



Optimization of the determination of chemical oxygen demand in wastewaters

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ABSTRACT

Chemical oxygen demand (COD) is one of the most relevant chemical parameters for the management of wastewater treatment facilities including the control of the quality of an effluent. The adequacy of decisions based on COD values relies on the quality of the measurements. Cost effective management of the minor sources of uncertainty can be applied to the analytical procedure without affecting measurement quality. This work presents a detailed assessment of the determination of COD values in wastewaters, according to ISO6060:1989 standard, which can support reduction of both measurement uncertainty and cost of analysis. This assessment includes the definition of the measurement traceability chain and the validation of the measurement procedure supported on sound and objective criteria. Detailed models of the measurement performance, including uncertainty, developed from the Differential Approach, were successfully validated by proficiency tests. The assumption of the measurement function linearity of the uncertainty propagation law was tested through the comparison with the numerical Kragten method. The gathered information supported the definition of strategies for measurement uncertainty or cost reduction. The developed models are available as [electronic supplementary material](#), in an MS-Excel file, to be updated with the user's data.

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1. Introduction

Water is, since ancient times, the most strictly managed resource of sedentary human societies. The impact of water quality on the environment and on public health justifies the investment in managing and controlling the safety of its domestic, public and industrial use. The sustainable management of water resources must be supported on the production of safe and adequately abundant drinking water and on the treatment of wastewaters. In some regions, this management is particularly difficult since the same environmental compartment is the source of water and the receptor of wastewater. The impact of wastewaters emissions on the receptor aquatic medium is managed through the enforcement of legislation that establishes limits for its pollution

charge. The most relevant pollution impact of domestic wastewaters results from organic matter. The concentration of organic matter in wastewaters is mostly tested by the determination of either biological oxygen demand (BOD) or chemical oxygen demand (COD) which estimate the extent of biological or chemical oxidation respectively. Those determinations are performed by empirical methods [1] (also known as “operationally defined measurement procedures” [2]) that consist of pragmatic and reliable analytical solutions for the management of the eutrophication risk of the receptor aquatic medium. The ability of testing wastewaters in a couple of hours, instead of the five days required for BOD₅, makes this analytical evaluation of COD most popular and useful despite the fact that it also involves the oxidation of inorganic matter.

The concentration of the organic matter can also be roughly estimated by total carbon (TC) or total organic carbon (TOC) quantified by elemental instrumental analysis. Nevertheless, TC and TOC values do not express the oxidable fraction of the organic matter responsible for the eutrophication of the receptor medium and cannot replace BOD and COD testing. Although no direct relation between the TC, TOC, COD and BOD values is known, empirical models relating these parameters, applicable to samples with similar composition, like wastewaters from a specific stage of the treatment process, can be developed [3].

Determination of COD in wastewaters is most often estimated from their oxidability by potassium dichromate (PDC) in specified concentration, catalytic, acidic and temperature conditions. Several standard procedures are available to perform this evaluation,

Abbreviations: BOD, biological oxygen demand; COD, chemical oxygen demand; CV, coefficient of variance; DL, determination limit; FAS, ferrous ammonium sulphate; MLOD, maximum admissible LOD; LOD, limit of detection; NKM, numerical Kragten method; PHP, potassium hydrogenophthalate; PDC, potassium dichromate; PV, parametric value for the monitoring of drinking water according to Directive 98/83/EC [19]; RELACRE, Portuguese Association of Accredited Laboratories; SD, standard deviation; Solution A, $K_2Cr_2O_7 \cong 0.04 \text{ mol L}^{-1}$, $HgSO_4 \cong 80.0 \text{ g L}^{-1}$, $H_2SO_4 \cong 1.80 \text{ mol L}^{-1}$; Solution B, $AgSO_4 \cong 10.0 \text{ g L}^{-1}$, $H_2SO_4 \cong 17.4 \text{ mol L}^{-1}$; Solution C, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O \cong 0.12 \text{ mol L}^{-1}$, $H_2SO_4 \cong 0.360 \text{ mol L}^{-1}$; Solution D, solution of PHP with a COD value of $\cong 500 \text{ mg L}^{-1}$; Solution E, solution of PHP with a COD value of $\cong 30 \text{ mg L}^{-1}$; TC, total carbon; TOC, total organic carbon; UPL, uncertainty propagation law.

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Nomenclature

a	reported result from the proficiency test
A_{Cr}	molar mass of the chromium
A_K	molar mass of the potassium
A_O	molar mass of the oxygen
b	reference value from the proficiency test
c	COD value in $\text{mg O}_2 \text{ L}^{-1}$
CStd	control standard
f_{DE}	factor for the combined efficiency of oxidation and digestion, and endpoint detection steps for blank test, sample test and FAS standardization
f_{SS}	factor for subsampling step
j	input quantity
k	coverage factor
m_{PDC}	mass of PDC used to prepare Solution A
M_{PDC}	molar mass of PDC
n	number of replicated analysis of the PHP standard
P_j	percentage contribution of component j
Pur	purity of PDC reagent
s_{IP}	standard deviation quantifying the intermediate imprecision
s'_{IP}	relative standard deviation quantifying the intermediate imprecision
s_r	standard deviation quantifying the repeatability of measurements of COD in the PHP standard solution
$s_{r(ww)}$	standard deviation quantifying the repeatability of measurements of COD in wastewater samples
u_i	standard uncertainty associated with the variable i
U_i	expanded uncertainty associated with the variable i
u'_j	relative standard uncertainty associated with the variable i
U'_j	relative expanded uncertainty associated with the variable i
U_{Tg}	target expanded uncertainty
$U_{Tg(HS)}$	target expanded uncertainty for the analysis of heterogeneous wastewater samples
u'_{PHP}	relative standard uncertainty associated with PHP standard solution concentration
$u(R_w)$	standard uncertainty associated with the intermediate precision (Nordtest Report TR 537 notation) [20]
$u(\text{bias})$	standard uncertainty associated with the measurement bias (Nordtest Report TR 573 notation) [20]
$V_{1(\text{blk})}$	volume of blank test aliquot
$V_{1(\text{spl})}$	volume of sample aliquot
$V_{2(\text{blk})}$	volume of Solution A used for blank test aliquot oxidation
$V_{2(\text{spl})}$	volume of Solution A used for sample aliquot oxidation
$V_{3(\text{blk})}$	volume of Solution C used to titrate digested and diluted blank test aliquot
$V_{3(\text{spl})}$	volume of Solution C used to titrate digested and diluted sample aliquot
V_A	aliquot of Solution A titrated with Solution C to estimate the FAS concentration
V_B	volume of Solution C used to titrate V_A from Solution A
V_x	volume of Solution A used to dilute m_{PDC}

in open or in closed systems [4]. The open system procedure is popular for not needing digestion temperature control since adequate temperature is ensured by sample reflux after reagents have been added [4,5].

COD values are used to monitor wastewaters before (influent) and after (effluent) treatment and, therefore, their reliability is important for protecting the environment and to guarantee the economical sustainability of the treatment facility. In fact, the cost of wastewater treatment contracted by the polluting industry is frequently settled in terms of the pollution charge quantified by its COD value. Likewise, the management of wastewaters facilities, such as the schedule of maintenance activities or the use of parallel treatment units, is also frequently based on COD values [6]. Directive 91/271/EEC [7] defines $125 \text{ mg O}_2 \text{ L}^{-1}$, as the maximum COD value for the discharge of urban wastewaters.

The reliability of the evaluations supported on COD values can be checked by the adequacy of the defined measurement traceability and the estimated measurement uncertainty. According to the latest edition of the International Vocabulary of Metrology [2], metrological traceability is defined as the “property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty”. The reference can be a defined unit, a reference material or a measurement procedure, ensuring the comparability of measurements traced to the same reference [2]. Whenever a measurement result is traceable to a reference different from the one considered in the legislated limits, evaluation is arbitrary. The adequacy of the estimated uncertainty is verified by comparison with a maximum target uncertainty value [2].

Droic et al. [8] developed a simplified model for the evaluation of the uncertainty associated with COD determinations where all precision components are combined in a single uncertainty component. The proposed approach does not allow optimization of this major component.

In this work a detailed model of the performance of the determination of COD in wastewaters, following ISO6060:1989 standard [5], is developed, which includes the assessment of the impacts from using the same PDC solution for ferrous ammonium sulphate (FAS) standardization and blank and sample oxidation. The Differential Approach was used for the evaluation of the measurement uncertainty [9,10], allowing the assessment of the individual precision components of the various analytical steps. The combination of the uncertainty components obtained by the uncertainty propagation law [11,12] was compared with the one obtained by the numerical Kragten method [12,13] for checking function linearity assumption. The developed metrological model was used to optimize the measurement procedure for cost and uncertainty having the intended use of measurements in mind. Before measurement uncertainty evaluation, the metrological traceability was clearly defined to guarantee the comparability of measurement results traced to the same reference.

2. Theory

2.1. Determination of chemical oxygen demand in wastewaters

The determination of COD consists of the following steps (Fig. 1) [5]:

- (1) Boiling a mixture of 10 mL of undiluted or diluted water sample, 5 mL of Solution A ($0.04 \text{ mol L}^{-1} \text{ K}_2\text{Cr}_2\text{O}_7$; $80.0 \text{ g L}^{-1} \text{ HgSO}_4$; $1.80 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$) and 15 mL of Solution B ($10.0 \text{ g L}^{-1} \text{ AgSO}_4$; $17.4 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$) for 2 h, under open reflux conditions. The concentration of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution must be known with its uncertainty. The other concentrations should be within the last significant figure considering minimum variation (e.g., $80.0 \pm 0.1 \text{ g L}^{-1}$ of HgSO_4).
- (2) Dilution of the digested solution, by adding approximately 75 mL of water, after reaching room temperature.

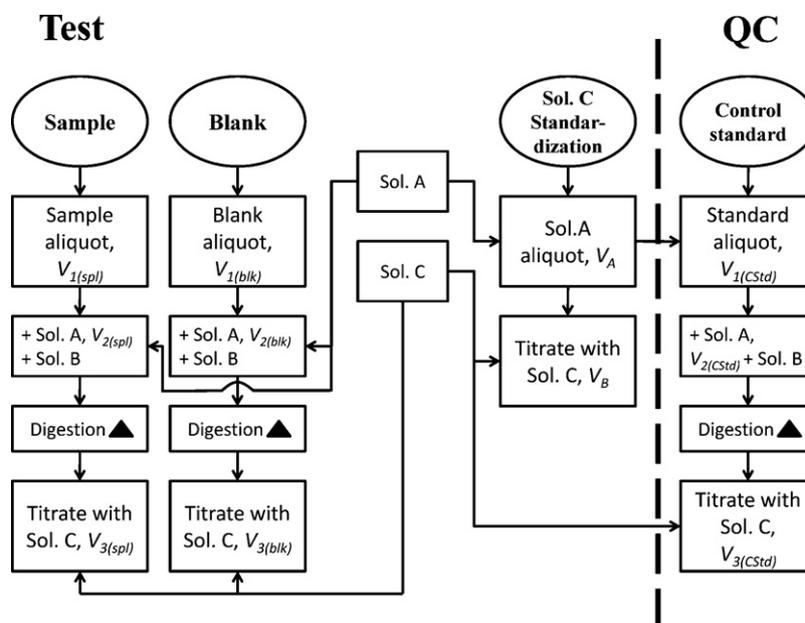


Fig. 1. Schematic description of the measurement procedure including the test quality control (QC). See Nomenclature for symbols.

- (3) Titration of the diluted solution with a standard FAS solution [Solution C: $0.12 \text{ mol L}^{-1} (\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$; $0.360 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$]. Solution C is standardized daily with Solution A for FAS concentration.
- (4) Blank test performance by running steps 1–3 for the analysis of 10 mL of deionised water.
- (5) Weekly analysis of a potassium hydrogenophthalate (PHP) standard solution (Solution D: $2.08 \text{ mmol L}^{-1} \text{KC}_8\text{H}_5\text{O}_4$, or Solution E: $0.125 \text{ mmol L}^{-1} \text{KC}_8\text{H}_5\text{O}_4$) with an expected COD value of $\cong 500 \text{ mg L}^{-1}$ or $\cong 30 \text{ mg L}^{-1}$ (each mol of $\text{KC}_8\text{H}_5\text{O}_4$ is equivalent to 7.5 mol of O_2) to check measurement performance. The uncertainty associated with the reference COD value must be known.

2.2. Traceability of measurements

The measurement results obtained by the reference measurement procedure [5] are traceable to the values defined by the operationally defined measurement procedure [14]. This statement highlights the fact that a measurement result must be traceable to a value and not to a procedure. Alternatively, the traceability of measurements can be defined as given by the application of the method [15] ensuring that all input quantities are traceable to adequate references, either SI units or other stable ones. This way of describing measurement traceability has the merit of calling the attention for the need of ensuring that all measured input quantities are traceable to an adequate reference; masses (g), molar masses (g mol^{-1}), volumes (L dm^3), period of time (s) and temperature (K), are traceable to the respective SI unit. The purity of chemicals are traceable to the value defined by the manufacturer. Nevertheless, only the purity of PDC and PHP has a relevant impact on the measurement result. Since highly pure chemicals were used and purity statements are soundly estimated in these compounds, the chemical composition can be considered traceable to the mass fraction SI unit. Therefore, only measurements from this procedure are comparable [2].

2.3. Validation of the measurement procedure

The validation of the measurement procedure involves the definition of a determination limit, DL, positioned above the

limit of detection (LOD), and the evaluation of the measurement repeatability, intermediate precision, trueness and uncertainty.

The determination limit (DL) concept is different from the statistical limit of detection (LOD) and it is useful for analytical fields, such as the analysis of drinking waters, where maximums LOD (MLOD) are defined in the legislation, in the specification or by the client. In those cases, the analytical range is, usually, set to start at the MLOD and, subsequently, the performance at this level is checked for being, at least, as good as expected at an LOD, proving that the lower limit of the analytical range (i.e., DL) is equal or above the LOD. This strategy avoids the need for performing the unnecessary and demanding control of the measurement performance near the statistical LOD, thus saving resources every time MLOD is above LOD.

The precision and trueness, at DL and higher concentration levels, were tested in repeatability and intermediate precision conditions. The repeatability is useful for defining criteria for checking replicated measurements obtained in repeatability conditions. The intermediate precision at DL is used to check its positioning above the LOD. The DL was tested in intermediate precision conditions to guarantee the estimation of a constant limit independently of daily precision variations. Since the coefficient of variation at LOD is 33% {assuming an homogeneous variance between the LOD value estimated by three times the standard deviation, in concentration units, SD, [16] and the concentration at which SD was estimated, the CV at LOD is $[\text{SD}/\text{LOD}] = [\text{SD}/(3 \times \text{SD})] = 33\%$ } and it decreases with increasing concentration, a coefficient of variation smaller than 33% at DL guarantees its positioning above LOD. The reliability of measurements is checked through the estimated measurement uncertainty. The fitness of measurements for the intended use is assessed through the comparison of the estimated measurement uncertainty with the target measurement uncertainty [2] (i.e., maximum admissible measurement uncertainty).

The adequacy of the measurement procedure for its intended use was decided on the basis of the following criteria:

- (1) Coefficient of variation in repeatability conditions for the analysis of homogeneous samples $\leq 5\%$;
- (2) Determination limit, $\text{DL} \leq 31 \text{ mg L}^{-1}$ (1/4 of the legal limit);

(3) Expanded measurement uncertainty \leq target measurement uncertainty (U_{Tg}) (Section 3.1).

No criterion for separately testing measurement precision and trueness considering the intended use of measurements was defined. These performance parameters are tested together in the evaluation of the magnitude of the measurement uncertainty. This approach has the advantage of accepting larger deviations on measurement trueness in highly precise measurements and vice versa. The DL (lower limit of the analytical range) is also used to limit the range of the applicability of the target measurement uncertainty. Whenever the measured quantity value, x (i.e., the best estimation of the measurand) added by the expanded measurement uncertainty ($x+U$), for a confidence level of 95%, is below the DL ($x+U < DL$), it can also be reported as " $x < DL$ ". This decision is associated with a confidence level of approximately 97.5% [17]. No target measurement uncertainty is defined for concentrations below DL.

The precision in repeatability conditions is used for the calculation of the critical range of replicated measurements (repeatability limit for duplicate measurements) [18] and for assessing the uncertainty from subsampling. The repeatability observed from the analysis of homogeneous PHP control standards is compared with the repeatability observed from the analysis of wastewater samples for the assessment of the subsampling uncertainty (Section 2.4).

The evaluation of the measurement uncertainty, the last stage of the validation of the measurement procedure, will be thoroughly described in Section 2.4. Section 2.3.1 describes how the target measurement uncertainty was defined.

2.3.1. Definition of the target measurement uncertainty

European Directive 91/271/EEC [7] that regulates the monitoring of wastewaters, establishes that COD value in the effluent should have a maximum O_2 equivalent value of 125 mg L^{-1} . This directive does not establish target values for the measurement uncertainty. Therefore, a target measurement uncertainty should be defined having the intended use of measurements in mind. A criterion equivalent to the one established for the analysis of drinking water was considered to make the selected target measurement uncertainty easily accepted by clients and by the analytical community.

2.3.1.1. Monitoring of drinking waters example. Directive 98/83/EC [19] that settles limit values for different parameters (i.e., parametric value, PV) in drinking waters, also defines maximum values for the detection limit [10% or 25% of the PV depending on the parameter], for the difference between the mean value of a large number of repeated measurements and the true value (trueness) [10% or 25% of the PV] and defines a maximum value for twice the standard deviation of replicated measurements obtained in repeatability or intermediate precision conditions [10% or 25% of PV]. The target values for measurement precision and trueness are applicable near the PV.

The defined limit values for measurement mean error and precision can be used to establish the target measurement uncertainty for drinking waters, U_{Tg} , by combining the maximum allowed variations as uncertainty components associated with measurement bias and intermediate precision, respectively, as proposed in the Nordtest Report TR 537 [20] (Eq. (1)):

$$U_{Tg} = 2\sqrt{u(R_W)^2 + u(\text{bias})^2} = 2\sqrt{\left(\frac{0.1 \times PV}{2}\right)^2 + (0.1 \times PV)^2} \quad (1)$$

where a relative difference of 10% was considered (0.1 can be substituted by 0.25 for relative target deviations of 25%). This cri-

terion is to be applied near PV (i.e., at least within the interval $PV \pm U_{Tg}$).

2.3.1.2. Monitoring of wastewaters. Although the target measurement uncertainty for the analysis of wastewaters can be larger than the one for drinking water, maximum relative deviations of 10% were considered in this work. Since this reference value is the most demanding it should be consensual although it may be too strict for some analysts. Eq. (2) presents the calculation of the target measurement expanded uncertainty, U_{Tg} , for the determination of COD in wastewaters:

$$U_{Tg} = 2\sqrt{\left(\frac{0.1 \times 125}{2}\right)^2 + (0.1 \times 125)^2} = 28.0 \text{ mg L}^{-1} \quad (2)$$

For the analysis of heterogeneous wastewaters samples an additional maximum subsampling relative standard uncertainty of 10% was considered [Eq. (3)]:

$$U_{Tg}(\text{HS}) = 2\sqrt{\left(\frac{0.1 \times 125}{2}\right)^2 + (0.1 \times 125)^2 + (0.1 \times 125)^2} = 37.5 \text{ mg L}^{-1} \quad (3)$$

where $U_{Tg}(\text{HS})$ is the target expanded uncertainty for the analysis of heterogeneous wastewater samples. In case subsampling uncertainty makes $U_{Tg}(\text{HS})$ not achievable, laboratory sample homogenization procedure should be revised (e.g., use mechanical sample shaker) and/or sample aliquot should be increased. The $U_{Tg}(\text{HS})$ is applicable, at least, in the interval $(125.0 \pm 37.5) \text{ mg O}_2 \text{ L}^{-1}$. For COD values where this condition is not valid, a target relative expanded uncertainty, $U'_{Tg}(\text{HS})$, of 20% is settled. The measurement uncertainty should comply with either U_{Tg} or U'_{Tg} .

2.4. Evaluation of the measurement uncertainty

The evaluation of the measurement uncertainty involves performing the, extensively described in various guides [11,12,21], following steps: (1) definition of the measurand; (2) definition of the measurement function; (3) identification of the sources of uncertainty; (4) quantification of the uncertainty components; (5) combination of the uncertainty components; (6) expansion of the combined standard uncertainty; (7) review of the uncertainty budget and (8) evaluation of the magnitude of the estimated measurement uncertainty. The last stage is frequently omitted but it is extremely important since it is the verification of the adequacy of the measurement quality for its intended use.

2.4.1. Definition of the measurand

The measurand is the "chemical oxygen demand, determined using measurement procedure ISO6060:1989 standard, in a specific wastewater sample coded on laboratory reception". In this case, the sampling procedure is excluded from the measurement procedure. Subsampling is included in the measurement procedure and is particularly relevant for the analysis of heterogeneous laboratory samples.

2.4.2. Definition of the measurement function

Eq. (4) presents the measurement function used to estimate COD in wastewater samples. This equation, simplified in the used standard [5], reflects the impact on measurement results, of using the same Solution A in the digestion of the analytical portion, in the blank test and in FAS standardization; symbols are explained in the

Nomenclature.

$$c = \left\{ \left(\frac{3A_O m_{PDC} \text{Pur}}{M_{PDC} V_x} \right) \left[\left(\frac{V_{2(\text{spl})}}{V_{1(\text{spl})}} - \frac{V_{2(\text{blk})}}{V_{1(\text{blk})}} \right) + \left(\frac{V_{3(\text{blk})}}{V_{1(\text{blk})}} - \frac{V_{3(\text{spl})}}{V_{1(\text{spl})}} \right) \frac{V_A}{V_B} \right] \right\} f_{DE} f_{SS} \quad (4)$$

Factor f_{DE} (expectedly an approximately unitary factor; $f_{DE} \cong 1$) aims at reflecting the combined impact of the various oxidation and digestion steps, and the visual endpoint detections performance on the measurement uncertainty. The unitary factor f_{SS} ($f_{SS} = 1$) reflects the impact of subsampling on measurement.

2.4.3. Identification of the sources of uncertainty

The cause and effect diagram from Fig. 2 presents the identified sources of uncertainty. The effects considered as affecting the uncertainty associated with the volumetric steps and the weighing operations are the ones advanced at the examples of the Eurachem/CITAC Guide CG4 [12]. Factor f_{DE} is divided in several effects affecting sample and blank test, and FAS standardization: oxidation and digestion precision and trueness, and endpoint detection precision and trueness.

2.4.4. Quantification of the uncertainty components

The uncertainty associated with volumetric steps, weighing operations, oxygen molar mass, PDC molar mass and purity were estimated as proposed on the Eurachem/CITAC Guide CG4 examples [12]. Factor f_{DE} was estimated by the ratio between the estimated mean and the expected COD values from the analysis of an homogeneous PHP standard solution. The standard uncertainty $u_{f_{DE}}$ was estimated by difference between the intermediate precision, s_{IP} , estimated from the analysis of a PHP standard solution and the combined standard uncertainty, u_{Inc} , associated with the components of the volumetric and gravimetric steps that contribute to the intermediate precision. Since the intermediate precision, s_{IP} , was estimated by using the same PDC reagent and balance, the terms Pur and the linearity components associated with m_{PDC} are not randomized in s_{IP} . Therefore, both these components were not considered in estimating u_{Inc} . The subsampling uncertainty is negligible in the analysis of this homogeneous PHP solution. Eq. (5) describes how the relative standard uncertainty associated with f_{DE} , $u'_{f_{DE}}$ (the apostrophe stands for relative quantities) was estimated:

$$u'_{f_{DE}} = \frac{u_{f_{DE}}}{f_{DE}} = \sqrt{(s'_{IP})^2 - (u'_{Inc})^2 + \frac{(s'_{IP})^2}{n} + u'_{PHP}} \quad (5)$$

where u'_{Inc} is the combined relative standard uncertainty associated with all quantified components affecting s_{IP} and u'_{PHP} is the relative standard uncertainty associated with PHP standard solution concentration. The subtraction from Eq. (5) is only statistically meaningful if $(s_{IP})^2$ is statistically larger than $(u_{Inc})^2$. This condition is tested through a one-tailed F -test assuming that u_{Inc} is associated with an infinite number of degrees of freedom. The subsampling uncertainty was estimated by difference between the repeatability observed from the analysis of homogeneous PHP standard solution, s_r , and the repeatability of measurements of heterogeneous wastewater samples, s_r . This difference was performed in a homoscedastic COD range tested with an F -test for 99% confidence level.

2.4.5. Combination of the uncertainty components

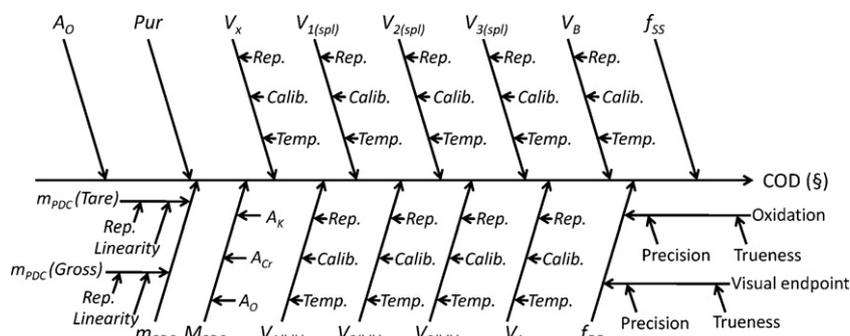
The uncertainty components were combined by the uncertainty propagation law that allowed understanding how sensitivity coefficients $[(\partial c/\partial j)$ Eq. (6)] that affect each of the uncertainty component contributions can be minimized. The assumption of function linearity of the uncertainty propagation law was tested by comparing the combined standard uncertainty estimated by the uncertainty propagation law [11,12] with the one estimated from the numerical Kragten Method [12,13].

2.4.5.1. Uncertainty propagation law. Since the studied variables are independent, the following general equation was considered [Eq. (4)] [11]:

$$u_c = \sqrt{\sum_j \left(\frac{\partial c}{\partial j} \right)^2 u_j^2} \quad (6)$$

where $j = A_O, m_{PDC}, \text{Pur}, M_{PDC}, V_x, V_{2(\text{spl})}, V_{2(\text{blk})}, V_{1(\text{spl})}, V_{1(\text{blk})}, V_{3(\text{blk})}, V_{3(\text{spl})}, V_A, V_B, f_{DE}$ and f_{SS} . Table 1 represents the partial derivatives of the measurement function [Eq. (4)] considering all input quantities, j . The developed algorithm is presented, as [electronic supplementary material](#), in an MS-Excel file (version 2007; UPL sheet) which can be used to follow the performed calculations or to perform other uncertainty evaluations once it is updated with specific data.

2.4.5.2. Kragten method. The numerical combination of the standard uncertainties associated with the input quantities was performed in an Excel spreadsheet (MS-Excel) as described in various guides and papers [12,13]. The performed calculations are presented, as [electronic supplementary material](#), in an Excel file (version 2007; Kragten sheet).



Rep. – repeatability; Tol. – calibration component; Temp. – temperature effect;

ξ – COD in wastewater samples estimated by ISO 6060:1989 standard.

Fig. 2. Schematic representation of the identified sources of uncertainty.

Table 1
Partial derivatives of the input quantities for the measurement function required for measurement uncertainty combination by the uncertainty propagation law.

j	$\frac{\partial c}{\partial j}$	j	$\frac{\partial c}{\partial j}$
A_O	c/A_O	$V_{3(\text{blk})}$	$(\alpha V_A) / (V_B V_{1(\text{blk})})$
m_{PDC}	c/m_{PDC}	$V_{3(\text{spl})}$	$(-\alpha V_A) / (V_B V_{1(\text{spl})})$
P_{ur}	c/P_{ur}	$V_{1(\text{spl})}$	$[-\alpha / (V_{1(\text{spl})})^2 (V_{2(\text{spl})} - (V_A V_{3(\text{spl})}) / V_B)]$
M_{PDC}	$-c/M_{\text{PDC}}$	V_A	β / V_B
V_x	$-c/V_x$	V_B	$-(\beta V_A) / (V_B)^2$
$V_{2(\text{spl})}$	$\alpha / V_{1(\text{spl})}$	f_{DE}	c/f_{DE}
$V_{2(\text{blk})}$	$-\alpha / V_{1(\text{blk})}$	f_{SS}	c/f_{SS}
$V_{1(\text{blk})}$	$\left[\alpha / (V_{1(\text{blk})})^2 \right] [V_{2(\text{blk})} - (V_A V_{3(\text{blk})}) / V_B]$		
$\alpha = (3 A_O m_{\text{PDC}} P_{\text{ur}} / M_{\text{PDC}} V_x) f_{\text{DE}} f_{\text{SS}}$			$\beta = \alpha \left[(V_{3(\text{blk})} / V_{1(\text{blk})}) - (V_{3(\text{spl})} / V_{1(\text{spl})}) \right]$

2.4.6. Expansion of the combined standard uncertainty

The combined standard uncertainty, u_c , was multiplied by a coverage factor, k , of 2 to estimate the expanded uncertainty U_c ($U_c = 2u_c$) for a confidence level of approximately 95%.

2.4.7. Review of the uncertainty budget

The review of the uncertainty budget is based on the calculation of the percentage contribution of the individual components, P_j , estimated by Eq. (7).

$$P_j = \frac{\left(\frac{\partial c}{\partial j}\right)^2 u_j^2}{u_c^2} \quad (7)$$

The balance of the uncertainty components can be used to detect mistakes on the performed calculations and to define a strategy for cost or uncertainty magnitude reduction. The Kragten method estimates P_j numerically.

2.4.8. Evaluation of the magnitude of the estimated measurement uncertainty

This stage involves the comparison of the relative or absolute expanded measurement uncertainty with the respective target value (Section 3.1).

3. Experimental

3.1. Material and reagents

Analytical grade reagents were used. Blank tests allowed checking and correcting any sources of contamination. Contaminations were kept at negligible level. Equipment met ISO6060:1989 standard [5] requirements. A and AS class volumetric material and a calibrated analytical balance were used for relevant volumetric and gravimetric steps.

3.2. Validation of the measurement procedure

The validation of the measurement procedure was based on the analysis of two PHP control standards (COD – CStd1: $29.97 \pm 0.36 \text{ mg O}_2 \text{ L}^{-1}$ and CStd2: $499.6 \pm 1.2 \text{ mg O}_2 \text{ L}^{-1}$) in repeatability and/or intermediate precision conditions, and in the analysis of wastewater samples in repeatability conditions. The studied lower concentration ($\sim 30 \text{ mg O}_2 \text{ L}^{-1}$) corresponds to the DL. The repeatability estimated for COD values of CStd2 and wastewater samples was checked for equivalence by performing an *F*-test for a confidence level of 99%.

The repeatability coefficient of variation, s'_r , estimated from 18 duplicate analysis of CStd2 is 1.37% (i.e., below 5%). The repeatability coefficient of variation, $s'_{r(\text{ww})}$, estimated from the relative difference of duplicate measurements of wastewater samples with COD values ranging from 46 to 89 or 91 to 293 $\text{mg O}_2 \text{ L}^{-1}$ is 10.0%

or 6.74%, respectively and was estimated from 14 or 19 duplicate analysis, respectively. The repeatability coefficient of variation for COD values ranging from 748 to 1452 $\text{mg O}_2 \text{ L}^{-1}$, estimated from 31 duplicate tests involving a sample aliquot of 2 mL (instead of 10 mL), is 3.65%. Since the absolute repeatability standard deviation, $s_{r(\text{ww})}$, is constant between 46 and 293 $\text{mg O}_2 \text{ L}^{-1}$ and $s'_{r(\text{ww})}$ decreases for increasing concentrations, it was assumed that, between 30 and 293 $\text{mg O}_2 \text{ L}^{-1}$, $s_{r(\text{ww})}$ is equal to 7.54 mg L^{-1} and, above this concentration level, $s'_{r(\text{ww})}$ is, by excess, 6.74%. The difference between measurements repeatability of PHP standard and wastewater samples is attributed to the sample heterogeneity responsible for subsampling uncertainty. The magnitude of the subsampling uncertainty is assessed together with the other uncertainty components having the target measurement uncertainty in mind.

The coefficient of variation of the intermediate precision, $s'_{\text{IP}(\text{ww})}$ at $\sim 500 \text{ mg O}_2 \text{ L}^{-1}$ (CStd2), estimated from 47 tests performed along 48 months, is 2.61%. The coefficient of variation of the intermediate precision at $\sim 30 \text{ mg O}_2 \text{ L}^{-1}$ (CStd1), estimated from 24 tests performed along 10 months, is 22.5%, proving that the DL is larger than the LOD.

No relevant systematic effects at the analysis of CStd1 and CStd2, in repeatability or intermediate precision conditions, were observed from the comparison of the mean with ideal 100% analyte apparent recovery [22] taking into account the standard uncertainty associated with the mean apparent recovery [23].

Completing of the measurement procedure validation, the evaluation of the measurement uncertainty is described in the following section.

3.3. Evaluation of the measurement uncertainty

The $s'_{r(\text{ww})}$ observed for wastewater samples with COD values larger than 293 $\text{mg O}_2 \text{ L}^{-1}$ is statistically larger than the s'_r being estimated a u'_{SS} of 6.60%, by difference $[u'_{\text{SS}} = \sqrt{(s'_{r(\text{ww})})^2 - (s'_r)^2}]$, for COD values between 293 and 500 $\text{mg O}_2 \text{ L}^{-1}$ associated with sample aliquots of 10 mL. For COD values ranging from 30 to 293 $\text{mg O}_2 \text{ L}^{-1}$, $s_{r(\text{ww})}$ is not statistically larger than s_r . However, since there is a chance of 1% of having a Type I error [24] in the *F*-test, it was estimated a u_{SS} value of 3.15 $\text{mg O}_2 \text{ L}^{-1}$ by difference between s_r and $s_{r(\text{ww})}$ for this range.

The standard uncertainty associated with f_{DE} was estimated by difference from the intermediate precision, s_{IP} , estimated from the analysis of PHP control standards CStd1 or CStd2 and the respective u_{Inc} [Eq. (5)]. The u_{Inc} was estimated excluding u_{SS} , u_{pur} and the balance calibration component of $u_{m_{\text{PDC}}}$ not randomized in s_{IP} . It was concluded that although s_{IP} is not statistically larger than u_{Inc} for CStd1, $u'_{f_{\text{DE}}}$ estimated from Eq. (5) is 4.634% and 2.410% for CStd1 and CStd2 respectively. Since $u'_{f_{\text{DE}}}$ is expected to decrease

exponentially with the concentration, it was estimated by excess considering the linear relation: ($u'_{f_{DE}} = 0.04776 - 0.00004732c$)

The quantified sources of uncertainty were combined either by the uncertainty propagation law (UPL) or the numerical Kragten method (NKM). The relative deviations between standard uncertainties estimated by both uncertainty combination procedures are negligible, being smaller or equal to $5 \times 10^{-4}\%$. The equivalence of performed estimations confirms the validity of the measurement function linearity assumption of both UPL and NKM. This assumption was further tested for NKM by estimating the sensitivity coefficients after either the addition or subtraction of the standard uncertainty to the respective input quantity [13]. This change only produces relative deviations smaller or equal to $2 \times 10^{-4}\%$.

For concentrations between 30 and 500 mg O₂ L⁻¹, either the absolute expanded uncertainty is smaller than the $U_{Tg}(HS)$ (Eq. (3)) or the relative expanded uncertainty [$U'_{Tg}(HS)$] is smaller than 20%, being fit for the indented use. Fig. 3 presents the comparison of the estimated (U) and target measurement uncertainty [$U_{Tg}(HS)$]. According to the developed metrological model, supported on approximations of the variation of u_{SS} and $u_{f_{DE}}$ with the COD value, the absolute expanded uncertainty increases with concentration from 12 to 71 mg O₂ L⁻¹.

Fig. 4 presents the percentage contribution (P_j) of the various uncertainty components for a COD value of 125 mg O₂ L⁻¹ (the legal

limit) [7]. It can be observed that $u_{f_{DE}}$ is the major uncertainty component responsible for 43% of the global uncertainty. The following uncertainty components, in terms of relevance, are u_{SS} , $u_{V_{3(blk)}}$ and $u_{V_{3(spl)}}$ responsible for 15–16% of the global uncertainty. The other uncertainty components are negligible since they are smaller than 1/5 of the major one.

Fig. 3 presents the variation of the percentage contribution (P_j) of the major uncertainty components and of the absolute expanded uncertainty (U) between COD values of 30 and 500 mg O₂ L⁻¹.

The percentage contribution of $u_{V_{2(blk)}}$ and $u_{V_{2(spl)}}$, and of $u_{V_{3(blk)}}$ and $u_{V_{3(spl)}}$ are equivalent and consistently decrease with the COD value. The percentage contribution of $u_{f_{SS}}$ and $u_{f_{DE}}$ have a minimum and a maximum near 250 mg O₂ L⁻¹ respectively due to the proposed model of the variation of u_{SS} and $u_{f_{DE}}$ with the COD value. The u_{SS} clearly dominates the uncertainty budget for COD values above 350 mg O₂ L⁻¹. This component depends on the heterogeneity of the COD value of the wastewater samples and cannot be extrapolated to different types of wastewaters.

For COD values near the DL, the measurement uncertainty can only be minimized if u_{SS} , $u_{V_{3(blk)}}$ and $u_{V_{3(spl)}}$ are simultaneously reduced. The u_{SS} can be reduced by increasing sample aliquot. The increase of $u_{V_{1(spl)}}$ should not affect significantly the reagent proportions that would affect the oxidation efficiency. Increasing

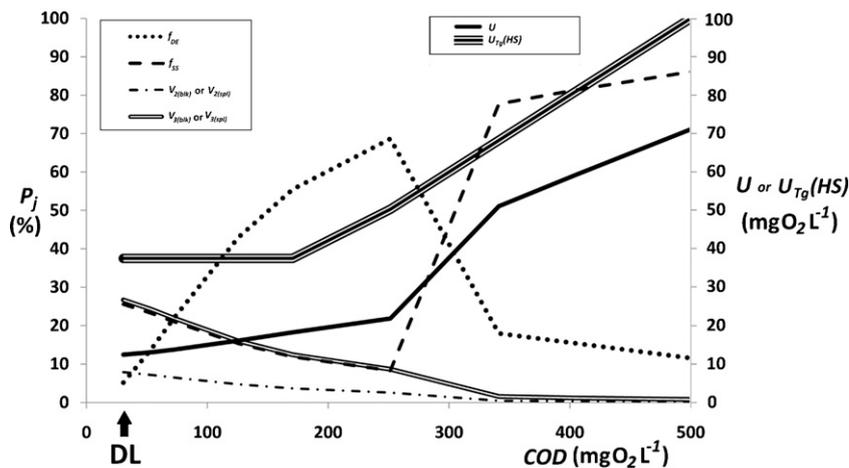


Fig. 3. Variation of the percentage contribution, P_j , of the major uncertainty components, of the measurement expanded uncertainty (U) and of the target measurement expanded uncertainty [$U_{Tg}(HS)$] with the COD value.

	P_j (%)
A_O	4.35E-06
f_{DE}	43.0
f_{SS}	15.3
m_{PDC}	0.0361
M_{PDC}	7.70E-07
Pur	0.0514
$V_{1(blk)}$	0.00812
$V_{1(spl)}$	0.0903
$V_{2(blk)}$	4.74
$V_{2(spl)}$	4.74
$V_{3(blk)}$	16.0
$V_{3(spl)}$	15.9
V_A	0.0403
V_B	0.0741
V_x	0.00692
Total:	100

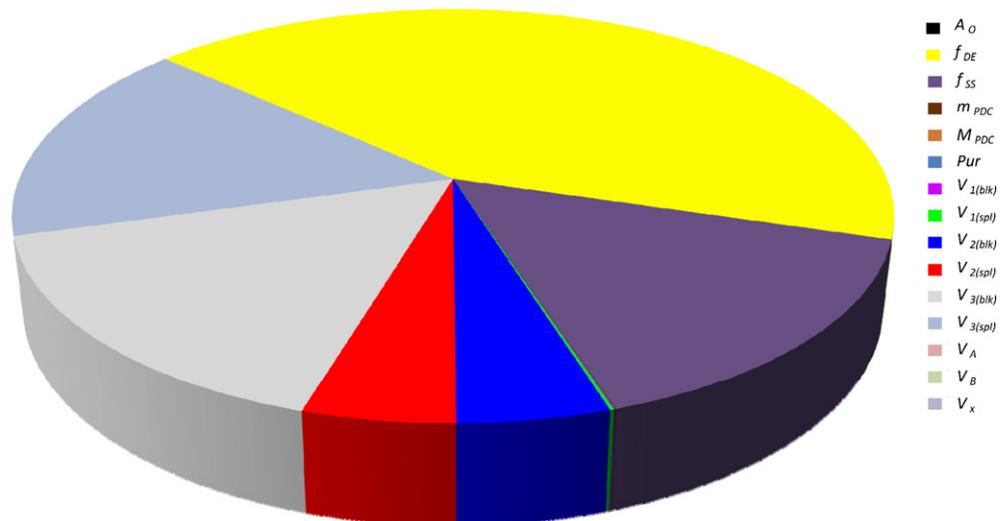


Fig. 4. Percentage contribution, P_j , of the uncertainty components for a COD value of 125 mg O₂ L⁻¹ (legal limit) [7].

sample aliquot to 20 mL, after sample dilution of 25–50 mL, would not affect the LOD if dilution is performed with a negligible uncertainty. This low uncertainty can be easily achieved by using class A volumetric material. The extra 10 mL of the digestion mixture should not affect the oxidation efficiency significantly.

The $u_{V_{3(\text{blk})}}$ and $u_{V_{3(\text{spl})}}$ components can be decreased by reducing the associated standard uncertainty and/or sensitivity coefficient. The standard uncertainty can be reduced by using a calibrated burette, where the mean error is measured for the used burette, instead of using a burette from a calibrated lot for which only some other burettes are metrologically checked and associated with a tolerance of the nominal value for the lot. This would reduce the calibration uncertainty component. A burette with a smaller tube diameter would be associated with a smaller repeatability uncertainty. The sensitivity coefficients associated with $u_{V_{3(\text{blk})}}$ and $u_{V_{3(\text{spl})}}$ can be reduced by reducing the concentration of the PDC solution (Solution A), that would decrease “ α ” (See Table 1) by decreasing (m_{PDC}/V_x) ratio, together with the reduction of the concentration of the FAS solution (Solution C) that would guarantee the reduction of the ratio (V_A/V_B). The increase of the blank and sample aliquot ($V_{1(\text{blk})}$ and $V_{1(\text{spl})}$) also contributes to $u_{V_{3(\text{blk})}}$ and $u_{V_{3(\text{spl})}}$ components reduction like occurred for u_{SS} .

Since $u_{m_{\text{PDC}}}$ and u_{pur} are not relevant uncertainty components, a cheaper balance and PDC reagent with higher purity uncertainty can be used without affecting significantly the measurement uncertainty.

The reduction of the uncertainty associated with measurements near DL can be useful for the control of the performance of wastewater treatment facilities focused in ensuring minimal contamination of the environment.

For samples with COD values near $125 \text{ mg O}_2 \text{ L}^{-1}$, a reduction of the $u_{f_{\text{DE}}}$ would need to be performed to guarantee a significant reduction of the expanded uncertainty. The reduction of the uncertainty associated with the control standard CStd1 COD value should be performed since this is clearly the major source of uncertainty in $u_{f_{\text{DE}}}$ at this COD value. This can be easily achieved by weighing a larger portion of PHP in CStd1 preparation.

For COD values larger than $350 \text{ mg O}_2 \text{ L}^{-1}$, the subsampling uncertainty dominates the uncertainty budget. Reduction of this component was previously discussed.

3.4. External experimental validation

The developed model for the measurement performance was externally validated through the determination of COD values in wastewaters samples from three proficiency tests promoted by RELACRE (Portuguese Association of Accredited Laboratories) between June 2008 and November 2009 [25–27]. Since proficiency test samples are homogeneous, u_{SS} is considered negligible for

Table 2
Results from the participation in three proficiency tests, promoted by RELACRE [25–27], for the external assessment of the measurement performance model.

PT reference	Result ($\text{mg O}_2 \text{ L}^{-1}$)	
	Reported result ^{*†} ($a \pm U_a$)	Reference value [*] ($b \pm U_b$)
AR2008-Junho	406 \pm 26	405 \pm 60
	404 \pm 26	
AR2008-Outubro	309 \pm 23	339 \pm 30
	314 \pm 23	
AR2009-Novembro	475 \pm 26	493 \pm 40
	492 \pm 26	

^{*} Uncertainty for a confidence level of approximately 95% estimated considering a coverage factor of 2.

[†] Duplicate measurements.

these analysis. Table 2 presents the reported measurement results and the reference values for the tests.

The reference value, reported with uncertainty, was estimated by a reference laboratory. The reported and reference results are compatible [2] since the amplitude of the measured quantity values are smaller than the respective expanded uncertainty of the difference considering a coverage factor of 2 for a confidence level of approximately 95%. Eq. (8) presents the assessment criteria for the first replicate measurement of AR2008-Junho:

$$\{|a - b| = |406 - 405| = 1\} \\ \leq \left\{ 26 = 2\sqrt{\left(\frac{26}{2}\right)^2 + \left(\frac{60}{2}\right)^2} = 2\sqrt{\left(\frac{U_a}{2}\right)^2 + \left(\frac{U_b}{2}\right)^2} \right\} \quad (8)$$

The uncertainty associated with the mean result of replicate measurements should include the reduction of the uncertainty components associated with replicated analytical steps or effects considering the standard deviation of the mean [28]. This work does not discuss the involved algorithm in detail.

4. Conclusion

The Differential Approach for the evaluation of the measurement uncertainty allowed the development of a detailed model for the performance of the determination of COD in wastewater samples. The uncertainty propagation law and the numerical Kragten method were successfully applied to combine the quantified uncertainty components, producing equivalent uncertainty estimations, since the assumption of linear variation of COD value with input quantities uncertainty is valid. The developed model allowed understating the way percentage contributions of the uncertainty components and expanded uncertainty magnitude vary with the COD value. The quantified measurement uncertainties are fit for the assessment of wastewater compliance with Directive 91/271/EEC [7]. The model for the sensitivity coefficients estimated by the uncertainty propagation law allowed the development of a strategy for the expanded uncertainty magnitude and cost reduction. This work illustrates the usefulness of valid uncertainty propagation law models for uncertainty optimization. The developed measurement performance model was successfully validated through the analysis of wastewater samples from three proficiency tests.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.aca.2011.05.026.

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