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CONTINUOUS STIRRED REACTOR MODEL AS BASIS FOR OPTIMISATION OF ELECTRON CAPTURE DETECTOR OPERATION IN COULOMETRIC AND CONSTANT CURRENT MODES

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SUMMARY

    The paper analyses the theoretical reasons for the empirical observations that the operational conditions in the constant current mode are contradictory to those in the coulometric mode. On the basis of the continuous stirred reactor model the necessary conditions for the two different modes are formulated.

INTRODUCTION

    During the last few years considerable progress has been made in understanding the mechanism of the electron capture detector (ECD) and in improving the detector parameters. The main effort has been concentrated on improving the limits of detection and increasing the linear range. It was shown that the coulometric detector[1] is better with regard to the detection limit but the detector working with constant current[2] is better as far as the linear range is concerned. However, the decision which of these two parameters is more important must be taken before the detector is going to be built, because simultaneous optimisation of both of them is impossible. In this paper it is shown how the contradictory demands concerning conditions of operation of the ECD in the coulometric and constant current modes stem from the chemical stirred reactor model of the detector. This model, sometimes called Lovelock's model[1], describes the mechanism of the ECD by two differential equations derived from the conservation of number for the relevant species, assuming uniform concentration (good mixing) within the cell.

$$\frac{dn_e}{dt} = A/V - n_e (k_1 n_a + k_d) \tag{1}$$

$$\frac{dn_a}{dt} = B/V - n_a (k_1 n_e + k_x + u/V) \tag{2}$$

where

   n_e, n_a = number of electrons and sample molecules per unit volume inside the detector cell, respectively

   A, B = rates of injection of electrons and sample molecules, respectively

   k_1 = rate constant for removal of sample molecules in electron capture process

   k_d = pseudo-recombination rate constant

   V = detector volume

   u = flow-rate of carrier gas

   k_x = rate of destruction of sample molecules by other processes (this constant will be neglected in the further consideration)

Eqns. 1 and 2 may be treated as linear differential equations of the first order.

$$\frac{dx}{dt} = a - \lambda x \tag{3}$$

with the solution

$$x = a/\lambda \, (1 - e^{-\lambda t}) \tag{4}$$

The system may be regarded as having reached a steady state after times greater than $3 \times$ time constant $(1/\lambda)$, that is, for pulse intervals (t_p) given by

$$t_p \geqslant 3 \, \frac{1}{k_d + k_1 \, n_a} \tag{5}$$

The concentration of the electrons reaches the value

$$n_e = \frac{A/V}{k_d + k_1 \, n_a} \tag{6}$$

and the ionization current, provided that every pulse removes all electrons from the cell. becomes

$$I_e = \frac{Vn_e}{t_p} = \frac{A}{(k_d + k_1 \, n_a)t_p} \tag{7}$$

Under the assumption that B is constant or changes slowly, the concentration of sample molecules in the detector cell is given by

$$n_a = \frac{B/V}{k_1 \, n_e + u/V} \tag{8}$$

or, replacing B/V by $n_{cg} \cdot u/V$ (9)

(where n_{ca} is the concentration of sample molecules in the carrier gas entering the detector cell)

$$n_a = n_{cg} \frac{u/V}{k_1 \, n_e + u/V} \tag{10}$$

The concentration of sample molecules inside the detector is a holomorphic function of the ventilation rate constant u/V, which is, of course, the reciprocal of the residence time.

CONSTANT CURRENT MODE

In order to increase the linear range of the ECD, Maggs et al.[2] suggested the constant current mode, in which the ionization current is kept constant by varying the pulse frequency. As the electric current is given by

$$I_e = A \, 1/\varepsilon \, (1 - e^{-\varepsilon}) \tag{11}$$

where

$$\varepsilon = t_p \, (k_d + k_1 \, n_a) \tag{12}$$

constant current is guaranteed by constancy of the argument ε

$$t_p \, (k_d + k_1 \, n_a) = \text{const.} = \varepsilon_0 \tag{13}$$

For the pure carrier gas

$$n_a = 0$$

and

$$t_p \, (k_d + k_1 \, n_a) = k_d \, t_{p0} \tag{14}$$

where t_{p0} is the initial time interval.

If ventilation is the main process in the depopulation of the sample molecules in the ECD which occurs for

$$u/V \gg k_1 \, n_e \tag{15}$$

eqn. 10 can be simplified to

$$n_a = n_{cg} \tag{16}$$

which results in

$$t_p \, (k_d + k_1 \, n_{cg}) = t_{p0} \, k_d \tag{17}$$

or

$$\frac{v - v_0}{v_0} = \frac{k_1}{k_d} \cdot n_{cg} \tag{18}$$

where frequency $v = 1/t_p$ and $v_0 = 1/t_{p0}$, and also in

$$\Delta v = \varepsilon_0^{-1} \, k_1 \, n_{cg} \tag{19}$$

Eqn. 19 implies that for good sensitivity $\varepsilon_0 = k_d t_{p0}$ should be chosen as small as possible. However, sensitivity is not the only factor considered in selecting ε_0 in practice and others like the linear range and the magnitude of an error must be taken into account.

The span of frequency is limited by the initial frequency v_0, which is of our choice and the final frequency v_c, which is determined by the pulse width (provided that input time constant of the detector electric system is negligible). The pulse width (t_w) must be of a sufficient length to enable collection of nearly all electrons, and may be roughly estimated by the relation

$$t_w = \frac{d}{v_d} \tag{20}$$

where d is the distance between the electrodes and v_d is the electron drift velocity. It is usually of the order of magnitude of 1 μsec.

From eqn. 19 the relation for the maximum analysed concentration can be obtained as

$$n_{cg\ \mathrm{max.}} = \frac{v_c - v_0}{k_1}\,\varepsilon_0 \tag{21}$$

which implies that ε_0 should be rather large if higher concentrations are to be analysed.

The last but not least factor which should be taken into account is an error introduced by inaccuracy in keeping the current I_e constant, which causes the fluctuations of ε_0. Because the current is the function of ε, those fluctuations are given by

$$\delta I = f'(\varepsilon)\,\delta\varepsilon \tag{22}$$

where $f'(\varepsilon)$ is the derivative of the function $I = f(\varepsilon)$ given by eqn. 11. From eqn. 19 it is evident that the relative error of an assessed sample concentration is at least equal to the relative error of ε_0, which can be derived from eqn. 22 as

$$\frac{\delta\varepsilon}{\varepsilon} = \frac{1}{\varepsilon f'(\varepsilon)}\cdot\delta I \tag{23}$$

For a given fluctuation δI, the relative error of ε_0 is the least for the ε_0 for which $\varepsilon\cdot f'(\varepsilon)$ reaches maximum. This occurs for $\varepsilon_0 \approx 1$ and means that both very small and very large values of ε_0 should be avoided because for both of them $\varepsilon\cdot f'(\varepsilon)$ is nearly nil.

As the result of all these considerations $\varepsilon_0 \approx 1$ may be recommended, which means

$$t_{p0}\cdot k_d \approx 1 \tag{24}$$

It is interesting to see that if condition 15 is to be satisfied for every concentration n_{cg}, i.e.

$$\frac{u}{V} \gg k_1 \frac{A/V}{k_d + k_1\,n_{cg}} \tag{25}$$

it is enough to have

$$\frac{u}{V} \gg \frac{k_1}{k_d} \cdot \frac{A}{V} \tag{26}$$

or

$$u \gg A \, k_1/k_d \tag{27}$$

Conditions 24 and 27 are satisfactory for long linear range and accuracy in constant current mode.

COULOMETRIC MODE

The signal of an ordinary ECD depends not only on the concentration but also on the kind of a sample. For quantitative analyses it is necessary to calibrate the detector separately for every analysed compound. The calibration, even if performed with the exponential dilution flask, is tedious and time consuming. Then an attempt was made[1,3] at constructing the detector whose signal is not dependent on the analysed species. Theoretically it can be easily achieved by making the electron attachment the dominating process over the ventilation

$$k_1 \, n_e \gg u/V \tag{28}$$

because, after that, it follows from eqn. 8 that

$$n_a = \frac{B/V}{k_1 \, u_e} \tag{29}$$

and from eqn. 1 that

$$n_e = \frac{A - B}{k_d \, V} \, (1 - e^{-t_p k_d}) \tag{30}$$

and

$$I_e = \frac{A - B}{t_p \, k_d} \, (1 - e^{-t_p k_d}) \tag{31}$$

As for pure carrier gas

$$I_{e0} = \frac{A}{t_p \, k_d} \, (1 - e^{-t_p k_d}) \tag{32}$$

then the detector signal is given by

$$\Delta I = \frac{B}{t_p \, k_d} \, (1 - e^{-t_p k_d}) \tag{33}$$

In the case of the ECD, coulometry means that

$$\frac{\text{Number of electrons not collected}}{\text{Time}} = \frac{\text{Number of molecules coming into the detector}}{\text{Time}} \tag{34}$$

To obtain coulometric response, an additional condition must be satisfied, viz.

$$t_p k_d \ll 1 \tag{35}$$

because it results in

$$\Delta I = B \tag{36a}$$

or

$$\Delta I = u n_{cg} \tag{36b}$$

For very small t_p

$$n_e = A/V \cdot t_p \tag{37}$$

what allows to rewrite condition 28 as

$$A \cdot k_1 t_p \gg u \tag{38}$$

It is not very difficult to satisfy these two conditions 35 and 38 if the rate constant for electron attachment is large as for SF_6, but it is hardly possible for species for which the rate constant is small. The chance to increase k_1 by proper choice of carrier gas and pressure in the detector seems to be little. Another way out is to maximise the ratio A/k_d which determines the current and the electron density by the selection of a strong ionization source and a carrier gas for which the recombination coefficient is small and the ionization cross-section high. It is interesting to notice that the two conditions do not explicitly include any volume term, but it should not be forgotten that the fundamental assumption about the ideal mixing in the detector cell is true only for small volumes.

CONCLUSIONS

The continuous stirred reactor model can be very useful in the determination of the operational conditions for the ECD in the constant current mode. It gives an

TABLE I

CONDITIONS OF THE ECD OPERATION

Constant current mode of ECD	Coulometric mode of ECD
$t_{p0} k_d \approx 1$	$t_p k_d \ll 1$
$k_1 n_e \ll u/V$	$k_1 n \gg u/V$
$A \dfrac{k_1}{k_d} \ll u$	$A k_1 t_p \gg u$
k_d large	k_d small
k_1 small	k_1 large
A small	A large

explanation of the fact that the operational conditions in these two modes are contradictory, what was known much earlier empirically from a comparison of the performance of commercial detectors.

The summary of the contradictory conditions which must be satisfied in these two modes of operation is given in Table I.

The last three conditions in Table I for the constant current mode are in obvious contradiction to the demand of the best detectivity. However, this disadvantage must be accepted in return for longer linear range.

REFERENCES

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3 J. E. Lovelock, R. J. Maggs and E. R. Adlard, *Anal. Chem.*, 43 (1971) 1962.