Interlaboratory tests of emission measurements in France using a testing bench

Jean Poulleau

INTERLABORATORY TESTS OF EMISSION MEASUREMENTS IN FRANCE USING A TESTING BENCH

Jean Poulleau Air Quality Department INERIS

(French National Institute for Industrial Environment and Risks)

ABSTRACT

It is well known that interlaboratory tests are a powerful tool to improve the quality of measurements. However they are difficult and costly to organise in the framework of emission measurements because of several reasons (too small measuring platforms, access to industrial plants...).
In order to facilitate these tests, French authorities asked INERIS to built a testing bench, which could simulate industrial gaseous emissions of easily modified composition.
The bench was originally designed mainly for having a constant concentration of gaseous pollutants (SO_2, NO_x, HCl, VOC). Work is in progress for semi-volatile pollutants injection.
The bench is designed and equipped in such a way that five teams may work in parallel, which allows having statistical comparison. For the time being, it is mainly used for:

- validation of measurement methods before their standardisation
- proficiency testing for laboratories in view of their accreditation/approval

A description of the bench and examples of results will be given.

1 INTRODUCTION

To be accredited, the laboratories which are involved in emission measurements have to provide the uncertainty attached to their measuring values. They can find some information in the most recent CEN standard, but they still do not know if they are implementing the standardised procedure properly unless they participate to interlaboratory campaigns.

Thus, interlaboratory tests are a powerful tool to improve the quality of measurements.

These campaigns are not so easy to organise on a plant and are expensive. Only very few teams can be simultaneously involved and the range of concentrations covered by one plant is quite often very narrow.

Therefore, in order to make these tests easier and more frequent, French authorities asked INERIS to design and build a testing bench, which could simulate varied industrial gaseous effluents.

The bench, which is a horizontal loop, was originally designed mainly for measuring concentrations of gaseous pollutants (SO_2, NO_x, HCl, VOC) but some studies are in progress for semi-volatile pollutants injection.

Up to now, six interlaboratory campaigns with French bodies and one with European laboratories have been organised, measuring O_2, CO, SO_2, NO_x, H_2O. Some interlaboratory campaigns are also under way for mercury and for PAH generated by a wood stove.

The bench is designed and equipped in such a way that five teams may work in parallel, which allows having statistical comparisons.

For the time being, it is mainly used for:

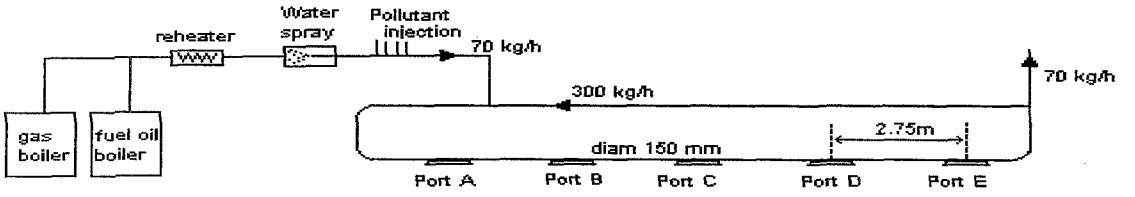
- validation of measurement methods before their standardisation
- proficiency testing for laboratories in view of their accreditation/approval

This presentation gives the main results and statistical evaluation of six campaigns for the determination of O_2, SO_2, NO_x, CO, TOC and H_2O.

2 PRESENTATION OF THE TESTING BENCH

A bench loop has been drawn up and built in 1998 in INERIS, which has the capacity to generate dynamically gaseous effluents from exhaust gases of a gas boiler or a fuel-oil boiler. These exhaust gases can be humidified and doped by pollutants coming from pure gases in cylinders: CO, CH_4, NO, NO_2, HCl or liquids (specific VOC).

Generated gases are injected into a stainless steel loop (150 mm internal diameter) coated with PTFE, where 300 kg/h gases are circulating. This horizontal loop is temperature controlled by mean of electric heating resistances. This bench is equipped to receive 5 different teams.



Each team has at its disposal:

- a rectangular sampling port (100 x 400 mm) situated at 1.20 m height with the possibility to have 2 or 3 holes in it.
- electric supply (230V 16A) and compressed air (6-7 bars).

The static pressure inside the duct is maintained between 1 and 4 mmCE in order to avoid interferences from one team to the others.

Characteristics of exhaust gases can be quickly modified. Ten to fifteen minutes only are necessary to reach a new steady configuration.

3 THE PARTICIPANTS

French participants : AIF, AINF, APAVE Normandie, APAVE Nord-Picardie, APAVE Lyonnaise, APAVE St Ouen, ATOFINA, Calydra, CERECO, CETIAT, Compagnie Française du Méthane, DGA, ELF ANTAR, GdF, INERIS, IRH Environnement, Laboratoire de la ville du Havre, Laboratoire National d'Essais, LECES environnement, MSIS, SOCOR, RHODIA,VERITAS.

European participants: CESI (I), INERIS (F), KEMA (NL), Miljo Kemi (DK), TÜV Bayern (D°)

4 THE TESTS

Tests performed between French laboratories were focusing on automatic measurements of O_2 (5-13%), CO_2, CO (10 - 500 mg/m^3), NO_x (75 - 1000 mg/m^3), SO_2 (40 - 1000 mg/m^3) and COVT (0 - 50 mgC/m^3). The choice of analytical techniques were left open.

For the European test performed for CEN standard validation purposes, the institutes had to use reference method in the following concentrations:

- SO_2 (0-2000 mg/m^3)	Thorin and Ionic Chromatography Method
- NO_x (0-1300 mg/m^3 NO_2 equiv.)	Chemiluminescence
- O_2 (3-12 %)	Paramagnetism
- CO (0-400 mg/m^3)	Infra-Red Absorption
- H_2O	Absorption and condensation

For each campaign, 10 to 12 half-hour tests were carried out, mostly at steady concentrations. Furthermore, INERIS has checked the calibration bottles of each participant with its own instruments.

5 RESULTS

5.1 CALIBRATION BOTTLES

The uncertainties attached to the concentration values, given by the manufacturer, are often small: +/-1 to 2% relative, even smaller in some cases.

To perform good measurements, we noticed that we could give the following advice: use a automatic instrument whose range corresponds approximately to twice the Emission Limit Value (ELV) and whose sensitivity may be adjusted with a calibration bottle whose concentration is approximately equal to the ELV.

For NO_x, we have two possibilities:

- To use one bottle with a mixture of NO and NO_2. In that case we suppose that both channel (NO and NOx) give an equivalent signal when injecting NO (it isn't always true). And we must have also enough NO_2 in NO in order to check the efficiency of the conversion oven.
- to use two separate bottles, the first one with NO in order to adjust both NO and NO_x channels, the second one with NO_2 in order to calculate the efficiency of the conversion oven.

It's a pity to see some laboratories that have only a NO bottle and don't control NO_2. Moreover some are measuring NO and add 5% to give NO_x values!

Even if the French standard and the new CEN Standard for TOC measurement demand to adjust the sensitivity of the FID with propane, half of French bodies still use methane. This can induce quite high deviations because the ratio of response factor between propane and methane is not always equal to 3 on every FID.

The comparison of calibration gases has been made on INERIS analysers who were previously adjusted. The linearity of these analysers has been previously checked according to internal quality assurance procedures. The results have been considered as abnormal when the deviation between the reading and the expected value was larger than the square root of the sum of the square value of the uncertainties given by the manufacturers.

We found that one fourth of the checks gave anomalies.

5.2 ANALYSERS ZERO AND SENSITIVITY ADJUSTMENTS AND CHECKS

The tests forecast an adjustment at the beginning of each day and a check at the end in order to detect possible zero and sensitivity drift.

Only a few laboratories, except the European bodies involved in CEN are correcting their values for drift when it is necessary. Some laboratories don't respect the warming time of their instruments, which induce a rather high drift in measurements.

5.3 MAIN RESULTS FOR EACH COMPONENT

For each component the average value obtained by the laboratories with the confidence interval attached to this average value has been calculated. This value gives an idea of the dispersion of results.

Table 1 below gives the confidence intervals for the first five tests between common French bodies and the European test performed with what we can consider as recognised laboratories.

		Regulation (2)		Relative confidence intervals (1)					
	Studied range	Limit value	Ic max (1)	Interlab 1	2	3	4	5	European test
O_2	4-13%	-	-	0<Ic<3	0<Ic<3.9	0<Ic<3	2<Ic<14	1<Ic< 3.9%	0.6<Ic<1.1
CO_2	4-10%	-	-	1<Ic<4	1<Ic<3	3<Ic<9	2<Ic<6.5	3.1< Ic<8.4	
NO_x	80-1000 mg/m^3	200 mg/m^3	20 %	2<Ic<8	5<Ic<10	3<Ic<13	11>Ic<82	1.4<Ic<12.3	1.4<Ic<2.6
CO	30-500 mg/m^3 10-30 mg/m^3	100 mg/m^3	10 %	3<IC<39 2<Ic<2.7	6<IC<34 34<Ic<73	9<IC<28 15<Ic<40	4.5<IC<179 17<Ic<40	5.4<Ic<60 60<Ic<135	2.5<Ic<3.6 2.4
SO_2	300-1000 mg/m 70-300 mg/m^3	200 mg/m^3	20 %	4<Ic<6 5<Ic<20	6.5<Ic<10.6 10.6<Ic<68	18<Ic<30 30<Ic<90	11<Ic<25 25<Ic<48	11<Ic<21 11<Ic<90	9 (IEC/Thorin) 10 (IEC/Thorin)
COVT	5-40 mg/m^3	20 mgC/m^3	30 %	9<Ic<25	10<Ic<75	12<Ic<50	16<Ic<44	10.3<Ic<47.3	

(1) Ic : 95% confidence interval attached to the average results

(2) half an hour limit values given by the European directive on wastes

Table n°1 : confidence intervals attached to the average results

This table shows that the results obtained during the European campaign with recognised bodies are much better than those obtained by common French labs.

Several explanations can be given:

- For the same pollutant, all European labs implemented the same measurement principles, in this case: the reference method.
- The recognised laboratories do perform the measurements with more expertise. They actually do know their instruments and have control procedures to follow their instruments up. Furthermore, they have a better knowledge of standards and regulation requirements. Leak tests of the sampling lines are generally done. Drifts are calculated and results are corrected when it is necessary.
- The concentration ranges and the calibration gases are well adapted to the measuring task.

For the European tests, the test programme has been modified in order to calculate repeatability and reproducibility according to ISO 5725-2 procedure. The reproducibility confidence interval is quite useful because each laboratory, performing the same method, has the possibility to give an uncertainty attached to its results.

Table 2 below gives the main results of the European campaign. We can find the results of different approaches to calculate the uncertainty of the measurement:

- ISO 14956 approach: **2.u**. It's a GUM approach, calculating the overall uncertainty from all the individual sources of uncertainty.
- Confidence interval attached to the average result **t.s/vn**

- Repeatability confidence interval according to ISO 5725: $\mathbf{t.s_r}$.
- Reproducibility confidence interval according to ISO 5725: $\mathbf{t.s_R}$.

	Concentration	Confidence Interval ISO 14956	Confidence Interval attached to the mean	Repeatability Confidence interval ISO 5725-2	Reproducibility Confidence interval ISO 5725-2
		2*u %rel	t.s /vn %rel	$t.s_r$ %rel	$t.s_R$ %rel
O_2 %	3		1.1	0.8	1.7
	6		0.9	0.5	1.3
	9	2.9	0.8	0.4	1.3
	12		0.6	0.3	1.0
CO mg/m^3	20		8.7	2.6	14.9
	60		4	1.1	6.9
	100	2.5	2.1	0.8	3.6
	350		0.9	0.6	1.5
NO mg/m^3 as NO_2	25		2.4	3.3	4.0
	100	1.7	2.5	1.9	3.7
	450		2.8	1.5	4.2
	1300		3.6	1.4	5.1
NO_x mg/m^3 as NO_2	30		2.6	3.0	4.0
	100	1.7	1.4	1.9	2.3
	450		1.6	1.5	2.5
	1300		1.8	1.4	2.9
SO_2 Thorin mg/m^3	20		19	3.0	36.8
	50		11	4.2	29.0
	200		10	4.8	13.3
	2000		9	5.0	17.3
SO_2 IEC mg/m^3	20		27	27.6	38.9
	50		21	12.0	26.2
	200		9.1	4.4	13.2
	2000		8.8	9.2	13.1
H_2O %	8		12	8.5	17.7
	12		9	9.2	13.4
	14		10	9.6	14.1
	22		10	10.3	14.9

Table n°2: European interlaboratory tests results

This table shows that :

- The uncertainty budget made according to ISO 14956 often lead to figures lower than those given by ISO 5725-t.s_R approach. We should observe the opposite because this approach is supposed to sum up all the possible sources of uncertainty. Therefore, it shows that either all sources have not been taken into account or the estimation has not been correctly managed.

- A factor 1.5 to 4 exists between repeatability and reproducibility, except for Thorin method where a factor 12 has been reached. This large dispersion may be due to the bad control of this rarely used method.

- In the last column we see that we fulfil the uncertainty requirements of the European Directive on Waste. Half confidence interval requirements are: 10% for CO, 20% for SO_2 and NO_x, and 30% for COVT.

6 OBSERVATIONS AND RECOMMENDATIONS

In conclusion, we can draw the following observations and recommendations:

- Anomalies met with some calibration gases have a rather limited influence on deviations between labs, except for TOC, where propane has to be used for adjustment of the sensitivity.

- Deviation between laboratories are not always constant from one day to another, for the same level of concentrations, which seems to show that some labs carry untidy adjustments. We have to remind that it is better to inject calibration gases at the inlet of the sampling line, in order to take into account possible loses in the line, above all with SO_2 or NO_2, to check that the analyser gives the same signal on calibration mode and on measurement mode. Moreover, because final results are given by the recording system, it seems important to calibrate referring to data logging and recording system.

- For some components, confidence intervals are rapidly increasing at low concentrations, because of a lack of sensitivity of the instrument, of cross interferents, of instrument adjustment (for FID), parameters whose influence on the results are known only when the performance characteristics have been previously determined. It would be useful for laboratories to have assessment or type approval reports from TÜV, MCERTS, INERIS... If these reports are not available, laboratories will have to perform linearity check, calculation of quantification limit and so on according to ISO 9169. At last, it's quite easy, when adjusting the sensitivity of one analyser to inject the calibration gas not only to the analyser but also to all the others in order to detect possible interference.

- A special attention has to be paid for SO_2 measurements by an automatic instrument:

- By choosing the right gas treatment to get rid of moisture
- By choosing the length and material of the sampling line (Viton will be banned)
- In adjustment procedure (wait enough time to reach stability and if possible, inject in the inlet of the line)
- In the choice of the analytical technique (we have to know interferents and instrument behaviour at low concentrations).

- Some important deviations at low concentrations seem to be due to the choice of a too high concentration range and calibration gas (see the recommendation of calibration gases above)

- These tests revealed erratic instruments functioning which have been sent back to manufacturers.

- Dispersion of humidity measurements are rather high: the efficiency of the condensation should be checked and leak test performed before sampling.

- For TOC measurements, the uncertainties on the measurements are very large. The gas burner geometry and adjustments are influential parameters. Therefore it is essential to know the response factor of all commercial FID according to the CEN requirements even if CEN requirements seem unrealistic.

These interlaboratory campaigns had the advantage to reveal the state of the uncertainty at the level of reference level and at the level of common practice in one country. The participants have drawn a lot of information on their own practice and will improve the quality of their measurements.

But these exercises must be periodically repeated to follow the progress in the management of measurement procedures.

About the author

Jean Poulleau has many years experience working as a development engineer in the field of combustion techniques then in air pollution measurements: evaluation of the performance characteristics of gas analysers, stack sampling and analysis.
He is strongly involved in standardisation activities, at the french , european and international levels.
E-mail adress: jean.poulleau@ineris.fr