

We first checked whether the the method for estimation of the cell capacity was correct.The method was performed in the same way as was done with the real cells,with capacitors of 50 and 166 μF. The experiment yielded the right values for these capacities.

The noise at the detector output was also measured as was done before, with the 166 μF capacitor.The value obtained fits nicely into

TABLE 1

Cell Impedances of the Electrochemical Cells,Measured at a Frequency of 1000 Hz

Coulometric Cell		Amperometric Cell	
WE - REF	13 k	WE - REF	300 k
REF- AUX	12 k	REF - AUX	18 k
AUX- WE	4.5 k	AUX - WE	300 k

WE: working electrode; AUX: auxiliary electrode; REF: reference electrode

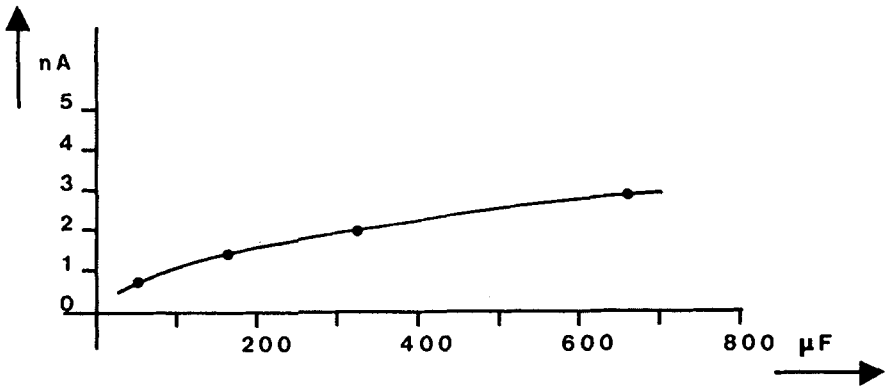

FIGURE 5 Relationship between the peak-to-peak noise at the detector output of the electronical circuit of the coulometric detector when connected to the simulated cell and the value of the capacitor in the simulated cell.

the plot of fig.2 ; i.e. it is in accordance with the value of the noise observed with the real cell having the same cell capacity. Next,additional capacitors were introduced in the simulation network,and the output noise was measured.The results are plotted in fig.5. As can be seen the noise level increases as expected with the capacity.However,the relation between noise and capacity departs slightly from linearity,which indicates that the model described by eqns(12-13) is a bit too crude.Nevertheless we believe that this experiment further corroborates the importance of capacity for the noise level.

CONCLUSION

It is useful to draw some conclusions with respect to the choice of electrode material,electronic equipment and electrode area.This discussion focusses on thin layer cell,but similar arguments apply to other cases,such as the wall jet geometry.

Eqn(13) summarized the proportionality between noise and area.A first approach for obtaining better detection limits of course

would consist in an attempt to decrease the factor β . As this is proportional to the capacity per unit area of the electrode in the carrier solution,careful selection of electrode material,while retaining the activity in electrochemical conversions of analytes, may lead to improvements.In the screening and development of electrode materials more attention should be given to the capacity these materials have per unit area.

The factor β is also proportional to the voltage noise,introduced via the reference electrode or otherwise (the term $\overline{e^2_{n,tot}}$ or $\overline{e^2_{n,ref}}$ in eqns (6) and (13) respectively).A thorough examination of reference electrodes and amplifiers with respect to their contribution to voltage noise appears to be important.

A next approach is of course the optimisation of the signal, while keeping the electrode area as small as possible.The signal can be expressed as:

$$i_s = F_c \, n \, F \, c_i \, Y \qquad (14)$$

where F_c is the flow rate,n is the number of electrons,F is the Faraday,c_i is the concentration of analyte i and Y is the electrochemical conversion yield.

As all factors in eqn(14) can be considered as constants except Y,the expression for Y as a function of cell geometry in the laminar flow region (the case of interest for analytical work) should be considered.The most general expression is given by Lankelma and Poppe (13,20) as:

$$Y = 1 - \exp(-Sh \, D \, A_{el} \, / \, 2 \, F_c \, d) \qquad (15)$$

where D is the diffusion coefficient and d is the layer thickness. Sh is the (dimensionless) Sherwood number,which describes the mass transfer.For not too low values of the argument in eqn(15) this is equal to 4.86;for lower values the graphs given by Stephan (20) for infinite Schmidt number can be used.These then give results which are virtually equal to those obtained with the Levêque expression, (21,22) and which involve a proportionality of Y with the length

to the two third power,which is equivalent to $A_{el}^{2/3}$ when the electrode width is constant.

The minimum detectable concentration c_i of the analyte is obtained by division of the eqns (14) and (13).Leaving out the factor $\beta/n\,F$,which is now considered to be constant,and inserting a factor 3 for statistical confidence leads to:

$$c_i \propto 3\,A_{el}/Y\,F_c \qquad (16)$$

For a value of the diffusion coefficient of 10^{-9} m^2s^{-1} and a flow rate of 1 ml/minute,this expression was calculated.The results are given in fig.6 . At high values of A_{el} ,the coulometric region, the detection limit increases with area.In that range the additional area generates more noise,but adds nothing to the signal because the

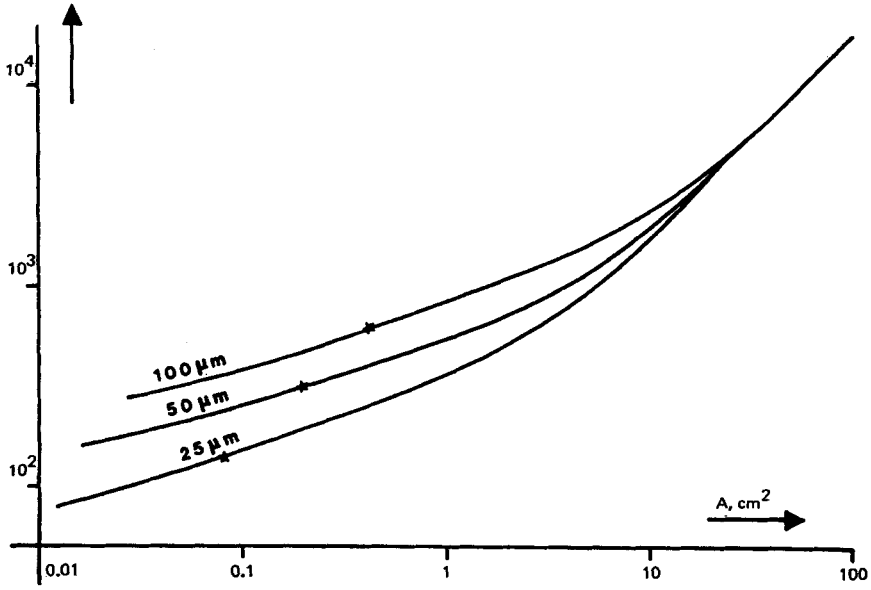

FIGURE 6 The geometry-dependent factor in the expression for the detection limit, $3A_{el}/F\,Y$ (eqn(16)) as a function of the area of the electrode for liquid film thicknesses of 25,50 and 100 µm. Electrode width is assumed to be equal to channel width.The parts of the curves at the left hand side of the stars are based on extrapolated Sherwood numbers (ref.20).

solution is already fully depleted.The curves move smoothly into the range where signal is proportional to $A_{el}^{2/3}$ .This is the amperometric region.

It is tempting to look for conditions where Sh is large,as was done by Weber and Purdy (23) and Hanekamp and Nieuwkerk (24) , which occurs for small areas and small film thicknesses.In both papers it was pointed out that a decrease of the area should be accomplished via the electrode length ,not the width.However,drastic changes in A_{el} , and thus of absolute current levels,would be needed for a moderate reduction in c_i,as the latter decreases with a one third power of A_{el}.We therefore believe such an attempt would not be very succesful.Amplifier current noise soon would predominate.

A more substantial (power 2/3) improvement can be obtained by the use of smaller film thicknesses.,because the absolute value of the current may remain sufficiently large to avoid electronic measurement noise problems.The improvement when going from 100 to 25 μm thickness is illustrated in fig.6.The most important obstacle while going into this direction appears to involve the mechanical problem of avoiding leakages and short-circuiting as a result of machining imperfections and increased pressure build up in the cell.

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