Detailed Evaluation of the Uncertainty for the Determination of Chemical Oxygen Demand in Wastewater

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INTRODUCTION

Chemical oxygen demand (COD) is one of the most relevant chemical parameters for the characterisation of wastewaters before (influent) and after (effluent) treatment in order to monitor its quality and compliance with the law.

Reliable COD values are important for protecting the environment and to guarantee the economical sustainability of the treatment facility.

In this work the potassium dichromate open reflux method was validated by studying the parameters of its quantitative performance. Models for the metrological performance of the determination of COD in wastewater were developed aiming at producing detailed estimates of the uncertainty associated with results obtained in a Portuguese Wastewater Treatment Plant.

METHODOLOGY

The determination of COD in wastewaters was determined according to the standardized method ISO 6060:1989, that consists on the steps described in Fig.1:

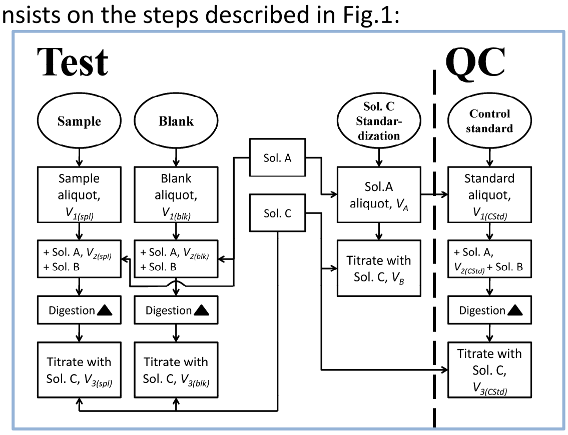

Fig. 1. Schematic description of the measurement procedure including the test quality control (QC).

The Fig. 1 shows the description of the measurement procedure where Solution A is 0.04 mol L^{-1} $K_2Cr_2O_7$; 80.0 g L^{-1} $HgSO_4$; 1.80 mol L^{-1} H_2SO_4; Solution B: 10.0 g L^{-1} $AgSO_4$; 17.4 mol L^{-1} H_2SO_4 and Solution C (FAS): 0.12 mol L^{-1} $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$; 0.360 mol L^{-1} H_2SO_4. Fig. 2 represents the identifies sources of uncertainty.

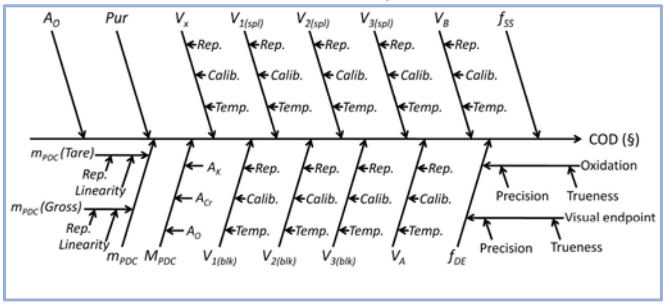

Fig. 2. Cause and effects diagram for determination of chemical oxygen demand, where **§** is COD in wastewater samples; **Rep.** – repeatability; **Temp.** – temperature effect.

$$C=\left\{\left(\frac{3\cdot A(O)\cdot m_{K_2Cr_2O_7}\cdot Pur}{M(K_2Cr_2O_7)\cdot V_X}\right)\cdot\left[\left(\frac{V_{2(spl)}}{V_{1(spl)}}-\frac{V_{2(blk)}}{V_{1(blk)}}\right)+\left(\frac{V_{3(blk)}}{V_{1(blk)}}-\frac{V_{3(spl)}}{V_{1(spl)}}\right)\cdot\frac{V_A}{V_B}\right]\right\}\cdot f_{DE}\cdot f_{SS}$$

Eq. 1. The measurement function used to estimate the concentration *C* in COD (mg O_2.L^{-1}) in wastewater samples. Where A_O – molar mass of the oxygen; *Pur* – purity of Potassium dicromate (PDC) reagent; $V_{1(blk)}$ – vol. of blank test aliquot; $V_{1(spl)}$ – vol. of sample aliquot; $V_{2(blk)}$ – vol. of Sol. A used for blank test aliquot oxidation; $V_{2(spl)}$ – vol. of Sol. A used for sample aliquot oxidation; $V_{3(blk)}$ – vol. of Sol. C used to titrate digested and diluted blank test aliquot; $V_{3(spl)}$ – vol. of Sol. C used to titrate digested and diluted sample aliquot; V_A – aliquot of Sol. A titrated with Sol. C to estimate the FAS concentration; V_B – vol. of Sol. C used to titrate V_A from Sol. A; V_X – vol. of Sol. A used to dilute m_{PDC}; f_{DE} – factor for the combined efficiency of oxidation and digestion, and endpoint detection steps for blank test, sample test and FAS standardisation; f_{SS} – factor for subsampling step.

RESULTS

Fig. 3 presents the comparison of the estimated (U) and target expanded uncertainty for the analysis of heterogeneous wastewater samples [U_{Tg}(HS)] measurement uncertainty.

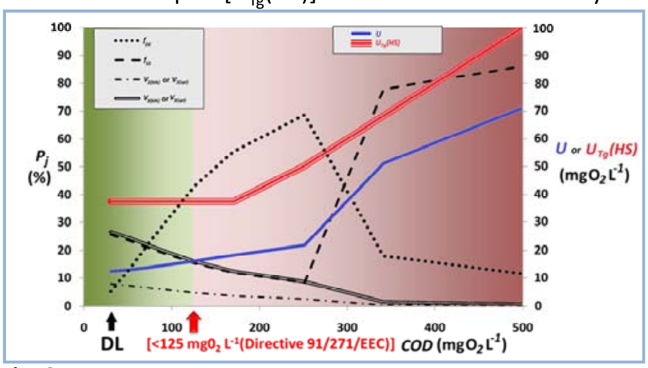

Fig. 3. Variation of the percentage contribution, Pj , of the major uncertainty components, of the measurement expanded uncertainty (U) and of the target measurement expanded uncertainty [U_{Tg}(HS)] with the COD value.

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 are presented in Fig. 4.

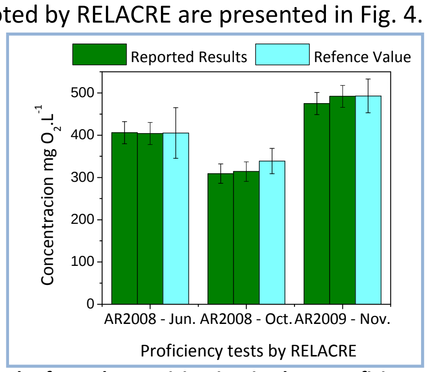

Fig. 4. Results from the participation in three proficiency tests, promoted by RELACRE (Portuguese Association of Accredited Laboratories).

CONCLUSIONS

Results show that the model estimated by the Differential Approach and uncertainty propagation law :

1. allowed understating the way percentage contributions of the uncertainty components and expanded uncertainty magnitude vary with the COD value.
2. was successfully validated through the analysis of wastewater samples from three proficiency tests.
3. allowed the development of a strategy for the expanded uncertainty magnitude and cost reduction.

The experimental part of this work was performed in the "Empresa concessionária dos Sistemas de Abastecimento de Água e de Saneamento do Concelho de Setúbal".