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**DEFINITION AND DETERMINATION OF
RESPONSE TIME OF ION
SELECTIVE ELECTRODES**

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Definition and determination of response time of ion selective electrodes

1. Introduction
2. Concept of response time
3. Determination of response time
 - 3.1. Dipping technique
 - 3.2. Injection technique
4. Limits of the activity step method
5. Attempts towards a definition of response time
6. Comparison of response time data calculated according to different mathematical models and response time definitions

1 INTRODUCTION

The analytical value of terms used to assess the performance characteristics of ion selective electrodes such as selectivity factor, lower limit of detection, response time, life time, etc., depends on the constancy of these factors. But these factors are greatly dependent of the methods used for their determination [1]. In order to be able to compare these factors the experimental methods must be carefully selected [2,3]. Under these conditions one can expect to obtain analytically useful parameters which permit the comparison of the performance characteristics of different types of ion-selective electrodes (ISE's).

The need to specify the measuring technique and experimental conditions seems to be especially important for the determination of response time since the published values of this parameter, even for the same type of electrodes, may differ by orders of magnitude [4,5].

2 CONCEPT OF RESPONSE TIME

The dynamic response of ion-selective electrodes or, more precisely, that of the potentiometric cells containing them may be studied by different methods [6-8]. The activity step method is the most important one for determining practical response time data. In this method the potential-time function of the electrochemical cell is studied as an effect of an activity step change produced in the sample, thus one works at $i=0$ current membrane conditions corresponding to the usual potentiometric conditions.

Applying the activity step method the measured overall response time data are determined not only by the properties of the ion-selective indicator electrode but also by the design of the electrochemical cell, the measuring technique, the experimental conditions selected and by the time dependence of other sources of potential in the cell such as diffusion and streaming potential furtheron by the electronics used for recording the transient signal (Fig.1). These factors altogether define the transient function of the whole system (electrochemical cell + electronics)[9].

MEASURING SYSTEM

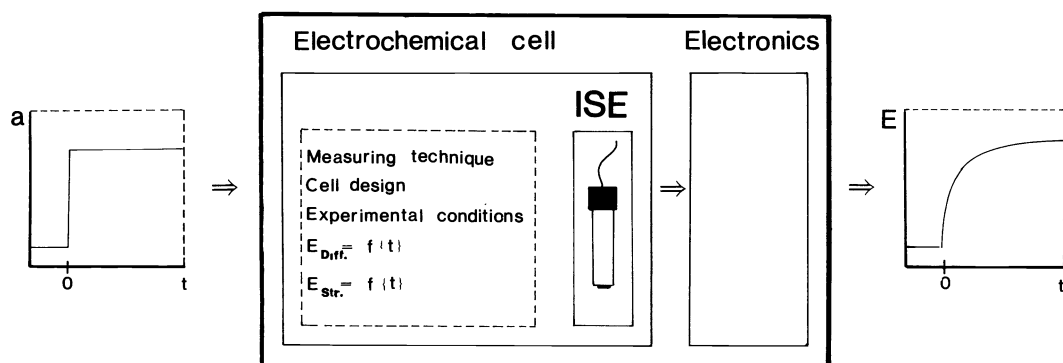


Fig. 1 Model for the definition of the response time of ion-selective electrodes, electrochemical cells and measuring systems

In principle, three limiting cases may be discussed:

- the dynamic response (response time) of a potentiometric system is determined principally by the measuring technique and experimental conditions applied. This means that the dynamic response of the ISE is extremely fast compared to the other parts of the system;
- the time constants of the transient functions of the two parts of the electrochemical cell (Fig.1) are comparable;
- the dynamic response of a potentiometric system is determined principally by the properties of the indicator electrode. In this case the time constant of the indicator electrode response function is much larger than that of the other parts of the electrochemical cell.

Consideration of the response time of an ion-selective electrode is appropriate only in the last limiting case above. However, in practice it is quite difficult to differentiate between the individual limiting cases since the types of the indicator electrodes, the concentration level of the primary ion and the design of the electrochemical cell together determine which of the three conditions apply. Moreover, in a paradoxical way it may be hard to differentiate between the individual limiting cases even in the knowledge of these experimental conditions.

In practice however when it is necessary to decide whether the measured potential is an equilibrium value, corresponding to the primary ion activity of the bulk and independent of the time constant of the measuring system, then the time constant of the whole potentiometric system is of importance. In the activity step method the transient function of the electrochemical cell is influenced by the dynamic properties of the indicator electrode and by the following factors:

- a/ to what extent the activity step can be considered as ideal, with a rising section of infinite slope at the electrode membrane surface;
- b/ the dynamic properties of other potential sources developing in the electrochemical cell such as streaming potential and liquid-junction potential.

The shape of the activity step is influenced mainly by the manner in which the activity step is produced e.g. dipping method, injection method or other special techniques.

3 DETERMINATION OF RESPONSE TIME

3.1 Dipping method [10, 11, 12]

The indicator electrode is conditioned in a solution of activity a_i^0 . After careful wiping or washing it is immersed into the stirred sample solution of activity a_i^∞ at the time $t=0$. The timer is started at the instant of immersion. (To avoid undesirable perturbations on the response, induced by wiping, the adhering droplets of conditioning solution can be removed by shaking the electrode during transfer [12].) To avoid problems due to the fact that during the experiment the electric circuit is broken and to improve reproducibility several special flow-through techniques have been developed [7,13,14,15,16]. The equipment developed by Tóth et al. [7,16] is probably closest to the dipping method in so far as instead of changing the position of the electrode that of the sample solutions is altered with the help of two mobile jets perpendicular to the electrode surface.

3.2 Injection method [11, 17, 18]

A volume of concentrated solution of primary ion, smaller than the cell volume, is injected by means of a syringe into the rapidly stirred test solution in which the cell assembly had been previously conditioned. The timer is started at the instant of injection of the concentrated sample.

4 LIMITS OF THE ACTIVITY STEP METHOD

By applying the activity step method reproducible response time data can be achieved only under exactly controlled hydrodynamic conditions using the same container, solution volume, injected volume, stirrer, stirring speed, electrode surface area and depth and angle of the measuring electrode. Ideal activity steps can be approximated only with special techniques [7, 13-16] but even in these cases it can only be realised on the boundary of the stagnant solution layer (Prandtl-layer) adhering to the electrode surface [11]. Thus, the observed time constants often correspond to film diffusion values as the stagnant film of initial solution changes by diffusion-migration to the new stepped value, accordingly only the distortion of the activity step is recorded. The thickness of the stagnant solution layer depends on:

- flow or mixing rate of the sample solution;
- design of the electrochemical cell;
- geometry of the indicator electrode;
- electrode membrane surface conditions;
- temperature and viscosity of the sample solution.

Other time dependent potential sources such as streaming and liquid junction potentials have not yet been considered in discussing the dynamic response of ion-selective electrodes. Efforts have usually been made for their minimalization or elimination.

The less ideal the activity step, the greater the contribution of transport processes, taking place within the cell in determining the transient function of the potentiometric system. Accordingly, the mathematical description of the potentiometric system as reflecting an activity step change, can be made by describing the activity of the primary ion at electrode surface as a function of time [4,11,19]. The more the activity step approaches the ideal step function the more the indicator electrode's properties control the response time of the cell [20,21].

The relation between the response time of the indicator electrode and that of the other parts of the whole system, cannot be estimated as long as these values cannot be measured separately. For a generally valid definition of response times of potentiometric systems it is necessary to describe mathematically the potential-time functions incorporating all the experimental parameters affecting the dynamic behaviour of the potentiometric cell. This would allow comparison of response time data measured under different experimental conditions or calculated according to different definitions. Since it is not yet possible to derive such generally valid mathematical equations, due to the problems discussed above, there is a considerable demand for a generally acceptable response time experimental method, especially for comparing data from the many automated analytical methods incorporating potentiometric electrodes. However, at the moment such internationally accepted standard methods are not available. The response time measurements are performed by measuring devices and electrodes of very different constructions [7,10-21]. Thus, earlier suggestions for the definition of response time [2,3,18] in addition of their advantages have some drawbacks, too.

5 ATTEMPTS TOWARDS A DEFINITION OF RESPONSE TIME

Although the general mathematical description of the transient function of the whole potentiometric measuring set-up employed in practice is rather complicated, the mathematical equations derived for describing potential-time curves in some well-defined limiting cases can be useful for calculating steady-state or equilibrium potential values.

a/ The dynamic response of the potentiometric system is mainly controlled by the measuring technique and experimental conditions (fast indicator electrodes, and slow measuring set-up).

In general this is the case when glass-, precipitate based or liquid ion-exchanger electrodes are used in relatively concentrated ($c > 10^{-4}$ M) solutions in the absence of interfering ions and under practical analytical conditions e.g. in cells without mixing, in slightly stirred solutions, or

in flow-through cells at low flow-rates. Thus, the rate of electrode response is controlled by film diffusion [11,19]:

$$E_t = E_\infty + S_{\text{eff}} \left[\log \frac{1 - \left(1 - \frac{a_i^0}{a_i^\infty}\right) e^{-t/\tau'}}{1} \right] \quad (1)$$

where

$$\tau' \approx \frac{\delta^2}{2D'}$$

E_t electrode potential measured at the time t after the sample activity change;

E_∞ final or equilibrium electrode potential value corresponding to activity value a_i^∞ ;

S_{eff} slope of the electrode response function;

a_i^0, a_i^∞ activity of the primary ion in the bulk of sample solution before ($t < 0$) or following ($t > 0$) the activity step, respectively;

δ thickness of the aqueous adhering layer;

D' mean diffusion coefficient in the aqueous adhering layer.

A similar exponential equation is valid when the time constant of the measuring electronics control the dynamic behaviour of the system [22].

This can occur when electrodes having extremely high resistance are used:

$$E_t = E_\infty - (E_\infty - E_0) e^{-t/RC} \quad (2)$$

where E_0 the electrode potential primary to the activity step;

R the internal resistance of the electrochemical cell;

C the total capacitance of cell and amplifier input

b/ The dynamic behaviour of the potentiometric system is mainly controlled by the indicator electrode itself (slow electrodes, specially designed cell and fast electronics).

Under certain experimental conditions such as high mixing or flow rates, the rate of mass transport from the bulk of the solution to the electrode surface can be neglected in comparison with other electrode reaction steps [20,21].

ba/ Transient functions of cells with precipitate based ISE's in the range of the lower detection limit.

Several authors have pointed out that deviations can be observed from the so-called diffusion model (Equ.1) especially if one works in the range of the detection limit of the electrodes [20,23,24]. Under these conditions the experimentally recorded data can be fitted by a hyperbolic function such as that first by Müller [25]:

$$E_t = E_0 + \left[E_\infty - E_0 \right] \frac{t/\tau'}{1+t/\tau'} \quad (3)$$

where the time constant τ' is a function of the primary ion activities a_i^0, a_i^∞ and the dissolution rate constant of the precipitate used as membrane material [23,24].

bb/ Transient functions of cells containing neutral carrier based ion-selective electrodes.

The transient functions of cells containing neutral carrier electrodes can be described by regarding the diffusion process within the ion-selective membrane as rate controlling [11,26]:

$$E_t = E_\infty + S_{\text{eff}} \log \left[1 - \left(1 - \frac{a_i^0}{a_i^\infty}\right) \frac{1}{\sqrt{t/\zeta + 1}} \right] \quad (4)$$

where

$$\zeta = \frac{D K^2 \delta^2}{D'}$$

- D mean diffusion coefficient within the membrane;
- K partition parameter [11];

In practice if one of the above limiting cases applies a mathematical equation can be fitted to the experimental data with the required accuracy and it is immaterial which of the current definitions is used for determining response time data:

- "The length of time (t^x) which elapses between the instant at which an ion-selective electrode and a reference electrode are brought into contact with a sample solution (or at which the concentration of the ion of interest in a solution in contact with an ion-selective electrode and reference electrode is changed) and the first instant at which the potential of the cell becomes equal to its steady-state value within 1 mV." [3] (Fig.2).
- "The length of time (t_α) that elapses between the instant at which an ion-selective electrode and a reference electrode are brought into contact with a sample solution (or at which the concentration of the ion of interest in a solution on contact with an ion-selective electrode and a reference electrode is changed) and the first instant when the potential of the cell has reached 90% of the final value" [2] (Fig.2). As can be seen in Fig.2.

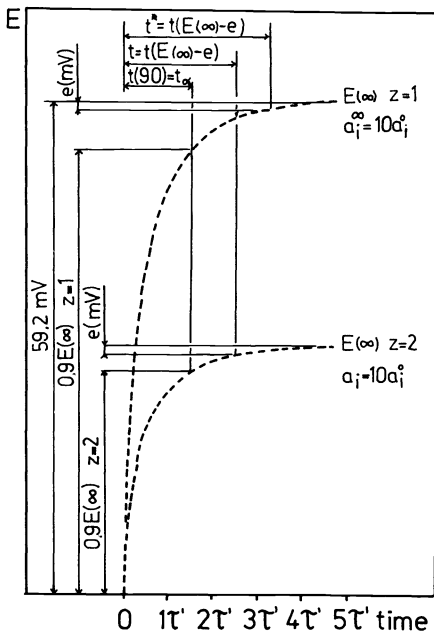


Fig. 2 Theoretical response time curves of uni-, and divalent ion selective electrodes calculated with equation 1. t_α (t_{90}) = the time required to attain 90% of the final potential (E_∞). t^x ($t_{E_\infty - e}$) = the time required to attain the final potential value to within $\pm e$ mV.

the first definition results in different response time values for univalent and divalent ion-selective electrodes even if the time constant of the mathematical equation describing the response time curve, is the same. Naturally if the mathematical equation for describing transient signals is available it does not matter which of the definition is used for the determination of response time since the different data can be intercompared. However even in these cases it is rather complicated to determine the time constant because it can only be done by curve fitting methods [21,27].

When one does not know the mathematical equation describing the transient function or the time constant of the transient function, however the above definitions of response time [2,3] are of not much practical value. Surely if the response time of the cell is short, then there is not much use of t^x [3] or t_α [2] values, since one can wait as long as the new steady-state potential value (E_∞) is developed (t_∞). Whenever the response time of the cell is long then in a paradoxical way it is impossible to determine t^x or t_α without a knowledge of E_∞ [28].

All the problems related to the definition of response time, discussed above can be overcome by defining the response time as a time interval necessary to reach a predetermined slope (differential quotient $t(\Delta E/\Delta t)$) value after the introduction of the activity step (Fig.3). The new definition has a number of advantages:

- it is very easy to determine;
- it can be determined without knowing the E_∞ value;
- it has the same significance as the time constant of a theoretical equation;
- it can also be used in the case of response time curves consisting of sections, controlled by different processes,
- it has the practical analytical advantage in that, it helps the analyst in determining the potential reading to be taken [29].

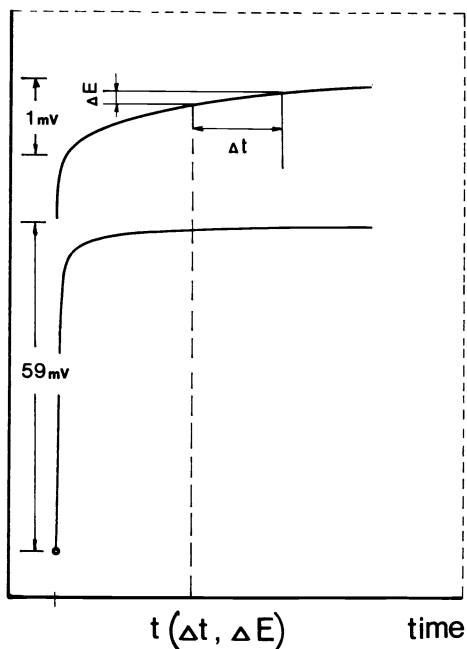


Fig. 3 Definition and determination of $t(\Delta E/\Delta t)$ [28]

For practical analytical purposes slope (differential quotient) values should be selected which fall on the asymptotic part of the transient function. As with the decrease of the preselected differential quotient values ($t(\Delta E/\Delta t)$) the response time data increase drastically, thus the selection of a practical differential quotient value is determined by the analytical accuracy required.

By studying the influence of different experimental parameters on the dynamic response of ISE's, Lindner, Tóth and Pungor [16,20,26] used the slope values of the response time curves to characterize the dynamic response function. They pointed out that the slopes provide the same information as the time constant of the fitted theoretical curves [30]. Lateron, Uemasu and Umezawa [28] have compared response time data determined according to the earlier definition (i.e. t^x and t_α) with those corresponding to a predetermined slope values e.g. $t(0.3 \text{ mV}/2 \text{ min})$.

In addition to the advantages of the new slope based definition there are also some drawbacks:

- by selecting a predetermined fixed differential quotient value, it is rather hard to predict the exact error in the analytical determination if the potential data corresponding to the defined differential quotient values are used for calculation instead of E_∞ ;
- The error in the analytical determination depends on the magnitude of the activity step (a_i^0/a_i^∞), and on the slope of the electrode potential response function (i.e. on the charge number of the primary ion (z_i) as well as on the electrode membrane conditions). However, these drawbacks also hold true for the earlier definition of response time.

6 COMPARISON OF RESPONSE TIME DATA CALCULATED ACCORDING TO DIFFERENT MATHEMATICAL MODELS AND RESPONSE TIME DEFINITIONS

A few model calculations in Table I and II were made for the limiting cases a/ and b/ with the help of equations 1 and 4 to provide a better insight into the problems of response time definitions, factors effecting response time data and analytical accuracy.

The following equations derived from equations 1 and 4 were used for calculating t^x and t_α values:

$$t(\xi) = \tau' \cdot \ln \frac{1 - a_i^0/a_i^\infty}{1 - (a_i^0/a_i^\infty)^\xi} \quad (5)$$

$$t(\xi) = \tau' \left[\frac{(a_i^0/a_i^\infty)^\xi - a_i^0/a_i^\infty}{1 - (a_i^0/a_i^\infty)^\xi} \right]^2 \quad (6)$$

where $t(\xi)$ is the response time calculated according to the different definitions, while

$$\xi = \frac{E(t) - E(\infty)}{E(0) - E(\infty)}$$

For calculating $t(\Delta E/\Delta t)$ values, however, the derivative of equations 1 and 4 were used.

It is apparent from this report, that a generally applicable procedure is conspicuous by its absence. We recommend to use for purposis of comparison the "differential quotient" $t (\Delta E / \Delta t)$, as the most satisfactory approach for the time being.

TABLE I. Theoretical response time values calculated with equation 1 (values in s, calculated with $\mathcal{J}' = 1s^b$)

a_i^∞ / a_i^0	t_α^a			t^{*a}			$t (\Delta E / \Delta t)$		
	[%]			[mV]			[mV/min]		
	50	90	99.5	1	0.5	0.1	1/1	0.5/1	0.1/1
Activity increase									
10	0.27	1.47	4.36	3.16	3.84	5.44	8.07	8.76	10.37
100	0.09	1.47	3.77	3.25	3.93	5.54	8.16	8.88	10.47
Activity decrease									
0.1	1.43	3.41	6.66	5.42	6.12	7.74	10.37	11.06	12.67
0.01	2.39	5.13	8.36	7.82	8.52	10.14	12.77	13.46	15.07

a/ In the case of t_α and t^{*} the response time data increase proportional with \mathcal{J}'

b/ Time constant value used for practical analytical conditions [11,19]

TABLE II. Theoretical response time values calculated with equation 4 (values in s, calculated with $\mathcal{J} = 10 ms^b$)

	t_α^a			t^{*a}			$t (\Delta E / \Delta t)$		
	[%]			[mV]			[mV/min]		
	50	90	99.5	1	0.5	0.1	1/1	0.5/1	0.1/1
Activity increase									
10	10^{-3}	0.11	60.3	5.1	20.9	532	29.1	46.2	136
100	10^{-4}	0.03	18.1	6.2	25.4	644	31.0	49.3	145
Activity decrease									
0.1	0.1	11.4	6025	509	$2.1 \cdot 10^3$	$5.3 \cdot 10^4$	128	206	617
0.01	1.0	283	$1.8 \cdot 10^5$	$6 \cdot 10^4$	$2.5 \cdot 10^5$	$6.4 \cdot 10^6$	530	886	2793

a/ In the case of t_α and t^{*} the response time data are proportional with \mathcal{J}

b/ Time constants measured with neutral carrier electrodes [11,26]

REFERENCES

1. E.Pungor, K.Tóth, A.Hrabéczy-Páll, Pure and Appl.Chem. 51, 1913 (1979)
2. G.G.Guilbault, IUPAC Int.Bull., No.1, 69 (1978)
3. IUPAC, Pure and Appl.Chem., 48, 127 (1976)

4. A. Shatkey, *Anal. Chem.*, 48, 1039 (1977)
5. E. Lindner, K. Tóth, E. Pungor, *Bunseki Kagaku*, 30, S67 (1981)
6. K. Tóth, I. Gavallér, E. Pungor, *Anal. Chim. Acta*, 57, 131 (1978)
7. R. P. Buck, "Ion-Selective Electrodes in Analytical Chemistry" Freiser ed., Plenum, New York, 1978
8. K. Camman, G. A. Rechnitz, *Anal. Chem.*, 48, 856 (1976)
9. E. Pungor, Y. Umezawa, *Anal. Chem.*, 55, 1432 (1983)
10. B. Karlberg, *J. Electroanal. Chem.* 49, 1 (1974)
11. W. E. Morf, E. Lindner, W. Simon, *Anal. Chem.*, 47, 1596 (1975)
12. R. C. Hawkings, L. P. U. Corriveau, S. A. Kushneriuk, P. W. Wong, *Anal. Chim. Acta*, 102, 61 (1978)
13. G. A. Rechnitz, G. C. Kugler, *Anal. Chem.*, 39, 1682 (1967)
14. J. Mertens, P. van den Winkel, D. L. Massart, *Anal. Chem.*, 48, 272 (1976)
15. A. Denks, R. Neeb, *Fresenius Z. Anal. Chem.*, 285, 233 (1977)
16. E. Lindner, K. Tóth, E. Pungor, *Anal. Chem.*, 48, 1071 (1976)
17. B. Karlberg, *J. Electroanal. Chem.*, 45 127 (1973)
18. B. Fleet, T. H. Ryan, M. J. D. Brand, *Anal. Chem.*, 46, 12 (1974)
19. P. L. Markovic, J. O. Osburn, *AICHE J.*, 19, 504 (1973)
20. E. Lindner, K. Tóth, E. Pungor, *Anal. Chem.*, 54, 72 (1982)
21. A. Denks, R. Neeb, *Fresenius Z. Anal. Chem.*, 298, 131 (1979)
22. W. E. Morf, W. Simon, "Ion-Selective Electrodes in Analytical Chemistry" Vol I., H. Freiser ed., Plenum, New York, 1978.
23. J. Buffle, N. Parthasarathy, *Anal. Chim. Acta*, 93 111 (1977)
24. N. Parathasarathy, J. Buffle, W. Haerdi, *Anal. Chim. Acta*, 93, 121 (1977)
25. R. H. Müller, *Anal. Chem.*, 41, 113A (1969)
26. E. Lindner, K. Tóth, E. Pungor, W. E. Morf, W. Simon, *Anal. Chem.*, 50, 1627 (1978)
27. A. Shatkey, M. Azor, *Anal. Chim. Acta*, 133, 183 (1981)
28. I. Uemasu, Y. Umezawa, *Anal. Chem.*, 54, 1198 (1982)
29. J. Havas, L. Kecskés, J. Erdélyi, *Hung. Sci. Instr.*, 51, 27 (1981)
30. E. Lindner, K. Tóth, E. Pungor, Y. Umezawa, *Anal. Chem.*, 56, 808 (1984)