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# Quality Assurance of Automated Measuring Systems: practical implementation of prEN 14181:2001.

## Results of field experience at two Italian plants.

Cipriano D.<sup>(1)</sup>, Ferrari A.<sup>(2)</sup>, Negri A.<sup>(1)</sup>

(1) CESI Spa, Environment Business Unit

(2) ARPA (Regional Environment Protection Agency) Lombardia, Servizio Aria

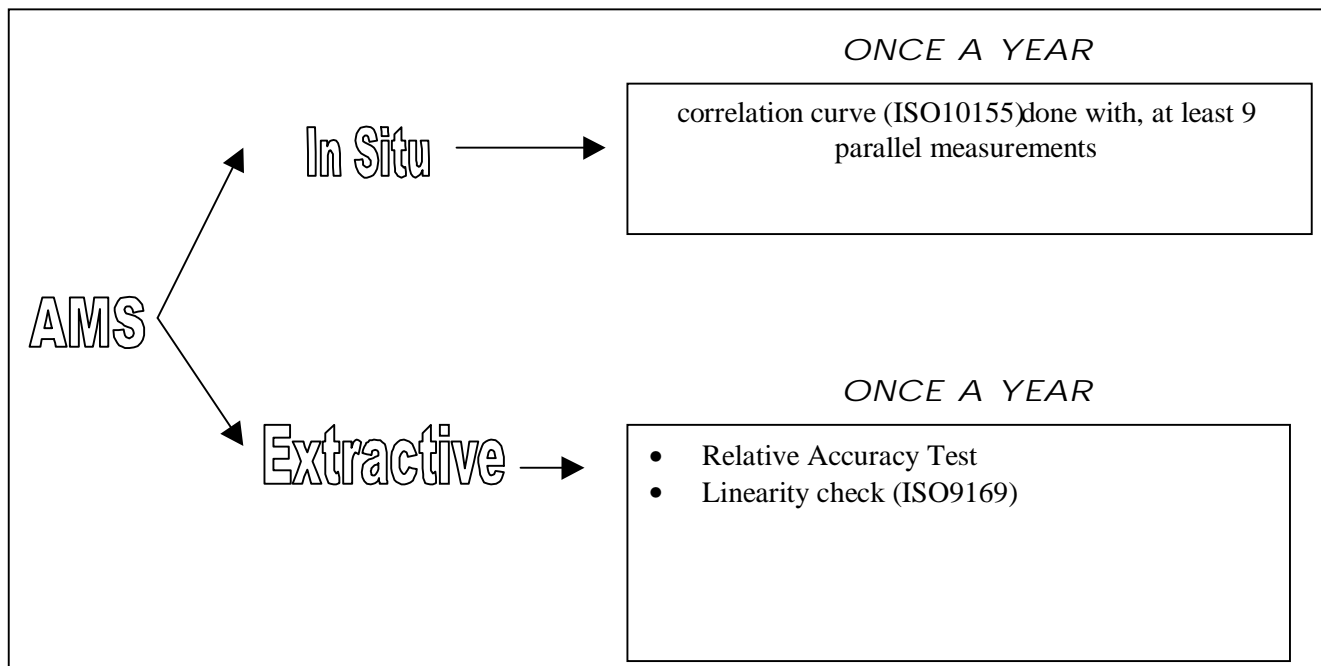
The aim of the prEN14181:2001 standard is to describe the quality assurance procedures for Automated Measuring Systems (AMS), in order to meet the uncertainty requirements on measured values given by EC Directives on Incineration and Large Combustion Plants.

On-site procedures (i.e. QAL2 for the AMS installation, QAL3 for the AMS operation and AST Annual Surveillance Test), that are based on quality assurance and statistic principles, are very different from the corresponding Italian national legislation (Decree of Environment Ministry of December 21, 1995).

### 1. The Two schemes

The Italian decree 12/21/1995 divides the AMS into two big families: one composed by the in-situ analysers and one by the extractive ones.

For each family the decree requires different approaches for the validation of the AMS; these two schemes are showed in the following figure:



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In particular, the extractive AMS are checked using a 'Relative Accuracy Test' derived from USEPA methodology. The procedure requires some parallel measurements done with the AMS and an independent 'Reference Method'.

The formula used to check the 'goodness' of the AMS is the following:

$$I_{AR} = 100 \cdot \left( 1 - \frac{\frac{1}{N} \sum |M_{rif,i} - M_i| + C_c}{\frac{1}{N} \sum M_{rif,i}} \right)$$

where:

$M_{rif,i}$	$i^{th}$ measure from the reference analyser/method
$M_i$	$i^{th}$ measure from the AMS
$C_c$	Confidence interval(at 95%) of the differences
$N$	number of measurements

In order to be validated, the AMS shall obtain a  $I_{AR}$  value over 80.

Problems arises whenever the concentration values of pollutant(s) are of the same order of magnitude of the precision/accuracy of the AMS: in this case is very easy to see that this test is not applicable.

The new draft standard prEN14181 is really innovative because of the introduction of quality assurance concepts in the field of emission monitoring.

The standard application scheme is divided into 3 different steps, namely QAL2, QAL 3 and AST: the first is relative to field validation, the second is relative to ongoing procedures and the third is relative to periodical controls (see the text of the standard for details)

A six-months experimental on-site application of this standard (especially QAL2 and QAL 3 ) on two real cases (a GT Combined Cycle Power Plant and a Municipal Wastes Incinerator) has been performed, in comparison with the Italian Law recommended procedures, in order to evaluate either the benefits and the costs of this new approach.

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## 2. The cases

Two different plants were chosen for this research:

### Plant n°1

Type:	Urban Waste Incinerator
Fuel:	Waste
Year of construction:	2000
Power:	11MW <sub>(electrical)</sub>
Type of gas cleaning:	Electrostatic precipitator, Ammonia injection and Baghouse filter
Main gas composition	Temp 110°C, Humidity 22%, O <sub>2</sub> 10% <sub>dry</sub> NO <sub>x</sub> 110±20 mg/m <sup>3</sup> , SO <sub>2</sub> <30 mg/m <sup>3</sup> , HCl <5 mg/m <sup>3</sup> , CO < 10 mg/m <sup>3</sup>
AMS installed:	extractive hot FTIR for all compounds but O <sub>2</sub> , measured by paramagnetic effect, and TOC, measured by a FID analyser

### Plant n°2

Type:	Dry Low NO <sub>x</sub> Gas Turbine with combined cycle
Fuel:	natural gas
Year of construction:	1990
Power:	55MW <sub>(electrical)</sub>
Type of gas cleaning:	n.a.
Main gas composition	Temp 130°C, Humidity 25%, O <sub>2</sub> 16% <sub>dry</sub> , NO <sub>x</sub> 15±5 mg/m <sup>3</sup> , CO < 10 mg/m <sup>3</sup>
AMS installed:	extractive cold NDIR for NO and CO; O <sub>2</sub> , measured by paramagnetic effect, and TOC, measured by a FID analyser

### 3. The QAL 2 vs the I<sub>AR</sub>

Both the Italian and the UE draft schemes require to make the validation tests with parallel measurements from the AMS and a second, independent measuring system (SRM), able to operate according to standard reference method.

So it was possible to apply both the procedures using the same experimental data.

In order to have long measurements series, automatic analysers were employed as SRM. For the compounds for which the measuring technique is a manual method (SO<sub>2</sub>, HCl), such techniques were used for calibrate the correspondent automatic analyser. For this scope the methods used were:

Pollutant	Method used for the Reference System
NO <sub>x</sub>	Extractive cold Chemiluminiscent (ISO10849)
SO <sub>2</sub>	Extractive cold NDIR (ISO7935) calibrated via manual analysis (ISO11632)
CO	Extractive cold NDIR (ISO12039)
O <sub>2</sub>	Extractive cold Paramagnetic
HCl	Extractive hot FTIR calibrated via manual analysis (EN1911)
TOC	Extractive hot FID

All the data were (from the AMS and SRM) were recorded every 5 seconds. These data were divided into one-hour average values after the elimination of out-layers.

#### 3.1. Plant n°1

The first plant was controlled for NO<sub>x</sub>, SO<sub>2</sub>, CO, O<sub>2</sub>, TOC and HCl.

The results of the parallel measurements are shown in the following figures.

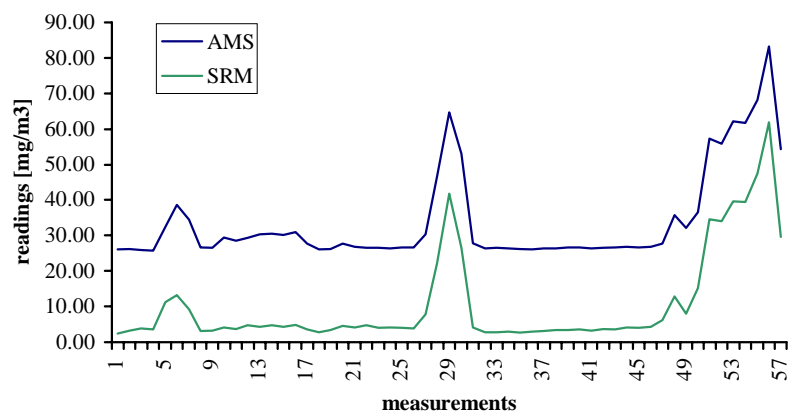
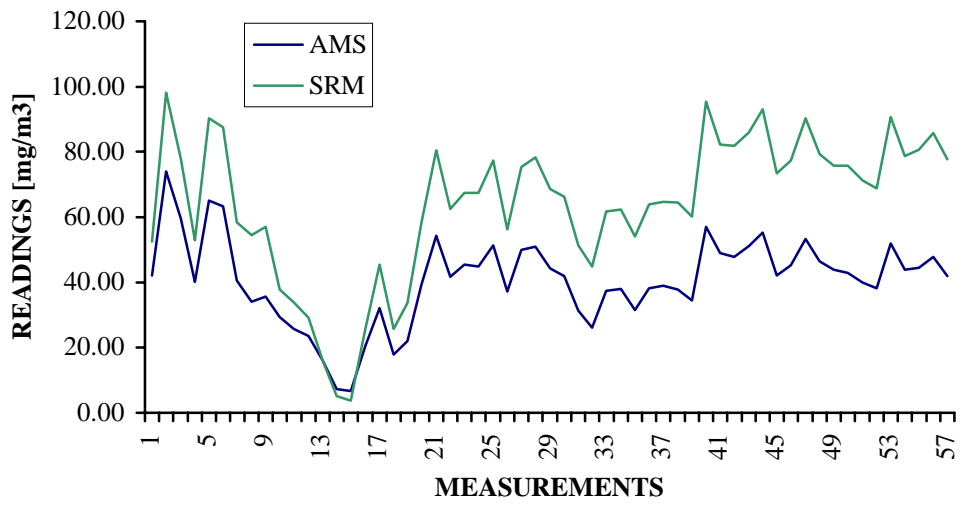
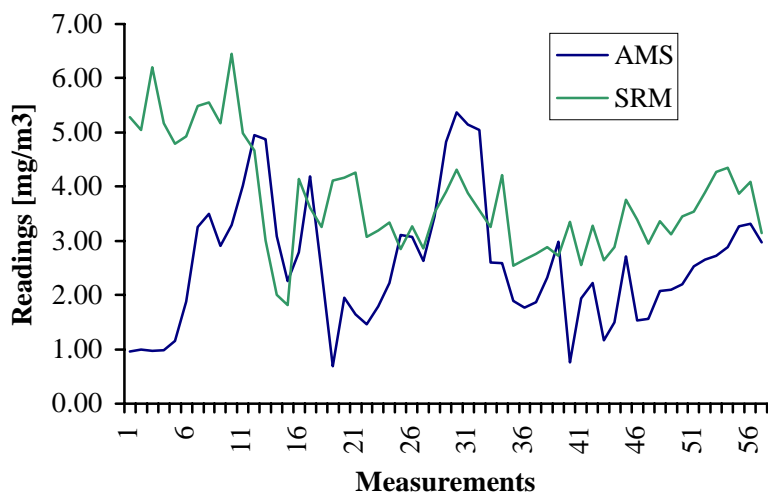


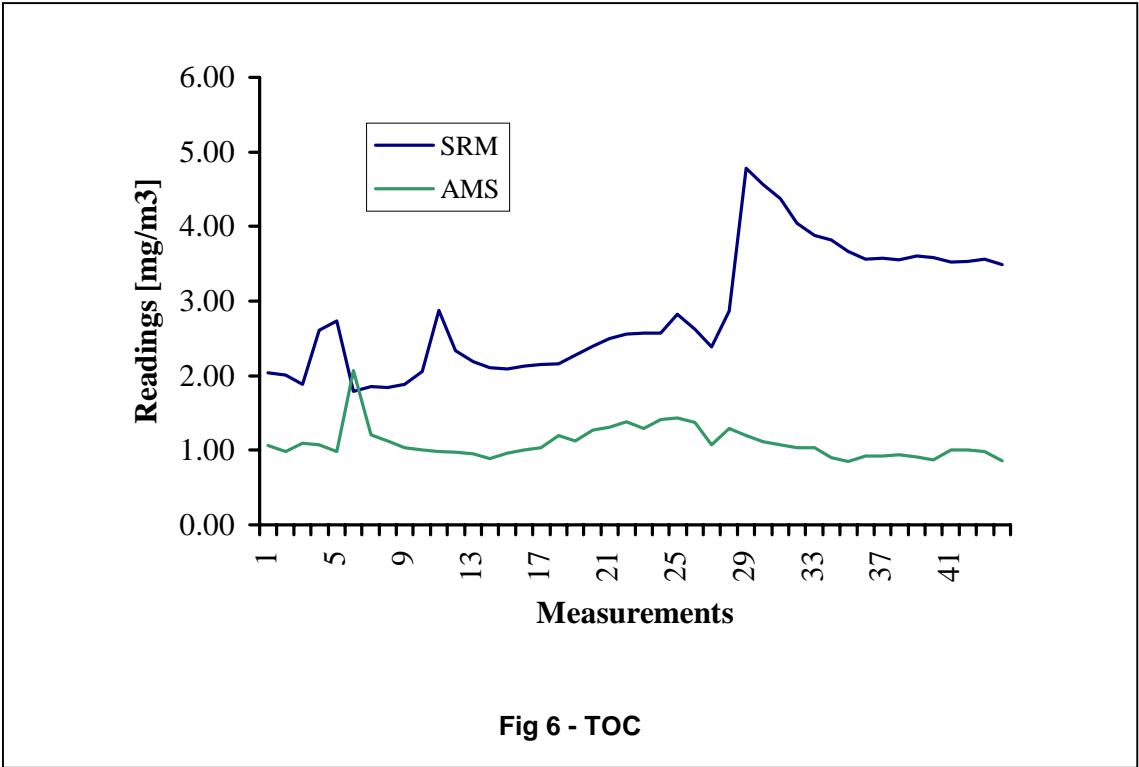
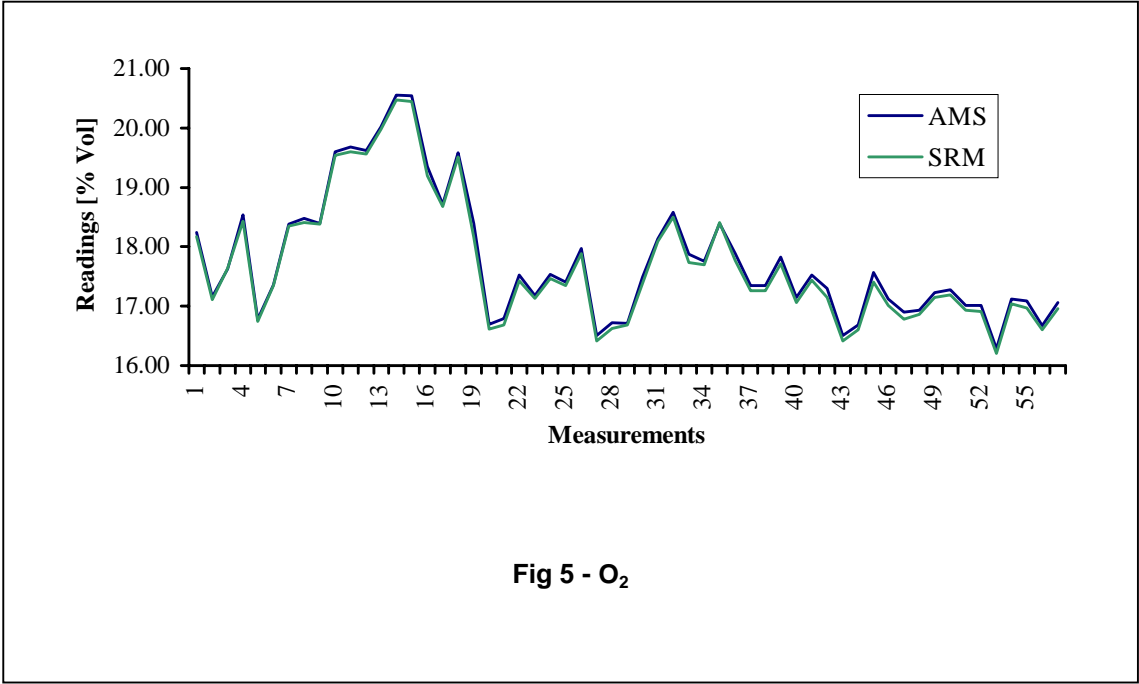
Fig 2 - SO<sub>2</sub>



**Fig 3 - NOx**



**Fig 4 - HCl**



The analysis done with the  $I_{AR}$  procedure takes to the following results:

Compound	$I_{AR}$ value	Requirements Fulfilled
SO <sub>2</sub>	-123.21	NO
NO <sub>x</sub>	59.05	NO
HCl	65.33	NO
O <sub>2</sub>	99.47	YES
COV	-85.57	NO

For the QAL2 procedure, the linear regression between the AMS and SRM values has been computed according to the following model:

$$Y_{AMS} = Y_{SRM} \cdot m + q$$

The values for  $m$ ,  $q$  and  $r^2$  obtained are:

Compound	$m$	$q$	$r^2$
SO <sub>2</sub>	1.02	23.88 mg/m <sup>3</sup>	0.99
NO <sub>x</sub>	1.59	-0.56 mg/m <sup>3</sup>	0.89
HCl	0.05	3.65 mg/m <sup>3</sup>	0.25
O <sub>2</sub>	1.00	-0.12 %	0.99
COV	0.41	7.92mg/m <sup>3</sup>	0.1

The bad results for HCl and COV are related to extremely low values during the test.

After that, the variability test for the acceptance of the correlation curves was calculated. The results are as follows:

Pollutant	SO <sub>2</sub>
ELV	300 mg/m <sup>3</sup>
$Y_{max}-Y_{min}$	58.51 mg/m <sup>3</sup>
$\alpha$	-23.88 mg/m <sup>3</sup>
$\beta$	1.02
$s_d$	1.32 mg/m <sup>3</sup>
$\sigma_0K$	15.13 mg/m <sup>3</sup>
Result	ACCEPTED

Pollutant	NO <sub>x</sub>
ELV	300 mg/m <sup>3</sup>
$Y_{max}-Y_{min}$	94.42 mg/m <sup>3</sup>
$\alpha$	-0,56 mg/m <sup>3</sup>
$\beta$	1.58
$s_d$	7.39 mg/m <sup>3</sup>
$\sigma_0K$	15.13 mg/m <sup>3</sup>
Result	ACCEPTED

Pollutant	HCl
ELV	21 mg/m <sup>3</sup>
Y <sub>max</sub> -Y <sub>min</sub>	3.17 mg/m <sup>3</sup>
α	2.84 mg/m <sup>3</sup>
β	0.21
s <sub>d</sub>	0.67 mg/m <sup>3</sup>
σ <sub>0</sub> K	0.76mg/m <sup>3</sup>
Result	ACCEPTED

Pollutant	O <sub>2</sub>
ELV	21 %
Y <sub>max</sub> -Y <sub>min</sub>	4.26%
α	-0.12 %
β	1.00
s <sub>d</sub>	0.042 %
σ <sub>0</sub> K	1.06 %
Result	ACCEPTED

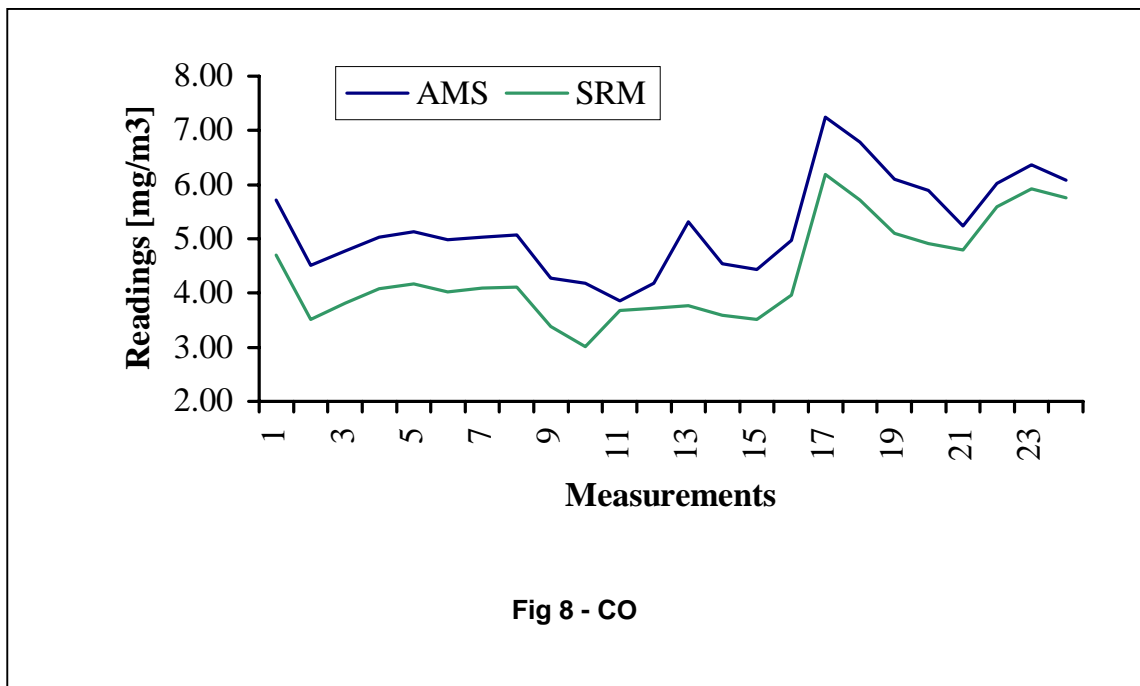
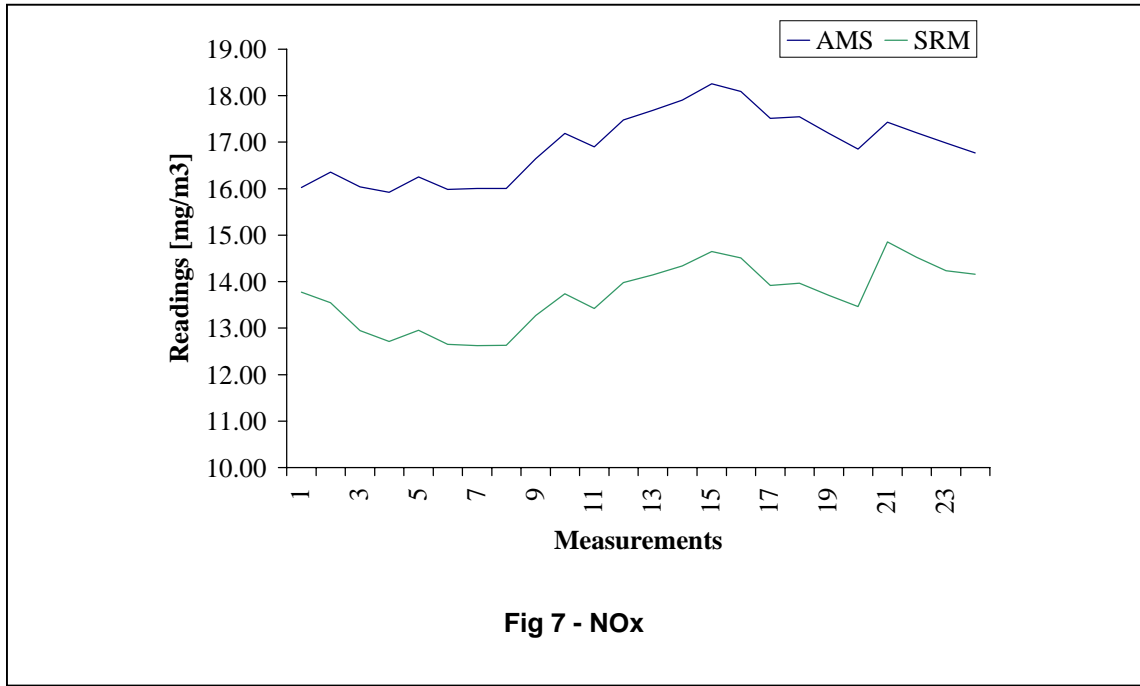
Pollutant	COV
ELV	300 mg/m <sup>3</sup>
Y <sub>max</sub> -Y <sub>min</sub>	1.23mg/m <sup>3</sup>
α	0 mg/m <sup>3</sup>
β	0.38
s <sub>d</sub>	0.44 mg/m <sup>3</sup>
σ <sub>0</sub> K	0.76 mg/m <sup>3</sup>
Result	ACCEPTED

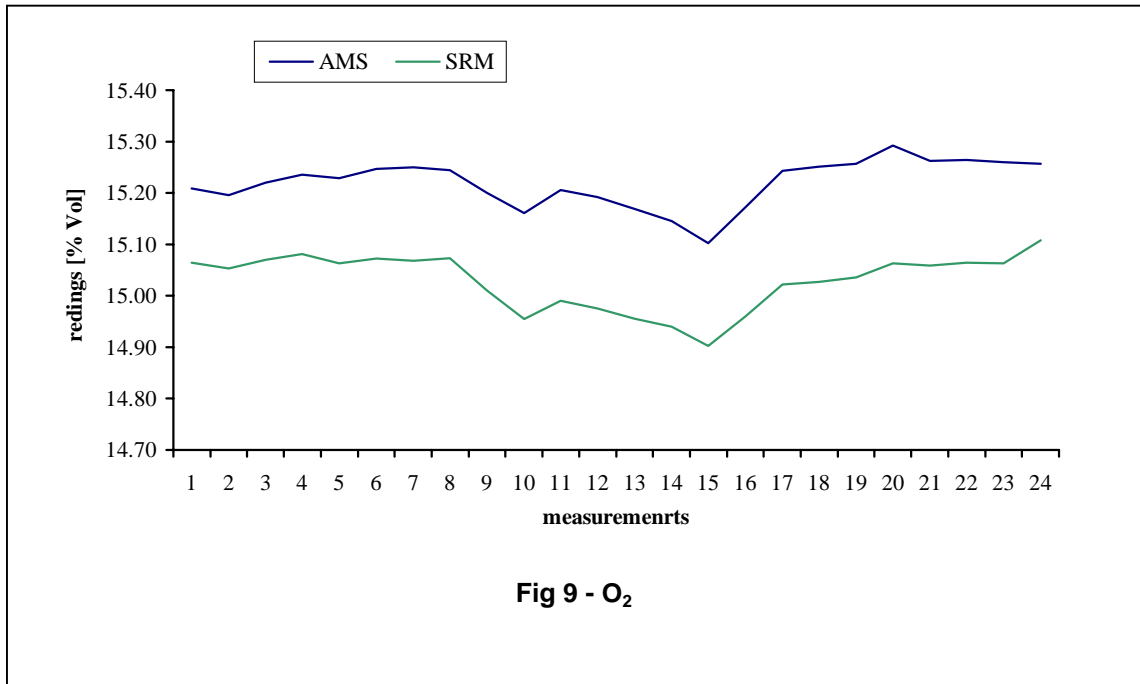


### 3.2. Plant n°2

The second plant was controlled for NO<sub>x</sub>, CO and O<sub>2</sub>.

The results of the parallel measurements are shown in the following figures.





**Fig 9 - O<sub>2</sub>**

The analysis done with the I<sub>AR</sub> procedure takes to the following results:

Compound	I <sub>AR</sub> value	Requirements Fulfilled
NO <sub>x</sub>	75.22	NO
O <sub>2</sub>	98.65	YES
CO	77.47	NO

For the QAL2 procedure, the linear regression between the AMS and SRM values has been computed according to the following model:

$$Y_{AMS} = Y_{SRM} \cdot m + q$$

The values for m, q and r<sup>2</sup> obtained are:

Compound	m	q	r <sup>2</sup>
NO <sub>x</sub>	0.79	0.33 mg/m <sup>3</sup>	0.71
O <sub>2</sub>	1.03	-0.63 %	0.73
CO	0.97	-0.73 mg/m <sup>3</sup>	0.88

The bad results for HCl and COV are related to extremely low values during the test.

After that, the variability test for the acceptance of the correlation curves was calculated. The results are as follows:

Pollutant	NO <sub>x</sub>
ELV	300 mg/m <sup>3</sup>
Y <sub>max</sub> -Y <sub>min</sub>	2.23mg/m <sup>3</sup>
α	0 mg/m <sup>3</sup>
β	0.81
s <sub>d</sub>	0.37 mg/m <sup>3</sup>
σ <sub>0</sub> K	15.09 mg/m <sup>3</sup>
Result	ACCEPTED

Pollutant	O <sub>2</sub>
ELV	21 %
Y <sub>max</sub> -Y <sub>min</sub>	3.17 %
α	0%
β	0.21
s <sub>d</sub>	0.67 %
σ <sub>0</sub> K	0.76 %
Result	ACCEPTED

Pollutant	CO
ELV	150 mg/m <sup>3</sup>
Y <sub>max</sub> -Y <sub>min</sub>	3.18 mg/m <sup>3</sup>
α	0 mg/m <sup>3</sup>
β	0.84
s <sub>d</sub>	0.34 mg/m <sup>3</sup>
σ <sub>0</sub> K	1.06 mg/m <sup>3</sup>
Result	ACCEPTED

#### 4. The QAL3 procedure

The QAL3 procedure is a 'on going' test that should, in the intention of the draft, assure that the AMS operates correctly between two annual controls. It should, in fact, be able to detect any systematic deviation from the normal values of zero and span , either considering their absolute values and stability.

In effect the test is divided into two different parts: one for the control of drift and the other for the control of precision (see fig.10)

The whole procedure is controlled by a factor ( $\sigma_{AMS}$ ) that derives directly from the characteristics of the analysers and is defined by the formula:

$$\sigma_{AMS} = \sqrt{\left(\sum u_n^2\right)}$$

Where  $u_n$  is the generic value for the uncertainty that relative to the factor n (temperature, pressure, instability, etc, etc)

Due to the lack of data about  $\sigma_{AMS}$  coming from the application of QAL1 procedures, especially for instruments like FTIR, the first problem was to fix a reasonable value for  $\sigma_{AMS}$  in order to test the method.

In order to obtain these results, we used the following procedure:

1. the two AMS were calibrated
2. every week, for about 6 months, the readings coming from zero and span calibration were collected without applying the QAL3
3. at the end of the period a new calibration was performed in order to assure that the AMS operating characteristics were maintained.
4. from experimental data a suitable  $\sigma_{AMS}$  were derived for each pollutant
5. some AMS 'failures' were simulated, using the experimental data and the  $\sigma_{AMS}$  values in order to verify the capability of the test to detect these faults.

#### 4.1. the estimation of $\sigma_{AMS}$

Even after a six-months campaign, the data collected were not enough to have a good estimation of  $\sigma_{AMS}$ . Because the QAL3 test takes into consideration the 'noise' of the system and can be considered a 'probabilistic' procedure, it is necessary to use a large quantity of data, thus having a representative population to consider.

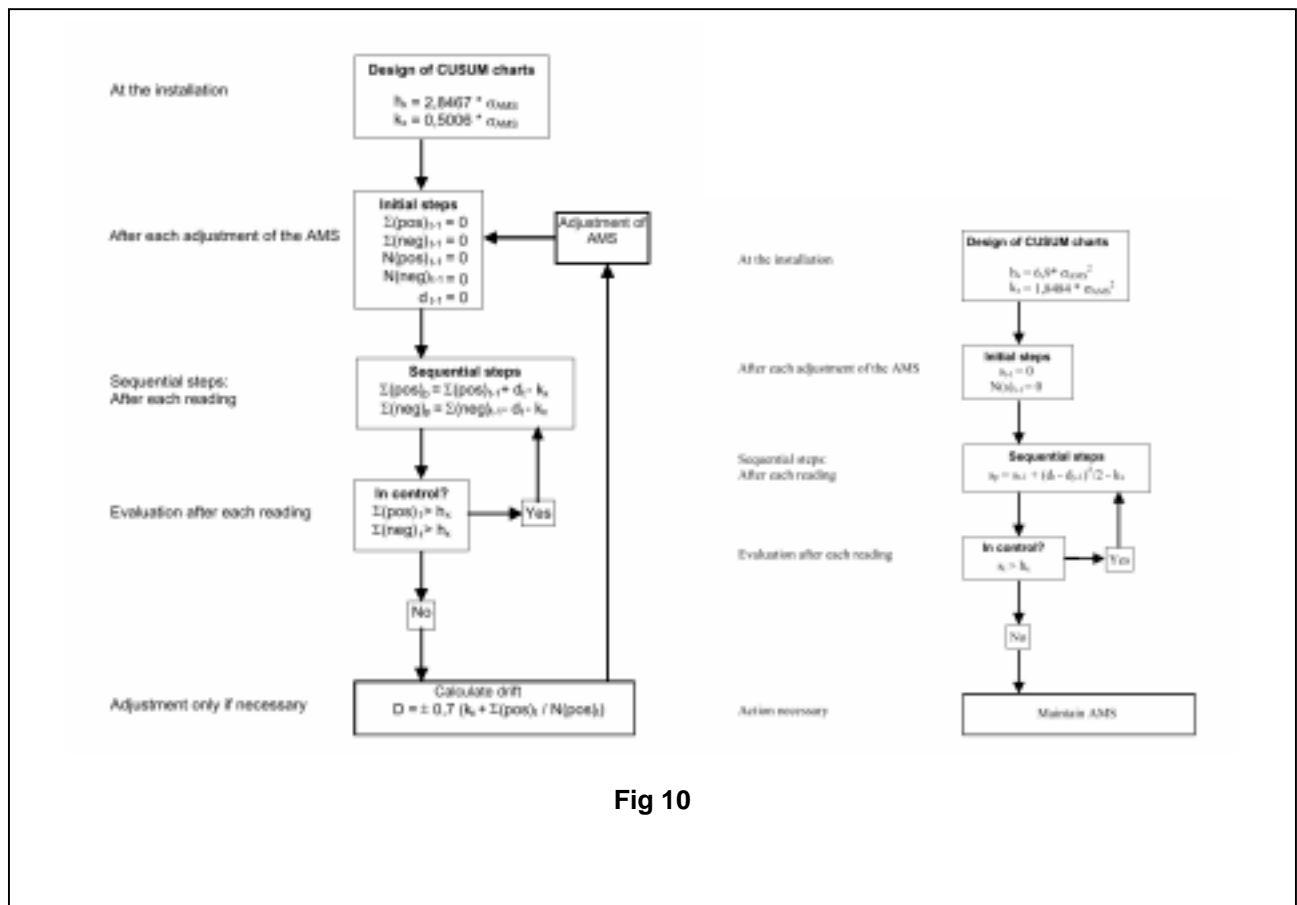


Fig 10

To overcome such a difficulty, we have supposed that the drift of the analysers can be represented using the following considerations:

1. the drift arises from two terms: a systematic drift and a random one
2. the two terms are independent
3. the systematic term can be represented using a sinusoidal function of time
4. the random term can be assumed to have a constant probability between  $-X$  and  $X$

This model is represented by the following formula:

$$X_i = A \cdot \delta_i + B \cdot \sin\left(\frac{i}{n} \cdot 2\Pi\right) + C$$

Where:

- $X_i$  is the generic value at the  $i^{th}$  week
- $\delta_i$  is a random function with values uniformly distributed between  $-1$  and  $+1$
- $A$  is the weight of the random function
- $B$  is the weight of the systematic drift
- $n$  is the period of the systematic drift
- $C$  is the nominal value

Using some data from the manufacturers of the AMS, it was also assumed  $A=B$  and  $n=30$ , so the formula becomes:

$$X_i = A \cdot \left( \delta_i + \sin\left(\frac{i}{30} \cdot 2\Pi\right) \right) + C$$

The  $A$  parameter was evaluated starting from the measured data for span values using common statistics and the results are:

#### Plant n°1

Compound	CO	HCl	NO <sub>x</sub>	SO <sub>2</sub>
Full scale	200 mg/m <sup>3</sup>	60 mg/m <sup>3</sup>	800 mg/m <sup>3</sup>	400 mg/m <sup>3</sup>
A value	4.5 mg/m <sup>3</sup>	3 mg/m <sup>3</sup>	5 mg/m <sup>3</sup>	10 mg/m <sup>3</sup>
	2.25%f.s.	5%f.s.	0.625%f.s.	2.5%f.s.

#### Plant n°2

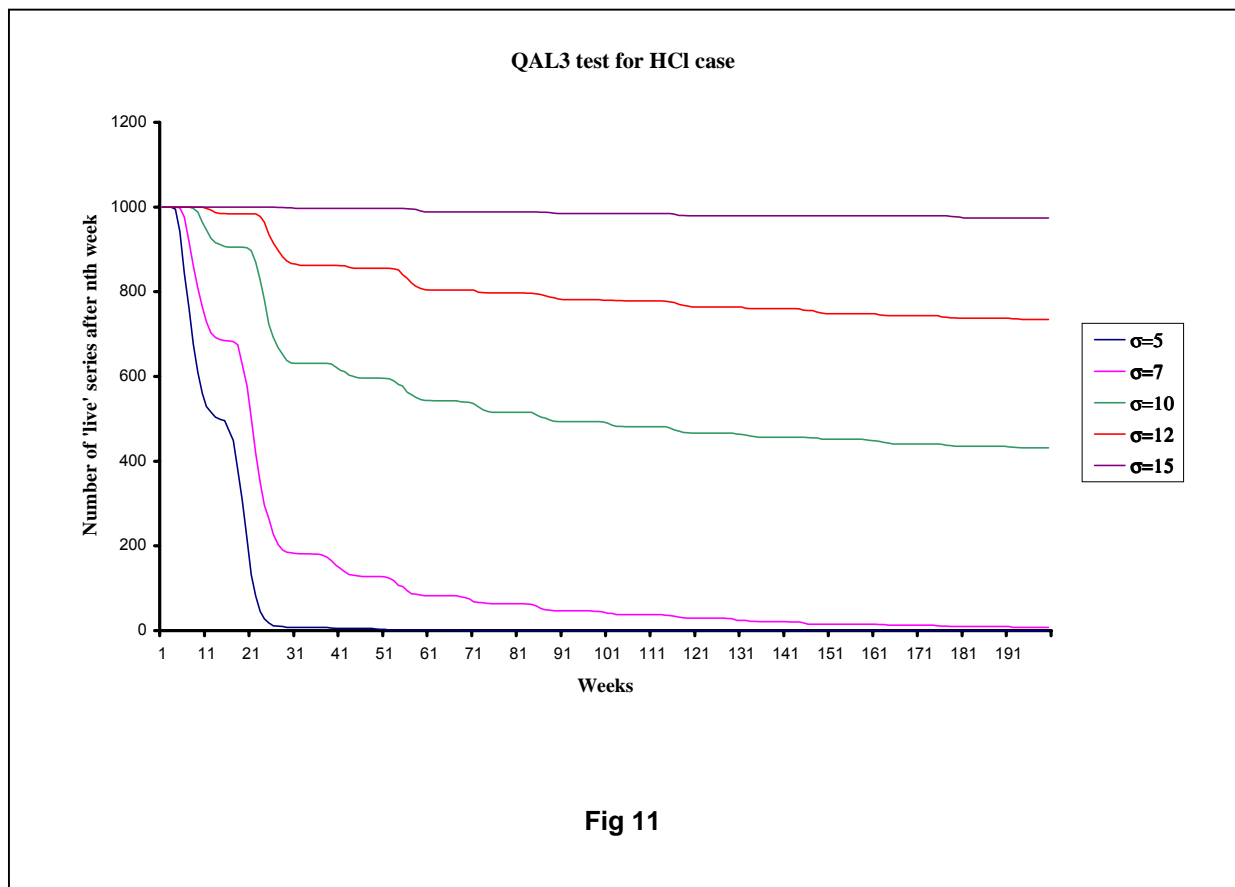
Compound	CO	NO <sub>x</sub>
Full scale	250 mg/m <sup>3</sup>	220 mg/m <sup>3</sup>
A value	3.5 mg/m <sup>3</sup>	2 mg/m <sup>3</sup>
	1.4%f.s.	0.91f.s.

For each compound showed, 1000 series of 200 values each were generated using a computer program. The QAL3 procedure was then applied at every series.

**For sake of clarity the full procedure for HCl only will be shown:**

1. Starting from the values of A, B and n, 1000 series made each by 200 elements were built
2. Some reasonable candidate values of  $\sigma_{AMS}$  were selected (in this case 5, 7, 10, 12 and 15 mg/m<sup>3</sup>)
3. The QAL3 test is the applied using one value of the candidate  $\sigma_{AMS}$  for every series
4. For every series it was recorded the week in which the test fails
5. After the analysis of all the series, a 'failure' statistic was built
6. Steps 3..5 were repeated for every candidate value of  $\sigma_{AMS}$

The results of such work is shown:



**Fig 11**

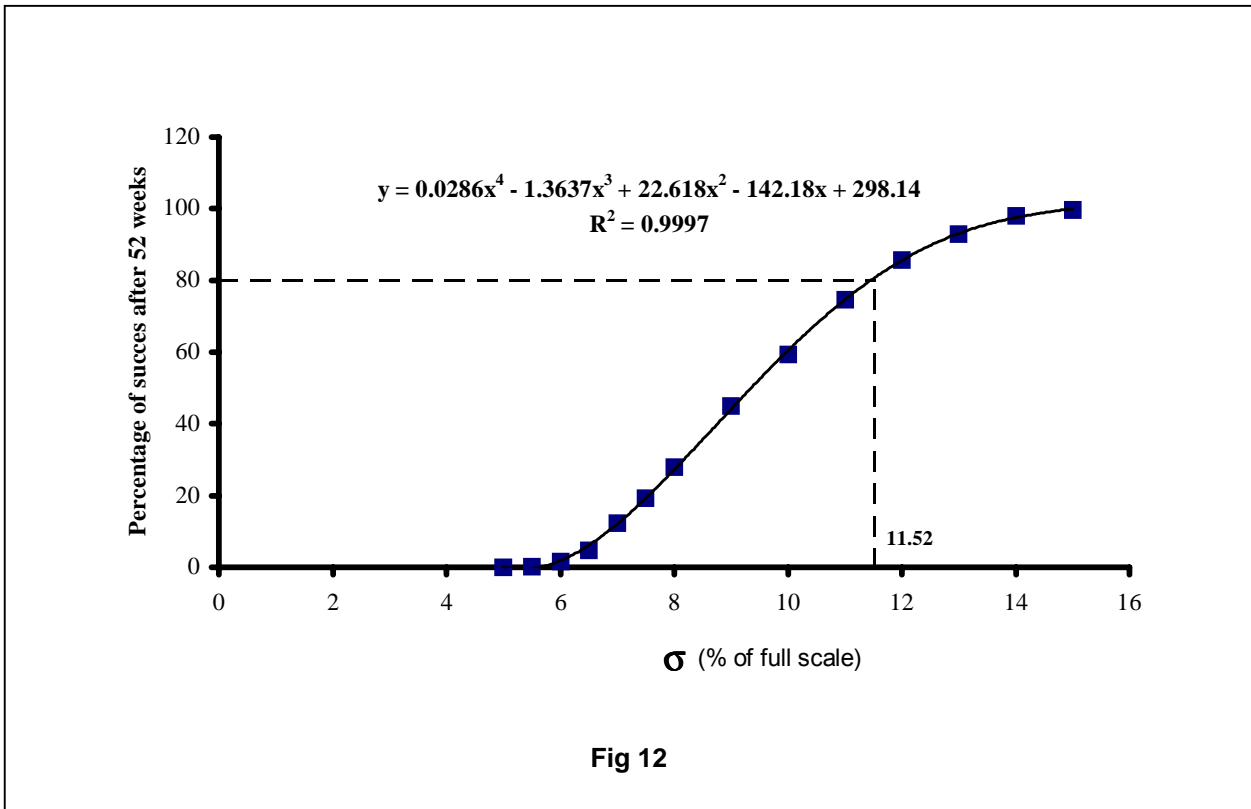
This sketch give the probabilities that, at a certain value of  $\sigma_{AMS}$ , the test fails after N<sup>th</sup> weeks. If we assume that such results come out from a properly operating instrument, we can use this for evaluating the optimal value of  $\sigma_{Ams}$ .

In fact, we can do some considerations:

1. For every value of  $\sigma_{AMS}$  we have a certain probability, different from zero, that the test fails even if the instrument continue to work properly
2. The standard gives one year as he maximum time between two calibrations
3. From a formal point of view, if the test fails, it was required to adjust the instrument, but in practice, newest instruments (like FTIR) don't give many possibilities to compensate eventual

drifts: so, in case of test failure, it's impossible to adjust simply the instrument, but it's necessary to maintenance it with obviously problems of costs. From this point of view, a test failure can be considered as a instrument failure.

From these considerations, we looked at the  $\sigma_{AMS}$  value that gives the 20% of failure probability after 52 weeks. The results are shown:



The values obtained, for each pollutant, are:

**Plant n°1**

Compound	HCl	NO <sub>x</sub>
Full scale	60 mg/m <sup>3</sup>	800 mg/m <sup>3</sup>
$\sigma_{AMS}$ value (% f.s.)	11.52%f.s.	1.44%f.s.
$\sigma_{AMS}$ value	7 mg/m <sup>3</sup>	12 mg/m <sup>3</sup>

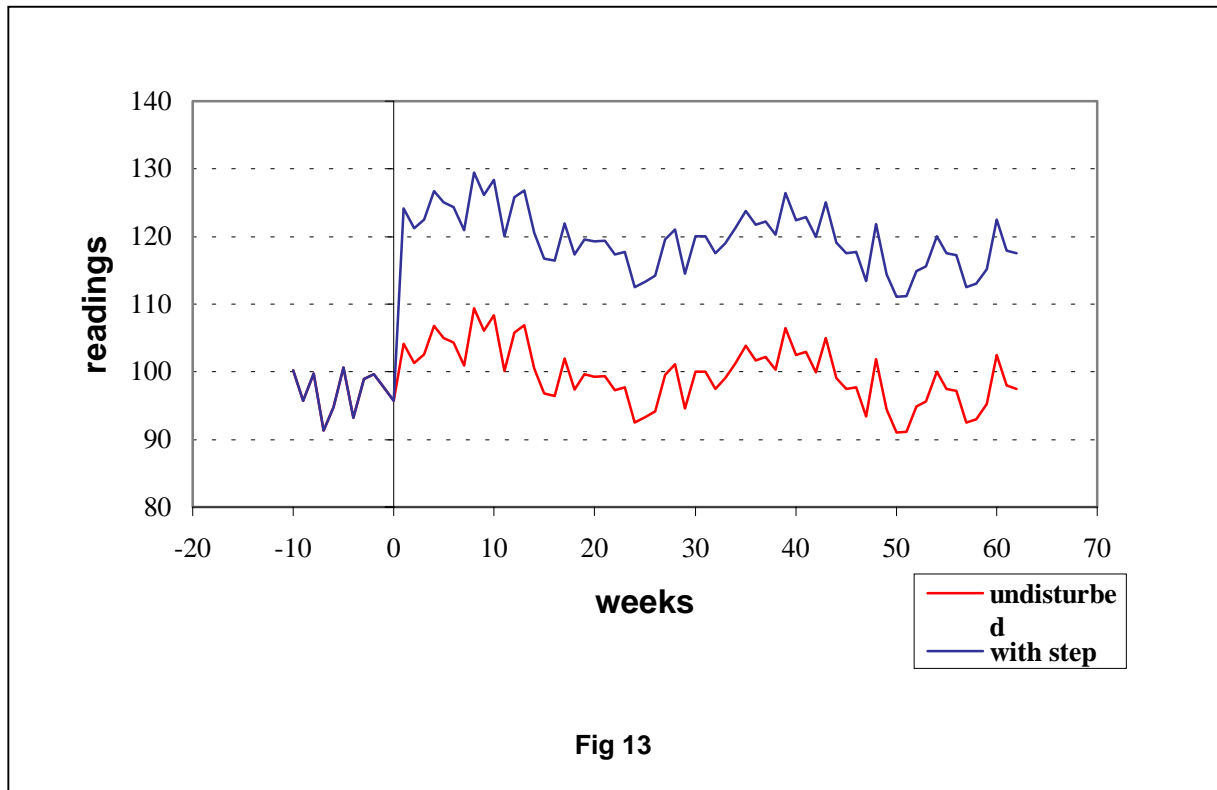
**Plant n°2**

Compound	CO	NO <sub>x</sub>
Full scale	250 mg/m <sup>3</sup>	220 mg/m <sup>3</sup>
$\sigma_{AMS}$ value (% f.s.)	3.19%f.s.	2.08%f.s.
$\sigma_{AMS}$ value	8 mg/m <sup>3</sup>	5 mg/m <sup>3</sup>

#### 4.2. The simulation of failure

After the evaluation of  $\sigma_{AMS}$ , the QAL3 capability of detecting a failure was tested. Failures were simulated only for HCl and NO<sub>x</sub> (plant n° 1), because the values of the corresponding  $\sigma_{AMS}$  were respectively the highest and the lowest found.

The failure was simulated introducing, in the original series of data, a step after the first reading,.



Various steps were evaluated and the QAL3 was repeated on the modified values (see fig.13).

The new statistic obtained was correlated with the 'undisturbed' situation and it was possible to calculate the probability that a certain step drift can be detected by the test.

In other words, it was calculated the ratio between the probability of detection with the step and the original value.

The results for the HCl and NO<sub>x</sub> are shown in the figures 14 and 15

## 5. Conclusions

The implementation of prEN14181:2001 standard has been tested at two different Italian plants, namely a Gas turbine power generation plant and a MSW incinerator, in order to evaluate the suitability of the recommended methodologies and to highlight advantages and disadvantages with respect to the procedures required by Italian Law for AMS periodical controls.



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QAL 2 (and AST) procedures have been shown to perform very well, even in the case of very low emission values, where the test based on Relative Accuracy (RA) evaluation fails or is inapplicable.

Moreover, QAL2 procedures have been shown to be a cost-effective alternative to RA test.

QAL3 procedures also is, at least in principle, a cost-effective type of test.

In the majority of cases, in fact, plant personnel performs -on a routine basis- the AMS zero and span calibration, thus allowing these data to be used for the detection of AMS deviation, according to QAL3 procedures.

Some problems, however, have been evidenced by our pilot application. From these results, the QAL3 procedure seems to have some problems. In particular:

- 1) the precision test, using the  $\sigma_{AMS}$  found, was always much less critical than the drift test (the reason way we have focused our article in it) and is not able to give pragmatic information
- 2) the drift test has shown a not perfect capability of detect failures of the AMS
- 3) a procedure able to permit the changing of gas cylinders without restart the test should be useful

