![A.G.L.A.E. logo]

**A**ssociation **G**énérale des **L**aboratoires
d'**A**nalyses de l'**E**nvironnement

# TECHNICAL STUDY No.1

# Comparison between measurements of COD with classical method and with small scale sealed-tube method

**This document is delivered for information and is based on the results and the observations from A.G.L.A.E.'s interlaboratory proficiency testing schemes.**

**December 2013**

**Writers:**
Ronan Charpentier
Marie Le Gaillard

**AGLAE Association**
Parc des Pyramides
427 rue des Bourreliers
59320 Hallennes lez Haubourdin
FRANCE
☎ +33 (0)3 20 16 91 40
contact@association-aglae.fr
www.association-aglae.fr

In case of a divergence between the French and English versions of this document, the French version shall prevail.

## RESUME

Depuis 5 ans, A.G.L.A.E. organise des essais interlaboratoires sur des matrices de type eaux naturelles et eaux résiduaires pour les deux paramètres suivants : DCO (méthode classique) et ST-DCO (méthode petite échelle en tubes fermés). L'objectif de cette étude est de comparer ces deux méthodes à partir des résultats obtenus lors de ces essais interlaboratoires. Au total, 27 matériaux ont été analysés et pour chacun d'eux nous avons pu observer des écarts entre les résultats de mesure de ces deux techniques analytiques. En effet, sur eaux naturelles la DCO a tendance à donner des résultats plus élevés que l'analyse en ST-DCO alors que sur eaux résiduaires la tendance s'inverse. De même, il n'y a pas équivalence totale entre les valeurs de fidélité (coefficients de variation de reproductibilité et de répétabilité) des deux méthodes selon le type de matrice. Si la ST-DCO donne des résultats plus répétables et plus reproductibles que la DCO sur eaux naturelles, la fidélité des deux techniques devient similaire sur eaux résiduaires.

Les écarts observés semblent donc être liés au type de matrice utilisée pour les essais mais peuvent également être corrélés à d'autres facteurs tels que le taux de matières en suspension, la valeur de la demande chimique en oxygène et l'utilisation de méthodes de dosage différentes (influence du volume de prise d'essai et du mode de détection : photométrique, titrimétrique ou potentiométrique). Nous avons également retraité les données des essais en fonction de la marque de kit utilisé pour la mesure en ST-DCO mais cette étude n'a pas permis d'expliquer les écarts de fidélité et les écarts entre les résultats.

## ABSTRACT

For 5 years, A.G.L.A.E. has been organising interlaboratory testing schemes in natural waters and waste waters for the two following parameters: COD (classical method) and ST-COD (small scale sealed-tube method). The aim of this study is to compare the two methods based on the results which were obtained during these proficiency tests. In total 27 materials were analysed and for each one we could observe deviations between measurement results of the two analytical techniques. Indeed, in natural waters the COD tends to give higher results than the ST-COD analysis whereas in waste waters the tendency is reversed. In the same way, there is no complete equivalence between precision values (variation coefficients of reproducibility and repeatability) of both methods according to the type of matrix. If the ST-COD gives more repeatable and more reproducible results than COD in natural waters, the precision of both methods tends to be similar in waste waters.

The observed deviations seem to be related to the type of matrix used for the proficiency testing scheme but can also be correlated to other factors like the content in suspended matters, the value of the chemical oxygen demand and the use of different analytical modalities (influence of the volume of the test sample and the detection method: photometric, titrimetric or potentiometric). We also processed data from the proficiency tests according to the brand of the kit used for the measurement of ST-COD but this study did not enable to explain deviations between measurement results and precision deviations.

# INTRODUCTION

## Issue

Since 2009, we have organised interlaboratory testing schemes for the ST-COD (small scale sealed-tube method) in addition to the COD (classical method), in natural waters and in waste waters. During these tests, we could occasionally notice some deviations in the precision values and some differences between the laboratories' results for each method.

This technical study aims to compare the two methods thanks to the results obtained during our interlaboratory proficiency tests since 2009.

## DATA

### Relevant interlaboratory tests

We collected data from interlaboratory tests carried out in natural waters and in waste waters since 2009.
  - Interlaboratory tests in natural waters: **programme 1B**.
  - Interlaboratory tests in waste waters: **programme 2**.

In natural waters, 9 proficiency tests were carried out in which 15 materials were analysed by the participants. In waste waters, 12 proficiency tests were organised with a single sample to analyse for each one. All of them were carried out under the COFRAC[1] accreditation (the stability and the homogeneity of the materials were systematically checked).

The tables next pages describe the proficiency tests and gather data which were obtained for both types of matrices. Please note that the given precision values (consensus values, variation coefficients of reproducibility and repeatability) were calculated according to robust calculation algorithms.

### Description of the proficiency tests in waste waters

For each proficiency test, the participants received 2 bottles from the same batch and had to analyse them twice. The characteristics of the matrix are listed in the table 1:

| Proficiency test | Matrix | TSS (mg/L) | Number of participants | | Organism in charge of the sample preparation |
|---|---|---|---|---|---|
| | | | COD | ST-COD | |
| 09M2.1 | WW TP | 432 | 112 | 48 | S.I.A.A.P. |
| 09M2.2 | WW TP | 162 | 116 | 46 | |
| 09M2.3 | WW TP diluted 1:2 with decanted water | 131 | 108 | 52 | |
| 10M2.1 | WW TP | 212 | 106 | 51 | |
| 10M2.2 | WW TP | 160 | 109 | 66 | |
| 10M2.3 | decanted WW TP | 48 | 110 | 69 | |
| 11M2.1 | WW TP | 144 | 109 | 65 | |
| 11M2.2 | decanted WW TP | 46 | 106 | 68 | |
| 12M2.1 | WW TP | 240 | 111 | 76 | |
| 12M2.2 | WW TP | 198 | 107 | 78 | |
| 12M2.3 | WW TP diluted 2:3 with distribution water | 85 | 106 | 91 | |
| 13M2.1 | WW TP | 172 | 131 | 110 | |

TSS: total suspended solids
WW TP: waste water from treatment plant
Chloride concentration in the waste water: ~ 150 mg/L

<u>Table 1</u>: description of the proficiency tests in waste waters

---

[1] Comité Français d'Accréditation (French Accreditation Committee)

Note: in waste waters, more and more laboratories carry out analysis by ST-COD. This percentage increases from 30% in 2009 to 55% in 2013 (figure 1).
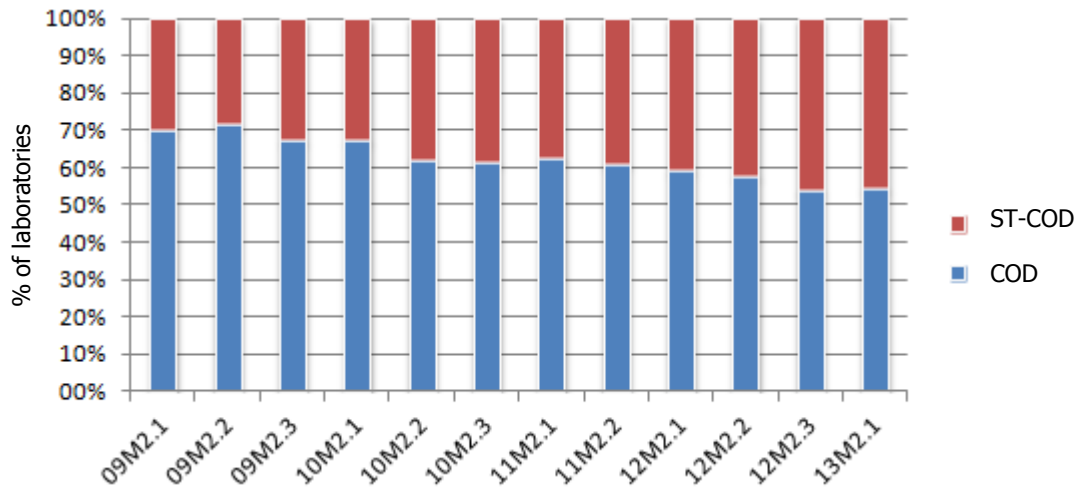


*Figure 1: use of COD and ST-COD methods for proficiency tests in waste waters*

## Obtained results in waste waters

The precision values (variation coefficients of reproducibility and repeatability) observed during these tests are as follow:

| Test | COD (mg of $O_2$/L) | | | ST-COD (mg of $O_2$/L) | | |
|------|-----------------|---------|---------|-----------------|---------|---------|
| | Consensus value | $CV_r$ (%) | $CV_R$ (%) | Consensus value | $CV_r$ (%) | $CV_R$ (%) |
| 09M2.1 | 393.0 | 1.5 | 5.9 | 403.3 | 2.5 | 7.3 |
| 09M2.2 | 275.1 | 1.4 | 6.0 | 278.3 | 1.8 | 6.5 |
| 09M2.3 | 261.2 | 1.8 | 6.0 | 265.2 | 2.7 | 12.1 |
| 10M2.1 | 438.8 | 1.5 | 4.6 | 452.7 | 1.5 | 8.0 |
| 10M2.2 | 281.1 | 1.8 | 5.7 | 289.5 | 2.1 | 10.1 |
| 10M2.3 | 139.8 | 2.0 | 8.4 | 139.1 | 1.5 | 11.0 |
| 11M2.1 | 461.1 | 1.3 | 4.4 | 475.1 | 1.3 | 7.6 |
| 11M2.2 | 127.4 | 2.5 | 9.5 | 124.0 | 2.3 | 15.0 |
| 12M2.1 | 444.6 | 1.4 | 5.5 | 447.5 | 1.9 | 8.8 |
| 12M2.2 | 361.3 | 2.1 | 6.6 | 364.1 | 2.1 | 8.8 |
| 12M2.3 | 142.1 | 2.6 | 7.7 | 137.1 | 2.6 | 10.4 |
| 13M2.1 | 327.5 | 1.7 | 6.4 | 333.5 | 1.9 | 7.3 |

*Table 2: results of the tests in waste waters*

## Description of the proficiency tests in natural waters

For tests from 2009 to 2011, the participants received 2 bottles from 2 similar batches (batches prepared from a same matrix) and had to analyse them twice. For the tests organised in 2012 and 2013, they had to analyse 2 bottles from the same batch twice.

The characteristics of the matrix are detailed in the table 3:

| Proficiency test | Matrix | TSS (mg/L) | Number of participants | | Organism in charge of the sample preparation |
|---|---|---|---|---|---|
| | | | COD | ST-COD | |
| 09M1B.1 | RW sieved to 2 mm | 8 | 98 | 50 | IPL Santé, Environnement Durables Nord |
| 09M1B.2 | RW sieved to 2 mm | 22 | 96 | 55 | |
| 10M1B.1 | RW sieved to 2 mm | 10 | 94 | 59 | |
| 10M1B.2 | RW sieved to 2 mm | 8 | 92 | 62 | |
| 11M1B.1 | RW sieved to 2 mm | 7 | 88 | 60 | |
| 11M1B.2 | RW sieved to 2 mm | 14 | 89 | 61 | |
| 12M1B.1 | 80% RW + 20% reverse osmosis water | 49 | 86 | 63 | A.G.L.A.E. |
| 12M1B.2 | 66% RW sieved to 2 mm + 33% reverse osmosis water | 12 | 88 | 60 | |
| 13M1B.1 | RW | 77 | 85 | 66 | |

*TSS: total suspended solids*
*RW: river water*

*Table 3: description of the tests in natural waters*

Note: in natural waters, more and more laboratories carry out a measure by ST-COD. This percentage increases from 34% in 2009 to 44% in 2013 (figure 2).
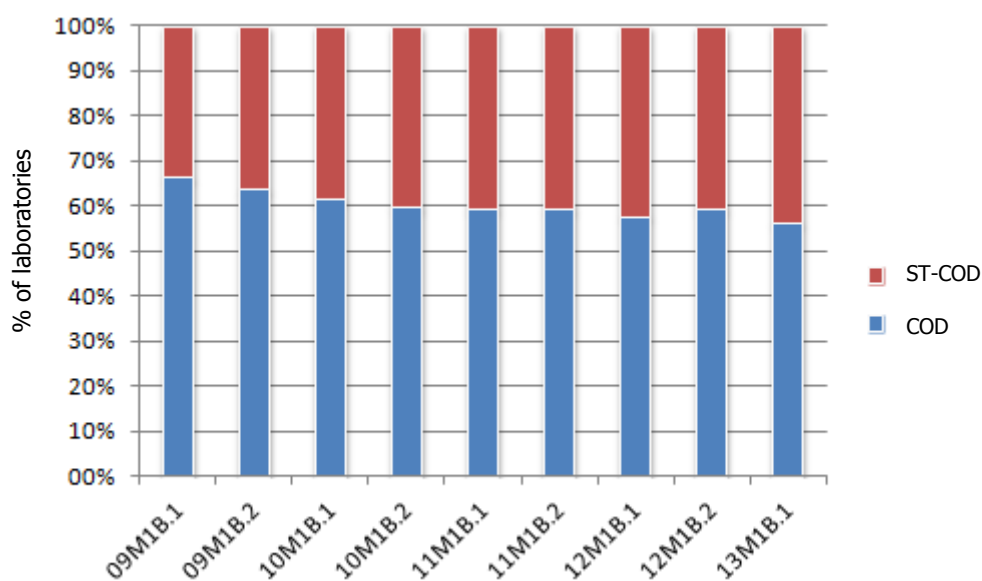


*Figure 2: use of COD and ST-COD methods for proficiency tests in natural waters*

## Obtained results in natural waters

The precision values (variation coefficients of reproducibility and repeatability) observed during these tests are as follow:

| Proficiency test | COD (mg d'O$_2$/L) | | | ST-COD (mg d'O$_2$/L) | | |
|---|---|---|---|---|---|---|
| | Consensus value | CV$_r$ (%) | CV$_R$ (%) | Consensus value | CV$_r$ (%) | CV$_R$ (%) |
| 09M1B.1 | 38.50 | 4.68 | 16.34 | 33.42 | 2.64 | 8.35 |
| 09M1B.1 | 35.59 | 3.87 | 19.96 | 30.02 | 3.41 | 11.07 |
| 09M1B.2 | 64.18 | 2.81 | 11.01 | 58.68 | 1.63 | 8.37 |
| 09M1B.2 | 62.07 | 3.02 | 10.08 | 54.62 | 4.14 | 7.57 |
| 10M1B.1 | 36.22 | 5.27 | 20.29 | 31.82 | 2.67 | 9.77 |
| 10M1B.1 | 35.56 | 4.97 | 18.98 | 32.21 | 3.07 | 8.67 |
| 10M1B.2 | 41.54 | 4.08 | 18.03 | 35.19 | 2.51 | 9.54 |
| 10M1B.2 | 40.74 | 4.34 | 19.60 | 34.76 | 2.75 | 10.17 |
| 11M1B.1 | 36.86 | 4.98 | 19.08 | 31.10 | 2.84 | 8.07 |
| 11M1B.1 | 36.11 | 5.19 | 19.96 | 30.09 | 2.82 | 9.39 |
| 11M1B.2 | 53.05 | 4.60 | 15.25 | 47.79 | 2.14 | 11.39 |
| 11M1B.2 | 53.36 | 4.77 | 15.56 | 48.07 | 3.16 | 11.03 |
| 12M1B.1 | 58.10 | 3.95 | 10.16 | 55.87 | 1.77 | 6.39 |
| 12M1B.2 | 79.59 | 2.66 | 8.12 | 72.27 | 2.25 | 5.92 |
| 13M1B.1 | 45.40 | 4.44 | 19.60 | 36.33 | 2.6 | 11.01 |

_Table 4_: results of the tests in natural waters

**Note:** for the tests from 2009 to 2011, COD and ST-COD were measured on two bottles from two similar batches that is why for each test there are two consensus values for each method.

## RESULTS & DISCUSSIONS

### Deviations between measurements

Some deviations between the values obtained by COD and ST-COD were observed. These deviations increase or decrease with the type of water, depending on how high the COD and TSS values are.

◇ In general, for a **matrix such as waste water** the difference between COD and ST-COD is negative. The observed values for ST-COD are lightly higher than the ones observed for COD. However, this deviation stays minor: it varies between -3 and 4% of the mean of the consensus values for ST-COD and COD (table 5 and figure 3).

| Test (natural waters) | COD (mg of O$_2$/L) | ST-COD (mg of O$_2$/L) | Deviation (mg of O$_2$/L) | Relative deviation |
|---|---|---|---|---|
| 09M2.1 | 393.0 | 403.3 | -10.3 | -2.6% |
| 09M2.2 | 275.1 | 278.3 | -3.2 | -1.2% |
| 09M2.3 | 261.2 | 265.2 | -4.0 | -1.5% |
| 10M2.1 | 438.8 | 452.7 | -13.9 | -3.1% |
| 10M2.2 | 281.1 | 289.5 | -8.4 | -2.9% |
| 10M2.3 | 139.8 | 139.1 | 0.7 | 0.5% |
| 11M2.1 | 461.1 | 475.1 | -14.0 | -3.0% |
| 11M2.2 | 127.4 | 124.0 | 3.4 | 2.7% |
| 12M2.1 | 444.6 | 447.5 | -2.9 | -0.6% |
| 12M2.2 | 361.3 | 364.1 | -2.7 | -0.8% |
| 12M2.3 | 142.1 | 137.1 | 5.0 | 3.6% |
| 13M2.1 | 327.5 | 333.5 | -6.0 | -1.8% |

*Table 5: deviations between the results in waste waters*

**Comparison between COD and ST-COD in waste waters**



$$\frac{COD - STCOD}{mean(COD,STCOD)}$$
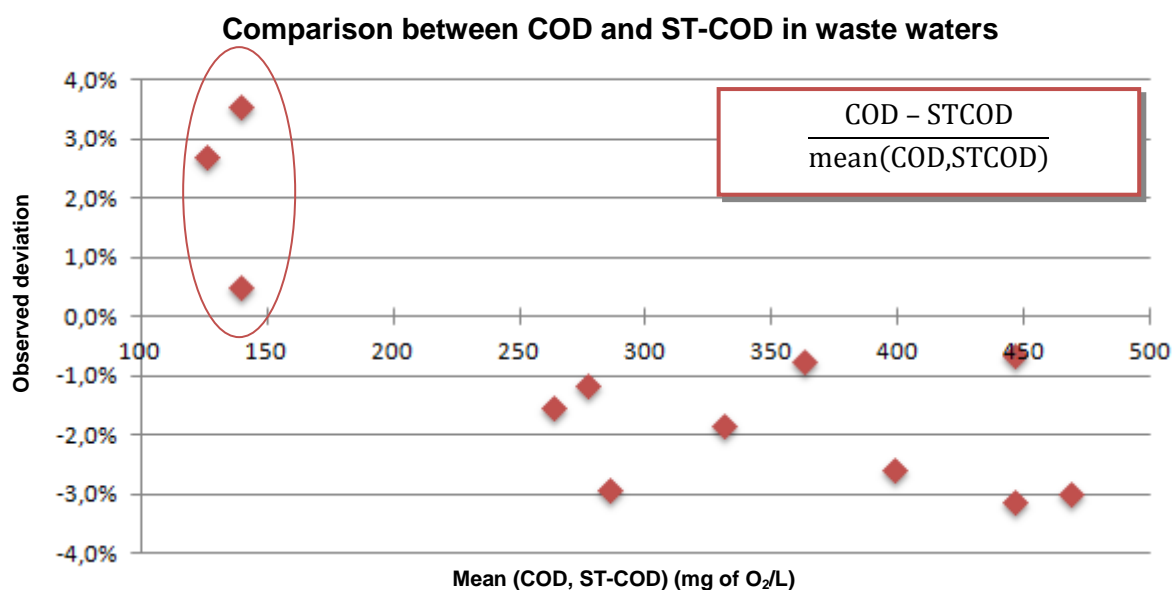
*Figure 3: deviations between the results in waste waters (relative deviations)*

For three tests (10M2.3, 11M2.2 and 12M2.3), the COD value is higher than the ST-COD value. This observation seems to be related to the type of matrix. Indeed, the water used for these tests came from a treatment plant and was settled, the TSS and COD values were significantly lower than for the other tests. The observed deviation between COD and ST-COD values is quite constant on the whole range of work, from 250 to 500 mg of $O_2$/L (without taking into account of the tests 10M2.3, 11M2.2 and 12M2.3), and is around -4.1 mg of $O_2$/L as shown below (figure 4).

**Comparison between COD and ST-COD in waste waters**
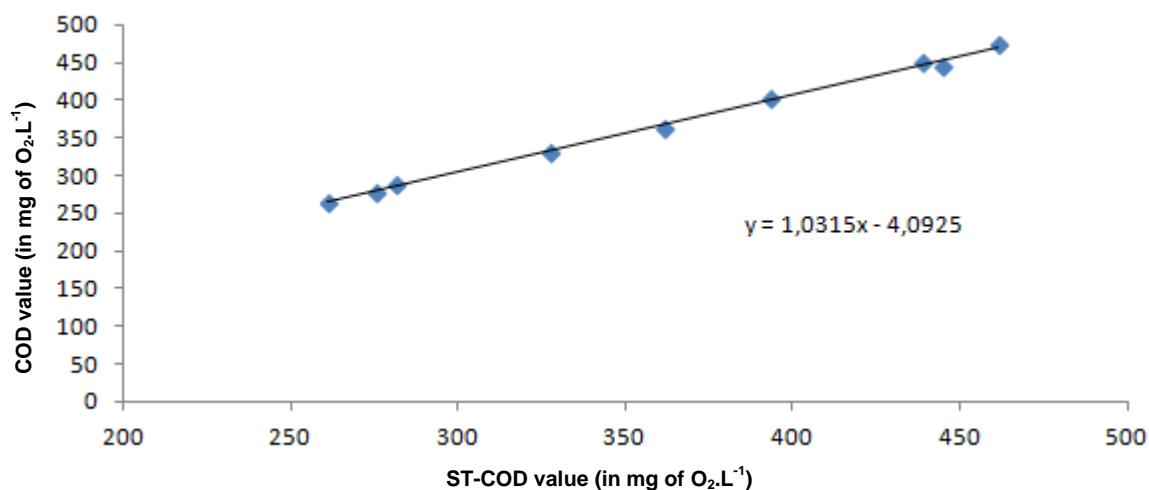


$y = 1,0315x - 4,0925$

Figure 4: linear regression – comparison between the COD and ST-COD values

◊ Conversely, for a **matrix such as natural water**, the values obtained for ST-COD are lower than the ones observed for COD. This deviation varies between 4 and 22% of the mean of the consensus values for ST-COD and COD (table 6 and figure 5).

| Tests (natural waters) | COD (mg of $O_2$/L) | ST-COD (mg of $O_2$/L) | Deviation (mg of $O_2$/L) | Relative deviation |
|---|---|---|---|---|
| 09M1B.1 | 35.59 | 30.02 | 5.57 | 17.0% |
| 09M1B.1 | 38.50 | 33.42 | 5.08 | 14.1% |
| 09M1B.2 | 62.07 | 54.62 | 7.45 | 12.8% |
| 09M1B.2 | 64.18 | 58.68 | 5.50 | 9.0% |
| 10M1B.1 | 35.56 | 32.21 | 3.36 | 9.9% |
| 10M1B.1 | 36.22 | 31.82 | 4.40 | 12.9% |
| 10M1B.2 | 40.74 | 34.76 | 5.98 | 15.8% |
| 10M1B.2 | 41.54 | 35.19 | 6.35 | 16.6% |
| 11M1B.1 | 36.11 | 30.09 | 6.02 | 18.2% |
| 11M1B.1 | 36.86 | 31.10 | 5.76 | 17.0% |
| 11M1B.2 | 53.05 | 47.79 | 5.26 | 10.4% |
| 11M1B.2 | 53.36 | 48.07 | 5.29 | 10.4% |
| 12M1B.1 | 58.10 | 55.87 | 2.23 | 3.9% |
| 12M1B.2 | 79.59 | 72.27 | 7.33 | 9.6% |
| 13M1B.1 | 45.40 | 36.33 | 9.06 | 22.2% |

Table 6: deviations between the results in natural waters

**Comparison between COD and ST-COD in natural waters**



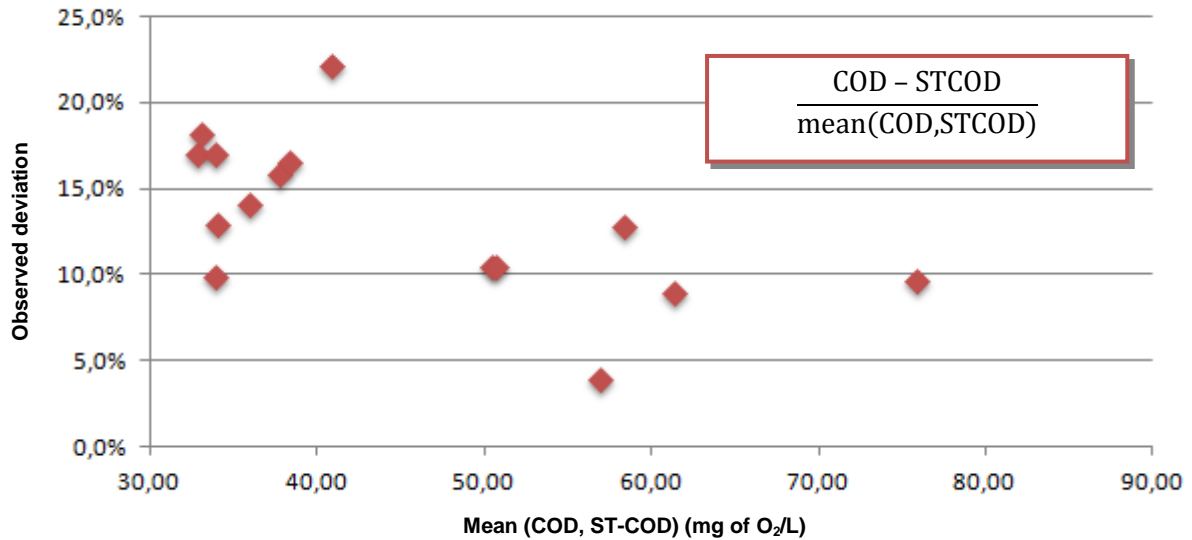$$\frac{COD - STCOD}{mean(COD,STCOD)}$$

*Figure 5: deviations between the results in natural waters (relative deviation)*

For chemical oxygen demands between 35 and 80 mg of $O_2$/L (content of TSS rather low), there is no direct correlation between the COD value and the size of the (relative) deviation between the two methods, even if in most cases the highest deviations are obtained with the lowest COD and ST-COD values.

The observed (absolute) deviation between the COD and ST-COD values is quite constant on the whole range of work, from 30 to 80 mg of $O_2$/L and is around 4.5 mg of $O_2$/L as shown below on the linear regression (figure 6):

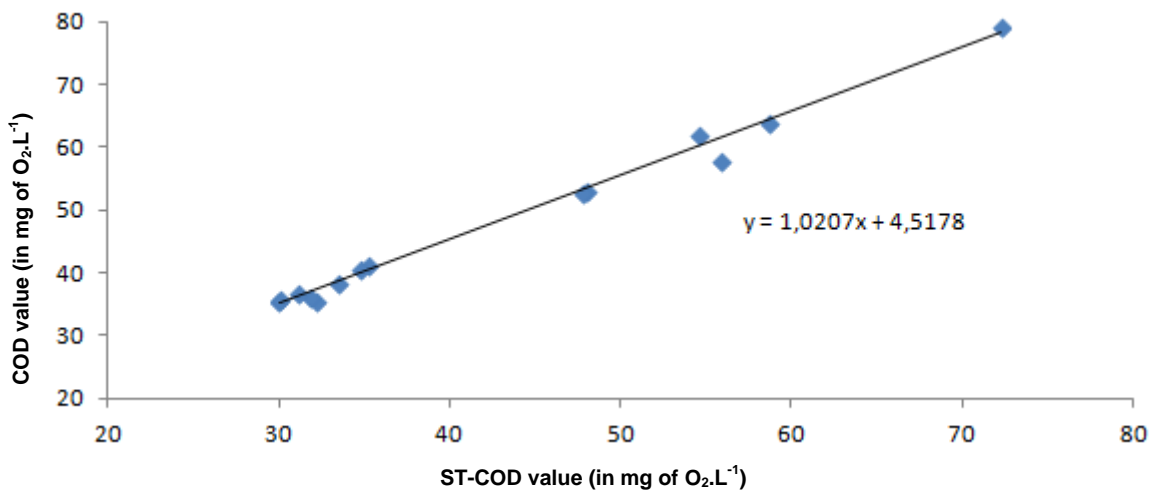**Comparaison ST-DCO (microtubes) et DCO sur eaux naturelles**



$y = 1,0207x + 4,5178$

*Figure 6: linear regression – comparison between the COD and ST-COD values*

◇ **Conclusion for all types of matrices**

**Deviation between the methods according to the mean of (COD, ST-COD) – All types of matrices**
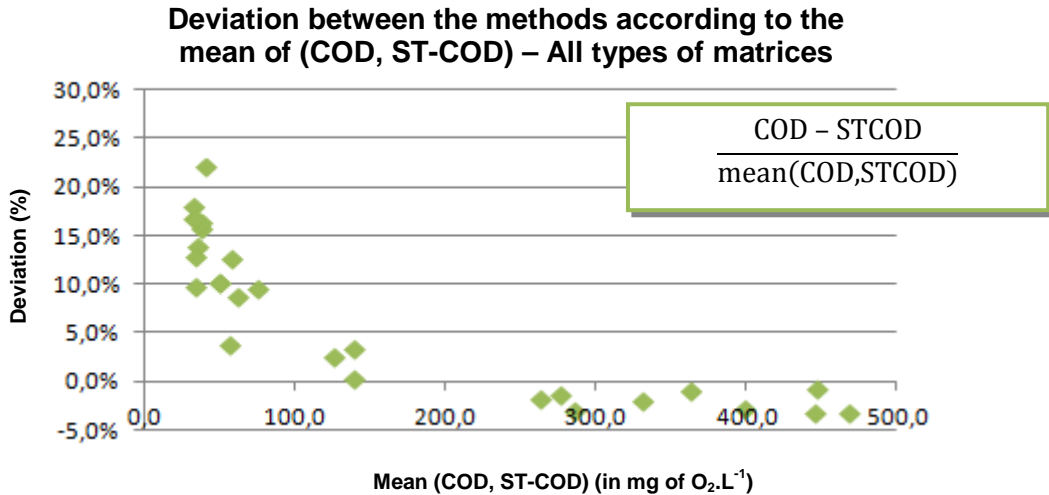


*Figure 7*: comparison between the COD and ST-COD values according to the chemical oxygen demand

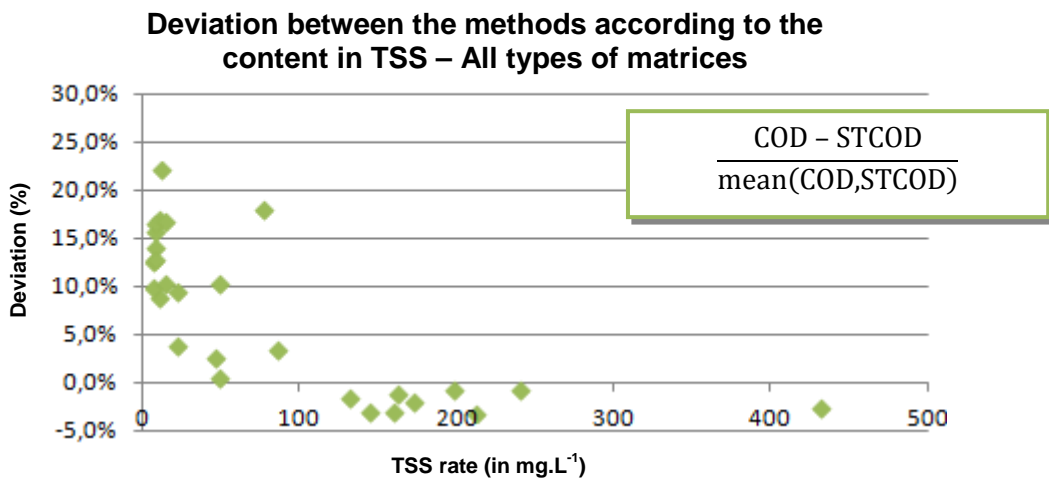**Deviation between the methods according to the content in TSS – All types of matrices**



*Figure 8*: comparison between the COD and ST-COD values according to the content in TSS

**Conclusion on the deviations between the results (figures 7 and 8)**
It appears that for a content in total suspended solid lower than 100mg/L, which corresponds to a chemical oxygen demand inferior to 200mg of $O_2$/L), the ST-COD measures give lower results than the ones obtained with classical methods. The deviation between these two methods increases up to 10-15% when the concentration level (in TSS and in chemical oxygen demand) decreases.
When the total suspended solid rate is higher than 100mg/L (chemical oxygen demand superior to 200mg of $O_2$/L), the ST-COD measures give higher results than the COD method but the deviation is reduced: around -2.5%.

## Deviations in the precision values

◇ We noticed higher deviations on the precision values (variation coefficients of reproducibility and repeatability) which were observed during interlaboratory tests, especially for **matrices such as natural waters**: variation coefficients are clearly higher for COD than for ST-COD (figures 9 and 10).
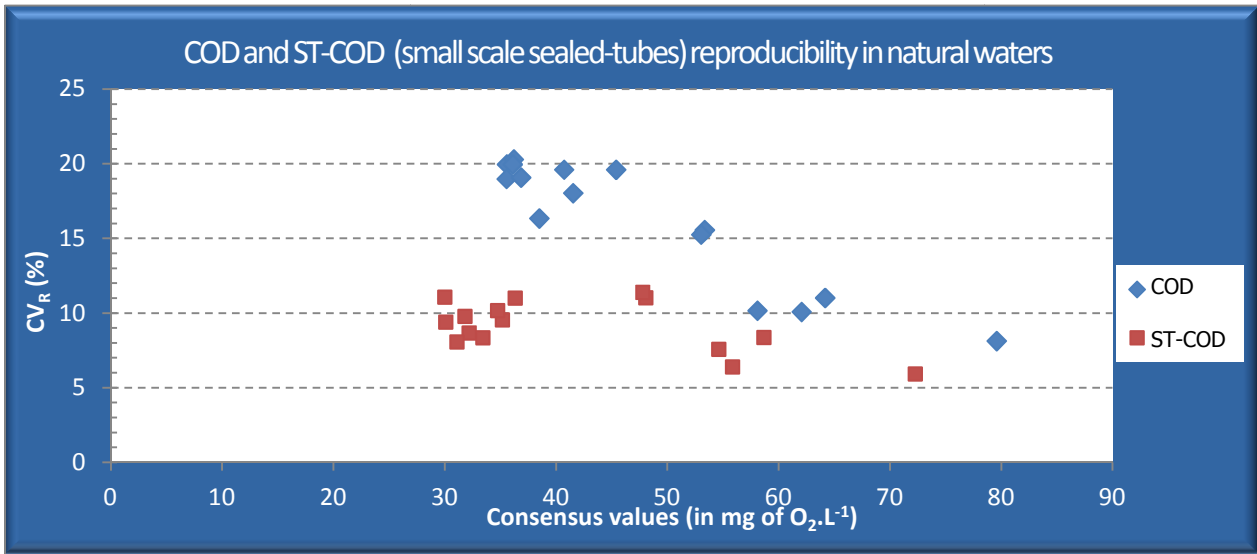


*Figure 9*: reproducibility values ($CV_R$%) in natural waters
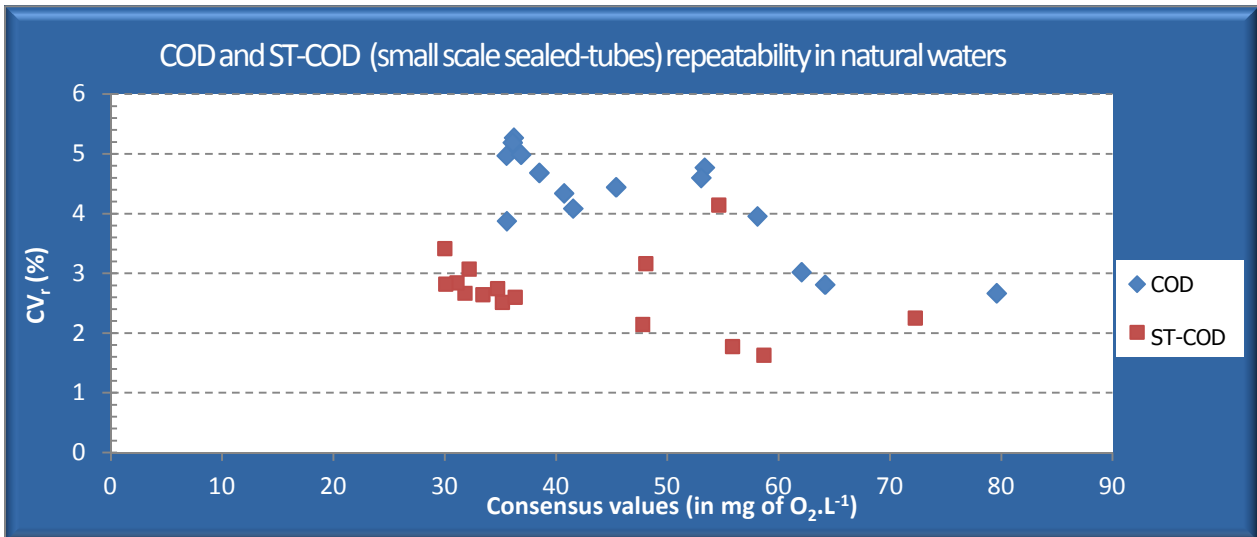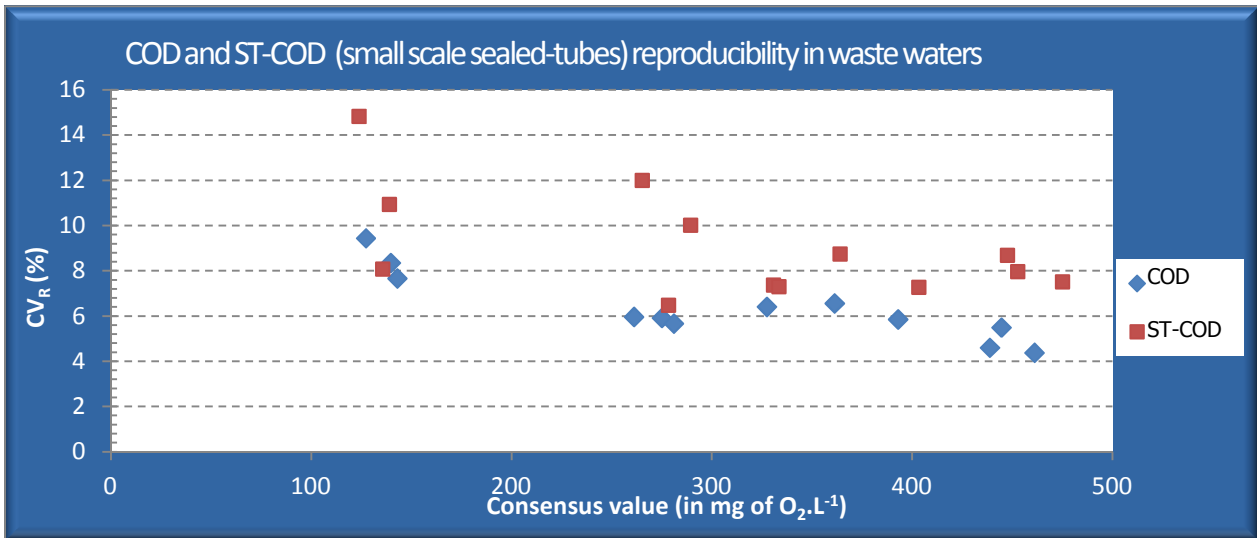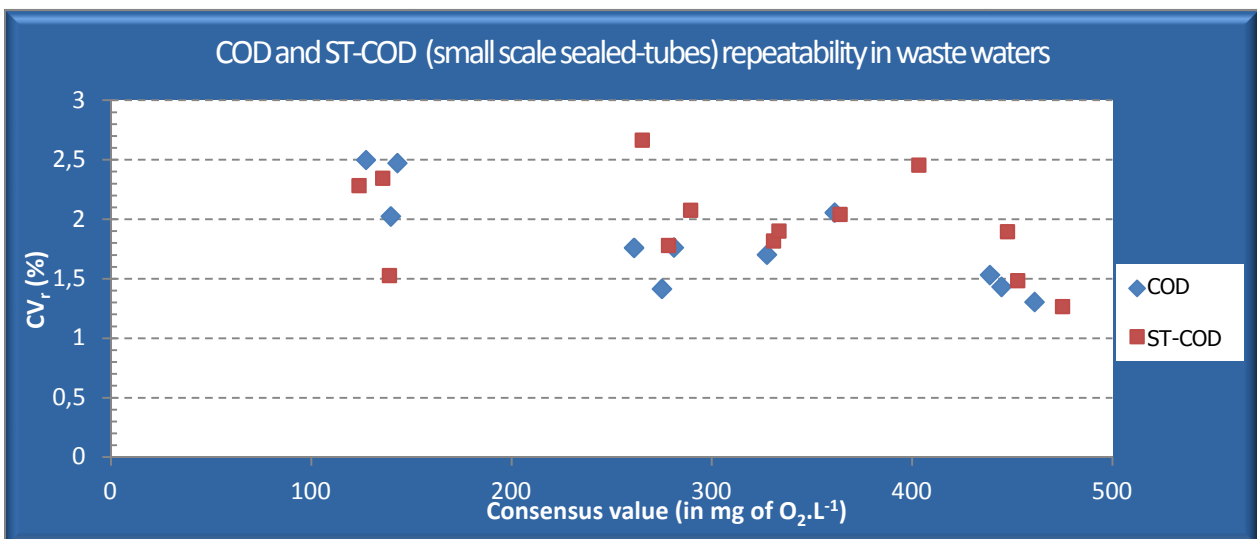


*Figure 10*: repeatability values ($CV_r$%) in natural waters

◊ In **waste waters**, these deviations between COD and ST-COD are lower overall (figures 11 and 12). For high chemical oxygen demand values (superior to 250mg of $O_2$/L) we observed that the variation coefficients for ST-COD are slightly higher than the ones obtained for COD ($CV_R$% around 10% for ST-COD, and about 6% for COD). On the other hand, for lower values, there is no deviation. These low values correspond to the tests for which the waste water was decanted (very low content in TSS as well as in natural waters). As a consequence, we cannot exclude that it may be a 'matrix' effect.



*Figure 11*: reproducibility values ($CV_R$%) in waste waters



*Figure 12*: repeatability values ($CV_r$%) in waste waters
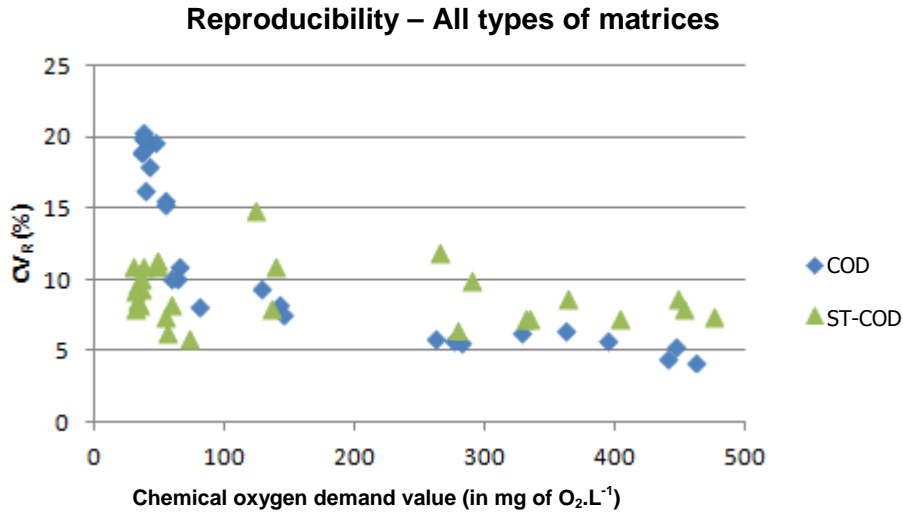
◇ **Conclusion for all types of matrices**

### Reproducibility – All types of matrices



*Figure 13: reproducibility values ($CV_R$%) in waste and natural waters*

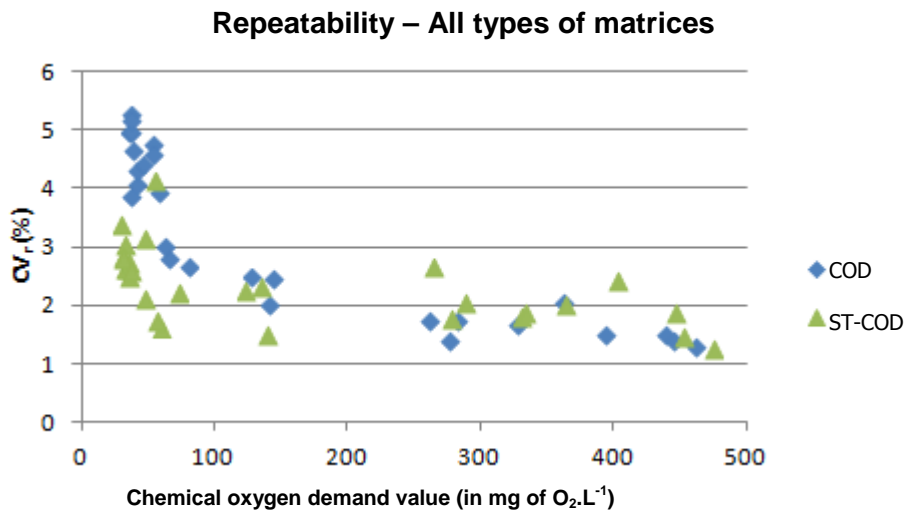### Repeatability – All types of matrices



*Figure 14: repeatability values ($CV_r$%) in waste and natural waters*

---

**Conclusion on the deviations between precision values (figures 13 and 14)**

As with any parameter, it appears that the reproducibility of the chemical oxygen demand becomes worse when the concentration decreases. Above 100mg of $O_2$/L, COD and ST-COD have a similar reproducibility value ($CV_R$%) around 8% (6% for COD and 10% for ST-COD). On the other hand, below 100mg of $O_2$/L, we can see that the reproducibility of COD becomes significantly worse and reaches 20%.

As for repeatability, it follows the same tend but with values 3 to 4 times lower ($\frac{CVR\%}{CVr\%}$ = 3 to 4).

---

The statistical treatments carried out between the variation coefficients obtained with the 2 methods appear significant at the 5% significance level.

## Discussion

### ◊ **Normative reminder**

The most used standards by the participants for the determination of the chemical oxygen demand are the NF T90-101 and the NF ISO 15705. They give some indications concerning the limit of both methods and the interferences with other substances.

- NF T90-101 'Qualité de l'eau – Détermination de la demande chimique en oxygène (DCO)'

Limit of the method: 'the determination of COD according to this standard is applicable to water for which the COD is between 30 and 700 mg of $O_2$/L and in which the chloride concentration does not exceed 2000 mg/L (the chloride oxidation into chlorine produces a positive deviation). The use of cleaned glassware is primordial (equipment cleaning with a reflux of potassium dichromate solution). Some very volatile organic substances can be evaporated during the oxidation.'

- NF ISO 15705 'Qualité de l'eau – Détermination de l'indice de demande chimique en oxygène (ST-DCO)'

Limit of the method: 'if the water contains nitrogenous compounds or heterocycles hard to oxidise in huge quantities, the ST-COD value is a wrong estimation of the theoretical chemical oxygen demand. The representativeness of a 2mL-sample is limited, especially if the content in total suspended solid is very high. The ST-COD determination according to this standard is applicable for a chemical oxygen demand inferior to 1000mg of $O_2$/L and in which the chloride concentration does not exceed 1000 mg/L. Some volatile organic substances can be evaporated during oxidation. Ammonium ions are not oxidised (they come from organic nitrogen).'

In our tests, the chemical oxygen demand is between 30 and 500 mg of $O_2$/L, the work range is consistent with the specifications of the standards NF T90-101 and NF ISO 15705 as if on natural waters the consensus values are often close to the inferior limit. Besides, we noticed that the precision values in natural waters, with a COD value close to 30mg of $O_2$/L, are the least satisfactory (but remain acceptable). That is usual, we know that the uncertainty of measurement increases for the lowest values. It should be noted that the concentration of chloride ions is low enough so as not to interact.

### ◊ **Comparison between methods**

#### ◊ **General principles**

Both methods present several differences in their implementation (table 7) even though their principles are quite close. Some of these differences can be at the origin of the bias we observed for the deviation between results but also for the precision of the measurements.

| Stage | COD | ST-COD |
|---|---|---|
| **Digestion** | Used products for the reflux:<br>- sulfuric acid<br>- silver sulfate (oxidation catalist)<br>- potassium dichromate<br>- mercury (II) sulfate (chloride elimination) | The sealed-tube contains:<br>- sulfuric acid<br>- silver sulfate (oxidation catalist)<br>- potassium dichromate<br>- mercury (II) sulfate (chloride elimination) |
| | Test portion: 10mL | Test portion: 2mL |
| | Digestion: 2h heating reflux | Digestion: 2h at 150°C |

| Stage | | COD | ST-COD |
|---|---|---|---|
| | | Complete with 75mL of water. | Centrifuge the tubes. |
| **Detection** | photometric | - | Decant the sample into a volumetric flask if the measure of the absorption cannot be carried out directly in the digestion tube → applies to solutions with low turbidity. |
| | titrimetric | Titrate the excess dichromate with a solution of iron II ammonium sulfate (indicator: ferroin). | Rinse the tube with 1mL of water. Titrate with a solution of iron II ammonium sulfate (indicator: ferroin). |
| | potentiometric | Measure the redox potential of the solution. Find the necessary volume from the graph redox potential/volume of the iron (II) ammonium sulfate solution. | - |

_Table 7_: comparison of the methods

◇ **Test portion**

The test portion is lower with ST-COD (2mL) than with COD (10mL). Getting a representative portion may be more difficult, especially if there is a high TSS content in the solution. Indeed, in natural waters, ST-COD gives better precision values than COD and particularly for the repeatability. Conversely, in waste waters, the tendency reverses or becomes quite low. A pre-treatment of the samples which aims to dissolve a part of the particles prior to take a test portion (for example an acidification) can allow to limit the impact of a catch with a reduced volume on the precision of the analyses.

◇ **Detection methods**

For ST-COD, most laboratories use a single method: spectrophotometry. For COD, two methods are generally used: titration and potentiometry. The use of several detection methods to determine the chemical oxygen demand can have an influence on the precision values.
Indeed, if a method tends to give results slightly lower than another one, the distribution of the whole data is affected by the distribution of the results of each individual method but also by the deviation between them which can create an over-scattering.

In consequence, we studied the influence of the methods of detection used by the participants on the precision values with the data from the last proficiency tests (13M2.1 and 13M1B.1). The test 13M2.1 is considered as a test with high content of TSS, it means, sufficiently representative of the matrix such as 'waste water'. The test 13M1B.1 was prepared with a non-diluted river water, not decanted.

Some deviations between the results obtained by different detection methods were statistically observed for a natural water matrix (figure 15).
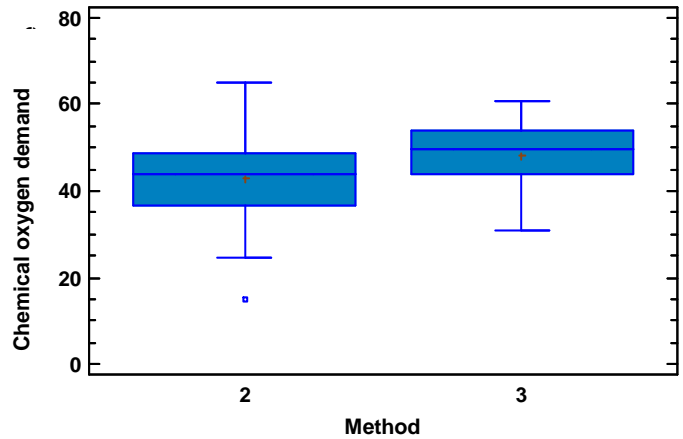
## Waste water

**Box plot**
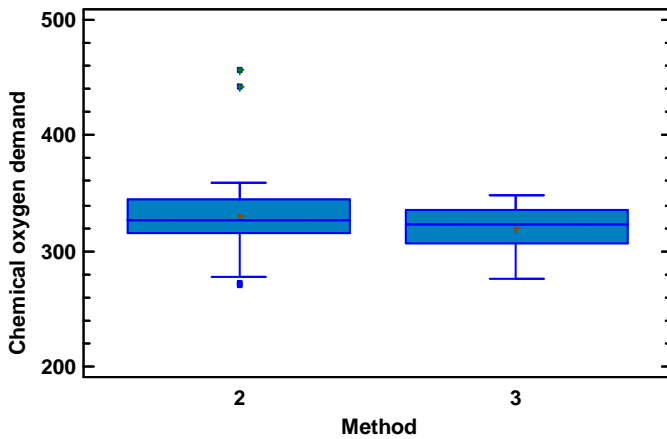


**Caption:**
2: COD (titration)
3: COD (potentiometry)

## Natural water

**Box plot**



**Caption:**
2: COD (titration)
3: COD (potentiometry)

*Figure 15*: deviation between methods

In **natural water** (13M1B.1), the repeatability of the measurements for each individual method is around 3% except for the titration for which the $CV_r$% is about 5.5%. The variation coefficient of repeatability for all methods with COD (4.4%) is influenced by the repeatability of the titrimetric method. This can explain, in part, the deviation between the $CV_r$% of the ST-COD method and the $CV_r$% of the COD method.

On the other hand, a treatment for each type of method does not allow to explain the deviations between reproducibility values between COD and ST-COD, in spite of the deviations between the laboratories' means (m). Indeed, even if the analytical modalities are considered separately for COD, their $CV_R$% (about 17%) are still higher than the one we obtained for the spectrophotometry with ST-COD (11%).

| Detection method | % of laboratories | Consensus value | | | $CV_r$% | $CV_R$% |
|---|---|---|---|---|---|---|
| | | IC inf | m | IC sup | | |
| **ST-COD** | | | | | | |
| Spectrophotometry | 97% | 34.9 | 36.33 | 37.6 | 2.60 | 11.01 |
| **COD** | | | | | | |
| Titration | 55% | 39.9 | 43.03 | 46.0 | 5.50 | 17.00 |
| Potentiometry | 42% | 44.3 | 47.88 | 51.4 | 3.00 | 16.50 |
| All methods | 100% | 42.7 | 45.40 | 48.0 | 4.44 | 19.60 |

*Table 8*: comparison between the measurement techniques in natural waters

In **waste waters** (13M2.1) the distribution of the results and the repeatability of the measurements are slightly equivalent for the COD method and the ST-COD method: the $CV_r\%$ are of the same order and the $CV_R\%$ just have a gap of 1%. <u>The choice of the detection method does not have any effect.</u>

| Detection method | % of laboratories | Consensus value | | | $CV_r\%$ | $CV_R\%$ |
|---|---|---|---|---|---|---|
| | | $IC_{inf}$ | $m$ | $IC_{sup}$ | | |
| **ST-COD** | | | | | | |
| Spectrophotometry | > 98% | 324.7 | 333.5 | 342.3 | 1.9 | 7.3 |
| **COD** | | | | | | |
| Titration | 57% | 322.9 | 331.7 | 340.4 | 1.7 | 6.3 |
| Potentiometry | 36% | 316.1 | 325.7 | 335.2 | 1.6 | 5.5 |
| All methods | 100% | 321.0 | 327.5 | 334.0 | 1.7 | 6.4 |

<u>Table 9</u>: comparison between the measurement techniques in waste waters

**Note:** it is possible that the different detection techniques used for ST-COD (spectrophotometry) and for COD (potentiometry and titrimetry) may be directly as the root of the observed deviations concerning the precision values. Indeed, the spectrophotometry is sensitive to the presence of sediments or other suspended solids and the sample has to be centrifuged very well, conversely to the titration or the potentiometry. On the other hand, in the absence of particles we can suppose that it is a method more reproducible than potentiometry and titration. This could explain why in natural water (with a low content in suspended solids) the ST-COD gives more reproducible results while in waste waters it gives results slightly less reproducible.

◇ **Study of the suppliers of kits used for the ST-COD**

As well as to study the influence of the detection method, we processed data from the test 13M2.1 (waste water matrix) in order to see if the brand of the kit used by the participants could have any influence on the deviations between the results or the precisions values.

We processed data separately according to the supplier and we did not notice any statistically significant deviation. The brand of the kits used does not seems to play a crucial part; the means and the precision values are really close (table 10 and figure 16).

| | ST-COD (Supplier 1) | ST-COD (Supplier 2) | ST-COD (Supplier 3) |
|---|---|---|---|
| $IC_{inf}$ | 319.4 | 311.6 | 312.9 |
| $m$ | 330.2 | 334.0 | 345.5 |
| $IC_{sup}$ | 340.9 | 356.5 | 378.2 |
| $CV_r\%$ | 2.5 | 1.5 | 1.5 |
| $CV_R\%$ | 6.5 | 8.5 | 8.0 |
| Number | 27 | 12 | 7 |

<u>Table 10</u>: comparison of the suppliers of kits for ST-COD



**13M2.1 – ST-COD**
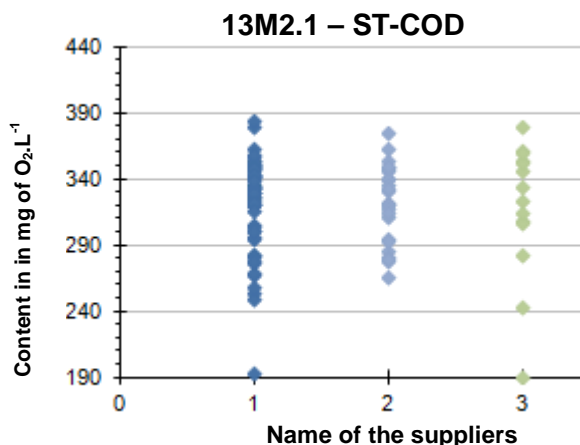
<u>Figure 16</u>: deviation between suppliers of kits

# CONCLUSION

The main observations done in our proficiency tests are summarised in the following table:

|  | **Natural waters** | **Waste waters**: TSS < 100 mg/L, COD < 200 mg of $O_2$/L | **Waste waters**: TSS > 100 mg/L, COD > 200 mg of $O_2$/L |
|---|---|---|---|
| **DEVIATIONS BETWEEN THE RESULTS** | The COD gives higher results than ST-COD | The COD gives slightly higher results than ST-COD | The COD gives slightly lower results than ST-COD |
| **PRECISION** | The ST-COD gives more repeatable and reproducible results than COD | The ST-COD gives slightly more repeatable and reproducible results than COD | The ST-COD gives quite equivalent or slightly higher precision values |

The deviations between the precision values and the results observed during our tests can be explained, in part, with:
- o **The test portion** which is low for the ST-COD and can produce a rise of the variation coefficient of repeatability for the tests carried out in waste waters (high content in total suspended solids): the $CV_r$% becomes equivalent or higher than the one obtained for the COD while in natural waters it is clearly lower.
- o **The use of different detection methods** for COD can explain, in part, the higher deviation of the results for this method in natural waters.

Actually it is difficult to evaluate the extent of the effect of these factors, especially the relation with the content in suspended solids.

It should also be noted that if laboratories use some kits with a different range of concentration, it can increase the variation coefficient of reproducibility ($CV_R$%) but also it can produce rather high deviations between the results of measurements. Nevertheless, we could not check this hypothesis yet and we are going to study it during the 2014 interlaboratory tests.

The brand of the kits used for the analysis with ST-COD does not seem to influence the deviations between the results or between the precision values.