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Comparing EN 17075 and VaMPIS approaches for *in situ* continuous monitoring of free chlorine in drinking water

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***Abstract* – The performances of commercially available on-line analysers for monitoring free chlorine in water was carried out following protocols described in EN 17075 standard. Measurement uncertainty was estimated under controlled conditions considering bias, repeatability, and deviation from linearity as well as key influential factors for amperometric chlorine measurement: pH and temperature. The performance under real conditions was estimated as the percentile 90 of the differences between the free chlorine concentration measured by the on-line analyser, and the reference value obtained using the DPD (N,N-diethyl-1,4-phenylenediamine) method with a portable spectrophotometer, in accordance with EN 17075 standard.**

The VaMPIS (Validation of Measurement Procedures that Include Sampling) simultaneous approach using the duplicate method was applied to data obtained in real conditions from two on-line amperometric analysers

The measurement uncertainties estimated by both approaches agreed well, considering the confidence intervals of each of the estimates.

I. INTRODUCTION

Chlorine is one of the most common products used for the disinfection of drinking water worldwide. Real-time monitoring has long demonstrated its usefulness, providing benefits such as controlling the level of chlorine addition to ensure that the residual concentration is maintained constantly within acceptable limits.

EN 17075 [1] standard describes requirement and protocols for evaluating the performances of continuous and portable measuring devices for monitoring different types of water, including continental fresh water, marine water, drinking water, urban or industrial wastewater, but also the monitoring of industrial processes (process water).

Performance tests according to this standard include tests carried out under controlled conditions in the laboratory to assess metrological characteristics as well as influent factors. Then a 3-month minimum in real conditions field trial is required to demonstrate that the performances evaluated under controlled laboratory conditions are maintained under operational conditions representative of a given application.

The recently published Eurachem VaMPIS guidance [2] includes the case of *in situ* measurements. Measurements that are made *in situ* do not require the extraction of a physical sample but involve placing some sort of measurement or sensing device at the original location of the sampling target. The effective integration of the sampling and analytical steps in an *in situ* measurement procedure means that an integrated approach for validation of the whole measurement procedure is applicable.

II. EN 17075 STANDARD - ASSESSING THE PERFORMANCES OF CLHORINE ANALYSERS

The performances of two amperometric on-line analysers with 3 electrodes covered with a membrane, and using gel to compensate for pH, were assessed under controlled conditions following protocols described in details by Guigues et al., 2022 [3] and in accordance with EN 17075 [1]. Repeatability, bias, deviation from linearity and limit of quantification (LOQ) were evaluated over the range 0.2 – 2 mg/L of free chlorine as follows:

- Step 1: A known volume of a commercially 2.6% bleach (sodium hypochlorite) stock solution is added to tap water. The concentration of free chlorine in then measured simultaneously by the analysers and using the reference titrimetric method (EN ISO 7393-1 [4]).
- Step 2: Step 1 is repeated 4 more times to get 5 test points covering for the entire measuring range.
- Step 3: Dilution with increasing quantities of tap water with low content of free chlorine is performed to achieve the same 5 test points but in descending order of concentration.

The procedure is then repeated twice more.

The influence of temperature and pH was also included, considering that drinking water pH is typically in between pH 7 and pH 8, and that amperometric sensors directly measure hypochlorous acid (HOCl) which has a temperature dependent dissociation constant (pKa = 7.5 at 25 °C).

Performances under controlled conditions for the two amperometric on-line analysers are summarize in Table 1.

Table 1. Performances of two on-line free chlorine analysers

Performances	Analyser A	Analyser B
Repeatability	2.8%	3.4%
Bias	1.8%	9.4%
Deviation from linearity	1.1%	1.4%
LOQ (mg/L)	0.12	0.25
pH influence (6.5-8.5)	7.9%	2.6%
Temperature influence (10-25°C)	6.0%	5.1%
Expanded measurement uncertainty U (k=2)	12%	15%

The error under real conditions was estimated during a 7-month field trial carried out from mid-May to mid-December 2019 at the outlet of a Drinking Water Treatment Plant operated by Veolia (Annet sur Marne, 40 km east of Paris, France). For that purpose, 56 comparative measurements were performed with both on-line free chlorine analysers and a reference method using the DPD (N,N-diethyl-1,4-phenylenediamine) colorimetric method (EN ISO 7393-2 [5]) and a portable spectrophotometer (NOVA 60, Merck).

To calculate the error under real conditions on site, first the difference between the free chlorine concentration measured by the on-line analyser and the reference value is calculated. Then, the 90th percentile of the absolute differences is computed in accordance with EN 17075. Results are presented in Table 2 for both analysers.

Table 2. Error under real conditions for two on-line free chlorine analysers

Performances	Analyser A	Analyser B
90th percentile (free chlorine: 0.5–1.0 mg/L; Temperature: 15-25°C; pH: 7.4– 7.8)	10%	15%

The 90th percentile is not different from the expanded measurement uncertainty estimated under controlled conditions for analyser B. The greater influence of pH for analyser A together with the more stable pH in real conditions can explain that the 90th percentile is lower than the expanded measurement uncertainty estimated under controlled conditions.

III. VAMPIS APPROACH TO VALIDATE CLHORINE ANALYSERS

During the 7-month field trial, duplicate measurements were carried out on a regular basis with both on-line analysers and the reference method. As it was possible to make some standard additions in a close test bench, the measuring range of the 26 duplicates was 0.5-2 mg/L.

Thus, the simultaneous VaMPIS approach using the duplicate method with a simplified balance design could be applied [2].

A. Analysis of Variance

Analysis of Variance (ANOVA) using RANOVA4 software [6] was used to estimate the random contribution to the measurement uncertainty for each free chlorine analyser (Table 3 and Table 4).

Table 3. Output of RANOVA4: Robust ANOVA for Analyser A

Mean	***0.9872***	Targets (*n*): ***26***	
Total SD (std d	***0.41155***		
	Btn Target		Measure
SD (or *u*)	***0.41057***		***0.028292***
% of total varia	***99.53***		***0.47***
U' (Exp rel uncertainty *k*=2)			***5.73***
Estimated exp rel uncertainty) 95% confidence (*k* = 2.05)			***5.88***

Table 4. Output of RANOVA4: Robust ANOVA for Analyser B

Mean	***1.0392***	Targets (*n*): ***26***	
Total SD (std d	***0.54437***		
	Btn Target		Measure
SD (or *u*)	***0.5426***		***0.043835***
% of total varia	***99.35***		***0.65***
U' (Exp rel uncertainty *k*=2)			***8.44***
Estimated exp rel uncertainty) 95% confidence (*k* = 2.19)			***9.24***

If the bias estimated under controlled conditions in Table 1 is included then the expanded measurement uncertainty is 6.4% and 16% respectively for analyser A and analyser B (using U with a 95% confidence interval (i.e. k>2)).

B. Bias estimation from real samples

As for Example A.2 in the VaMPIS document [2], it is more realistic to estimate the bias by comparison of the *in situ* measurement values against the reference measurement values made *ex situ* on physical samples taken at the same time than using the bias estimated under controlled conditions (Table 1).

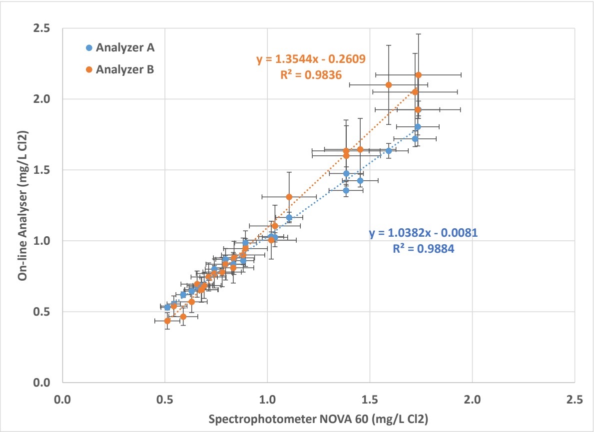

Fig.1. Relationship between free chlorine concentrations measured in situ by on-line analyser and ex situ using the reference method (NOVA 60). Excel LINEST function was used to establish the linear model. Error bars correspond to the expanded uncertainty (k=2) estimated according to EN 17075, without taking into account pH influence.

Fig.1 shows that analyser A is characterised by a slope (i.e. rotational bias) of 1.038 ± 0.022 allowing an overestimated of approximately 4% whereas Analyser B tends to over estimated free chlorine concentration by more than 35% (slope of 1.354 ± 0.036) over the range 0.2-2.0 mg/L. Both slopes are statistically different from unity (0.022/1.038 and 0.036/1.354 < $t_{24,5\%} = 2.06$)

In the case of analyser A, the intercept (i.e. translation bias) is not different statistically from zero (-0.008 ± 0.024, 0.024/0.008 > $t_{24,5\%} = 2.06$), whereas for analyser B, the intercept is statistically different from zero (-0.261 ± 0.037, 0.037/0.261 < $t_{24,5\%} = 2.06$).

The free chlorine concentration can be corrected for the rotational bias as follows:

[free chlorine] corrected = [free chlorine]in situ / slope (1)

The uncertainty of this correction is then respectively for analyser A and B 2.2% and 3.6%.

In the case of analyser B, the translational bias can be included as it is significantly different from zero.

[free chlorine] corrected = ([free chlorine]in situ – intercept)/ slope (2)

Then the expanded measurement uncertainty can be expressed using the following equation:

$$U_{\text{free chlorine}} = 2 \sqrt{(u_{\text{bias real samples}}^2 + u_{\text{RbosutANOVA}}^2)} \qquad (3)$$

The expanded measurement uncertainty is then 7.5% and 12% respectively for analyser A and analyser B.

An alternative way of estimating the measurement uncertainty based on real samples is to use the standard error Sey of the linear model using the excel function LINEST between the *in situ* free chlorine concentrations measured by on-line analyser and the DPD reference method, and without taking into account the associated uncertainties.

$$U_{\text{linear model}} = 2 * \text{Sey} / \text{robust mean} \qquad (4)$$

The calculation for each analyser are summarised in Table 3.

Table 3. LINEST standard error, robust mean, and uncertainty for analysers A and B using

Analyser	**Error Sey (mg/L)**	**Robust mean (mg/L)**	$U_{\text{linear model}}$
Analyser A	0.046	0.987	9.2%
Analyser B	0.071	1.039	14%

The expanded measurement uncertainty estimated using Robust ANOVA for the random contribution, and real samples under real conditions for the systematic contribution, instead of using the bias estimated under controlled conditions is similar for analyser B (16%) but much high for analyser A (11% versus 6.4 %).

IV. COMPARISON OF THE DIFFRENT APPROACHES

The comparison of the different approaches presented in this paper to estimate the measurement uncertainty of free chlorine in drinking water using on-line amperometric analysers is presented in Table 4.

It appears that there is some consistency between EN 17075 approaches and the LINEST standard error approach, with expanded uncertainty of 9.2% to 12 % for analyser A, and 14% to 15% for analyser B.

When using bias assessed under controlled conditions (pH of 7.6-7.8 and temperature of 22-23°C) then the expanded uncertainty for analyser A is underestimated, where as for analyser B, due to a large bias (9.4%) the expanded uncertainty is somehow similar to EN 17075 approaches and LINEST standard error approach.

If the bias is estimated with the slope of the linear regression between on-line analysers and reference values, then the expanded uncertainty is much lower for both analysers than the EN 17075 and LINEST approaches.

Table 4. Summary of the expanded relative uncertainty for analyser A and analyser B estimated using different methodologies

Methodology	**Expanded measurement uncertainty**	
	Analyser A	**Analyser B**
EN 17075 – controlled condition	12%	15%
EN 17075 – real conditions 90th percentile	10%	15%
RANOVA (random only)	5.9%	9.2%
RANOVA with bias assessed under controlled conditions	6.4%	16%
RANOVA with bias from real samples (slope of linear model)	7.5%	12%
LINEST standard error of real samples	9.2%	14%

Some of the apparent differences between these MU estimates might however not be statistically significant because of the confidence intervals of each of the estimates [7]. As an example, the confidence intervals of measurement uncertainty estimated with Robust ANOVA are respectively 4.9%-7.9% and 6.1%-13% for analysers A and B.

V. JUDGING THE FITNESS FOR PURPOSE

To judge the fitness for purpose, if the criteria is set to the expanded measurement uncertainty of the reference method, e.g. 12%, then only analyser A is fit for purpose, whichever methodology is used to estimate its expanded uncertainty.

However, if the target uncertainty is set to 20%, corresponding to the maximum 90th percentile obtained for eight on-line analysers [3], then both analysers are fit for purpose.

Finally, if the target uncertainty is defined so that the measurement uncertainty does not exceed 20% of the total variance over the range 0.1 – 2 mg/L free chlorine [2], which correspond to roughly 2.5 % of the total variance over the typical range of 0.1-0.7 mg/L of free chlorine at the outlet of drinking water treatment plants, then the target uncertainty is respectively 13% and 17% for analyser A and B. In that case both free chlorine analysers are fit for purpose.

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