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(Article begins on next page)

# Assessment of the uncertainty budget for the amperometric measurement of dissolved oxygen

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Received 26 March 2007; received in revised form 6 June 2007; accepted 12 June 2007

Available online 20 June 2007

## Abstract

This work aimed at identifying the main sources of uncertainty for the measurement of dissolved oxygen concentration in aqueous solutions. The experimental apparatus consists of an amperometric cell based on the Clark-type sensor. The corresponding uncertainty budget was assessed, this being a fundamental step for the validation of a measurement method. The principle of the measurement, as well as the procedure for the set-up and the characterisation of the cell, are described. The measurement equation was defined as a combination of Faraday's and Fick's laws, and a method was worked out for the empirical determination of the diffusivity parameter. In this connection, the solutions of oxygen were standardised by way of the Winkler's titration, as suggested by the ISO Guide 5813 and 5814. With this approach we aimed at contributing to the development of a potential primary method of measurement. A discussion of all the contributions to the overall uncertainty is reported, allowing operators to locate the largest ones and plan specific improvements.

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**Keywords:** Clark-type sensors; Amperometric measurement; Dissolved oxygen measurement uncertainty; Validation

## 1. Introduction

Oxygen is necessary to nearly all forms of life and a large number of chemical and biological reactions, including processes in water, are directly or indirectly influenced by the amount of oxygen. Thus, the evaluation of the amount of dissolved oxygen (henceforth: DO) in aqueous solutions is an essential monitoring task and its scope ranges from measurements in natural and industrial waters to medical applications, like in the case of oxygen content in blood and tissues [1–6]. Moreover, given the increasing prevalence of environmental legislation, many industries and agencies are now required to monitor the effect they have on the surrounding environment [7]. These monitoring schemes must be accurate to ensure that a correct picture of the habitat health is given, and reliable to reassure that measurements are valid.

The routine measurement of DO concentration is nowadays mostly performed *via* optical [8–10] or electrochemical sensors [3–6]. Both sensor types show similar accuracy [11] and exhibit remarkable advantages if compared to time-consuming redox chemical analysis, such as the Winkler's titration [12–14]. Nevertheless, only the Winkler's absolute method of analysis ensures quantification of DO independent of any calibration procedure involving the preparation of standard solutions of the measurand.

In spite of the extensive literature on DO concentration measurement, neither primary methods nor reference solutions have been developed to date. Calibration can be regarded as the most difficult step of DO analysis and, as a matter of fact, commercial standard solutions of DO are not available. This makes calibration procedures hardly adequate and often unreliable, while the validation of a measurement system requires reference solutions characterised by independent methods.

Many methods have been tested to obtain standard oxygen-containing solutions ([2] and refs. therein), but their conservation is a challenging task. Oxygen standard solutions, in fact, show severe limitations of time life because of the dynamic equilibrium established with the external environment. As a consequence, preparation, standardization and use must be almost

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simultaneous steps. Some of the proposed methods use stream of well-defined gas mixtures (clean air in the simplest case) flowing through a thermo stated water reservoir. However, especially at the oxygen trace level, these methods are expensive and erroneous because they need standardized gases and atmospheric oxygen interferes [2]. A more convenient and faster calibration uses water vapour saturated air rather than air-saturated water. However, different convection and diffusion conditions between gaseous and aqueous phases require empirical correction terms, while erroneous calibration could be achieved if the sensor was not carefully dried after the removal from the analyte. Besides, the evaporation heat of the wet sensor may cause temperature changes [15]. Attempts were also made to produce standard oxygen solutions by way of electrolytic generation [16–18]. This method is usually limited to low oxygen concentrations [16] and may need empirical correction if the current efficiency is below 100% [17]. The major advantages of such a calibration procedure are, first, that the oxygen concentration could be continuously varied adjusting the electrolysis current and the flow rate of the solution, and second, that the oxygen concentration is independent of gaseous equilibrium and temperature of the solution [18]. Finally, the catalysed decomposition of hydrogen peroxide was also suggested for the calibration of oxygen detectors [19].

Guidelines for the calibration of instruments for routine analysis are given in ISO 5814 Guide [20]. Despite the apparent simplicity of the measurement using commercial sensors, an interlaboratory *in situ* comparison demonstrated that it is not at all as robust as often considered: out of 63 measurement results obtained by the participants, 39% were unacceptable according to the performance evaluation criteria, because of deficiency in the instruments and methodology, or due to underestimation of uncertainty contributions [21].

Although optical devices are more suitable for measurement in difficult environmental matrixes, electrochemical sensors are preferable for metrological purposes, which are independent of the applicative requirements. In fact, intrinsic accuracy and stability of the electric signals even at very low current level, along with the well-established theoretical models, make electrochemical techniques pretty attractive for basic science in chemical metrology, which is asked by the scientific community to provide means for reference measurement methods and mutually acceptable results.

The measurement system we chose is the amperometric Clark-type cell that is the most commonly used electrochemical device for DO. It usually consists of a noble metal cathode and a reference silver/silver chloride anode submerged in an electrolyte, which are separated from the sample by a gas-permeable polymeric membrane [22]. The membrane protects the cathode to a large degree from fouling or poisoning by solution borne species and preserves its catalytic activity [2]. Unfortunately, for routine measurements on complex samples this electrochemical apparatus suffers contamination of the membrane, causing a change of sensitivity with time. This effect results in additional difficulties to provide reliable results, *i.e.* accurate to a known level of uncertainty, since sensors need frequent calibrations [2,3,23,24]. Such an obstacle was negligible in this work, as

the experimental design was thought for metrological purposes exploiting synthetic solutions.

Aim of this work is to identify, through the construction of the uncertainty budget, the main contributions that affect the accuracy and precision of the whole measurement procedure. The principles of the measurement, as well as the set-up and the characterisation of the cell, are described. Oxygen solutions were prepared by bubbling predetermined N<sub>2</sub>/O<sub>2</sub> mixtures in 0.2 mol L<sup>-1</sup> KCl aqueous solution. Quantification of the oxygen concentration actually obtained was achieved by way of the Winkler's method [12–14], as suggested by the ISO 5813 Guide [25]. Then, we were able to quantify the diffusivity parameter enabling the employment of the measurement equation defined as a combination of Faraday's and Fick's laws. The overall uncertainty budget was built around the measurement of DO concentration of an unknown sample.

The approach chosen would aim at developing a potential primary method [26,27] and this work can be regarded as a first attempt at assessing a complete uncertainty budget for DO concentration measurement. In this connection, the goal is focused on the measurement steps, which are considered in detail leading to the definition and quantification of each contribution to the measurement uncertainty.

## 2. Measurement principles and measurement equation

The Clark-type cell is based on amperometric measurement [22]. Oxygen molecules diffuse from the bulk of the solution through the cell membrane and the electrolyte solution to be reduced at the surface of the cathode. The electrochemical reduction gives rise to a current whose magnitude is proportional to the flow of oxygen arriving at the electrode, which is in turn proportional to the concentration of DO in the bulk solution. The semi-reaction occurring at the working electrode is given by:



The relationship between the overall charge  $Q$  and DO level is derived *via* Faraday's law (coulometric technique):

$$Q = \int_0^t i \, dt = mnF \quad (2)$$

where  $i$  is the current,  $m$  the number of moles of oxygen,  $n$  the number of exchanged electrons, and  $F$  is the Faraday's constant. According to the amperometric technique, the current is obtained by the derivative of Eq. (2):

$$i = nF \frac{dm}{dt} \quad (2a)$$

In steady state, the mass flow rate is determined by diffusion [2], and Fick's first law of diffusion relates the molar flow,  $(1/A_s)(dm/dt)$ , to the concentration gradient  $(dC/dx)_{x=0}$  and diffusivity  $D$ , according to Eq. (3):

$$\frac{1}{A_s} \frac{dm}{dt} = D \frac{dC}{dx} \quad (3)$$

where  $A_s$  is the surface of the cathode and  $D$  is given by:

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \quad (4)$$

where  $D_0$  is the standard diffusivity and  $E_D$  is the activation energy for the diffusion.

Combining Eqs. (2a) and (3), the expression for the current  $i$  becomes:

$$i = nA_sFD\left(\frac{dC}{dx}\right)_{x=0} \quad (5)$$

The concentration gradient at the electrode surface should be calculated first, in order to evaluate the current that is determined by diffusion of the electroactive species to or from the electrode. This is not always easy, but a general, simplified equation can be obtained if the Nernstian approximation of a linear concentration gradient in the diffusion layer is made [2]. Then Eq. (5) becomes:

$$i = nA_sFD\frac{C_\infty - C_0}{\delta} \quad (6)$$

where  $C_\infty$  and  $C_0$  are the concentrations in the bulk of the solution and at the cathode surface, respectively,  $\delta$  is the diffusion layer thickness, *i.e.* the electrolyte solution layer plus the membrane. Working in the limiting diffusion current region (LDCR), the concentration of oxygen at the cathode surface is zero, as all the oxygen that reaches the cathode surface is promptly reduced [2]. We can thus assume  $C_0 = 0$ . Furthermore, in a Clark-type cell, the thickness of the electrolyte is negligible compared to that of the membrane [3,7], since the electrode is in direct contact with the membrane itself. Therefore,  $\delta$  is assumed to be equal to the membrane thickness. The model equation becomes:

$$i = \frac{nA_sFDC_{DO}}{\delta} \quad (7)$$

where  $C_{DO}$  is the measurand.

### 3. Experimental

#### 3.1. Chemicals

KCl Suprapur from Merck was used for the preparation of solutions for voltammetry.  $\text{Na}_2\text{SO}_3$  anhydrous from Fluka (99% pure) was used to attain a zero DO concentration.

For the Winkler's titration,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , NaOH pellets (both from Merck), KI and concentrated sulphuric acid (both from VWR) were used.  $0.1 \text{ eq L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$  from Merck was diluted to  $0.0125 \text{ eq L}^{-1}$  and standardised against extra pure (99–100%)  $\text{KIO}_3$  from Riedel-de Haen.

All solutions were prepared using water freshly generated by a Millipore Milli-Q purification system. Oxygen and nitrogen gases were provided by Air Liquid.

#### 3.2. Instruments

Gas treatments and amperometric measurements were performed at the reference temperature of  $25^\circ\text{C}$ , using a MGW-20 Lauda thermostatic bath.

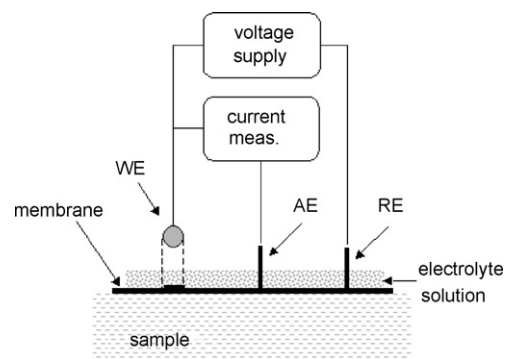


Fig. 1. Scheme of the amperometric cell. WE is the working Au electrode, RE the reference Ag/AgCl one and AE the auxiliary Pt one.

A flow-meter from Cole-Parmer ensured the control of the gas injection.

Cyclic voltammetric and chronoamperometric measurements were performed with an Autolab PGSTAT-10 potentiostat from Echo Chemie interfaced to a computer with GPES 4.9 software for the handling of the data.

#### 3.3. Cell set-up

The cell consists of a 60 mL vessel in Plexiglass. A scheme of the cell is shown in Fig. 1. Its design is able to guarantee airtight closure after filling. The working electrode (WE) is in gold having a diameter of 1.60 mm supplied from BASi. Before every measurement the WE is polished with alumina powder of particle sizes of 1 and  $0.05 \mu\text{m}$  on polishing cloth. After the surface had been rinsed, the electrode was cleaned in an ultrasonic distilled water bath for a few minutes to ensure the complete removal of the alumina particles. The reference electrode is a commercial Ag/AgCl/ $\text{Cl}^-$  ( $\text{KCl } 3 \text{ mol L}^{-1}$ ) electrode supplied from BASi. The auxiliary electrode is a Pt wire that provides a surface for a redox reaction to balance the one occurring at the surface of the WE, and does not need special care, such as polishing. The three electrodes are immersed in the electrolyte solution, 2 mL of  $0.2 \text{ mol L}^{-1} \text{ KCl}$ . Electrodes and electrolyte solution are kept separated from the sample by a Teflon membrane of  $10 \mu\text{m}$  thickness supplied from Goodfellow.

The chronoamperometric measurements were performed applying the working potential of  $-0.65 \text{ V}$  versus the Ag/AgCl/ $\text{Cl}^-$  electrode and recording the electric current.

#### 3.4. Preparation of standard solutions

Standard solutions were used to determine the diffusivity coefficient,  $D$  (see below). Since no reference solutions are commercially available, homemade standards were prepared, using a  $0.2 \text{ mol L}^{-1} \text{ KCl}$  aqueous solution as solvent and bubbling defined flows of oxygen and nitrogen for different durations. At the end of the treatment, the bottle was immediately capped, taking care of avoiding agitation of the sample. For each batch, two operations were conducted at the same time on separated aliquots: (i) the concentration of DO was determined by means of

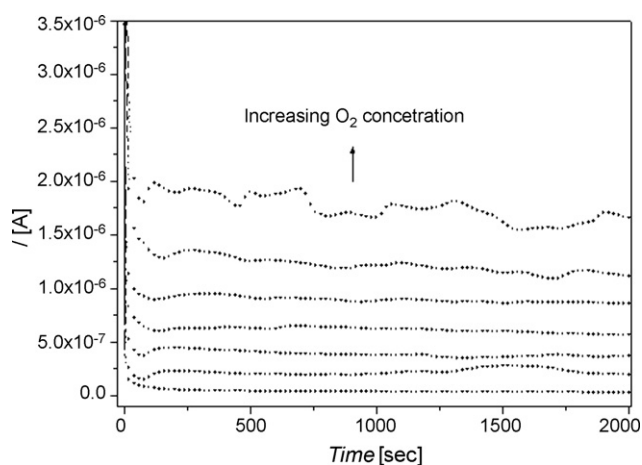


Fig. 2. Chronoamperometric curves for different concentrations of DO in the interval from  $\sim 0$  to  $11 \text{ mg L}^{-1}$ .

the Winkler's titration [12–14] and (ii) the corresponding electric current value was recorded in the Clark cell.

## 4. Results and discussion

### 4.1. Characterisation of the cell

Cyclic voltammograms of the sensor were initially recorded in a  $0.2 \text{ mol L}^{-1}$  KCl solution to verify the characteristic plateau of the LDCR. The plateau was found stretched from approximately  $-0.3$  to  $-1.1 \text{ V}$ . In this range of potentials, electron transfer at the electrode occurs so fast that diffusion becomes the rate-determining factor. These initial voltammograms ensured that the potentiostatic application of  $-0.65 \text{ V}$  to the WE during the amperometric measurements is within the LDCR.

Fig. 2 reports the chronoamperometric curves at different DO concentrations. After about 3 min, the sensor shows a good stability of the signal, maintained for at least 30 min. However, it is possible to observe that stability decreases with increasing oxygen content (upper curves).

Normally, yet at zero oxygen concentration in the sample, a residual current is present, mostly because of the DO in the electrolyte solution. The residual current was therefore measured for every set of experiments on a  $0.1 \text{ mol L}^{-1}$  sodium sulphite solution, which is able to reduce  $\text{O}_2$ , and the value of the recorded current was subtracted from the current signal at each oxygen concentration value.

Table 1  
Results of the intensity current measurements ( $i_i$ ), and Winkler's titration ( $C_i$ )

$i_i$ (A)	S.D.	$C_i$ ( $\text{g mm}^{-3}$ )	S.D.
$9.866 \times 10^{-8}$	$5.06 \times 10^{-9}$	$8.200 \times 10^{-11}$	$2.00 \times 10^{-11}$
$4.302 \times 10^{-7}$	$8.19 \times 10^{-8}$	$1.747 \times 10^{-9}$	$2.70 \times 10^{-11}$
$6.488 \times 10^{-7}$	$8.18 \times 10^{-8}$	$2.969 \times 10^{-9}$	$1.36 \times 10^{-10}$
$6.617 \times 10^{-7}$	$6.38 \times 10^{-8}$	$4.542 \times 10^{-9}$	$1.49 \times 10^{-10}$
$7.868 \times 10^{-7}$	$7.95 \times 10^{-8}$	$4.844 \times 10^{-9}$	$2.19 \times 10^{-10}$
$1.191 \times 10^{-6}$	$4.48 \times 10^{-8}$	$7.260 \times 10^{-9}$	$5.50 \times 10^{-11}$
$2.181 \times 10^{-6}$	$4.21 \times 10^{-8}$	$9.880 \times 10^{-9}$	$9.90 \times 10^{-11}$
$2.452 \times 10^{-6}$	$1.10 \times 10^{-7}$	$1.070 \times 10^{-8}$	$2.90 \times 10^{-11}$

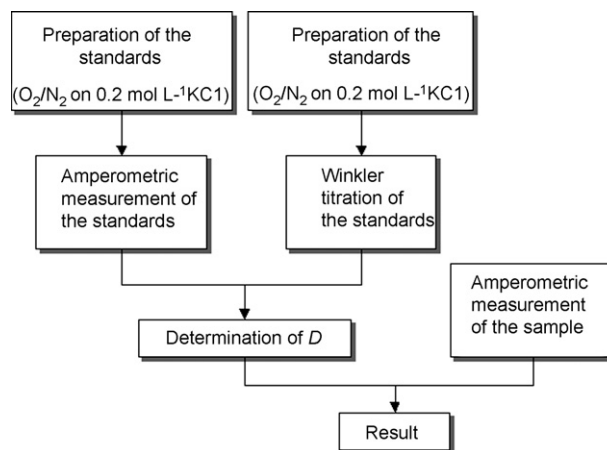


Fig. 3. Flowchart of the procedure for the determination of DO concentration.

Eight solutions having different concentration of DO in the range from 1 to  $11 \text{ mg L}^{-1}$  were measured according to the procedure described in Experimental Section 3. The results are reported in Table 1.  $C_i$  values were determined by the Winkler's titration and each result is the average of three independent replicates.  $i_i$  are the current values measured in the cell;  $i_i$  results are averaged over three independent replicates. The various steps of the procedure are summarized in the flowchart reported in Fig. 3 and are described in detail in the following paragraphs.

### 4.2. Determination of $D$

The definition of a primary method requires the establishment of a measurement equation together with preliminary quantification of each parameter. Analogously to the procedure applied to establish the standard potential,  $E^\circ$ , of the Harned cell dealing with the potentiometric measurement of pH [28],  $D$  was determined measuring the current intensity of a solution of DO of known concentration stated by way of a redox titration (Winkler's method). In order to probe validation quantities of the method under construction, various levels of DO concentration were tested.

Hence, in order to calculate the DO concentration in a sample, using Eq. (7), the diffusivity coefficient  $D$  was defined first.  $D$  was empirically determined starting from  $C_i$  and  $i_i$  values reported in Table 1, rearranging Eq. (7) in the form:

$$D = \frac{i_i \delta}{n A_s F C_i} \quad (8)$$

where  $i_i$  and  $C_i$  are, respectively, the measured current and the DO concentration of each standard solution,  $A_s$  is the WE surface ( $2.0096 \text{ mm}^2$ ),  $\delta$  is the membrane thickness ( $0.01 \text{ mm}$ ),  $n$  is the number of exchanged electrons ( $n=4$ ) and  $F$  is the Faraday's constant ( $96485.3415 \text{ s A mol}^{-1}$ ).

The values of  $D$  derived from the eight solutions are reported in Table 2. The results obtained for the solution at the lowest DO concentration was significantly different from the other ones and was excluded after verification by applying the  $Q$ -test. The mean value of  $D$  subsequently used was  $2.567 \times 10^{-6} \text{ mol mm}^2 \text{ s}^{-1} \text{ g}^{-1}$ .

Table 2  
Diffusivity parameter values,  $D$ , calculated from each oxygen standard solution

$C_i$ (g mm <sup>-3</sup> )	$i_i$ (A)	$D$ (mol mm <sup>2</sup> s <sup>-1</sup> g <sup>-1</sup> )
$8.200 \times 10^{-11}$	$9.866 \times 10^{-8}$	$1.559 \times 10^{-5}$
$1.747 \times 10^{-9}$	$4.302 \times 10^{-7}$	$3.191 \times 10^{-6}$
$2.969 \times 10^{-9}$	$6.488 \times 10^{-7}$	$2.831 \times 10^{-6}$
$4.542 \times 10^{-9}$	$6.617 \times 10^{-7}$	$1.887 \times 10^{-6}$
$4.844 \times 10^{-9}$	$7.868 \times 10^{-7}$	$2.104 \times 10^{-6}$
$7.260 \times 10^{-9}$	$1.191 \times 10^{-6}$	$2.126 \times 10^{-6}$
$9.880 \times 10^{-9}$	$2.181 \times 10^{-6}$	$2.859 \times 10^{-6}$
$1.070 \times 10^{-8}$	$2.452 \times 10^{-6}$	$2.969 \times 10^{-6}$

#### 4.3. Assessment of the uncertainty budget

Once the value of  $D$  was determined, it was used to calculate the concentration of DO,  $C_x$ , in an unknown sample, according to Eq. (7) in the form:

$$C_x = \frac{i_x \delta}{n A_s F D} + \Delta(\text{DO}_T) + \Delta(\text{DO}_p) \quad (9)$$

The parameters  $\Delta(\text{DO}_T)$  and  $\Delta(\text{DO}_p)$  are two additional terms that refer to the effect of temperature and atmospheric pressure on the concentration of DO in solution.  $\Delta(\text{DO}_T)$  and  $\Delta(\text{DO}_p)$  are defined so that their value is 0 while their contributions to the overall uncertainty have to be taken into account.

As concerns the evaluation of the uncertainty, combined standard uncertainties of the results were obtained by propagating individual contributions, according to the ISO/GUM Guide [29] and QUAM [30]. An evaluation of the uncertainty for the calibration procedure of a commercial sensor is presented in ref. [31].

The equations established for propagation of the uncertainty for the diffusivity coefficient  $D$  (Eq. (10)) and DO concentration in the sample (Eq. (11)) are:

$$u^2(D) = c^2(i_i)u^2(i_i) + c^2(\delta)u^2(\delta) + c^2(F)u^2(F) + c^2(A_s)u^2(A_s) + c^2(C_i)u^2(C_i) \quad (10)$$

$$u^2(C_x) = c^2(i_x)u^2(i_x) + c^2(\delta)u^2(\delta) + c^2(F)u^2(F) + c^2(A_s)u^2(A_s) + c^2(D)u^2(D) + c^2(\Delta(\text{DO}_T))u^2(\Delta(\text{DO}_T)) + c^2(\Delta(\text{DO}_p))u^2(\Delta(\text{DO}_p)) \quad (11)$$

Table 3  
Uncertainty budget for diffusivity coefficient,  $D$ , value

Quantity	Estimate ( $x_i$ )	Standard uncertainty ( $u_i$ )	Sensitivity coefficient ( $c_i$ )	Contribution ( $u_i(y)$ )
$i_i$ (A)	$7.87 \times 10^{-7}$	$7.95 \times 10^{-8}$	2.66	$2.12 \times 10^{-7}$
$\delta$ (mm)	0.01	$5.77 \times 10^{-5}$	$2.09 \times 10^{-4}$	$1.21 \times 10^{-8}$
$F$ (s A mol <sup>-1</sup> )	96485.3415	$8.30 \times 10^{-3}$	$2.17 \times 10^{-11}$	$1.80 \times 10^{-13}$
$A_s$ (mm <sup>2</sup> )	2.0096	$4.35 \times 10^{-2}$	$1.04 \times 10^{-6}$	$4.53 \times 10^{-8}$
$C_i$ (g mm <sup>-3</sup> )	$4.84 \times 10^{-9}$	$2.19 \times 10^{-10}$	$4.32 \times 10^{+2}$	$9.47 \times 10^{-8}$
$D$ (mol mm <sup>2</sup> s <sup>-1</sup> g <sup>-1</sup> )	$2.094 \times 10^{-6}$			$2.37 \times 10^{-7}$

where  $c(x)$  terms are the sensitivity coefficients, defined as:

$$c(x) = \frac{\partial f}{\partial x_j} \quad (12)$$

where  $x_j$  are the variables of the model, considering  $y = f(x_1, x_2, x_3, \dots, x_n)$  as the generic model equation.

A representative example of the uncertainty evaluation is reported, considering, first, the uncertainty associated with the determination of  $D$ , deriving from an independent measurement, and then, the uncertainty associated with the DO concentration value. Measurements, for the determination of both  $D$  and  $C_x$ , were performed at  $25 \pm 0.1$  °C.

In what follows we quantify the uncertainty of the  $D$  value. The complete uncertainty budget is reported in Table 3.

$i_i$ : The output current, average of three measurements, was  $7.87 \times 10^{-7}$  A. The combined uncertainty, equal to  $7.95 \times 10^{-8}$  A, is mainly due to repeatability of the readings. The resolution of the potentiostat was also taken into account, although its contribution resulted negligible with respect to the repeatability.

$\delta$ : The thickness of the membrane is 0.01 mm. The working electrode is directly in contact with the membrane, and the thickness of the electrolyte solution is of a few molecular layers so that it is negligible if compared to the membrane [3,7]. Nevertheless, we cannot neglect its contribution to the uncertainty. The combined uncertainty for  $\delta$  was estimated as 1% of its value.

$F$ : The Faraday's constant,  $96485.3415$  s A mol<sup>-1</sup>, and its combined uncertainty,  $8.30 \times 10^{-3}$  s A mol<sup>-1</sup>, were obtained from CODATA [32].

$A_s$ : The working electrode has a diameter of 1.60 mm with a tolerance of 0.03 mm declared by the manufacturer. As no supplemental indications are given, the tolerance value was propagated, considering a rectangular distribution, for the estimation of the uncertainty due to the electrode geometric area [30]. The standard uncertainty contribution is  $4.53 \times 10^{-8}$  mm<sup>2</sup>.

$C_i$ : The DO concentration of the selected standard (determined by the Winkler's titration) was  $4.84$  mg L<sup>-1</sup> with a standard uncertainty of  $0.49$  mg L<sup>-1</sup> (see Table 1). For the calculations, the concentration of oxygen and its uncertainty were expressed in g mm<sup>-3</sup> instead of mg L<sup>-1</sup> to harmonise the units. The large standard deviation is due to the low repeatability owing to air contamination.

Table 4  
Uncertainty budget for DO concentration in the sample

Quantity	Estimate ( $x_i$ )	Standard uncertainty ( $u_i$ )	Sensitivity coefficient ( $c_i$ )	Contribution ( $u_i(y)$ )
$i_x$ (A)	$1.50 \times 10^{-6}$	$4.14 \times 10^{-8}$	$5.02 \times 10^{-3}$	$2.08 \times 10^{-10}$
$\delta$ (mm)	0.01	$5.77 \times 10^{-5}$	$7.53 \times 10^{-7}$	$4.35 \times 10^{-11}$
$F$ (s A mol $^{-1}$ )	96485.3415	$8.30 \times 10^{-3}$	$7.81 \times 10^{-14}$	$6.48 \times 10^{-16}$
$A_s$ (mm $^2$ )	2.0096	$4.35 \times 10^{-2}$	$3.75 \times 10^{-9}$	$1.15 \times 10^{-10}$
$D$ (mol mm $^2$ s $^{-1}$ g $^{-1}$ )	$2.567 \times 10^{-6}$	$2.34 \times 10^{-7}$	$2.94 \times 10^{-3}$	$6.85 \times 10^{-10}$
$\Delta DO_T$ (g mm $^{-3}$ )	0	$8.70 \times 10^{-12}$	1	$8.70 \times 10^{-12}$
$\Delta DO_p$ (g mm $^{-3}$ )	0	$8.70 \times 10^{-12}$	1	$8.70 \times 10^{-12}$
$C_x$ (g mm $^{-3}$ )	$7.53 \times 10^{-9}$			
$u_c(C_x) =$				$7.44 \times 10^{-10}$
$U(C_x) =$				$1.49 \times 10^{-9}$

The expanded uncertainty,  $U(C_x)$ , corresponds to a coverage probability of approximately 95%.

The combined uncertainty of  $D$  results in  $2.37 \times 10^{-7}$  mol mm $^2$  s $^{-1}$  g $^{-1}$ .

As concerns the uncertainty of  $C_x$  (DO concentration in the unknown sample), Table 4 reports the complete uncertainty budget. Input quantities are below analysed in details.

$i_x$ : The output current for the unknown sample was  $1.50 \times 10^{-6}$  A, determined as an average of three replicates, with a standard uncertainty of  $4.14 \times 10^{-8}$  A. The instrumental resolution was negligible with respect to the standard deviation of the replicates. This current value corresponds to a DO concentration of  $7.53 \times 10^{-9}$  g mm $^{-3}$ .

$\delta$ ,  $A_s$ , and  $F$ : The same criteria adopted for the uncertainty of  $D$  were applied in this case, being the membrane, the electrode, and obviously the Faraday's constant, the same in both measurements.

$D$ : As previously described, the value of  $D$  used for the determination of the measurand was  $2.567 \times 10^{-6}$  mol mm $^2$  s $^{-1}$  g $^{-1}$ , and its combined uncertainty is  $2.37 \times 10^{-7}$  mol mm $^2$  s $^{-1}$  g $^{-1}$ .

$\Delta(DO_T)$ : The value of this variable is 0. In Ref. [2] studies are reported on the variation of DO concentration with respect to the temperature. Authors demonstrate that the DO concentration varies by about 2%/°C. Our measurements were performed at  $25 \pm 0.1$  °C leading to a possible variation of DO of 0.2%. Considering a rectangular distribution [30], the contribution to uncertainty of  $\Delta(DO_T)$  for DO concentration of  $7.53 \times 10^{-9}$  g mm $^{-3}$  is  $8.74 \times 10^{-12}$  g mm $^{-3}$ .

$\Delta(DO_p)$ : Also the value of this parameter is 0. Ref. [2] again reports studies on variation of DO concentration with respect to atmospheric pressure. The variation is about  $1 \times 10^{-3}$ % Pa $^{-1}$ . The measurements were performed at  $(101120 \pm 200)$  Pa, leading to a possible variation of DO of 0.2%. Considering a rectangular distribution, the contribution to uncertainty of  $\Delta(DO_p)$  for DO concentration of  $7.53 \times 10^{-9}$  g mm $^{-3}$  is  $8.74 \times 10^{-12}$  g mm $^{-3}$ .

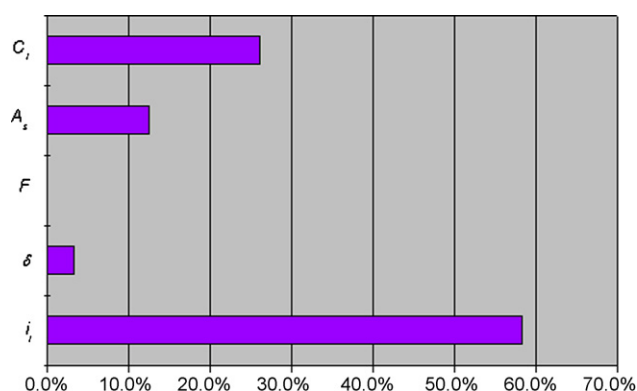


Fig. 4. Relative contributions to uncertainty in the determination of  $D$ .

The resulting DO concentration is  $7.53 \times 10^{-9}$  g mm $^{-3}$  and its combined uncertainty is  $7.44 \times 10^{-10}$  g mm $^{-3}$ . Expressing the DO concentration in mg L $^{-1}$ , it becomes 7.53 mg L $^{-1}$  with a combined uncertainty of 0.744 mg L $^{-1}$ .

The expanded uncertainty,  $U(C_x)$  (coverage probability of 95%,  $k=2$ ), for the measurement of DO concentration, is:

$$U(C_x) = 0.744 \times 2 = 1.49 \text{ mg L}^{-1}.$$

Figs. 4 and 5 show the relative contributions to the total uncertainty of  $D$  and  $C_x$ , respectively. Single terms are calculated and represented in the histograms as percent-

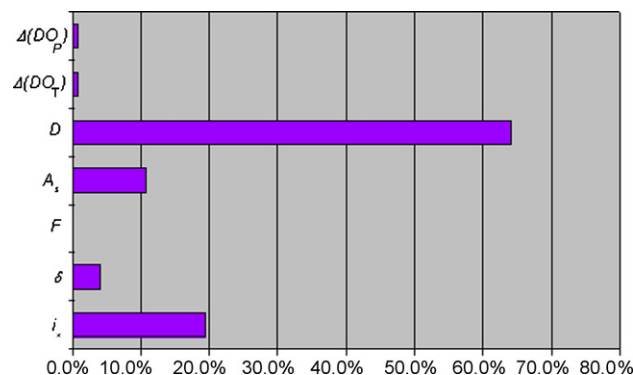


Fig. 5. Relative contributions to uncertainty in the determination of DO concentration in the sample.

age of the arithmetic sum of all the  $u_i(y)$  contributions (see Tables 3 and 4).

## 5. Conclusions

This work aimed at identifying the significant sources of uncertainty and at assessing the uncertainty budget of amperometric DO concentration measurement, this being a powerful tool of quality control in analytical chemistry and a central issue of metrological studies. The selected approach aimed at contributing to the development of a potential primary method of measurement.

A Clark-type sensor, based on an amperometric principle working in regime of diffusivity, was set-up for the measurement of DO concentration and characterised *via* cyclic voltammetry and chronoamperometry. The measurement equation was defined and a procedure was worked out for the empirical determination of the diffusivity parameter,  $D$ . All the input quantities were analysed in details in order to establish their contribution to the uncertainty budget.

As concerns  $D$ , it is possible to note that the most relevant contributions to its uncertainty are those related with the repeatability of  $i_i$  and  $C_i$  terms and derive from the manipulation of the oxygen solutions, or else from environmental contamination. In turn,  $D$  is the major contributor to the uncertainty of  $C_x$ .

Thanks to the provided uncertainty budget, it is possible to estimate the accuracy of DO concentration measurement (under unbiased conditions). Moreover, from the analysis of each input term, one can identify those steps of the method carrying the worst contributions to the overall uncertainty and try to plan specific improvements able to enhance accuracy and precision of the technique.

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