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# Combined sulfite method for the measurement of the oxygen transfer coefficient $k_La$ in bioreactors

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## Abstract

The combined sulfite method is proposed for the measurement of oxygen transfer coefficients,  $k_La$ , in bioreactors. The method consists of a steady-state and a dynamic measurement which are carried out under the same experimental conditions and thus yield data for both methods during one experiment. The applied experimental conditions are shown to avoid chemical enhancement during the steady-state measurement. Moreover, no parallel sulfite oxidation occurs during the oxygen saturation phase of the dynamic measurement. Under the applied experimental conditions, no information about the sulfite oxidation kinetics is required and possible metal ion impurities in sulfite salts do not influence the measurement. The characterization of a laboratory-scale bioreactor aerated with pure oxygen yields  $k_La$  values during the steady-state and the dynamic measurements that are in good agreement with the dynamic pressure method, the correctness of which is generally accepted. When air is used for absorption, the steady-state measurement yields  $k_La$  values that correlate to the correct variant of the standard dynamic method. The dynamic measurement with air absorption yields a  $k_La$  value which considers the influence of the non-uniform bubble size distribution present in bubble-aerated bioreactors.

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## 1. Introduction

Comprehensive data about the oxygen transfer capacity of a bioreactor are essential for the exper-

imental planning of aerobic bioprocesses regardless of scale. The oxygen transfer capacity is characterized by the volumetric oxygen transfer coefficient,  $k_La$ . Steady-state  $k_La$  measurement methods reach equilibrium between oxygen transfer and oxygen consumption resulting in a constant dissolved oxygen concentration in the liquid phase. Dynamic methods rely on the time-resolved measurement of the dissolved oxygen concentration after the introduction of a sudden change in oxygen concentration in the liquid phase.

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**Nomenclature**

$a$	volumetric mass transfer area ( $\text{m}^{-1}$ )
$C$	constant
C.V.	coefficient of variation
$c_{\text{O}}$	oxygen concentration (% air-saturation)
$c_{\text{O}}^*$	oxygen saturation concentration (% air-saturation)
$d_{\text{b}}$	mean diameter of gas bubbles (m)
$d_{\text{I}}$	diameter of the impeller (m)
DO	dissolved oxygen concentration (% air-saturation)
DPM	dynamic pressure method
DSM	dynamic sulfite method
$k_{\text{L}}a$	oxygen transfer coefficient ( $\text{s}^{-1}$ )
$\overline{\text{MD}}$	mean deviation
$n$	impeller speed ( $\text{s}^{-1}$ )
$N_{\text{P}}$	power number
$P_0$	power input under ungassed conditions (W)
$P_{\text{g}}$	power input under gassed conditions (W)
SDM	standard dynamic method
SSM	steady-state sulfite method
$t$	time (s)
$t_{\text{E}}$	response time of electrode (90%) (s)
$u_{\text{g}}$	superficial gas velocity ( $\text{m s}^{-1}$ )
$V$	volume (L)
$\dot{V}_{\text{g}}$	aeration rate ( $\text{L min}^{-1}$ )
<b>Greek letters</b>	
$\alpha$	constant
$\beta$	constant
$\varepsilon_{\text{g}}$	gas hold-up
$\rho$	density ( $\text{kg m}^{-3}$ )

Consequently, mixing of gas and liquid phase and the electrode response characteristics need to be considered.

The dynamic pressure method (DPM) yields physically correct  $k_{\text{L}}a$  values because the oxygen partial pressure distribution in the gas phase does not influence the results (Linek et al., 1989). Therefore, the same  $k_{\text{L}}a$  value is measured whether air or pure oxygen is used for aeration. Nevertheless, the oxygen electrode must be verified to provide a stable signal during pressure

change and the reaction vessel to be characterized needs to be accordingly equipped to enable suitable pressure changes (Linek et al., 1994).

The stationary sulfite feeding method (Imai et al., 1987) yields  $k_{\text{L}}a$  values corresponding to the dynamic pressure method if pure oxygen is used for aeration (Linek et al., 1990). Using air for aeration leads to increasing accumulation of small bubbles with increasing power input (Linek et al., 1989). Due to their high surface area, small bubbles quickly reach oxygen diffusion equilibrium and therefore mainly contain nitrogen during absorption of air. Thus, they act as oxygen sinks and decrease the overall oxygen transfer from the gas into the liquid phase. Since the high residence time and the lower oxygen partial pressure in small bubbles are usually not considered in the mass transfer models, the  $k_{\text{L}}a$  value is underestimated (Linek et al., 1987).

The steady-state sulfite method (SSM) has been shown to be able to reproduce the  $k_{\text{L}}a$  values of the dynamic pressure method if sulfite oxidation takes place in the non-accelerated reaction regime. Due to the complex reaction kinetics of the sulfite oxidation, there is a lot of controversy about the proper adjustment of the catalyst concentration (Linek and Vacek, 1981; Maier et al., 2001).

Another method yielding  $k_{\text{L}}a$  values equivalent to the dynamic pressure method is the dynamic sulfite method (DSM) with oxygen aeration (Havelka et al., 1998). After stoichiometric consumption of added sulfite at a catalyst concentration of  $10^{-3} \text{ M Co}^{2+}$ , the saturation of the liquid phase is monitored and the  $k_{\text{L}}a$  value is calculated. However, the published study requires the verification of sulfite consumption by an online absorbance measurement in a reactor bypass preventing the straightforward use of this method.

In this article, we report the characterization of a new approach for simple and reliable  $k_{\text{L}}a$  measurement, referred to as the “combined sulfite method” (CSM). This method consists of a combination of the steady-state and the dynamic sulfite method at the same experimental conditions. The simple variant of the steady-state sulfite method does not require any assumptions about the mixing of the gas phase nor the verification of the appropriate catalyst concentration at the respective reaction conditions. The resulting  $k_{\text{L}}a$  values are not influenced by the distribution of oxygen partial pressure in bubbles of different size and thus physically correct. The simultaneously per-

formed dynamic sulfite method yields  $k_La$  values under consideration of the small-bubble effect which occurs whenever nitrogen is present in the gas mixture used for aeration.

## 2. Materials and methods

### 2.1. Bioreactor

A lab-scale stirred-tank bioreactor with a nominal volume of 7.5 L was used (Labfors, Infors, Bottmingen, Switzerland). The clearance of the lowermost of three Rushton turbines is 25 mm. The spacing of the impellers was 60 mm.

### 2.2. Power input

The power dissipated in the medium was measured by the electric power draw of the electric drive of the bioreactor. This value was calculated as the difference of power drawn under experimental conditions and the power drawn without liquid. Experiments were carried out at 37 °C with aeration rates of 2.53 and 1.27 L min<sup>-1</sup> corresponding to 0.84 and 0.42 vvm, respectively.

### 2.3. Gas hold-up

Gas hold-up was measured by comparing the liquid height under experimental conditions with the liquid level under ungassed conditions. This method is known to give reproducible and accurate results despite its simplicity (Gogate et al., 2000). Gas hold-up,  $\varepsilon_g$ , was calculated by the following equation:

$$\varepsilon_g = \frac{V_{\text{gassed}} - V_{\text{ungassed}}}{V_{\text{ungassed}}} \quad (1)$$

The volumetric mass transfer area  $a$  can be correlated to the gas hold-up by Eq. (4) where  $d_b$  is the Sauter mean bubble diameter:

$$a = \frac{6\varepsilon_g}{(1 - \varepsilon_g)d_b} \quad (2)$$

### 2.4. Measurement of dissolved oxygen concentration (DO)

Dissolved oxygen concentration was measured with a fiberoptic probe (MircoXTX, Presens, Regensburg,

Germany) in the bioreactor. The probe tip was located 20 mm below the liquid surface at a distance of 5 mm to one of the three baffles. The optode was characterized by a response time  $t_E$  (90%) of 2–3 s which is lower than the typical response time of polarographic oxygen probes. Another advantage of the used optode is the small tip diameter of <200 µm which less influences the flow conditions in the bioreactor than a standard polarographic probe. Calibration was performed with a 100 and 0% air or oxygen saturated 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution, respectively. A 0% oxygen saturation was achieved by sparging of pure nitrogen.

### 2.5. $k_La$ measurement

All measurements were performed in 3 L of a 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution (VWR International GmbH, Darmstadt, Germany) to simulate non-coalescing conditions. Gas was supplied at aeration rates of 2.53 and 1.27 L min<sup>-1</sup> corresponding to superficial gas velocities of 0.1 and 0.2 cm s<sup>-1</sup>, respectively. The temperature was maintained at 37 °C. The impeller rotational speed was varied between 400 and 1500 min<sup>-1</sup> (6.7 and 23.3 s<sup>-1</sup>) with intervals of 100 min<sup>-1</sup>. The combined sulfite method with oxygen aeration was carried out with impeller speeds of only up to 800 min<sup>-1</sup> because of the high influence of the electrode response time at  $k_La$  values > 0.5 s<sup>-1</sup>.

For the dynamic sulfite method, a solution of 1.66 M Na<sub>2</sub>SO<sub>3</sub> (VWR International GmbH, Darmstadt, Germany) was prepared with deionized water after stripping the dissolved oxygen with pure nitrogen. Each measurement started with the saturation of the 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution, containing 10<sup>-3</sup> M CoSO<sub>4</sub> (VWR International GmbH, Darmstadt, Germany) as a catalyst, with air or pure oxygen, respectively. After the addition of an amount of sulfite solution sufficient to consume all dissolved oxygen, the dissolved oxygen tension dropped to zero. After the depletion of sulfite, the saturation phase was monitored. The injection of the sulfite was carried out through the sampling tube of the bioreactor, the end of which was located next to the lowermost impeller.

The standard dynamic method (SDM, technique 'A'), also referred to as nitrogen desorption method or gassing-out method, was conducted under the same conditions as above except that nitrogen was sparged into the vessel to desorb the dissolved oxygen.

The following equation can be fitted to the saturation curves by assuming a perfectly mixed gas and liquid phase in the reactor and accounting for the optode response time  $t_E$  by a first-order model (Fuchs and Ryu, 1971).

$$\frac{c_O^* - c_t}{c_O^* - c_O} = \left( \frac{1}{1 - t_E k_L a} \right) (e^{-(t - \Delta t) k_L a} - t_E k_L a^{\frac{(t - \Delta t)}{t_E}}) \quad (3)$$

The oxygen saturation concentration  $c_O^*$  refers to the inlet gas. The response time  $t_E$  is the time needed to monitor 90% of a step change in dissolved oxygen concentration. The experimental time  $t$  is introduced as a floating parameter by allowing a time lag  $\Delta t$  between the sparging of nitrogen and air (Linek et al., 1987) or the addition of sulfite and its stoichiometric consumption. A Levenberg–Marquardt algorithm (LabView 7.0, National Instruments, Munich, Germany) was applied for the non-linear fit of the experimental data.

Details about the steady-state sulfite method are reported elsewhere (Linek and Vacek, 1981; Maier et al., 2001). In this work, a catalyst concentration of  $10^{-3}$  M  $\text{CoSO}_4$  was used. For each set of reaction conditions, three different sulfite volumes were added subsequently into the saturated medium followed by 3 mL of deionized water to ensure the complete flushing of the sampling tube. The sulfite volumes yielded sulfite concentrations of 0.8–5.4 mM. The time until the start of the saturation phase was monitored. Assuming constant reaction rate and a negligible oxygen concentration during sulfite oxidation under the applied conditions, the following equation can be used to calculate the  $k_L a$  value while taking the stoichiometry of the sulfite oxidation into account:

$$k_L a = \frac{0.5 c_{\text{sulfite}} - c_O^*}{t c_O^*} \quad (4)$$

The oxygen saturation concentration  $c_O^*$  was experimentally determined in a solution of 0.5 M  $\text{Na}_2\text{SO}_4$  containing  $10^{-3}$  M  $\text{CoSO}_4$  as a catalyst at  $37^\circ\text{C}$ . To ensure negligible oxygen transfer but sufficient mixing, aeration was switched off and the impeller speed was set to  $300 \text{ min}^{-1}$ . Sulfite amounts that consumed less than 100% of the dissolved oxygen were added and the dissolved oxygen concentration after sulfite depletion was monitored. From a linear correlation between the sulfite concentration and the dissolved oxygen con-

centration after the reaction, the required amount of sulfite for total oxygen consumption was calculated. The determined oxygen saturation concentration was 0.146 mM.

### 3. Results and discussion

#### 3.1. Power input

Power input measurements yielded a power number,  $N_p$ , of 5.0. The generally applied equation to correlate gassed and ungassed power input (Michel and Miller, 1962) yielded the constants  $\alpha = 1.224$  and  $\beta = 0.432$  with a mean deviation of the experimental values of 8% (results not shown). The power number complies with literature results (Linek et al., 1996).

#### 3.2. Gas hold-up

The gas hold-up could be correlated to the power input into the liquid with a mean deviation of 7% by the following equation:

$$\varepsilon_g = 0.0366 \left( \frac{P_g}{V} \right)^{0.53} \quad (5)$$

The mean gas hold-up in a stirred tank with four Rushton turbines can be described by the same type of equation (Linek et al., 1996). The reported equation characterized by a constant of 0.446 and an exponent of 0.50 reveals a gas hold-up 13% higher than in the bioreactor used in this study. This higher gas hold-up found by Linek can be attributed to the higher number of impellers. The similarity of correlation (5) compared to literature indicates that the measurement of power input via the electric power draw of the drive yields reliable results.

#### 3.3. Characterization of the combined sulfite method

The presented method is a combination of a simple variant of the steady-state sulfite method and the dynamic sulfite method. The reaction conditions for the steady-state method need to ensure the avoidance of chemical enhancement, whereas the reaction conditions for the dynamic sulfite method need to ensure the stoichiometric consumption of all added sulfite

before the start of the saturation phase. Therefore, the combined sulfite method is carried out at a catalyst concentration of  $10^{-3}$  M and the addition of sulfite to yield concentrations in the range of mmoles.

### 3.3.1. Dynamic sulfite method

To circumvent the online verification of residual sulfite concentration in the reaction medium as proposed by Havelka et al. (1998), the influence of the cobalt catalyst concentration on the  $k_La$  value was verified experimentally in a lab-scale stirred-tank reactor (Fig. 1). The results show that catalyst concentrations  $<5 \times 10^{-4}$  M lead to lower  $k_La$  values than catalyst concentrations  $>5 \times 10^{-4}$  M.

The time profiles of the saturation phases at various catalyst concentrations show an increasing reaction rate with increasing catalyst concentration (Fig. 2). Due to the increasing slope of the saturation phases with increasing catalyst concentration, non-linear regression (Eq. (3)) leads to higher  $k_La$  values. The SDM under the same experimental conditions revealed constant  $k_La$  values at varying catalyst concentrations. This indicates that during the dynamic sulfite method, the sulfite oxidation at catalyst concentrations  $<5 \times 10^{-4}$  M is not complete at the start of the saturation of the liquid phase.

The stoichiometric consumption of added sulfite can be verified by exploiting the buffer potential of sulfite. Both the addition and the stoichiometric consumption of sulfite in an unbuffered solution can be monitored by a change of the pH. The addition of sulfite leads to an increase of the pH. After the consumption of sulfite, the pH drops back to its initial value. The pH profiles presented in Fig. 2 indicate a slow pH drop at catalyst concentrations below  $3.16 \times 10^{-5}$  M  $\text{Co}^{2+}$  during

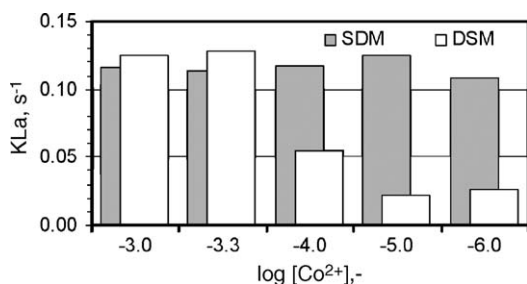


Fig. 1.  $k_La$  as function of cobalt catalyst concentration ( $\text{Co}^{2+}$ ). SDM: standard dynamic method; DSM: dynamic sulfite method.

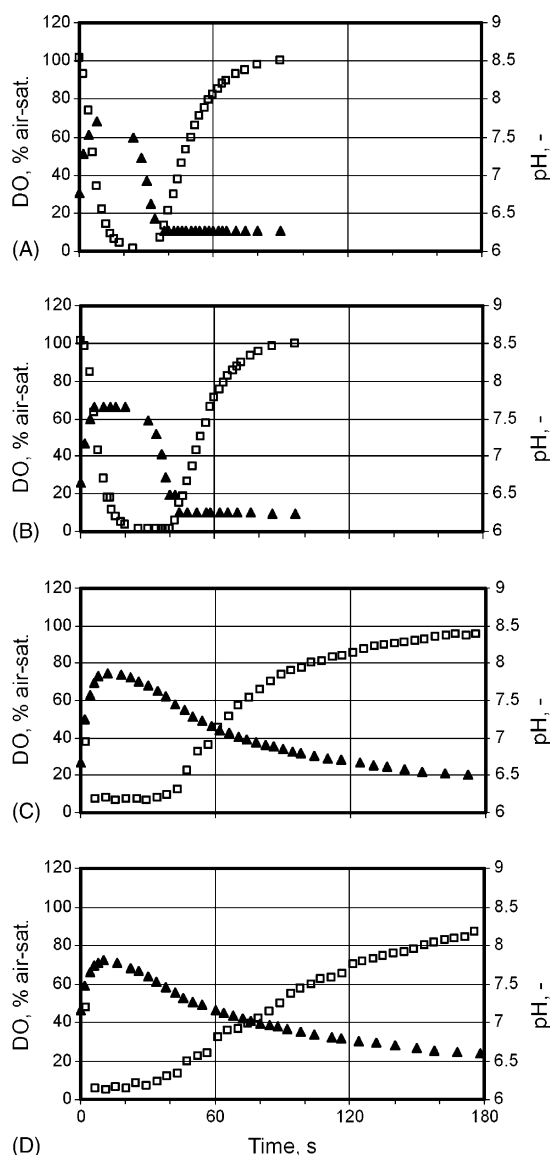


Fig. 2. Time-course of dissolved oxygen concentration (DO) and pH after sulfite addition at  $t=0$ : (A)  $10^{-3}$  M  $\text{Co}^{2+}$ ; (B)  $5 \times 10^{-4}$  M  $\text{Co}^{2+}$ ; (C)  $3.16 \times 10^{-5}$  M  $\text{Co}^{2+}$ ; (D)  $10^{-5}$  M  $\text{Co}^{2+}$ ; (□) dissolved oxygen concentration DO; (▲) pH.

saturation of the reaction medium. The sulfite oxidation occurring simultaneously to the oxygen saturation of the medium results in a lower apparent  $k_La$  value. Above a catalyst concentration of  $5 \times 10^{-4}$  M, the pH drops back to its initial value before the start of the saturation phase because the added amount of sulfite was stoichiometrically consumed.

For all following measurements, the catalyst concentration was therefore set to  $10^{-3}$  M to avoid simultaneous sulfite oxidation during the saturation of the liquid.

### 3.3.2. Steady-state sulfite method

The most common error connected to the established steady-state sulfite method is an improper adjustment of the catalyst concentration. Since the established method is conducted at high sulfite concentrations of 0.5 or 1.0 M, the catalyst concentration must be adjusted below a threshold value in order to prevent chemical enhancement. The here proposed variant of the sulfite method applies a much higher catalyst concentration of  $10^{-3}$  M. In that case, the sulfite concentration is the critical parameter to ensure the prevention of chemical enhancement. Fig. 3 illustrates the relation between the added sulfite concentration and the determined reaction time for an impeller speed of  $1000 \text{ min}^{-1}$  at an aeration rate of  $2.53 \text{ L min}^{-1}$ . The reaction time was shown to be a linear function of the sulfite concentration within the studied sulfite concentration range of 1.9–10.5 mM. The linearity indicates that the sulfite oxidation is not chemically enhanced in that case.

The limiting parameter for the reaction velocity of sulfite oxidation is most likely the sulfite concentration since the dissolved oxygen concentration during a measurement was in the range of 1.7–4.7%. For a catalyst concentration of  $5 \times 10^{-6}$  M, Imai et al. (1987) determined 5.5–32 mM as threshold sulfite concentration below which the reaction was not chemically enhanced. Although a lower threshold value of sulfite concentration would be expected at a higher catalyst concentration of  $10^{-3}$  M  $\text{CoSO}_4$ , Imai et al. observed

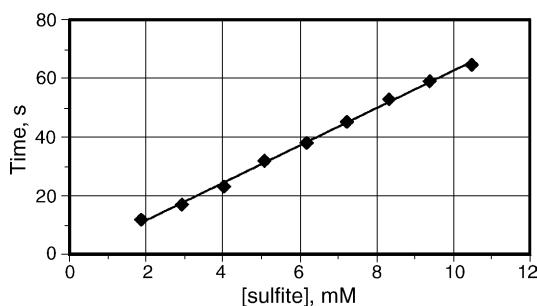


Fig. 3. Reaction time  $t$  for sulfite oxidation as a function of the concentration of added sulfite.

constant  $k_L a$  values even at catalyst concentrations of up to  $2 \times 10^{-3}$  M.

The established steady-state method may be hampered by the presence of metal ion impurities in sulfite salts whose concentrations may range in the same order as the required catalyst concentration which is stated between  $10^{-5}$  and  $10^{-7}$  M  $\text{Co}^{2+}$  in literature. The here proposed variant of the steady-state sulfite method with a catalyst concentration of  $10^{-3}$  M  $\text{Co}^{2+}$  avoids chemical enhancement by the limiting sulfite concentration. Moreover, possible impurities by metal ions would have no influence since their summarized concentrations are at least 100 times lower than the catalyst concentration used in this work.

### 3.4. Mass transfer

#### 3.4.1. CSM with oxygen aeration

The combined sulfite method was first carried out with oxygen aeration to characterize the  $k_L a$  value as a function of impeller speed at a superficial gas velocity of  $0.2 \text{ cm s}^{-1}$ . Fig. 4 shows the estimated  $k_L a$  value of the steady-state and the dynamic part of the experiments. The  $k_L a$  value increases continuously with increasing power input. A correlation of the common

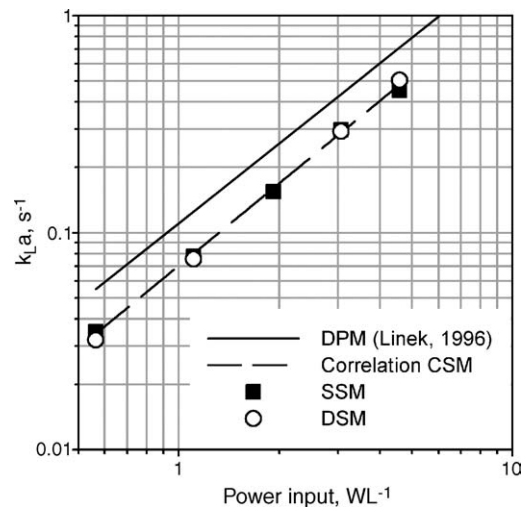


Fig. 4. Volumetric oxygen transfer coefficient  $k_L a$  as function of volumetric power input with pure oxygen aeration: (—) correlation of dynamic pressure method (Linek et al., 1996); (---) correlation of combined sulfite method; (■) steady-state sulfite method (SSM); (○) dynamic sulfite method (DSM).



Table 1

Constants of Eq. (6) for the correlation of  $k_L a$  values based on the steady-state results, the dynamic results and all results of the combined sulfite method with oxygen aeration

	Method	$C \times 10^3$	$\alpha$	$\beta$	$\overline{MD}$ (%)
This work	SSM	0.092	1.316	0.4	5
This work	DSM	0.162	1.240	0.4	6
This work	SSM and DSM	0.135	1.278	0.4	11
Linek et al., 1996	DPM	0.276	1.228	0.4	–24

$\overline{MD}$ : Mean deviation of experimental results from correlation.

type (Cooper et al., 1944):

$$k_L a = C \left( \frac{P_g}{V} \right)^\alpha u_g^\beta \quad (6)$$

where  $[k_L a] = s^{-1}$ ,  $[P_g/V] = W m^{-3}$  and  $[u_g] = m s^{-1}$ , can be established with the constants  $C$ ,  $\alpha$  and  $\beta$  given in Table 1. The exponent  $\beta$  was set to 0.4 to ensure a better comparability to correlations reported in literature (Linek et al., 1987, 1989, 1994).

The mean deviation between the experimental values and the correlations are 5% for the  $k_L a$  values identified by the SSM, 6% with the DSM and 11% if the data of both measuring techniques were correlated at the same time (CSM).

The  $k_L a$  values measured with the combined sulfite method follow the same trend as the  $k_L a$  values of the dynamic pressure method measured in a stirred-tank

reactor with four Rushton turbines (Linek et al., 1996) but are 24% lower on average (Fig. 4). A ratio of the volumetric mass transfer area can be calculated as a function of varying gas hold-ups with Eq. (2). The 13% lower gas hold-up in the bioreactor used in this work can thus be calculated to account for an approximately 17% lower volumetric mass transfer area  $a$  and thus  $k_L a$  value. The remaining error of 7% is in the range of experimental errors of  $k_L a$  measurement methods.

### 3.4.2. CSM with air aeration

The results of the combined sulfite method with air aeration for two different superficial gas velocities of 0.1 and 0.2  $cm s^{-1}$  are presented in Fig. 5. The  $k_L a$  values estimated by the steady-state method with air aeration increases linearly with increasing power input similarly to aeration with pure oxygen. However, the  $k_L a$  values obtained by the dynamic method

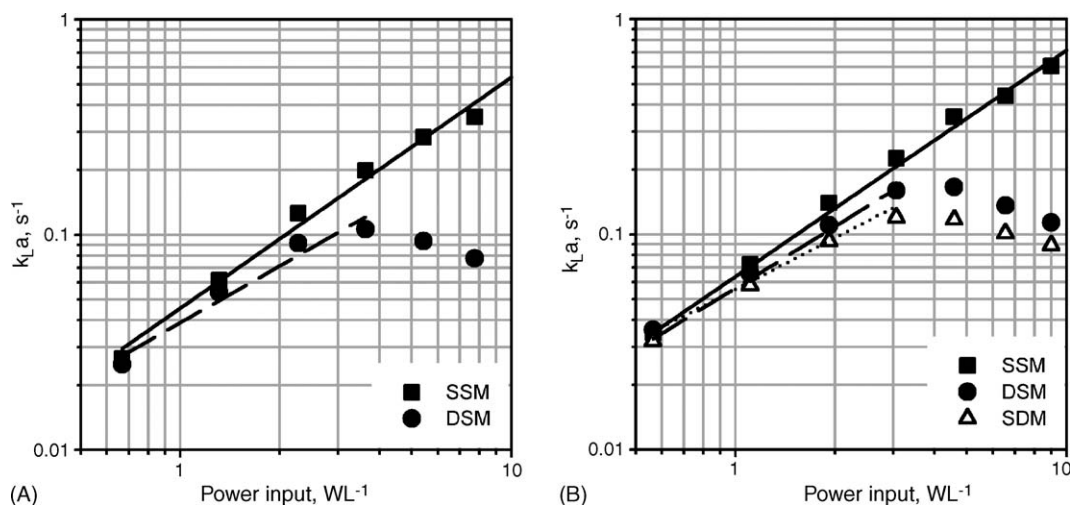


Fig. 5. Volumetric oxygen transfer coefficient  $k_L a$  as function of volumetric power input with air aeration for two superficial gas velocities: (A)  $u_g = 0.1 cm s^{-1}$ ; (B)  $u_g = 0.2 cm s^{-1}$ ; (■) data of steady-state sulfite method (SSM); (●) data of dynamic sulfite method; (△) data of standard dynamic method.

reaches maximum values for a power input of 3.5 and 4.5  $\text{W L}^{-1}$  for the used aeration rates, respectively. A further increase of the power input results in a decrease of the  $k_L a$  value. The dynamic method generally underestimates the values determined by the steady-state method at a power input  $>1 \text{ W L}^{-1}$ . At a power input of 9  $\text{W L}^{-1}$ , the degree of this underestimation is  $>400\%$  for both aeration rates. The maximum  $k_L a$  value at the higher aeration rate is shifted to a higher power input value compared to the lower aeration rate.

These results clearly indicate the presence of small bubbles in the liquid which influences the  $k_L a$  measurement with the dynamic method. During the oxygen saturation of the liquid phase, newly dispersed gas bubbles are forced to coalesce with the already present small bubbles which mainly contain nitrogen. As a result, the overall oxygen concentration in the dispersed gas phase is lower than in the inlet gas. Using the perfectly mixed model for the gas and liquid phase, an incorrect driving force is used to calculate the  $k_L a$  value which is, therefore, underestimated. Despite the presence of small bubbles, this phenomenon does not occur with the steady-state method. Due to the high catalyst concentration of  $10^{-3} \text{ M}$ , the oxygen in newly dispersed bubbles is rapidly oxidised by sulfite before any significant gas mixing can occur. Theoretically, higher power input could lead to a small-bubble effect if mixing times are low enough to reveal an influence of sulfite oxidation. In bioreactors like the one used in this study, the bubble size distribution at a relevant power input has thus no influence on the reaction time of the sulfite oxidation.

These experimental data were also correlated with Eq. (6) (Table 2). The mean deviation between experimental data up to a power input of 10  $\text{W L}^{-1}$  and the correlations are 13% (SSM), 6% (DSM) and 13% based on the combined sulfite method. Compared to literature, the  $k_L a$  values were 12% lower, which can again

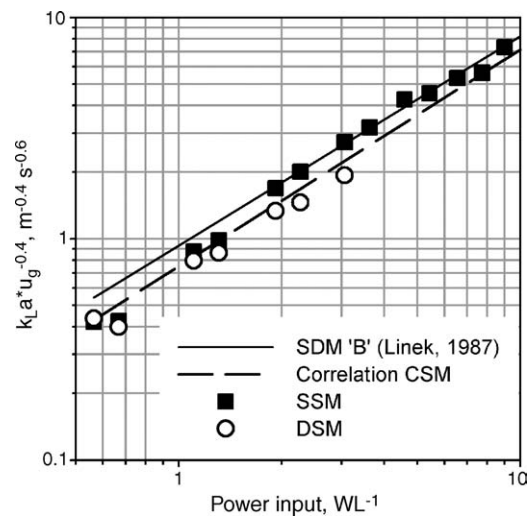


Fig. 6. Volumetric oxygen transfer coefficient  $k_L a$  corrected for superficial gas velocity as function of volumetric power input with air aeration: (—) correlation of correct variant of standard dynamic method (SDM, technique 'B'; Linek et al., 1987); (---) correlation of combined sulfite method; (■) data of both aeration rates for steady-state sulfite method (SSM); (○) data of both aeration rates for dynamic sulfite method (DSM).

be attributed to the lower gas hold-up of the bioreactor used in this work compared to the bioreactor used in the cited work (Fig. 6).

The physically correct  $k_L a$  value is obtained in the absence of mixing effects within the dispersed gas phase. From a biochemical engineering point of view, however, the conditions during a cultivation are of major interest. In this case, the real  $k_L a$  value is not equal to the physically defined value, but is indeed influenced by mixing effects with the remaining gas bubbles in the liquid phase. The better the dispersed gas phase represents the composition in a bioreactor during a cultivation, the more accurately the measured  $k_L a$  value will represent the real  $k_L a$  value during a

Table 2

Constants of Eq. (6) for the correlation of  $k_L a$  values based on the steady-state results, the dynamic results and all results of the combined sulfite method with air aeration

	Method	$C \times 10^3$	$\alpha$	$\beta$	$\overline{\text{MD}} (\%)$
This work	SSM	1.209	0.944	0.4	13
This work	DSM	0.957	0.951	0.4	6
This work	SSM and DSM	0.867	0.979	0.4	13
Linek et al., 1987	SDM technique 'B'	1.35	0.946	0.4	−12

$\overline{\text{MD}}$ : Mean deviation of experimental results from correlation.



cultivation. The combined sulfite method allows the determination of both, the correct  $k_L a$  value according to the precise physical definition and the real  $k_L a$  value in the presence of nitrogen in the gas mixture used for aeration.

#### 4. Conclusions

The combined sulfite method consists of a variant of the steady-state sulfite method and the dynamic sulfite method for the estimation of  $k_L a$  values. Both methods are conducted under the same experimental conditions in 0.5 M NaSO<sub>4</sub> as a model liquid for non-coalescing conditions. Both data sets are obtained within one experiment. During the steady-state part of the method, the combination of a high catalyst concentration of  $10^{-3}$  M Co<sup>2+</sup> and low sulfite concentration in the range of mmoles prevents chemical enhancement and negative effects of metal impurities in sulfite salts. The determination of sulfite oxidation kinetics is not necessary. The data are not influenced by the non-uniform bubble size distribution present in all bubble-aerated bioreactors and thus do not yield erroneous  $k_L a$  values as function of power input which are indicated by a  $k_L a$  maximum and decreasing  $k_L a$  values with increasing power input. Oxygen aeration leads to  $k_L a$  values that were satisfactorily correlated to the dynamic pressure method which has been shown to yield physically correct  $k_L a$  values (Linek et al., 1996). The  $k_L a$  values measured with air aeration were satisfactorily correlated to the correct variant of the standard dynamic method (Linek et al., 1987). The dynamic sulfite method yields real  $k_L a$  values which account for gas phase mixing effects and thus represent the cultivation conditions in a bioreactor in a more realistic way. Major practical advantages of the combined sulfite method are the relatively short experimental time in the range of a few minutes per measurement and the simple experimental approach. As a result, the combined sulfite method is an ideal tool to characterize bioreactors with regards to their oxygen transfer capacity

under ideal, i.e. without the influence of small bubbles and real-case conditions, i.e. with the influence of small bubbles.

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## Corrigendum

Corrigendum to “Combined sulfite method for the measurement  
of the oxygen transfer coefficient  $k_L a$  in bioreactors”  
[J. Biotechnol. 120 (4) (2005) 430–438]

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During the publication of the above mentioned article, Eq. (3) was printed incorrectly. The corrected Eq. (3) is hereby printed below.

$$\frac{c_0^* - c_0(t)}{c_0^* - c_0(0)} = \left( \frac{1}{1 - t_E k_L a} \right) (e^{-(t-\Delta t)k_L a} - t_E k_L a e^{-(t-\Delta t)/t_E}) \quad (3)$$

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