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## Uncertainty attached to the results of a calibrated AMS

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### **Abstract**

The calibration of a method by comparison with the reference method is commonly used in metrology. If the reference method is supposed to give the true value of the measurand by convention, the uncertainty attached to the results may be rather high. If the uncertainty sources that influence the result are randomly contributing to the overall uncertainty of the method, this drawback can be overcome by carrying out several successive measurements, the uncertainty attached to the average value being equal to that of a simple measurement divided by a factor  $1/\sqrt{n}$ . However, if the reference method is not described accurately enough and influent parameters not all identified, its implementation may lead to systematic deviations between laboratories. Thus, several manual reference methods prepared by CEN working groups have led to confidence intervals of reproducibility higher than expected : e.g. 20% for the manual method for SO<sub>2</sub> (EN 14791) determinations. The following question then arises: is it still relevant to use such methods to calibrate an AMS and to check if its variability is acceptable, according to EN 14181? Directives 2001/80/CEE and 2000/76/CEE fix a maximum uncertainty of 20% at the limit value for AMS measuring SO<sub>2</sub> and 30% for particulates... The presentation shows how to calculate the uncertainty attached to the results of a calibrated AMS on the whole measuring range and how the uncertainty of the reference method affects the quality of the QAL2 and consequently what is the maximum acceptable uncertainty for the SRM.

### **Résumé**

L'étalonnage d'une méthode par comparaison avec la méthode de référence est souvent employé en métrologie. Si la méthode de référence est censée donner la valeur vraie du mesurande par convention, l'incertitude attachée aux résultats peut être plutôt élevée. Cet inconvénient peut être surmonté aisément en effectuant plusieurs mesurages successifs dans le cas où les sources d'incertitude influençant le résultat du mesurage contribuent aléatoirement à l'incertitude globale de la méthode. L'incertitude attachée à la valeur moyenne sera ainsi égale à celle d'une mesure simple divisée par un facteur  $1/\sqrt{n}$ ; Cependant, si la méthode de référence n'est pas suffisamment bien définie ou les facteurs d'influence mal connus, la mise en œuvre de la méthode peut mener à des écarts systématiques de mesurage entre laboratoires. Ainsi les essais de validation de plusieurs méthodes de référence manuelles par les groupes de travail du CEN ont conduit à des incertitudes de reproductibilité plus élevées qu'escomptées : 20% pour la méthode manuelle pour la détermination du SO<sub>2</sub> (en 14791). La question suivante se pose alors : l'usage de telles méthodes pour étalonner les AMS et vérifier si leur variabilité est acceptable selon les exigences de l'EN 14181, est-il pertinent? Les directives 2001/80/CEE et 2000/76/CEE fixent une incertitude maximum de 20% et 30% à la valeur limite pour la mesure par un AMS du SO<sub>2</sub> et des poussières respectivement... La présentation montre comment calculer l'incertitude attachée aux résultats d'un AMS étalonné sur la gamme de mesure et comment l'incertitude de la méthode de référence affecte la qualité du QAL2 et par voie de conséquence quelle pourrait être la limite acceptable d'incertitude pour la SRM.

## Introduction

EN 14181, based on ISO 11095 requires using Standard Reference Methods (SRMs) to calibrate Automated Measuring Systems (AMS). To be relevant and effective, QAL2 should be carried out according to the following conditions:

- Use a spread of data over the whole range of the AMS.
- The AMS repeatability is noticeably lower than the SRM's.

These two conditions are not always fulfilled:

- It is difficult for an industrial process to operate in a way that provides very different levels of concentrations; moreover a voluntary big depreciation of the quality of the characteristics of the exhaust gases is undesirable.
- Repeatability of the AMS is often equal or lower than the repeatability of the SRM.

Another problem occurs with the regression model. How this model takes into account or not the lack of precision or trueness of the SRM.?

Actually, non-automatic SRM are often characterised by rather high values of repeatability and reproducibility standard deviations ( $s_r$  and  $s_R$ ) : HCl, Hg, SO<sub>2</sub>, H<sub>2</sub>O... For SO<sub>2</sub>, the 95% confidence interval of repeatability and reproducibility for a single measurement are very close to the maximum level of uncertainty required by the Directives for the AMS at the ELV. This means that on one hand the result obtained by one laboratory that has a bad repeatability may lead to reject wrongly an AMS during the variability test. On the second hand a bad reproducibility, due to a rather high inter-laboratory standard deviation  $s_L$  may lead to different calibration functions depending on whether one laboratory or another carries out the QAL2. Furthermore, if the team who performs QAL2 is not the same as for AST, the surveillance test may lead to invalidate the previous QAL 2 calibration function. Moreover, the experience of INERIS in the organisation of inter-laboratory campaigns shows that the actual reproducibility standard deviation obtained by accredited laboratories can vary from 1 to 3 times those reached by reference laboratories during the validation of the standard...

The following question then arises: is it still relevant to use such methods to calibrate AMS and to check if their variability is acceptable, as required by the EN 14181? The following pages shows how to calculate the uncertainty attached to the results of a calibrated AMS on the whole measuring range and how the uncertainty of the reference method affects the quality of the QAL2 and consequently what is the maximum acceptable uncertainty for the SRM.

## 1 - General model of regression function

We start with the common model :

$$y_i = a + b \cdot x_i + \varepsilon_i \quad (1)$$

where :

$x_i$  is the  $i^{\text{th}}$  result of the explanatory variable ;  $i = 1$  to  $n$  ;  $n \geq 15$  ;

$y_i$  is the  $i^{\text{th}}$  result of the variable to be explained ;  $i = 1$  to  $n$  ;  $n \geq 15$  ;

$\varepsilon_i$  is the deviation between  $y_i$  and the expected value; its mean value is zero and standard deviation  $\sigma$

$a$  is the intercept of the calibration function ;

$b$  is the slope of the calibration function.

This model rests in particular on the following assumptions:

- assumption 1:  $x$  is a variable known without uncertainty
- assumption 2: the values  $y_i$  have the same uncertainty on the whole range and are not correlated,

$$u(y_i) = \sigma \text{ et } u(y_i, y_j) = 0$$

The estimate of this model with n couples of points  $(x_i, y_i)$  resulted in calculating the 3 following parameters:  $\hat{a}$ ,  $\hat{b}$  and  $s$  (estimate of  $\sigma$ ).

The most the model fits the points, the lower  $s$  is :

An individual estimate of  $y$  for  $x_0$  with this model is :

$$\hat{y}_0 = \hat{a} + \hat{b} \cdot x_0 + \hat{\varepsilon}_0 \quad \text{where } \hat{\varepsilon}_0 \text{ equals zero but contributes to the uncertainty of } \hat{y}_0$$

An average estimate of  $y$  for  $x_0$  with this model is :

$$\hat{y}_0 = \hat{a} + \hat{b} \cdot x_0$$

And its uncertainty is :

$$u^2(\hat{y}_0) = u^2(\hat{a} + \hat{b} \cdot x_0)$$

$$u^2(\hat{y}_0) = u^2(\hat{a}) + u^2(\hat{b}) \cdot x_0^2 + 2x_0 \cdot u(\hat{a}, \hat{b})$$

or in a more explicit way :

$$u^2(\hat{y}_0) = s^2 \cdot \left( \frac{1}{n} + \frac{(x_0 - \bar{x})^2}{\sum_{i=1}^{i=n} (x_i - \bar{x})^2} \right) \rightarrow$$

$$u(\hat{y}_0) = s \cdot \sqrt{\frac{1}{n} + \frac{(x_0 - \bar{x})^2}{\sum_{i=1}^{i=n} (x_i - \bar{x})^2}}$$

where :

$$s = \sqrt{\frac{\sum_i (y_i - \hat{y}_i)^2}{n-2}}$$

## **2 - Calibration model of the AMS**

EN 14181 uses the model presented in the previous paragraph:

$y$  is the value of the SRM, reported in the conditions of the AMS,

$x$  is the value given by the AMS,

$\hat{y}$  is the calibrated value of the AMS. This calibrated value corresponds to an average estimate.

The results  $x$  given by the AMS, as well as the true values  $y$  given by the SRM are both associated to an uncertainty. This uncertainty is made up with 2 components:

- an uncertainty resulting from random errors (lack of precision); this component can be estimated by the repeatability standard deviation of the method.
- an uncertainty resulting from systematic errors (lack of trueness); this component is can be estimated by the inter-laboratory standard deviation of the method.

- We have to notice that, except for the lowest part of the range of concentrations, uncertainty is approximately proportional to the result of measurement.

In the context of stack measurements, the requirements corresponding to the assumptions of the general linear model, are not often fulfilled.

This situation leads us to two important conclusions:

- the method to be recommended to estimate the model is not necessarily the Ordinary Least Squares
- nevertheless, if the Ordinary Least Squares are used, it is necessary to add to the uncertainty of the model the part of uncertainty of  $y$  not taken into account by the model.

We will initially leave aside the issue of improvement of the method of estimation; one finds in the statistical literature several methods (see annex) and two of them have been tested in this study :

- Ordinary Least Square (OLS)
- Weighted Regression Line (WRL).

Let us suppose first that we follow this second method (Ordinary Least Square).

We are interested in the propagation of these uncertainties to the estimate.

- the uncertainty due to a lack of trueness of the AMS, should be negligible because QAL2 consists of improving the trueness of the AMS via its calibration with the SRM. Thus, this contribution to the uncertainty is taken into account in the uncertainty corresponding to the trueness of the SRM propagated with the modelled value of the AMS.
- the uncertainty due to a lack of precision of the AMS influences uncertainty  $s$  resulting from the model.

Lastly, it is necessary to analyse the uncertainty of the SRM- variable  $y$  of the model.

### **3 - Uncertainty of the SRM**

As we said formerly, the uncertainty of the SRM includes 2 components :

- a component resulting from random errors estimated by  $u(\text{SRM} - \text{repeatability})$ .
- a component resulting from systematic errors estimated by  $u(\text{SRM} - \text{interlab})$ .

In the model, the uncertainty of the SRM is represented by the term  $\varepsilon$  and its standard deviation  $\sigma$ . Its estimate  $s$  arises from the combined effects of :

- the precision of the results of the SRM,
- the precision of the results of the AMS,
- and how the regression line fit to the points.

The variation of SRM and AMS can be estimated by their repeatability, known from laboratory or field tests. This knowledge can be considered to be more robust than what is supposed to be obtained by the model and achieved during the QAL2 process (the number of parallel measurement is limited).

Therefore, in order to estimate the combined uncertainty due to the lack of fit of the regression line and variations of results of the SRM and AMS we will use the term  $s'$  defined by :

$$s' = \max \left[ s ; \sqrt{s^2(\text{AMS} \circ \text{repeatability}) + s^2(\text{SRM} \circ \text{repeatability})} \right]$$

Furthermore, because  $s$  is not constant in all the range of concentrations studied, it is more appropriate to use repeatabilities known from field tests when we want to estimate the uncertainty at a concentration that is outside the range studied during the calibration. It is the case when we want to estimate the uncertainty at the ELV, when this value doesn't belong to the studied range.

In that case, the uncertainty of the calibrated AMS can be estimated by a combination of  $u(\text{SRM} \circ \text{repeatability})$ ,  $u(\text{AMS} \circ \text{repeatability})$  and  $u(\text{SRM} \circ \text{trueness})$  added in a quadratic way.

$u(SRM \circ \text{trueness})$  can be estimated by  $u(SRM \circ \text{interlab})$  whose expression is given in ISO 5725-2 :

$$u^2(SRM \circ \text{interlab}) = \frac{1}{p-1} \cdot \sum_{i=1}^p (\bar{y}_i - \bar{y})^2 - \frac{1}{2} \cdot u^2(SRM \circ \text{repeatability})$$

$$\text{with : } u^2(SRM \circ \text{repeatability}) = \frac{1}{2p} \sum_{i=1}^p (y_{i1} - y_{i2})^2$$

#### 4 – Uncertainty of the calibrated AMS

The uncertainty  $u(\hat{y}_0)$  attached to the estimate  $\hat{y}_0 = \hat{a} + \hat{b} \cdot x_0$  can be calculated from:

$$u^2(\hat{y}_0) = u^2(\hat{a}) + u^2(\hat{b}) \times x_0^2 + 2x_0 \times u(\hat{a}, \hat{b}) + u^2(SRM \circ \text{interlab})$$

or:

$$u^2(\hat{y}_0) = \left( s^2 \left( \frac{1}{n} + \frac{(x_0 - \bar{x})^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right) \right) + u^2(SRM \circ \text{interlab})$$

The expanded uncertainty attached to a result given by the calibrated AMS is then :

$$U(\hat{y}_0) = 2 \times \sqrt{\left( s^2 \left( \frac{1}{n} + \frac{(x_0 - \bar{x})^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right) \right) + u^2(SRM \circ \text{interlab})}$$

#### Other sources of uncertainties

$U(\hat{y}_0)$  corresponds to the variance on the estimate  $\hat{y}_0$  not yet expressed in standardised conditions (p, T, H<sub>2</sub>O, O<sub>2</sub> réf.). To be compared to the limit value of uncertainty given by the Directives, corrections of p, T, H<sub>2</sub>O, O<sub>2</sub> réf. must be done. The effect of corrections due to pressure and temperature is low and more significant for H<sub>2</sub>O (see annex B). Last but not the least: O<sub>2</sub> corrections may increase greatly the uncertainty attached to the results given by the calibrated AMS, especially when the O<sub>2</sub> concentration is higher than 11%. In the example given in annex B, the uncertainty increases:

- by 45% when the O<sub>2</sub> concentration increases from 11 to 15%
- and by 117% when the O<sub>2</sub> concentration increases from 11 to 17%.

#### 5 – Results

In the following examples we suppose that we are in favourable conditions:

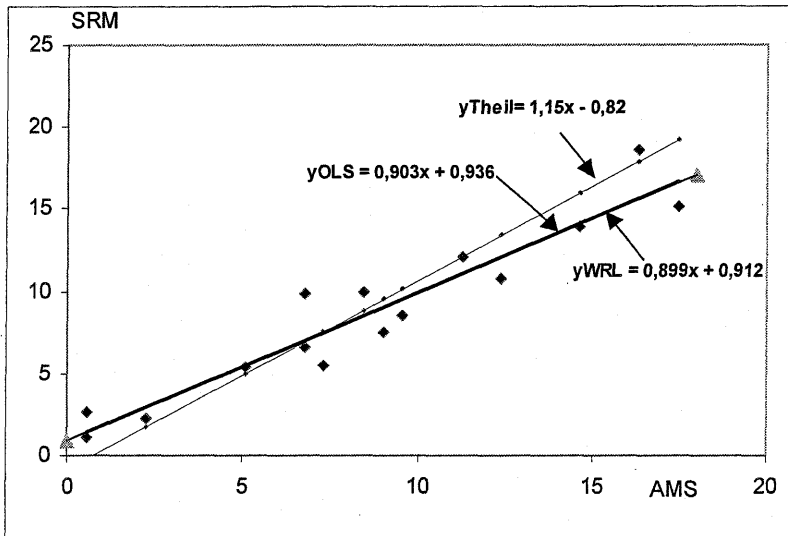
- no correction from wet to dry conditions (the SRM and AMS for SO<sub>2</sub> are supposed to give both results on a dry basis)
- and O<sub>2</sub> concentrations very close to 11%.

**5.1 Dust**

The first example is a QAL2 performed on an opacimeter measuring dust.

The use of the weighted regression line model leads to a equation that is very similar to that given by Ordinary Least Square (OLS) :

- $Y_{OLS} = 0,903 x + 0,936$
- $Y_{WRL} = 0,899 x + 0,912$
- $Y_{Theil} = 1,15 x - 0,82$  (model described in annex A)



The non-parametric method (Theil' method) is not efficient enough to fit the data.

But what about the other two models?

The weighted regression line WRL gives a lower value of s :

$s_{OLS} = 1,6 \text{ mg/m}^3$   
 and  $s_{WRL} = 1,2 \text{ mg/m}^3$ .

From EN 13284-1 we can draw the following information at the average concentration of  $8,5 \text{ mg/m}^3$  and at ELV for the SRM:

- $u(SRM \circ repeatability) = 9,3 \%$  and  $4,2\%$ , respectively,
- $u(SRM \circ int \text{ erlab}) = 13,3 \%$  and  $7,2\%$ .

The excel file gives us an expanded uncertainty  $U(y) = 33 \%$  at the average concentration of  $8,5 \text{ mg/m}^3$ .

At ELV,  $U(y) = 15,2\%$ . => We fulfil the requirement of the Directive ( $U < 30\%$ ).

We see in the table that the main contribution to the expanded uncertainty comes from the effect of  $u(SRM \circ int \text{ erlab})$ , that is to say the effect of laboratory.

With this example, we can study the effect of  $u(SRM \circ repeatability)$  and  $u(SRM \circ int \text{ erlab})$  :

If  $u(SRM \circ repeatability)$  decreases from 9,3 to 4% then  $U(y)$  stays at 33 %. This is due to the fact

that the estimate s already includes the repeatability of the SRM.

If  $u(SRM \circ \text{int erlab})$  decreases from 13,3% to 6% then  $U(y)$  decreases from 33 % to 22,9 %.

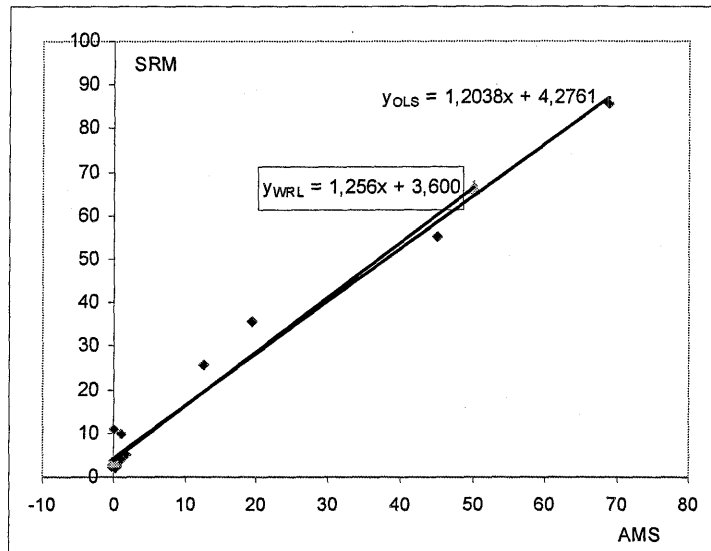
	at $x_{\text{aver}}$	at $x_{\text{aver}}$	at $x_{\text{aver}}$	at ELV	
$u(\text{SRM repeatability})$	9,3%	4,0%	9,3%	4,2%	
$u(\text{SRM interlab})$	13,3%	13,3%	6,0%	7,2%	
$s^2$ ou $u^2_{\text{SRM rep}}$	0,713	0,713	0,713	2,110	
$u^2(\text{AMS}^\circ \text{repeat.})$	0,029	0,029	0,029	1,440	
$u^2(\text{lab})$	1,325	1,325	0,270	18,66	
$u^2_{\text{total}}$	2,037	2,037	0,982	20,773	
$u(\text{AMS})$	1,43	1,43	0,99	4,56	mg/m <sup>3</sup>
$u(\text{AMS}) \%$	16,5	16,5	11,5	7,6	%
$U(\text{AMS})$	2,85	2,85	1,98	9,12	mg/m <sup>3</sup>
$U(\text{AMS}) \%$	33,0	33,0	22,9	15,2	%

### 5.2 SO<sub>2</sub>

The second example is a QAL2 performed on a SO<sub>2</sub> NDIR analyser.

The use of the weighted regression line leads to a equation slightly different from that given by Ordinary Least Square (OLS) :

- $Y_{\text{OLS}} = 1,2038x + 4,276$
- $Y_{\text{WRL}} = 1,256x + 3,600$



The weighted regression line WRL gives a lower value of s :

$$s_{\text{OLS}} = 3,7 \text{ mg/m}^3 \quad \text{and} \quad s_{\text{WRL}} = 1,8 \text{ mg/m}^3$$

From EN 14791, we can draw the following information at the average concentration of 14,4 mg/m<sup>3</sup> and at the ELV for the SRM:

- $u(\text{SRM} \circ \text{repeatability}) = 9,6 \%$  and  $6,4 \%$  respectively,
- $u(\text{SRM} \circ \text{int erlab}) = 12,8 \%$  and  $6,5 \%$ .



The excel file gives an expanded uncertainty  $U(y) = 48,8 \%$  at the average concentration of  $14,4 \text{ mg/m}^3$ .

At ELV :  $U(y) = 23,6 \%$ . => we do not fulfil the requirement of the Directive (20%). The main part of the uncertainty comes from the OLS model.

	at $x_{aver}$	at ELV	
u(SRM repeatability)	9,6%	6,4%	
u(SRM interlab)	12,8%	6,5%	
$s^2$	8,994	24,166	
$u^2(\text{AMS}^\circ \text{ repeat.})$	0,005	1,440	
$u^2(\text{lab})$	3,416	10,563	
$u^2\text{total}$	12,410	34,729	
u(AMS)	3,52	5,89	$\text{mg/m}^3$
u(AMS) %	24,4	11,8	%
U(AMS)	7,05	11,79	$\text{mg/m}^3$
U(AMS) %	48,8	23,6	%

## 6 – Variability test

### 6.1 Dust

OLS and WRL give similar calibration functions and relative difference between the estimates at standard conditions  $\hat{y}_{i,s}$  and  $y_{i,R,s}$  is slightly better for the WRL (see table below) : the average of relative difference is 1,20 % for the OLS Model and 0,42 % for the WRL model. Our conclusion is that in this example OLS Model improve slightly the estimate.

#### Variability test

$i$	$\hat{y}_{i,s}$	$\hat{y}_{i,s}$	SRM $y_{i,R,s}$ $\text{mg/m}^3$	Difference	Difference	Difference	Difference
	OLS	WRL		Di abs	Di rel.	Di abs	Di rel.
1	1,40	1,38	1,07	-0,33	-31,24	-0,31	-28,91
2	6,76	6,71	6,41	-0,35	-5,47	-0,31	-4,78
3	8,94	8,89	8,25	-0,69	-8,35	-0,64	-7,72
4	6,98	6,93	5,39	-1,59	-29,41	-1,54	-28,59
5	10,36	10,31	11,86	1,50	12,63	1,55	13,10
6	1,36	1,34	2,52	1,16	46,05	1,19	47,01
7	10,91	10,85	10,49	-0,42	-4,01	-0,36	-3,46
8	7,92	7,87	8,93	1,01	11,31	1,06	11,85
9	6,45	6,41	8,76	2,31	26,40	2,35	26,88
10	14,24	14,17	18,24	4,00	21,93	4,07	22,31
11	12,85	12,79	12,41	-0,44	-3,55	-0,38	-3,03
12	15,30	15,22	13,36	-1,94	-14,49	-1,86	-13,93
13	2,67	2,64	2,18	-0,49	-22,71	-0,47	-21,42
14	8,02	7,97	6,76	-1,26	-18,66	-1,21	-17,96
15	4,79	4,75	4,86	0,08	1,59	0,11	2,31
average				<b>0,17</b>	<b>-1,20</b>	<b>0,22</b>	<b>-0,42</b>
standard deviation				<b>1,57</b>	<b>21,73</b>	<b>1,58</b>	<b>21,51</b>
				<b>OLS</b>		<b>WRL</b>	

The variability test performed on absolute values gives a positive result ( $S_D < k_v \sigma$ ). The same test performed on the standard deviation calculated on the population of the relative values also gives a positive result.

$S_D$	1,574
$\sigma$	9,184
$k_V$	0,9761

1,574	<	8,964
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AMS pass the variability test

## 6.2 SO<sub>2</sub>

In this example we have rather high differences between the estimates at standard conditions  $\hat{y}_{i,s}$  and  $y_{i,R,s}$  (see table below) : the average of relative difference is 45 % for the OLS Model and 28 % for the WRL model!

Our conclusion is that in this example WRL improves significantly the estimate.

### Variability test

$i$	$\hat{y}_{i,s}$	$\hat{y}_{i,s}$	SRM $y_{i,R,s}$ mg/m <sup>3</sup>	Difference Di	Difference Di	Difference Di	Difference Di
	OLS	WRL		abs	rel.	abs	rel.
1	5,27	4,65	3,76	-1,51	-40,16	-0,89	-23,64
2	4,15	3,48	2,21	-1,94	-88,18	-1,27	-57,74
3	4,79	4,08	2,13	-2,66	-124,93	-1,95	-91,63
4	5,27	4,48	2,67	-2,61	-97,82	-1,81	-68,02
5	4,36	3,68	2,33	-2,03	-87,18	-1,35	-58,18
6	4,59	3,89	3,77	-0,82	-21,81	-0,12	-3,14
7	5,89	5,26	4,26	-1,63	-38,23	-1,00	-23,40
8	4,82	4,09	2,59	-2,23	-86,17	-1,50	-58,03
9	4,73	4,02	2,27	-2,46	-108,51	-1,76	-77,43
10	4,89	4,22	2,74	-2,15	-78,35	-1,48	-53,76
11	5,69	4,90	2,31	-3,38	-146,39	-2,59	-112,31
12	6,37	5,79	5,06	-1,31	-26,01	-0,74	-14,61
13	5,70	5,08	9,67	3,97	41,03	4,60	47,53
14	3,99	3,36	9,73	5,74	58,99	6,38	65,53
15	19,16	19,14	24,62	5,46	22,18	5,48	22,26
16	27,66	27,99	34,44	6,78	19,69	6,44	18,72
17	58,14	59,82	52,21	-5,94	-11,37	-7,61	-14,57
18	71,93	74,34	67,88	-4,04	-5,96	-6,46	-9,51
average				-0,71	-45,51	-0,42	-28,44
standard deviation				3,62	59,64	3,89	47,95
					OLS		WRL

The test of variability given by the EN 14181 accepts the results :

$S_D$	3,623
$\sigma$	5,102
$k_V$	0,9761

3,623	<	4,980
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**AMS pass the variability test**

This result is not consistent with the estimate of the uncertainty at the ELV that shows that we do not fulfil the Directive requirement.

If we consider the same variability test calculated with relative values, which is more relevant, because we give the same weight to all the values, then the test fails.

**7 - Conclusion**

This presentation proposes a rather comprehensive procedure to calculate the actual uncertainty of the calibrated AMS at the ELV. This procedure could be a more suitable way than the variability test to conclude on the conformity of an AMS at the ELV which does not give the actual uncertainty in the studied range and at ELV.

In the few examples that we have submitted in this position paper we had the possibility to vary the concentrations on the full range. In this propitious configuration we found that :

- The result of uncertainty of a calibrated AMS shows that the conclusion of the QAL2 test depends on the quality of the reference methods. A Reference method with a bad repeatability induces a rather high uncertainty  $s$  resulting from the model. Moreover, the variability test of the EN 14181 does not take into account the uncertainty coming from the lack of trueness of the SRM :  $u(SRM \circ interlab)$ , the contribution of which should be included in a comprehensive calculation of the uncertainty of the calibrated AMS. Unfortunately,  $u(SRM \circ interlab)$  is not always low and may create difficulties when the laboratory performing AST is not the same one as for QAL2. Thus the example given with the manual reference SO<sub>2</sub> method leads to the rejection of the AMS because of a too high uncertainty. The variability test proposed by EN 14181 is not relevant and leads to an opposite conclusion.
- O<sub>2</sub> corrections may increase greatly the uncertainty attached to the results given by the calibrated AMS, especially when the O<sub>2</sub> concentration is higher than 11%. In these cases the objective of the Directives cannot be fulfilled.
- a Weighed Regression Line is more appropriate and gives a better estimate of the true value than the Ordinary Least Square.

## Annex A : regression methods

### Non-parametric regression methods

Of the non-parametric methods available, perhaps the simplest is Theil's incomplete method. Theil's incomplete method determines the slope of a regression line as the median of the slopes calculated from selected pairs of points: the intercept of the line is the median of the intercept values calculated from the slope and the co-ordinates of the individual points.

The Theil's method has three distinct advantages: it does not assume that all the errors are only in the y direction (i-e uncertainty on x is possible) and either the x or y direction errors are normally distributed; and it is not affected by the presence of outlying results.

The method assumes that a series of points  $(x_1, y_1), (x_2, y_2), \dots$  is fitted by a line of the form  $y = a + b \cdot x$ . The first step in the calculation involves ranking the points in order of increasing  $x$ . If the number of points,  $x$ , is odd, the middle point, i.e. the median value of  $x$ , is deleted: the calculation always requires an even number of points. For any pair of points  $(x_i, y_i), (x_j, y_j)$ , where  $x_j \geq x_i$ ,

the slope,  $b_{ij}$  of the line joining the points can be calculated from : 
$$b_{ij} = \frac{(y_j - y_i)}{(x_j - x_i)}$$

Slopes  $b_{ij}$  are calculated for the pair of points  $(x_1, y_1)$  and the point immediately after the median  $x$ -value, for  $(x_2, y_2)$  and the second point after the median  $x$ -value, and so on until the slope is calculated for the line joining the point immediately before the median  $x$  with the last point. Thus, if the original data contained 11 points, five slopes would be estimated (the median point having been omitted). For eight original points there would be four slope estimates, and so on. These slope estimates are arranged in ascending order and their median is the estimated slope of the straight line. With this value of  $b$ , values  $a_i$  for the intercept are estimated for each point with the aid of the equation  $y = a + b \cdot x$ . Again the estimates of  $a$  are arranged in ascending order and the median value is chosen as the best estimate of the intercept of the line. The method is illustrated in the example and lead to a non satisfactory regression function (underestimation for low values and overestimation for high values).

### Weighed regression Method

Weighed regression method (WRM) is commonly used when the uncertainties of methods are not constant on the whole range of concentrations.

The regression line must be calculated to give additional weight to those points where the uncertainty is smallest : it is more important for the calculated line to be close to such points than to be close to the points representing higher concentrations with the largest uncertainties. This result is achieved by giving each point a weighing inversely proportional to the corresponding variance ,  $s_i^2$ .

Weights : 
$$w_i = \frac{1}{s_i^2}$$

Weighed slope :

$$b_w = \frac{\sum_i w_i x_i y_i \cdot \sum_i w_i - \sum_i w_i x_i \cdot \sum_i w_i y_i}{\sum_i w_i x_i^2 \cdot \sum_i w_i - (\sum_i w_i x_i)^2}$$

Weighed intercept :

$$a_w = y_w - b \cdot x_w$$

Comparison of the results of the unweighed and weighed regression calculation is very instructive : the weighed centroid  $(\bar{x}_w, \bar{y}_w)$  is much closer to the origin of the graph than the unweighed centroid  $(\bar{x}, \bar{y})$ .

**Annex B : Contribution of the correction on dry gas and of the correction to a reference concentration of oxygen to the total uncertainty attached to a result of a measurement**

- **Case of the conversion of the concentration of the pollutant to a reference concentration of oxygen**

The conversion of a concentration given at actual conditions of oxygen, to a reference oxygen concentration is calculated as follows:

$$C_{O_2,ref} = C_{O_2,meas} \frac{20,9 - O_{2,ref}}{20,9 - O_{2,meas}} \quad (1)$$

where

- $C_{O_2,ref}$  is the concentration of pollutant corrected to a reference oxygen concentration
- $C_{O_2,meas}$  is the concentration of pollutant measured in the stack at the actual oxygen concentration
- $O_{2,ref}$  is the reference oxygen concentration
- $O_{2,meas}$  is the oxygen concentration measured in the stack

The derivative of the equation (1) leads to :

$$u^2(C_{O_2,ref}) = \left( \frac{\partial C_{O_2,ref}}{\partial C_{O_2,meas}} \right)^2 \cdot u^2(C_{O_2,meas}) + \left( \frac{\partial C_{O_2,ref}}{\partial O_{2,meas}} \right)^2 u^2(O_{2,meas}) \quad (2)$$

$$\frac{\partial C_{O_2,ref}}{\partial C_{O_2,meas}} = \frac{20,9 - O_{2,ref}}{20,9 - O_{2,meas}} \quad (3)$$

$$\frac{\partial C_{O_2,ref}}{\partial O_{2,meas}} = \frac{(20,9 - O_{2,ref}) \times C_{meas}}{(20,9 - O_{2,meas})^2} \quad (4)$$

Equation (2) is equivalent to equations (5) or (6) :

$$u^2(C_{O_2,ref}) = \left( \frac{20,9 - O_{2,ref}}{20,9 - O_{2,meas}} \right)^2 \cdot u^2(C_{O_2,meas}) + \left( \frac{(20,9 - O_{2,ref}) \cdot C_{O_2,meas}}{(20,9 - O_{2,meas})^2} \right)^2 u^2(O_{2,meas}) \quad (5)$$

$$u^2(C_{O_2,ref}) = C_{C_{O_2,ref}}^2 \cdot \left( \frac{u^2(C_{O_2,meas})}{C_{O_2,meas}} + \frac{u^2(O_{2,meas})}{(20,9 - O_{2,meas})^2} \right) \quad (6)$$

Uncertainty associated with the concentration of the pollutant brought back to a reference concentration of oxygen depends on :

- uncertainty of the measurement of the pollutant
- the concentration of oxygen in the stack and of uncertainty associated with oxygen measurement

An example of calculation of uncertainty associated with measurement of a pollutant after conversion to a reference concentration of oxygen is given hereafter. For a concentration given at actual oxygen concentration, and knowing uncertainties of measurement of the pollutant and the oxygen concentration, we have calculated the uncertainty associated with the concentration corrected at the reference concentration of oxygen for various oxygen concentrations measured in the stack. The table shows that final uncertainty increases with the oxygen concentration in the stack, this independently of respective uncertainties of pollutant and oxygen measurements.

**Table 1** : Example of uncertainty values associated to the concentration of pollutant after conversion at a reference concentration of oxygen.

Concentration of pollutant C	200	mg/m <sup>3</sup> at actual O <sub>2</sub> concentration
type-uncertainty at actual O <sub>2</sub> réel u(C)	4,7	% of the concentration
type- uncertainty of O <sub>2</sub> measurement	2,5	% relative
O <sub>2,ref</sub>	11	% volume

O <sub>2 mes</sub>	C1 at 11%O <sub>2</sub> mg/m3	u(C1) mg/m3	u(C1) % relative
% volume	calculation with O <sub>2mes</sub>		
5	124,53	5,93	4,77
6	132,89	6,39	4,81
7	142,45	6,93	4,87
8	153,49	7,60	4,95
9	166,39	8,43	5,07
10	181,65	9,50	5,23
11	200,00	10,92	5,46
12	222,47	12,87	5,78
13	250,63	15,65	6,25
14	286,96	19,84	6,92
15	335,59	26,53	7,90
16	404,08	38,06	9,42
17	507,69	60,25	11,87
18	682,76	110,70	16,21
19	1042,11	265,09	25,44
20	2200,00	1226,59	55,75

• **Case of the conversion of the concentration of the pollutant on dry gas**

Conversion to dry gas of a concentration measured on wet gas is calculated as follows:

$$C_{dry} = C_{hum} \frac{100}{100 - H_2O_{meas}} \tag{7}$$

where

*C<sub>dry</sub>* is the concentration given on dry basis

$C_{hum}$  is the concentration measured in stack given on wet basis

$H_2O_{meas}$  is the water vapour concentration measured in stack

The derivative of the equation (7) leads to :

$$u^2(C_{dry}) = \left( \frac{\partial C_{dry}}{\partial C_{hum}} \right)^2 u^2(C_{hum}) + \left( \frac{\partial C_{dry}}{\partial H_2O_{meas}} \right)^2 u^2(H_2O_{meas}) \quad (8)$$

$$\frac{\partial C_{dry}}{\partial C_{hum}} = \frac{100}{100 - H_2O_{meas}} \quad (9)$$

$$\frac{\partial C_{dry}}{\partial H_2O_{meas}} = \frac{100 \times C_{hum}}{(100 - H_2O_{meas})^2} \quad (10)$$

Equation (8) is equivalent to equations (11) or (12) :

$$u^2(C_{dry}) = \left( \frac{100}{100 - H_2O_{meas}} \right)^2 u^2(C_{hum}) + \left( \frac{100 \times C_{hum}}{(100 - H_2O_{meas})^2} \right)^2 u^2(H_2O_{meas}) \quad (11)$$

$$u^2(C_{dry}) = C_{dry}^2 \times \left( \frac{u^2(C_{hum})}{C_{hum}^2} + \frac{u^2(H_2O_{meas})}{(100 - H_2O_{meas})^2} \right) \quad (12)$$

Uncertainty associated with the concentration expressed on dry basis depends on:

- uncertainty of the measurement
- concentration of water vapour in the stack and uncertainty associated with the result of the measurement

An example of calculation of uncertainty associated with a measurement after conversion to dry basis is given hereafter. For a given concentration measured on wet basis, and knowing uncertainties of measurement of the pollutant and water vapour, we calculate the uncertainty associated with the concentration corrected on dry basis for various water vapour contents measured in the stack. The table shows that final uncertainty increases with the water vapour content of gases, independently of the uncertainties of measurement of the pollutant and of water vapour.



**Table 2** : Example of uncertainty values associated to the concentration of pollutant after conversion on dry basis

Concentration of pollutant C 150 mg/m<sup>3</sup> on wet basis  
 type-uncertainty of the concentration of the pollutant u(C) on wet basis 4,7 % of the measured value  
 type-uncertainty associated water vapour measurement u(H<sub>2</sub>O) 10 % of the measured value

Water vapour % volume H <sub>2</sub> O mes	C1 mg/m <sup>3</sup> calculation with H <sub>2</sub> O	u(C1) mg/m <sup>3</sup>	u(C1) % relative
1	151,52	7,12	4,70
2	153,06	7,20	4,70
3	154,64	7,28	4,71
4	156,25	7,37	4,72
5	157,89	7,47	4,73
6	159,57	7,57	4,74
7	161,29	7,68	4,76
8	163,04	7,79	4,78
9	164,84	7,92	4,80
10	166,67	8,05	4,83
11	168,54	8,19	4,86
12	170,45	8,34	4,89
13	172,41	8,50	4,93
14	174,42	8,68	4,97
15	176,47	8,86	5,02
16	178,57	9,06	5,07
17	180,72	9,27	5,13
18	182,93	9,49	5,19
19	185,19	9,73	5,25
20	187,50	9,98	5,32
21	189,87	10,25	5,40
22	192,31	10,54	5,48
23	194,81	10,85	5,57
24	197,37	11,18	5,66
25	200,00	11,52	5,76
26	202,70	11,89	5,87
27	205,48	12,29	5,98
28	208,33	12,71	6,10
29	211,27	13,16	6,23
30	214,29	13,63	6,36
31	217,39	14,13	6,50
32	220,59	14,67	6,65
33	223,88	15,24	6,81
34	227,27	15,85	6,97
35	230,77	16,49	7,15

$$C1 = C \times \frac{100}{100 - H_2O_{mes}}$$

$$u^2(C1) = \left( \frac{100}{100 - H_2O_{mes}} \right)^2 u^2(C) + \left( \frac{100 \times C}{(100 - H_2O_{mes})^2} \right)^2 u^2(H_2O_{mes})$$

$$u^2(C1) = C1^2 \times \left( \frac{u^2(C)}{C^2} + \frac{u^2(H_2O_{mes})}{(100 - H_2O_{mes})^2} \right)$$