

### A1.2.4 The relaxation effect

When the electrode of a dissolved oxygen meter is suddenly transferred from a liquid with a particular dissolved oxygen concentration (for example saturated water) to a different environment (for example water without dissolved oxygen), it can be observed that a relatively long period is required before the reading has adapted to the new situation and indicates the true dissolved oxygen concentration in the new environment. This time period is called the relaxation period of the electrode. The relatively low response rate of the dissolved oxygen electrode may be a problem for OUR measurements. It can be observed experimentally that the rate of change of the meter reading is proportional to the difference that exists between the indicated value and the true dissolved oxygen concentration in the water, so that:

$$(DO_m/dt)_r = k_r \cdot (DO_m - DO) \quad (A1.6)$$

Where:

$DO_m, DO$  = dissolved oxygen reading on the meter respectively the true oxygen concentration

$k_r$  = relaxation constant of the electrode

If the true dissolved oxygen concentration is constant Eq. (A1.6) can be solved as:

$$(DO_m - DO)/(DO_{m0} - DO) = \exp(-k_r \cdot t) \quad (A1.7)$$

Where  $DO_{m0}$  = initial dissolved oxygen reading on the meter

The value of the relaxation constant can now be calculated as follows:

- (1) Fill a beaker with water not containing dissolved oxygen ( $DO = 0 \text{ mg.l}^{-1}$ ) and another one with saturated water;
- (2) Place the electrode in one of the beakers and wait until a constant reading is obtained;
- (3) Transfer the electrode suddenly to the other beaker and record the dissolved oxygen reading on the meter as a function of time;
- (4) Determine the relaxation time  $t_r$ , which is reached when the difference between the reading and the true value is a factor 0.37 of initial difference (the value of 0.37 corresponds to  $e^{-1} = 1/2.72 = 0.37$ ). At this moment the value of  $k_r \cdot t_r = 1$  and  $k_r = 1/t_r$ .

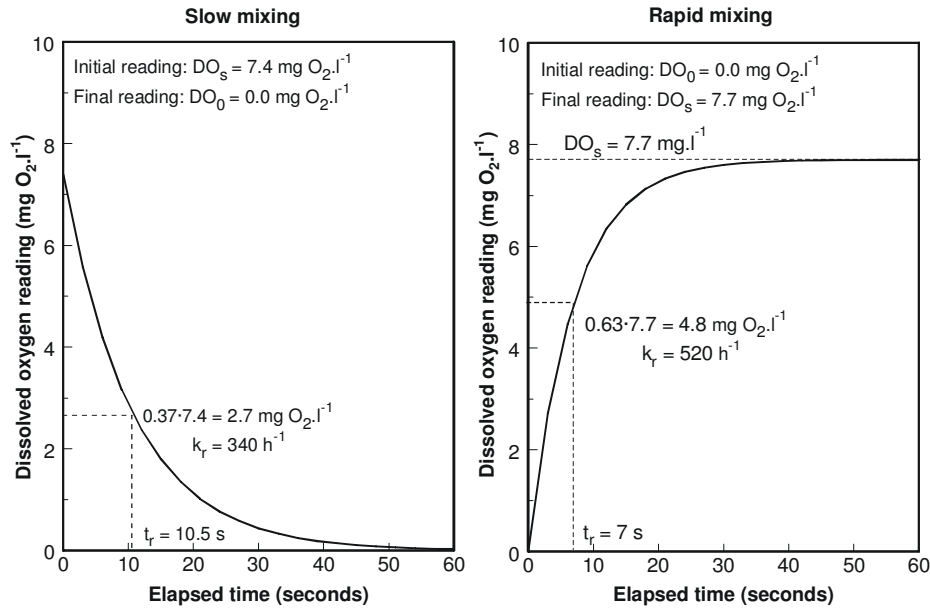


Figure A1.5 Experimental determination of the oxygen probe relaxation constant

In Fig. A1.5 two examples of the experimental determination of the  $k_r$  value are shown, for intense and for slow mixing of the beaker. Using the above procedure, values of  $k_r = 520 \text{ h}^{-1}$  and  $340 \text{ h}^{-1}$  were obtained for fast and slow mixing respectively.

It should be noted that apart from the mixing intensity, other factors also influence the value of the relaxation constant, such as the type of electrode, the condition of the membrane and the temperature. When the true dissolved oxygen concentration changes (as will be the case during OUR determinations), the differential equation can be written as:

$$(dDO_m/dt)_r = k_r \cdot (DO_m - DO) = k_r \cdot (DO_m - DO_0 - OUR_a \cdot t) \tag{A1.8}$$

Where  $DO_0$  = initial value of the actual dissolved oxygen concentration.

The solution to Eq. (A1.8) is:

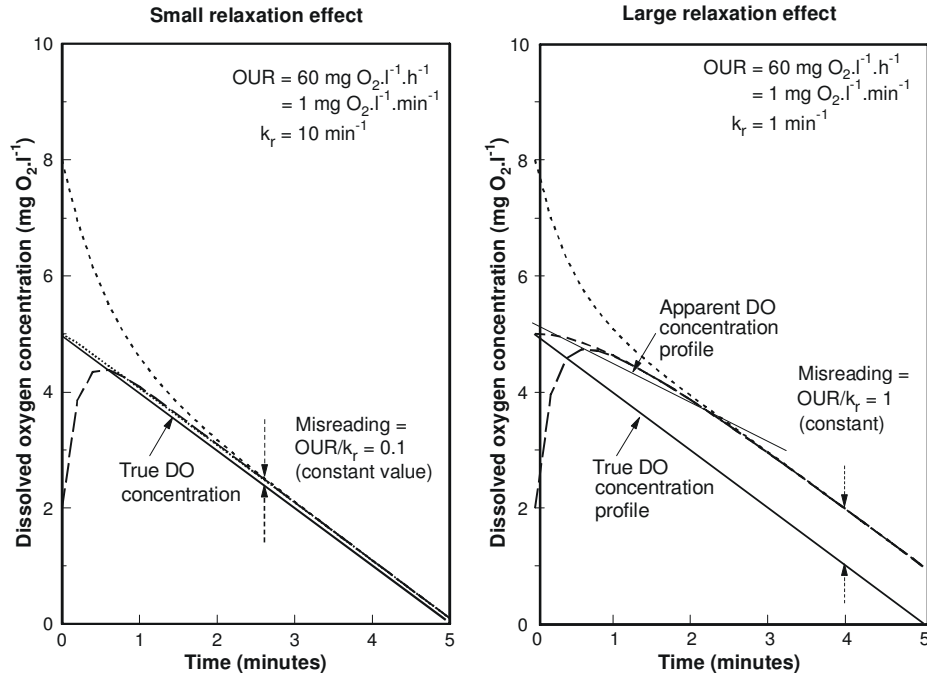
$$DO_m = DO + (OUR_t/k_r) \cdot (1 - \exp(-k_r \cdot t)) + (DO_{m0} - DO_0) \cdot \exp(-k_r \cdot t) \text{ or} \tag{A1.9}$$

$$DO_m - DO = (OUR_t/k_r) \cdot (1 - \exp(-k_r \cdot t)) + (DO_{m0} - DO_0) \cdot \exp(-k_r \cdot t) \tag{A1.10}$$

Equation (A1.10) shows that during the OUR test the measured dissolved oxygen concentration will never be equal to the true value of the dissolved oxygen concentration in the mixed liquor: there will always exist a difference between these two parameters. However, this does not invalidate the test. As the relaxation constant  $k_r$  generally has a large value (normally in the range of  $5 \text{ to } 10 \text{ min}^{-1}$  or  $0.08 \text{ to } 0.17 \text{ s}^{-1}$ ), the exponential factors in Eq. (A1.10) quickly become insignificant. For example: in order to decrease the relaxation effect by 99% (i.e.  $\exp(-k_r \cdot t) < 0.01$ ), it is required that  $t > 4.6/k_r = 20 \text{ to } 40$  seconds. Consequently after a period of 20 to 40 seconds 99 percent of the relaxation effect will have been eliminated. After this initial period a difference will remain between the reading on the meter and the true value, given as:

$$\Delta DO = OUR_t/k_r \quad (A1.11)$$

In Fig. A1.6 true and measured profiles of the dissolved oxygen concentration are shown as a function of time for two values of the relaxation constant. In both cases an OUR of  $1 \text{ mg O}_2 \cdot \text{l}^{-1} \cdot \text{min}^{-1}$  and a true initial dissolved oxygen concentration of  $5 \text{ mg O}_2 \cdot \text{l}^{-1}$  have been assumed. The profiles have been drawn for three initial readings: (1)  $DO_{m0} = 2 \text{ mg O}_2 \cdot \text{l}^{-1}$ ; (2)  $DO_{m0} = 5 \text{ mg O}_2 \cdot \text{l}^{-1}$  and (3)  $DO_{m0} = 8 \text{ mg O}_2 \cdot \text{l}^{-1}$ .



**Figure A1.6 Relaxation effect: true and measured dissolved oxygen profiles for different values of the relaxation constant  $k_r$**

It can be observed that the OUR determination may easily lead to a considerable error when the relaxation constant has a low value. Even when the initial dissolved oxygen meter reading is equal to the true dissolved oxygen concentration, there is a danger of misinterpretation of the apparent straight line that is obtained. In the case of Fig. A1.6 (right), the curve beginning at  $DO = 5 \text{ mg O}_2 \cdot \text{l}^{-1}$  could be interpreted as a straight line: the reduction of the dissolved oxygen concentration from 5 to  $3 \text{ mg O}_2 \cdot \text{l}^{-1}$  in a period of 3.2 minutes would then lead to an assumed OUR value of  $2/3.2 = 0.6 \text{ mg O}_2 \cdot \text{l}^{-1} \cdot \text{min}^{-1}$  instead of the true value of  $1 \text{ mg O}_2 \cdot \text{l}^{-1} \cdot \text{min}^{-1}$  (i.e. a decrease of  $5 \text{ mg O}_2 \cdot \text{l}^{-1}$  in 5 minutes).