Robustness of the QAL2 calibration (EN 14181)
Uncertainty on the results given by a calibrated AMS

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EMISSION MONITORING OF INDUSTRIAL INSTALLATIONS: A CONTEXT SWITCH

The European Directives on waste incineration (2000/76/CE) and on large combustion plants (2001/80/CE) require to refer to international and national standards for emission monitoring and they specify requirements for the performance characteristics and the total uncertainty attached to the results provided by the automated monitoring systems (AMS) used for continuous monitoring.

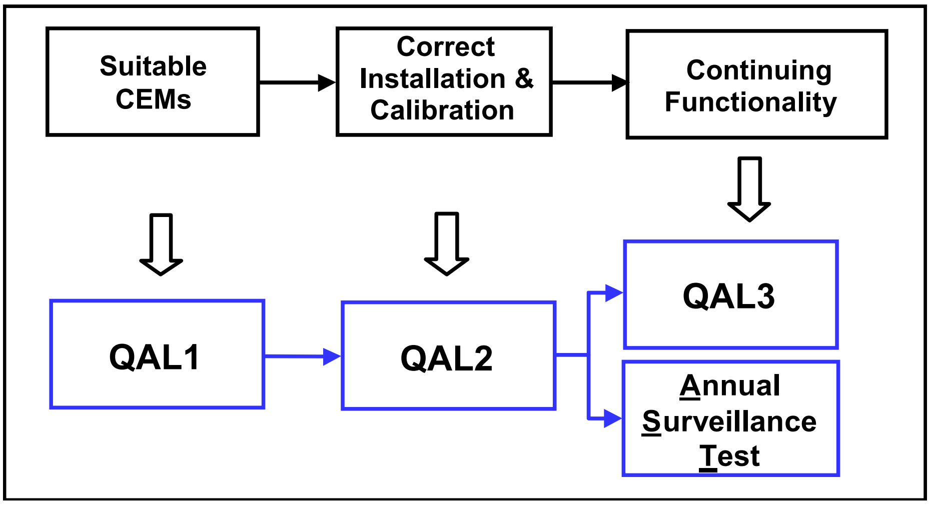
CEN TC 264 worked out in 2004 the EN 14181 standard which defines the various stages of quality assurance to be implemented to guarantee the reliability of the continuous emission monitoring. It applies to incineration and combustion plants but its use could be extended to other industrial plants after the publication of the future integrated European Directive which will replace the 7 already existing European directives.

The EN 14181 standard specifies three levels of quality assurance (indicated by initials QAL) and an annual test of monitoring: (annual monitoring test indicated by initials AST). They are as follows:

QAL1	A procedure to demonstrate that the AMS selected before their installation on site are adapted to the use for which they are intended, i.e. ready to measure with the required uncertainty.
QAL2	A procedure to check that the AMS are correctly installed and to calibrate them by comparison with the standard reference method (SRM). A test of variability is also carried out to check the compatibility of the AMS on site with the level of required uncertainty.
QAL3	A procedure using a control chart for the determination of the zero and span drift of the AMS, carried out with reference materials and allowing demonstrating that the AMS continue to provide reliable data with the level of required uncertainty.
AST	An annual test, corresponding to a mini QAL 2, to evaluate if the AMS functions satisfactorily.

These quality assurance levels follow a logical sequence to demonstrate the suitability of the AMS, its correct installation, commissioning, and calibration, followed by continuing and correct operation (see Figure 1).

Figure 1 – *the sequence of quality assurance levels in EN 14181*



EN 14181 is one of the principal new tools, at the disposal of the actors implied in emission controls on stacks to ensure the reliability and the quality of the measurement results.

QAL1, while being based on EN 15267 which sets the certification rules of the AMS in Europe actually almost requires certification. EN 15267-3 describes the procedure to determine the performance characteristics of the AMS and to calculate the total measurement uncertainty for variation of standard conditions of the influence factors. The total measurement uncertainty determined under the field conditions at the limit value must be lower than 75% of the uncertainty objective fixed by the directive to be sure that the AMS will pass the tests QAL2 and QAL3 during its operation on site.

The QAL2 stage, by fixing the calibration procedure per comparison with the SRM, limits the simple method of calibration with materials of reference to restricted cases (quoted by GA X 43-132, worked out by the AFNOR commission to specify the details of implementation of EN 14181).

For the compounds being the subject of a continuous-monitoring, with the implementation of EN 14181, the controls carried out for regulatory purposes by the approved organizations do not have, as a main goal to check the conformity of the installation any more, but rather to check the state of correct operation of the AMS installed in the plant. Consequently, the data provided by the AMS will be considered of a sufficient quality to check the conformity of an installation at any period of the year and to calculate annual flows of pollutants rejected by the installation.

OBJECTIVES OF THE STUDY

The prime objective of this study financed by the French Ministry in charge of Environment and by ADEME (French Environment and Energy Management Agency) was **to check the quality and the robustness of the QAL2 according to test conditions met on site**. For that, the various situations of the field were repeated:

- Case A : ideal conditions where the concentrations vary on all the range from 0 to daily ELV with 20 points
- Case B : concentration range varying on all the range from 0 to daily ELV with a limited number of points: 10 points
- Case C : concentration range restricted to 50% of the range from 0 to daily ELV with a limited number of points: 10 points
- Case D : concentration range reduced to a cloud of 5 points to which is added or not the zero point. For each case D1 (low concentrations) and D2 (high concentrations). the calibration functions obtained with or without the zero are compared and the Calibration function whose R^2 is largest is kept. In the thirds case studied D3, the 5 points are equally distributed on all the range of measurement.

From the digital processing of the results, it was given in which site configuration (possibility of varying the concentrations on site or not) or of uncertainty of the SRM, it can be most relevant to reduce the number of couples of points to even substitute for the suggested method of calibration QAL2, a simple adjustment by reference materials.

The second objective of the study aimed at using the test results in order **to estimate the uncertainty attached to a result given by an AMS** conformed with QAL1 requirements (thus linear and not very sensitive to interfering) when it is **calibrated according to QAL2**.

FACILITIES AND CONDITIONS OF TESTS

The QAL2 tests were related to 3 certified AMS from the Environnement S.A. company:

- A MIR-FT which can measure simultaneously by Fourier Transform Infra-red absorption (IRTF) the gases: HCl, HF, NH_3, SO_2, NO, NO_2, NOx, CO, TOC, H_2O, N_2O and the measurement of O_2 by an integrated Zirconia cell. Many other gases are also available on request.
- A MIR 9000 which measures continuously gas compounds by infra-red spectroscopy with gas filter correlation: HCl, HF, SO_2, NO, NO_2, NOx, CO, TOC, N_2O
- A Graphite 52 M for the measurement of TOC with a flame ionization detector.

The tests related to two compounds for which the SRM is manual: HCl and SO_2, three compounds for which the SRM is automatic: CO, NOx and TOC and finally, the peripheral compounds allowing the conversion of the data under the reference conditions (O_2 and H_2O).

Five approved organizations took part in the tests: ANECO, BUREAU VERITAS, CETIAT, INERIS and LECES.

To facilitate the test program, it was implemented on the test bench of INERIS which can provide gas effluents resulting from combustions or waste incineration. It is equipped to accommodate five teams simultaneously.

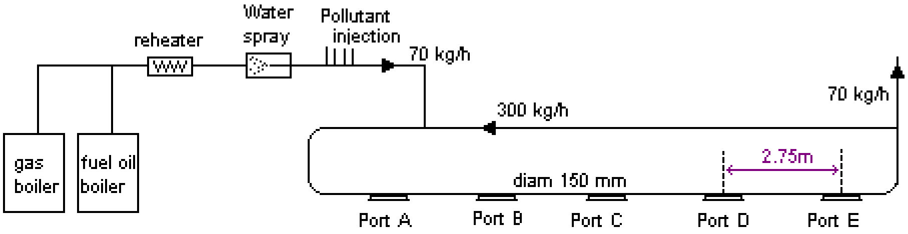


Figure 2 – *Test bench scheme*

To generate gases, the bench (cf. figure n°2) is equipped by two boilers of approximately 50 kW each, the first fed with natural gas, the second with light fuel. The gases resulting from this combustion can be heated, humidified to simulate effluents leaving a scrubber and the concentrations of some pollutants increased by the controlled gas addition (CO, NO, SO_2, HCl, etc) or vaporization of made up liquids (specific VOC).

The generated gases return in a steel loop, internally protected by a PTFE coating, where a flow of 300 kg/h. circulates. This loop is maintained in temperature by electric tracing. The internal diameter of the duct is 150 mm.

The concentrations of each compound varied from 0 to $ELV_{1/2h}$ for waste incineration. All the compounds were measured in parallel.

Table n°1: Table of the selected emission limit values for the measurement campaign

Compound	**Range**	**ELV day**	**ELV ½ h**
SO_2	400 mg/m_0^3	50 mg/m_0^3	200 mg/m_0^3
HCl	120	10	60
NOx	1000	200	400
CO	1000	50	150
TOC	40	10	20

RESULTS AND DISCUSSION

1. INFLUENCE OF THE NUMBER AND OF THE DISTRIBUTION OF THE POINTS ON THE STUDIED RANGE AND INFLUENCE OF THE SRM ON THE QUALITY OF THE CALIBRATION FUNCTIONS

- As recommended in the AFNOR guide GA X 43-132, the automatic AMS and SRM were adjusted before the calibration.

  This preliminary adjustment lead to Calibration functions with a slope close to 1 for the compounds which have an automatic SRM (O_2, NOx, CO, TOC).
- Calibration functions are of better quality when the SRM is automatic (R^2 coefficient much higher than 0,9).

	O_2	**CO**	**TOC**	**NOx**	**HCl**	**SO_2**
Calibration function ax+b						
a	0,9834	1,021	1,051	0,982	0,875	1,186
b	0,1748	5,248	1,61	-0,163	0,839	-6,26
coefficient R^2	0,944	0,9999	0,9975	0,9998	0,983	0,873

Table n°2: *Calibration functions obtained with MIR FT and Graphite52M (case A)*

The coefficient of determination of the equation of the calibration function is not affected by the number of points (20, 10 or 5 points) since those are equally distributed on the range of measurements. A contrario, when the range covered by the points gets narrow, the coefficient of determination is degraded. An example is given below with the TOC results:

TOC	**case A**	**case B**	**case C**	**case D1**	**case D2**	**case D3**
Calibration function				with/without pt 0	with/without pt 0	
a	1,051	1,024	1,063	1,337/0,9461	1,164/0,4625	1,0421
b	1,61	1,79	1,606	0,785/1,9883	0,099/9,4236	1,438
coefft R^2	0,9975	0,9977	0,9864	0,9051/0,8954	0,9949/0,8098	0,9983
variability test	0,40<1,50	0,34<1,47	0,28<1,47	0,58<0,93	0,43<1,43	0,43<1,43

Table n°3: *Calibration functions and results of variability tests with Graphite 52M*

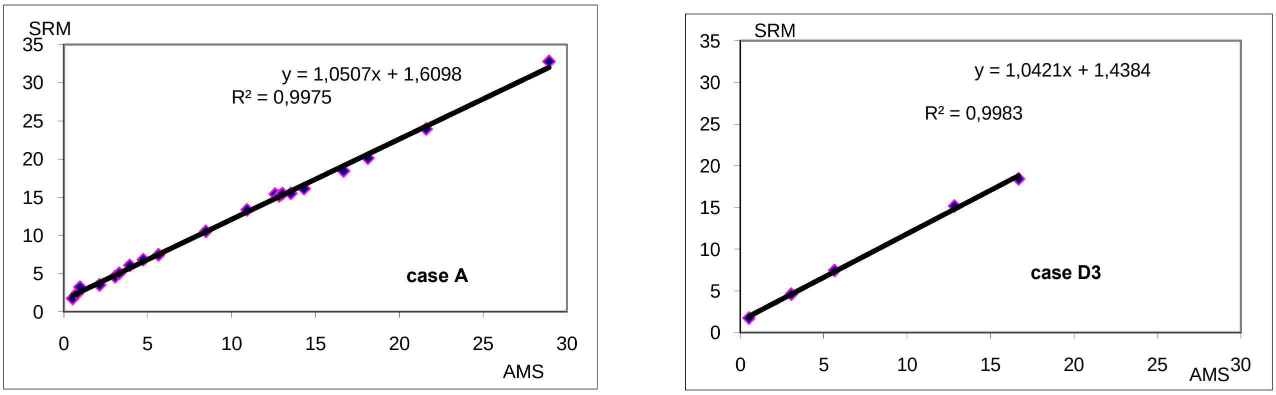


Figure 3 – *Influence of the number of points on the quality of the calibration function*

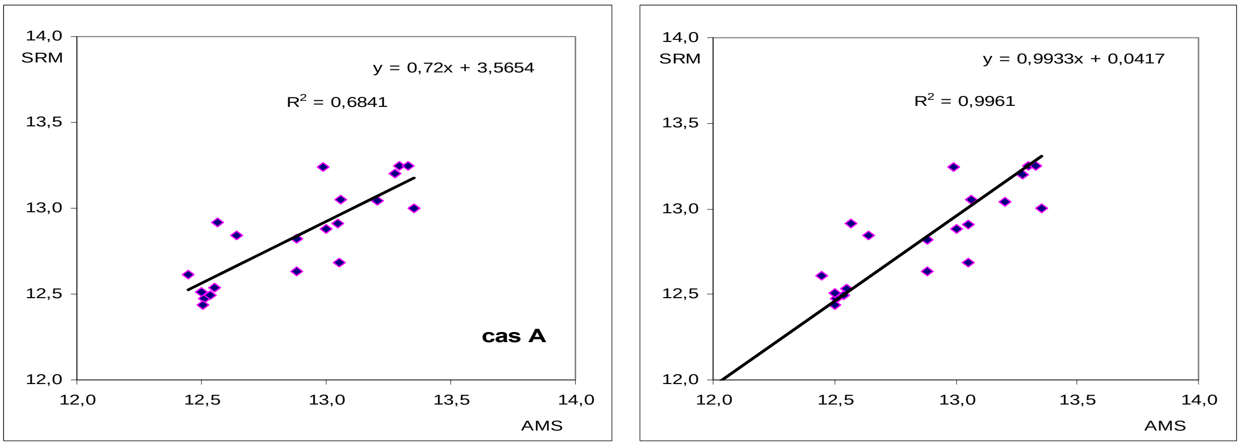
For the case D2, where the cloud of points is located in the highest part of the concentration range, the addition of the point (0,0) appreciably improves the quality of calibration function whose slope passes from 0,46 to 1,16 and R^2 from 0,81 to 0,99. For case D1, where the cloud of points is located in the lowest part of the concentration range, the addition of the point (0,0) does not improve the calibration function.

- In a more general way, for the compounds whose SRM is manual, the characteristics of the calibration functions vary more noticeably according to the configuration because of the variability of SRM data. The quality of the calibration functions, very poor when it is difficult to vary the concentrations, can be highly improved by the addition of the point (0,0), including for the most favorable configurations (A, B and C). An example is given below with the measurement of the water vapor concentration:

H_2O	case A	case B	case C	case D1	case D2
Calibration function ax+b	without/with p^t 0	without/with p^t 0	without/with p^t 0	without/with p^t 0	without/with p^t 0
a	0,7425 / 0,993	0,892 / 1,000	0,584 / 0,994	-0,297 / 0,995	0,34 / 0,995
b	3,2704 / 0,042	1,394 / 0,007	5,39 / 0,015	17,26 / 0,008	8,371 / 0,016
coefft R^2	0,6783 / 0,996	0,8378 / 0,999	0,423 / 0,998	0,169 / 0,999	0,211 / 0,998
Variability test	0,172 < 1,527	0,141 < 1,502	0,173 < 1,5	0,176 < 1,425	0,229 < 1,424

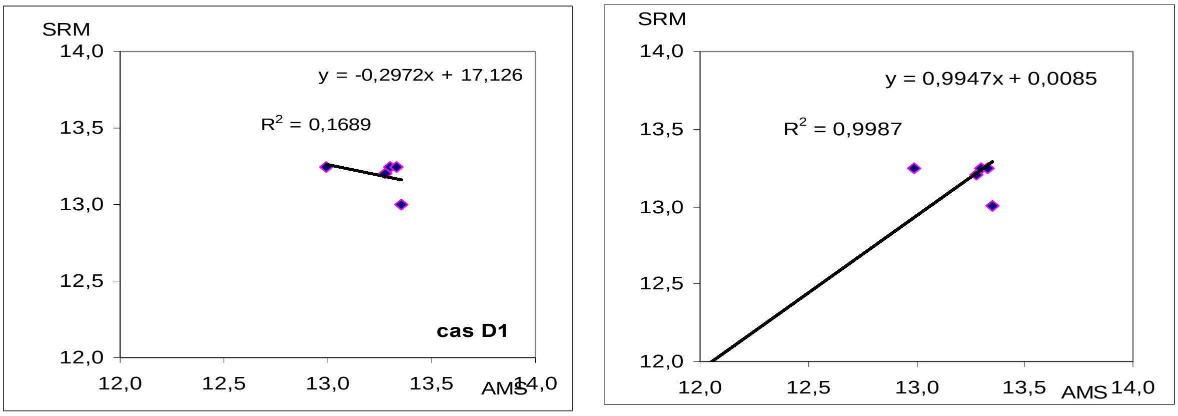
Table n°4 *: Calibration functions and results of variability tests obtained with MIR FT (H_2O)*

The addition of the point (0,0) highly improves the equations of calibration functions, including for configuration A. For D1 and D2, one passes from a slope of -0,297 to 0,995 and from 0,34 to 0,995 respectively. The determination coefficients pass from 0,169 to 0,999 and from 0,211 to 0,999 respectively.



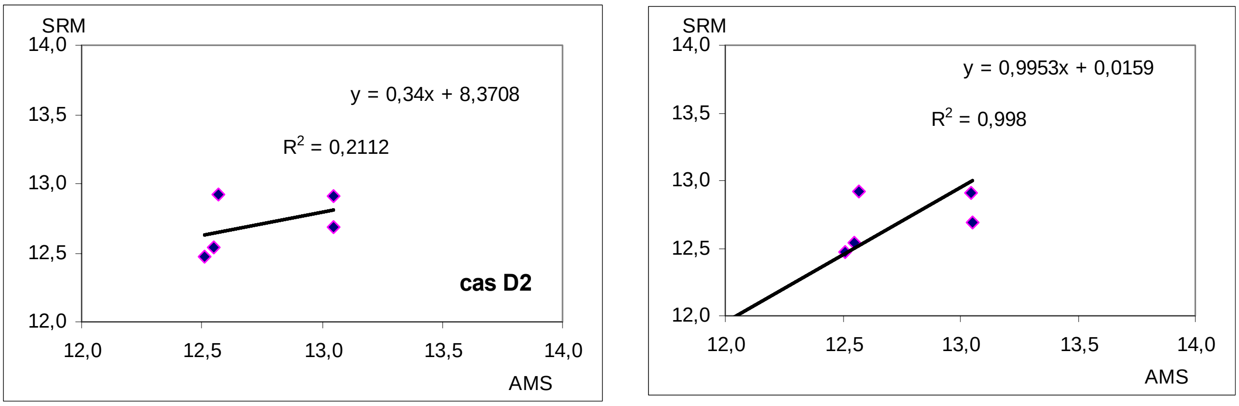
Case A without point (0,0)

Case A with point (0,0)



Case D1 without point (0,0)

Case D1 with point (0,0)



Case D2 without point (0,0)

Case D2 with point (0,0)

Figures n°4 *: Calibrations functions obtained with MIR FT (H_2O)*

VARIABILITY TEST AND SUSPECT VALUES

- The tests of variability carried out with the whole set of data lead to some negative results for the compounds for which the SRM is manual.

  In this case, the uncertainty of the implemented SRM, strongly influences the dispersion of the couples of points around the calibration function. When a manual SRM is implemented, suspect values are almost systematically detected by the test proposed by GA X 43-132. Although the test of variability is not very demanding, the result with this test can be negative by not removing any of the couples of points resulting from the tests. Thus, for HCl and SO_2, we withdrew two pairs of values (tolerated by GA X 43-132). Without these withdrawals of suspect values, the results of the tests of variability on HCl and SO_2 are negative. In the case of an SRM with a high uncertainty, it is relevant to be able to remove one to two suspect couples not to weigh down over the AMS the threat of a rejection for lack of fidelity, which is actually due to the SRM and its implementation. After removal of one to two suspect data, the result of the test becomes positive. The test suggested in the guide GA X 43-132 is thus relevant. On the other hand, it would be more relevant, with the sight of the treated examples, not to exclude the couples from points remaining in the interval + 0,5 σ_0 around the calibration function (the guide indicates + 0,25 σ_0).
- For the compounds with automatic SRM, the tests of variability are always positive.

2. COMPARISON OF THE RESULTS OF QAL2 OF DIFFERENT PARTICIPANTS

Table n°5 hereafter provides the averages of the calibrated values of the participants at the level of the daily ELV (ELV_d), for the various configurations:

Compound measured	**O_2**	**CO**	**NO**	**TOC**	**SO_2**	**HCl**
ELV_d in mg/m_0^3 at 11% of O_2	-	50	200	10	50	10
Calibrated value (case A) **QAL2 with 20 points** distributed on all the range	10,4	53,9	202,7	10,2	52,1	9,90
Calibrated value (case B) **QAL2 with 10 points** distributed on all the range		54,2	203,4	10,2	48,4	9,79
Calibrated value (case C) **QAL2 with 10 points** distributed on 50% of the range		49,9	212,2	10,1	51,9	10,68
Calibrated value (case D1 with pt 0,0) *Case D1 without pt (0,0)* **QAL2 with a cloud of 5 points** distributed on the lowest part of the range		51,8 *40,9*	178,0 *200,0*	9,6	48,9 *50,9*	8,43 *2,81*
Calibrated value (case D2 with pt 0,0) *Case D2 without pt (0,0)* **QAL2 with a cloud of 5 points** distributed on the highest part of the range		53,7 *58,3*	202,5 *209,5*	10,3	52,7 *20,7*	9,17 *11,5*

Table n°5: *Average calibrated values for the various configurations*

We see that the influence of the configuration of the points on the slope of the calibration function or on the calibrated value remains often limited, if the operator adds the point (0,0) or forces the calibration function to pass by 0, since the measuring points are limited to a group of points of low size. The possibility of adding the point (0,0) is mentioned in GA X 43-132, whatever the configuration met during the tests, in the express condition of checking that the AMS gives a signal 0 with a reference material representing zero state.

ESTIMATE OF THE MEASUREMENT UNCERTAINTY THROUGH THE CONFIDENCE INTERVAL ON THE CALIBRATED VALUES

The summary table n°6 hereafter gives an estimate of the confidence interval on the values calibrated for the various configurations:

The confidence interval is evaluated by considering in first estimate, 2 times the standard deviation of the calibrated values at the daily ELV obtained by the participants

Compound measured	**O_2**	**CO**	**NO**	**COT**	**SO_2**	**HCl**
ELV $_d$ in mg/m_0^3 at 11% of O_2	-	50	200	10	50	10
Confidence interval % on calibrated value **QAL2 with 20 points** distributed on all the range (case A)	5,6	3,1	6,7	21,2	13,9	16,3
Confidence interval % on calibrated value **QAL2 with 10 points** distributed on all the range (case B)		3,0	6,0	24,9	14,4	18.4
Confidence interval % on calibrated value **QAL2 with 10 points** distributed on 50% of the range (case C)		2,7	8,4	19,6	27,6	27,9
Confidence interval % on calibrated value **QAL2 with a cloud of 5 points** distributed on the lowest part of the range (case D1+ pt 0,0) *case D1*		19,9 *25,0*	6,1 *15,2*	42,6	14,9 *25,1*	19,3 *628*
Confidence interval % on calibrated value **QAL2 with a cloud of 5 points** distributed on the highest part of the range (case D2+pt 0,0) *case D2*		3,6 *6,0*	6,4 *11,2*	19,7	16,6 *238*	16,1 *32,2*

Table n°6: *Confidence intervals on the calibrated values for the various configurations*

- **We note that:**

  Confidence intervals allocated to the calibrated values, which can be considered as expanded uncertainties, are appreciably more important for the compounds where the SRM is manual. However, we have an exception with Graphite 52 M, where the measurand is a concentration index of VOCs and for which we know that measurement is very dependent on the configuration of the FID used and where the concept of accuracy of the SRM is quite relative (the response factors can be different from one model of analyzer to another).

  We note that the calibrated value resulting from calibration QAL2 varies slightly for cases A, B, C or D2 for the compounds where the SRM is automatic.

  The calibrated value resulting from calibration QAL2 varies more as soon as one varies the number of data, for the compounds where the SRM is manual.

- **The impact of the configuration of the number and distribution of points on the effective range is less important when the uncertainty of the SRM is low.**

We note that it is not inevitably necessary to have a high number of points to obtain a calibrated value close to the expected concentration and an acceptable uncertainty. We notice that in the case of a 5 points cloud, close to the top-of-the-range, since it is associated the point (0,0), the quality of the results in terms of accuracy and uncertainty was similar to the one we have in case A, where the 20 points are equally distributed on all the range. On the other hand, the cloud of points located at the bottom-of-the-range often led to calibrated values far away from the expected concentration and whose associated uncertainty can be very important.

3. COMPARISON OF UNCERTAINTIES AT THE LEVEL OF THE DAYLY ELV EVALUATED BY A UNCERTAINTY BUDGET OF THE AMS (QAL1) OR OBTAINED DURING CONTROL QAL2

The second objective of the study aimed at using the test results in order to calculate on the one hand the uncertainty attached to a result given by a certified AMS (conform with QAL1, thus linear and with a low cross-sensitivity), and on the other hand the uncertainty when it is calibrated according to QAL2.

Our objective is to check coherence between the results of uncertainty resulting from exercises QAL1 and QAL2. For that it is advisable to calculate the uncertainty which one expects at the level of the limit value, starting from the budget of uncertainties determined on the basis of the evaluation of performance characteristics (QAL1) and to compare it with the uncertainty estimation that we have on the calibrated value of the AMS at the ELV.

Uncertainty at the ELV is given by taking into account the actual variation range of the influence factors and not the default variation range used during the AMS certification, to know if the AMS is in conformity with the European directives objectives.

Table n°7 hereafter provides the results of uncertainty for the 2 approaches:

Compound measured	**O_2**	**CO**	**NO**	**TOC**	**SO_2**	**HCl**
ELV $_d$ in mg/m$_0^3$ at 11% of O_2	-	50	200	10	50	10
Uncertainty required by European Directives for AMS	-	10	20	30	20	40
Uncertainty % **QAL1 actual case,** taking into account lack of homogeneity ➔ $U_{QAL1}(\hat{y}_{VLEj})$		**5,8**	**6,5**	**7,9**	**9,1**	**11,4**
Confidence interval % on calibrated value **QAL2 with 20 points** equally distributed on the range ➔ $U_{QAL2}(\hat{y}_{VLEj})$ (case A)	**5,6**	**3,1**	**6,7**	**21,2**	**13,9**	**16,3**
Confidence interval % on calibrated value **QAL2 with a 5 points cloud in, the lowest part of the range** ➔ $U_{QAL2}(\hat{y}_{VLEj})$ (case D1)		**19,9**	**6,1**	**42,6**	**25,1**	**19,3**
Confidence interval % on calibrated value **QAL2 with a 5 points cloud in, the highest part of the range** ➔ $U_{QAL2}(\hat{y}_{VLEj})$ (case D2)		**3,6**	**6,4**	**19,7**	**16,6**	**16,1**

Table n°7: *Comparison of uncertainty results for the QAL 1 adapted to the measuring site and the QAL 2.*

We note that, when the uncertainty of the SRM is rather low (case of the majority of the automatic methods) then $U_{QAL1}(\hat{y}_{VLEj}) \approx U_{QAL2}(\hat{y}_{VLEj})$, and when the uncertainty is higher (case of the manual methods and FID) then $U_{QAL2}(\hat{y}_{VLEj}) \approx$ 1,5 to 2 times $U_{QAL1}(\hat{y}_{VLEj})$.

This report leads to favour SRMs with low uncertainties, which is often the case for the automatic SRM.

Bibliographie

EN 14181 Quality Assurance of AMS

NF GA X 43-132 Stack emissions - Quality assurance of the automatic measurement systems - Application of the standards EN 14181, EN 13284-2 et EN 14184