PRACTICAL IMPLEMENTATION OF EN 45001 QUALITY STANDARD IN EMISSION MEASUREMENTS

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Abstract

Since 3 years the EN45001 standard for quality in analysis and testing is being implemented in Flanders by emission testing laboratories, as required by environmental legislation. During the implementation of the standard the officially approved laboratories were audited by the reference laboratory Vito. The audits revealed several difficulties of applying EN45001 to emission measurements. A brief summary of the frequently encountered problems is given. In the first phase problems were mainly related to non conformities with the standard which are relatively easy to correct. Some of the remaining problems deal with interpretation of the standard for the specific field of application. The solutions that were proposed by the reference laboratory are given for some of these matters, more specifically concerning the validation of methods, the recommended quality control steps and the use of calibration gases.

Legal requirements for quality in emission measurements

EN45001 defines itself as a quality standard that should be applied when testing measured values against a legal requirement. Vice versa it is obvious that environmental legislation should specify a quality standard for emission measurements. In Flanders, the northern region of Belgium, the requirement for environmental labs to work according to the EN45001 standard was first anounced in the draft decree on environmental policy in 1995, and in 1999 the application of EN45001 and the keeping of a quality manual for environmental measurements was imposed by law. However the law does not state that it is necessary for a lab to be accredited. Since more than 3 years now the standard is being implemented by emission laboratories. For the certification of the implementation of the standard the laboratories where given the choice to obtain an accreditation from Beltest, the Belgian accreditation body (or a similar EAL body for foreing labs), or to have their quality system audited by representatives from the reference laboratory Vito. The latter system focused mainly on technical aspects, and aimed at improving the quality of measurements as quickly as possible. For the labs an advantage of this system was that there were no costs for the audits, and that a limited amount of expert advice could be obtained in the process. Of a total of 20 labs, only 4 or 5 have followed the Beltest path, but less than half were succesful. For both options however the implementation of the standard gives rise to different interpretations. The final result after accreditation can be a somewhat random combination of procedures proposed by the lab, and adaptations to the visions of the auditing team. The labs that were already accredited by an EAL body had to adapt to a number of specific interpretations of the standard, such as the use of calibration gases. It is the role of the reference laboratory to harmonize these differences, in order to obtain emission measurements of comparable and good quality.
The EN45001 standard is now gradually replaced by ISO17025. At the technical level for emission measurements, this hardly entails any changes. This standard is a bit more precise in some of its requirements, but it also recognizes that in specific fields explanations are necessary. However ISO17025 explicitly discourages the writing of documents with more requirements for specific disciplins.

Homologated laboratories in Flanders

Briefly the system of licensing laboratories for air pollution measurements in Flanders is such that the Minister of the Environment grants the official recognition for a period of 5 years after the application for a defined scope has been approved. The scope can be selected from 22 packages of parameters, e.g. "basic emission parameters", "small combustion plants", "dioxins in emission". The environmental administration checks whether the application is complete and if general conditions of competence, independance, language etc. are fulfilled. Technical advice is then asked from the reference laboratory Vito, which will inspect the quality manual, the methods and the equipment used. After this technical tests are organized. These tests consists mainly of the measurement of test gases from a calibration gas generator, and eventually the analysis of some reference samples. Conditions have been laid down about acceptable deviations from the reference values. As a rule 20% deviation is acceptable, but for some packages like the testing of automatic emission monitors, only 10% is

allowed. These criteria were put forward more than 5 years ago, with respect to environmental legislation where a maximum total measurement uncertainty of 30 % is specified. After 5 years of tests these criteria still appear to be good discriminators between good and bad quality control of emission measurements and they will not be altered in the near future. For some packages where knowledge of special methods or codes is needed, the experts of the candidate lab must pass an additional multiple choice exam. The number of actually homologated labs is about 20, among which a few from the Netherlands and Germany.

Introduction of EN45001 standard

In 1993 due to a change in legislation there was a high demand for source testing and several analytical laboratories with little previous experience applied for homologation in emission testing. The quality from these labs was irregular, and large differences of results for the same source were not uncommon. In a 1997 meeting with the reference lab the laboratories were given some "first aid" advice on how to improve on the quality of emission measurements. Summarized these basic recommendations were:

- have written procedures of all methods
- calibrate all essential measuring equipment like:
  - temperature
  - manometers
  - volume meters
  - pitot tubes
- validate methods
  - explore limits of validity of method
  - document measurement uncertainty
- keep maintenance record and do functional checks on instruments
- keep track of data chain
  - use a standard form to register test data on site
  - always conserve raw data
- always leak test equipment first

The objective was set to have all labs working according EN45001 by the end of 1999, and to have a first round of audits in 1998.

Frequently encountered problems

A list of some frequently encountered problems during audits of emission labs is given in table 1. In the first phase of implementation many beginners problems were detected that were relatively easy to correct. Some non conformities with the standard keep appearing however and are indicated as "phase 2" in the table. Problems of a more general nature with the quality system like training, quality manual etc. are not mentioned here. The table is given as an illustration of some practical requirements only. Other auditors should be warned to strictly follow their own views, since some errors are contagious because auditors spread them (i.e. they look for the same errors in all labs) and this may lead to an excessive culture of particular problems.

Table 1 Some frequently encountered problems in emission measurements

Phase 1 Basic shortcomings at the introduction of EN45001	Phase 2 Recurring or lasting problems
• No written procedures available • Different uncalibrated instruments in use • No calibration or zero gases used on site • Time and duration of test not registered • No leak test • Calibration of electrochemical analysers with gas cylinders only once a year • Linearity of analyser or method not tested • Unusual definitions of detection limits, etc. • No internal auditing of tests • No registration of calibration on site • Use of non-standard methods without validation • Unregistered samples, unregistered instruments • VOC's sampled with personal samplers without volume measurement • No heated probes where required	• Unsufficient warming up of analyzers before measurement • Linearity not properly defined and tested (linear regression) • Measurement outside calibration or linear range • Calibration not traceable to national standards (electrochemical analysers, temperature, volume meters, manometers) • Not enough points for traverse measurements • Obvious mistakes not corrected and not reported to the client • Detection limit unknown or too high (fluoride) • Mixing of different standard methods leading to wrong results (Chlorine) • Non validated gross deviations from standard methods • Improper estimates of measurement uncertainty (generally underestimated) • Damaged or faulty equipment in use or not recalibrated • Temperature of heated probes not well monitored

Method validation

In quite general terms the standards states that quantitative test methods have to be validated adequately, every time this is technically justified and pertinent in the context of the application. During a 1997 auditors meeting Beltest, the Belgian accreditation organisation for EN4500x and ISO17025 certification proposed the following table of properties that have to be determined in a validation scheme for chemical analysis. This scheme is not absolute, but an accredited lab has to demonstrate a substantial part of this validation work.

Table 2 Method validation in chemical analysis (Beltest recommendation 1997)

	New method	Standard method	Adapted method
Trueness	**A**	**A**	**A**
Repeatability	**A**	**A**	**A**
Reproducibility intra lab	**A**	**A**	**A**
Limit of detection	**O**	**O**	**O**
Limit of quantitation	**O**	**O**	**O**
Linearity	**O**	-	**O**
Selectivity	**A**	-	-
Ruggedness	**A**	-	**O**

A : Always test
O: Optional, test if technically relevant in the field of application
-: not required

For emission measurements carrying out all the work required to complete this table with quantitative data is not a feasible option. The main problem compared with lab analysis is that a reference material for the measurands is hard to obtain. Table 3 gives a reduced set of characteristics that are to be validated for emission measurements.
For some gaseous components like CO, SO_2, NO, HCl gas mixtures in cylinders can be purchased and used as a test material. With a diluter several concentrations can be generated and used to test some of the parameters in the list. However out of 20 labs only a few have gas diluters at their disposal. Some others have combined their efforts with equipment vendors to test their analysers with several independent gas mixtures in cylinders. For dust and dust bound components validation of trueness, detection limit and repeatability is equally important but generally it can only be carried out on the subparts of the test like the weighing of blank and loaded filters, the analysis, and the sample volume measurement.
Although the efforts in validating gas analysers are considerable, the results are in most cases worthwhile since they provide realistic information about the limits of the method and the measurement uncertainty.
An important consideration is the technical relevance of all these tests. For the classical optical methods (IR and UV) a check of linearity and selectivity are most critical. The testing of trueness and detection limit is very useful in estimating the measurement uncertainty. Repeatibility and linearity normally are tested according to ISO 5725 and 9169 definitions respectively. However the number of tests required are either not specified or too high (15-30 or more) and we would recommend a minimum of 6 data points.
Limit of detection is of little importance when pollutants to be measured have higher concentrations like NO and SO_2 in coal combustion, but it may be very important for the same pollutants when low concentration sources are measured. The same applies for HCl and HF, where the emission limit values are often close to the detection limits of the method.

Table 3 Recommended method validation for emission measurements

	Gases - Instrumental methods CO, SO_2, NO…	Gases Wet chemical HCl, HF, Hg	Dust and dustbound metals
Trueness	**A**	**O** **A** (analysis)	**A** (weighing) **A** (analysis)
Repeatability	**A**	-	**A**
Linearity	**A**	**O** (analysis)	**O** (analysis)
Limit of detection	**R**	**A** (analysis)	**A** (w & a)
Selectivity[1)]	**R**	**O**	-

O Optional due to difficulty in realising the measurand
A Always try to test or determine otherwise
R Always test if relevant for this method or measurand
- not required
1) always test in cases where known interferences exist, e.g. NO_2 with SO_2 by NDUV

The frequency of these tests is to be decided by the lab. Considering the amount of work involved a frequency of once every 2 years, or whenever new instruments or methods are introduced appears adequate for most criteria. However a good lab will do some extra checks on its instruments before any critical applications. When the highest analytical quality is needed, e.g. for the calibration of fixed continuous analysers by comparative measurements, the method validation steps need to be more elaborate than for routine measurements.

Quality control steps

In quality control of results we distinguish three levels:

1. first line: reference samples are analysed of which the concentration is known to the analyst (control charts)
2. second line: samples with concentration unknown to the analyst are analyzed; the concentration however is known by the quality manager of the lab
3. third line: samples of unknown composition are analysed; e.g. by participating in ring tests

With emission gases it is not always possible to have all 3 levels of quality control operational. Vito's recommendation is based on Beltest's standpoint that at least 2 out of 3 levels have to be implemented. Practically this means that e.g. a control chart system has to be kept in combination with participation in ring tests for any parameter of the scope. Therefore we consider it of utmost importance to provide ring tests for as many emission parameters as feasible. Table 4 is an overview of the first 5 year plan of ring tests.

Table 4 Ring test program LABS during last 5 years

Year	Ring test parameters
1997	- Inorganic flue gases SO_2, CO, NO_x, O_2 - VOC'
1998	- Wet chemical determination SO_2 - HCl - VOC - identification of VOC - Total organic carbon by FID
1999	- Inorganic flue gases SO_2, CO, NO_x, O_2 - Dust (filter weighing)
2000	- VOC's in dry and wet gases - Physical parameters T, flow, V
2001	- Inorganic flue gases SO_2, CO, NO_x, O_2 - Asbestos in air (filters) - Gaseous mercury

The role of these ring tests has changed somewhat over the years. First it was a deliberate element of quality improvement, and some labs neglected to participate. Now participation has become compulsory, with possible consequences for the homologation of the lab. When too large deviations are present, this indicates that the quality of a given test is not under control and the labs are warned that corrective actions are needed. An external auditor will always check past ring test scores as an indicator of the capabilities of a lab.

Reliability and traceability of calibration gases

As a small country Belgium has no national standards for the gases SO_2, NO, NO_2, CO etc. at current emission levels. The laboratories used to purchase their calibration gases from 4 or 5 different suppliers, of whom no one (until 2 years ago) was even certified to analyse their own products according to EN45001. It had occurred a few times during ring tests that labs had a bad score purely due to the quality of the calibration gases. VITO was one of the victims in 1998 when we had a significant negative error on total hydrocarbons with the FID, due to a 11 % deviation from the certified value in a propane-nitrogen mixture. The supplier was contacted and had to admit that there was a difference for this cylinder between the preparation value and the analysis value. The latter had been put on the certificate, contrary to the producers own rules. Another supplier caused us problems with a too high NO calibration gas cylinder. In a meeting with the reference gas producers in 1998, it appeared that most companies did not have the analytical possibilities at the same EN45001 level as the emission testing labs, and relied exclusively on gravimetric preparation of the gas cylinders. The response to the demand to have their labs accredited was not very positive. At least two estimated the financial implications were too heavy, and they

proposed to import certified mixtures from abroad. In one case this would entail a price tag of 1000 Euro for a cylinder.
The maximum deviation from the true value for calibration gases was another point of discussion. Ideally this would be situated below 5 %. This uncertainty level (or even 2 %) is frequently given on certifcates. However since several cases have been detected with deviations outside the limits on the certificate, this raises the question how many percent of reference gas cylinders outside the specifications are tolerable. Regarding the number of labs and cylinders, in my opinion 1 out of 20 is too much. Therefore the following uncertainties about the certified concentrations would be reasonable requirements for most calibration gases in emission monitoring:

- 5 % uncertainty at the 99 % confidence level, or
- 2 % uncertainty at the 95 % confidence level

The matter of which calibration gas to use is not completely resolved. In the production the ISO/DIS 6142 (1998) standard "Gas analysis - Preparation of calibration gas mixtures - Gravimetric mehod" is followed but there is no ISO or EN standard defining the different levels of reference gases and the corresponding requirements. After several labs received remarks about using untraceable calibration gases or certificates that did not show an analysis by an accredited lab, some producers have now taken further incentives toward certification of the quality of cylinder analysis and preparation.

Use of calibration gases in the field is crucial for the quality of results from gas analysers. Since the instruments suffer from transport and dirty gases of different origin, the stability of zero and span needs to be monitored by a check at the start and the end of each measurement campaign on site. The procedure as in figure 1 was agreed with the labs. Whether the results have to be corrected for zero and span drift must be decided by criteria specified in the procedures. The use of an independent control gas and a control chart was introduced in analogy with other chemical analysis. The added value of this will be re-evaluated in the future.

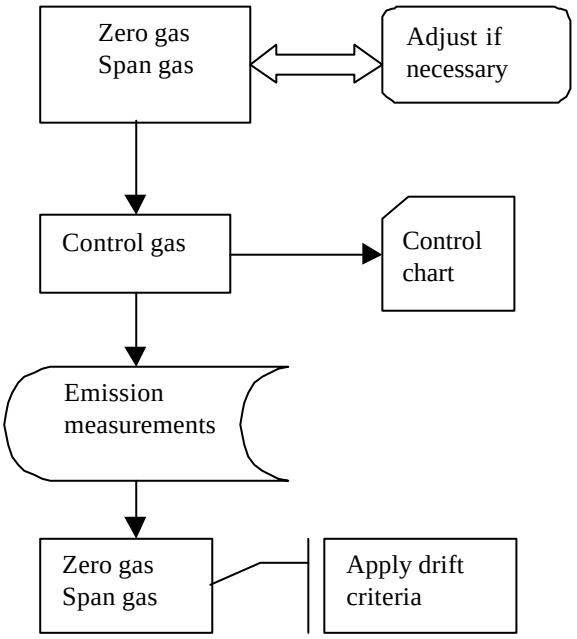

Figure 1. Proposed path for calibration of gas analysers on site

Comments on some other problems

Leak test "impossible" or dangerous
Not all labs rigorously leak test all of their equipment before starting a sampling test. Cases have been encountered where the leak test was done only in the lab, or on the day before the measurement. What is required is a check of the complete sampling train just before it will be used, wihtout any dismantling between the test and the sampling. Some EN standards even prescribe double leak checks. Since it is such an obvious source of errors we demand that labs provide traceable proof of leak check, i.e. they have to note the time and the quantitative result of the test. A simple "OK" on the protocol is not sufficient as it is all too easy to come by without executing the test.
Several labs are afraid to leak test sampling trains with impingers, especially when these are filled with dangerous liquids such as nitric acid or dichromate in sulfuric acid. The reason is that they normally leak check by stoppering the probe with the thumb, and are unable to release the vacuum smoothly, thus causing the liquid to burst in a big splash through the end of the train, possibly damaging valves, pumps or meters. The solution is of course that they have to constuct a stopper for each probe that allows for slow breaking of the vacuum.

Electrochemical analysers
Several labs only have electrochemical instruments at their disposal. The problem with the older and cheaper instruments of this type was that the cells showed drift and were sensitive to interferences. The use of electrochemical instruments therefore was restricted to combustion plants with a heat output below 10 MW. (However sellers of these instrument are referring to technological advancement and are asking to remove this restriction in the future).

Working with rented equipment
There are several companies in Europe that rent emission monitoring equipment. In principle the same quality of measurement must be expected from rented equipment, but mostly for the operator time is too short to make sure that the rented instrument functions as well as the usual one. For short rental periods it is practically impossible to guarantee EN45001 requirements, e.g. to have adequate written procedures and method validation. The following tips apply to make a rented instrument compatible with an existing quality system:
- try to rent exactly the same instrument as the one that is normally used
- prepare for a set of tests to demonstrate that the instrument is functioning properly
- if unknown instruments are to be rented, take time to learn to know the instrument and validate.

Organisation of audits

Practically the audits in most laboratories were done with 2 to 3 auditors, depending on the size of the lab and the scope, during one full day. A total of 6 qualified auditors took part, 5 of which are technical auditors, and one is a principal auditor, who coordinates and audits more general aspects like training of personel, flow of samples, etc. Nearly all of the auditing time was spent inside the lab. In the beginning the auditing of the paperwork and the instruments in the lab brought up so many problems that there was no further need to check the work in the field. After the first round of audits the "distance to target" for most labs appeared so large that it was hard to overcome in one year, and therefore a second series of audits had to be organised to follow up the progress. Even in the second year practically no time was left to audit measurements in the field. Beltest here takes a different approach. After the first application for accreditation Beltest proposes a pre-audit with a limited crew, to check if a full size audit is worthwhile. After this at least one auditor will allways spent half a day on site, prior to the audit in the lab. The experience is that field audits are difficult to organise and do not allow to cover many tests, but on the other hand they show an essential part of the capabilities of the labs. For the year 2001 it is planned to start with a system of audits during measurements in the field.
The deadline for compliance with EN45001 had to be extended with another year until the end of 2000, in order to allow laboratories to realise the necessary quality improvements. By the end of 2000 labs that did not comply would loose their homologation, but fortunately this has not been the case.

Author

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