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CHEMICAL OXYGEN DEMAND - EVALUATION OF INTERFERENCES AND MEASUREMENT UNCERTAINTY

ABSTRACT

The determination of the Chemical Oxygen Demand (COD) in industrial wastewaters requires a detailed study of the presence of interfering species that can significantly affect the estimation of the target oxidability of the sample. Whenever, the oxidability of the organic matter of the wastewater is the goal of the analysis, the elimination of oxidants from the matrix is determinant. The elimination of interferences is performed during method development and subsequently validated through a detailed study of the measurement performance.

The reliability of results depends on an adequate definition of the measurements traceability and on a proper validation of the measurement procedure that includes the evaluation of the measurement uncertainty. In this work, the uncertainty was estimated using the top-down approach based on intralaboratory validation data, namely the measurement trueness and precision [1].

Results show that the measurement, including the evaluated uncertainty, is fit for the assessment of the compliance of industrial wastewaters with the legislation [2].

This work highlights the need for a detailed understanding of the sample matrix and a careful measurement procedure development before measurement validation and uncertainty evaluation.

INTRODUCTION

Chemical Oxygen Demand (COD) of a water is defined as the amount of oxygen equivalent to potassium dichromate which reacts under specific conditions with the oxidable matter in the sample: 1 mol $K_2Cr_2O_7$ ↔ 1,5 mol O_2. However the application of this relation requires the elimination of other oxidants from the matrix, e.g. hydrogen peroxide, H_2O_2. [3]

Chloride ions are a common know interference.

The measurement results traceability was defined considering available references for COD determination in wastewaters.

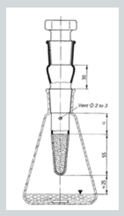
The measurement procedure validation involved checking the most relevant performance parameters for its fitness for the intended use.

The uncertainty was quantified using the top-down approach based on in-house validation data supported on the measurement precision and trueness estimated in intermediate precision conditions.

MATERIAL AND METHODS

Potassium dichromate method in open reflux conditions.

Studied interferences:



• **Chloride ion, Cl^-**

HCl absorber with calcium hydroxide- DIN 38 409-H41-2.

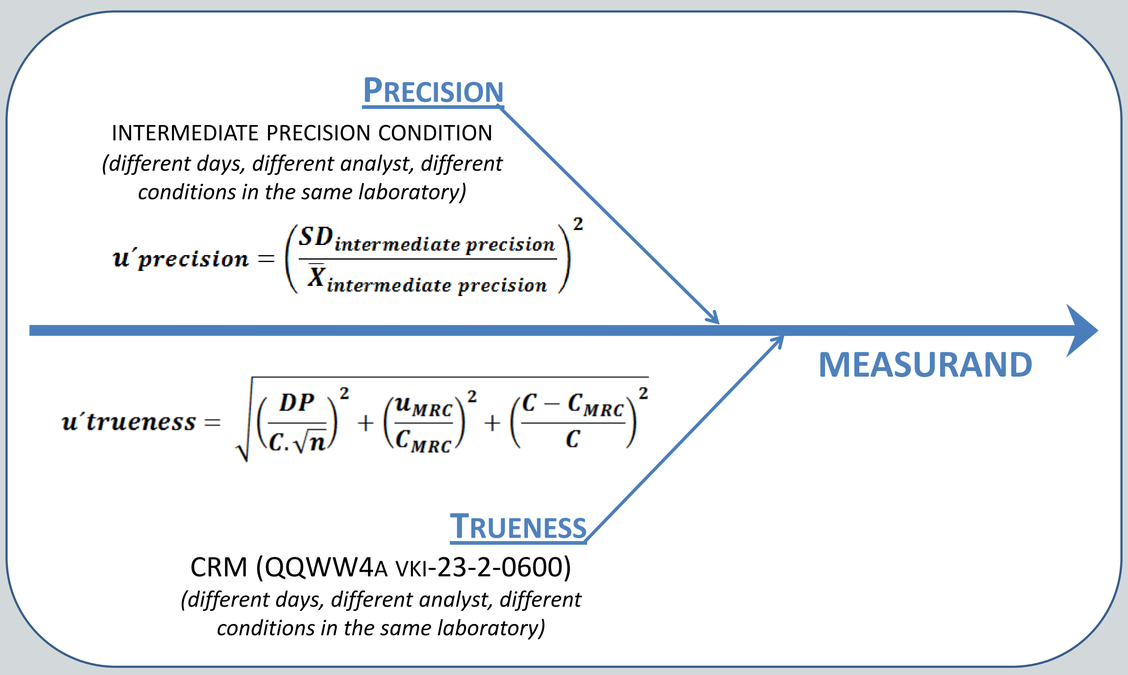
Residual chloride ions removed by mercury (II) chloride.

• **Hydrogen peroxide, H_2O_2**

Positive interference removed by pre-treatment of the sample with sodium sulfite.

Method validation:

- Analytical limits;
- Working range;
- Robustness;
- Accuracy (precision and trueness) . [4]

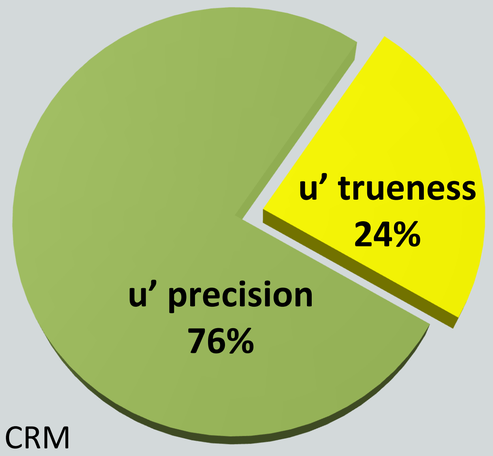


RESULTS

	PRECISION	TRUENESS
		QQWW4A, VKI-23-2-0600
NUMBER OF RESULTS (N)	15	10
AVERAGE ($\overline{X}$)	28.0 mg O_2/L	53.2 mg O_2/L
STANDARD DEVIATION (SD)	2.8 mg O_2/L	1.8 mg O_2/L
RELATIVE STANDARD DEVIATION (RSD)	10.1%	3.5%
CERTIFIED VALUE	---	50.5 mg O_2/L
CONFIDENCE INTERVAL	---	(49.0– 51.9) mg O_2/L

$$u' = \sqrt{u'_{precision}{}^2 + u'_{trueness}{}^2}$$

INTERMEDIATE PRECISION	$u'_{precision}$	0.1010
TRUENESS	$u'_{trueness}$	0.0565
STANDARD MEASUREMENT UNCERTAINTY	u'	0.1158
EXPANDED MEASUREMENT UNCERTAINTY (k= 2, with a confidence level of ≈ 95%)	U'	**23 %**



Verification of uncertainty estimation with the CRM (this comparison is only indicative):

$$\frac{(\overline{X}_{lab} - X_{certifiedvalue})}{U_{lab}} = 0.22 < 1$$

CONCLUSIONS

The developed measurement procedure proved to efficiently remove inferences of chloride and hydrogen peroxide.

The measurement performance observed during method validation proved the adequacy of the measurement procedure for its intended use. The RSD of replicated measurements obtained in intermediate precision conditions is smaller than a target value of 25% and the mean relative measurement error is smaller than 10%. The measurement method also proved to be fit for the routine evaluation of wastewaters compliance with legislated COD value considering the magnitude of the measurement uncertainty. The developed model for uncertainty quantification identified precision component has the major one, responsible for 76% of the total uncertainty.

REFERENCES:

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4. IPAC, 2007, OGC 007 - Guia para a quantificação de incerteza em ensaios químicos.