Uncertainty budgeting for instrumental methods in emissions. A practical approach for measuring institutes.

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Abstract: A procedure based on zero and span readings before and after each measurement campaign has been developed and described. The procedure is rather flexible, and it can be used for the instrument in general, for the instrument when used in certain applications, or when used for one specific measuring task. Further more the procedure also gives a procedure for determining the detection limit of the instrument – under field conditions. For normal use the alternative procedure does not require additional activities in the field – just more calculations. The alternative procedure does not cover all uncertainty sources, and consequently additional calculations are needed.

Keywords: Uncertainty calculations, Field tests, Emissions.

1. Introduction

The international standard EN ISO 14956 [1] was accepted as an international standard in August 2002 and shall be implemented as national standards in the CEN countries at the latest by February 2003. Knowing that the accreditation bodies in Denmark and Sweden will request – or at least strongly encourage – the measuring institutes to use this standard for their uncertainty budgeting, the two national environmental protection agencies[1] decided to establish a project, where the procedures in the standard are described, and also an alternative and "easier-to-access" procedure is given.

The argumentation for an alternative procedure is, that it is difficult for the individual institute to establish the necessary information required to make a valid calculation. Further more the differences in the uncertainties calculated by different institutes are assumed not to originate from differences in the instruments and procedures used but from differences in the calculations.

The main task of the project was to establish a procedure, which should be relatively simple – or at least simple to harmonise, that gives a measure for the uncertainty of an instrument under field conditions. The intention of the alternative procedure is to substitute as many uncertainty sources as possible by information of the performance of the instrument during measurement campaigns.

2. Existing procedures.

2.1 Available standards and reference documents.

The basic reference documents for estimating the uncertainty in emission measurements are GUM [2] and QUAM [3], which both are rather theoretically – especially from the view of a

[1] The Danish costs are a part of the activities in the national reference laboratory within dk-TEKNIK. The Swedish part is a direct contract with the Swedish EPA.

practically oriented measuring expert. QAUM introduces although the use of “cause and effect diagram” in uncertainty budgeting.

Cause and effect diagrams are designed in order to assist in building the budgets, and it is recommend to begin with a relative simple diagram as illustrated in figure 1 (copied from [3], and therefore the abbreviations is irrelevant for this paper).

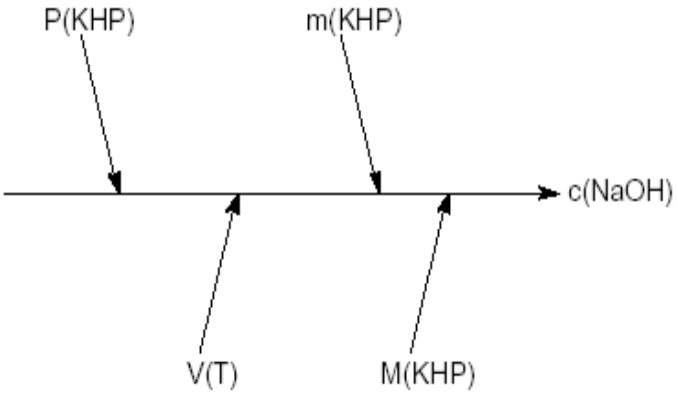

Figure 1. The simple first step in setting up the cause and effect diagram.

The parameters m(KHP) and V(T) are also measurements, and similar diagram can be design for each of those, and incorporated in the diagram in figure 1. The resulting diagram is given in figure 2.

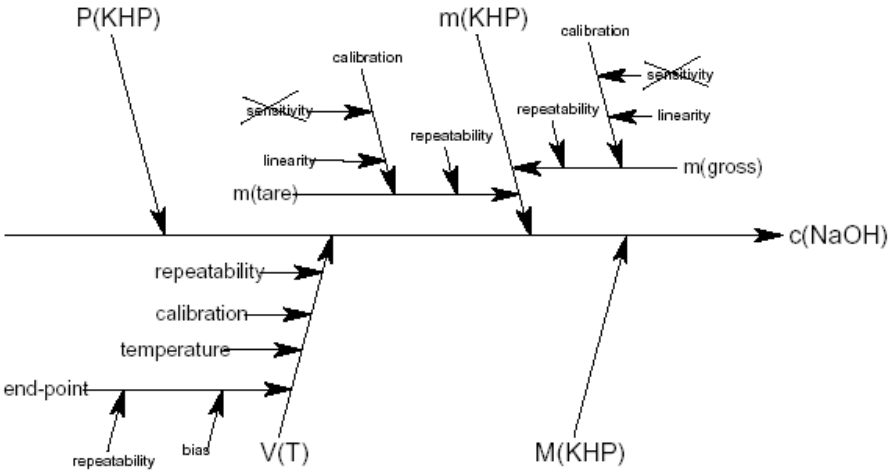

Figure 2. Cause and effect diagram when uncertainty sources from m and V are included.

These diagrams are widely used in chemical laboratories, and in order to minimise the number of uncertainty sources to be quantified, each laboratory very often determine the total uncertainty originating from one group. In this example it could be that the uncertainty from V(T) is determined by in-house experiments, and the result from here is used in the uncertainty budget.

Making such diagrams for instrumental methods for emission measurements becomes very complicated. ISO 14956 [1] gives a procedure how to combine the uncertainty of every possible influencing source on the measuring result. The standard deals with the following uncertainty sources:

- Non-linearity
- Reproducibility standard deviation
- Instability

- Pressure dependence (ambient and stack pressure)
- Temperature dependence (ambient and stack temperature)
- Interfering components – includes also possible chemical reaction at sampling filter
- Losses in sample line and other instabilities in sampling line
- Variations in power supply
- Leakage
- Uncertainty of calibration gasses

Having this information ISO 14956 give a rather precise procedure on how to calculate the total uncertainty.

2.2 Identified problems.

The principle in ISO 14956 is, that each uncertainty source has an impact on the combined measurement uncertainty. The impact is calculated from the uncertainty sources through a sensitivity factor and the difference between the calibration situation and the measuring situation.

An example is temperature dependence. The manufacturer of the instrument specifies the temperature dependence to be less than 1% of measured value per 10 °C change in ambient temperature. The instrument is calibrated at 20 °C, and the instrument is operating in an environment with variations from 0 to 40 °C. The impact from the ambient temperature then becomes ± 20 °C divided by 10 °C times 1% of measured value, equals ± 2% of measured value[2].

This procedure seems very logic, but coming to the practical use several question arises.

- What is the temperature at calibration? Is it when the instrument was calibrated initially, or is it the temperature on site, when I do my zero and span checks – or is it somewhere in between?
- What is the variation in the temperature? One measuring location is outside, and the temperature is varying between 2 and 4 °C. The next day the location is inside, and the temperature is varying between 35 and 40 °C. Shall the temperature from 2 to 40 °C be used?
- Which measured value to use? Always use the emission limit – that's where the uncertainty is most important. Day one is at a waste incinerator, and day two is a power plant with two very different limit values?

This is only one example, other uncertainty sources raises similar questions. Such questions resulted in, that very few – if any – measuring institutes did reliable uncertainty calculations. The most institutes did not any calculations at all.

Further more two institutes having the same type of equipment should theoretically obtain the same uncertainty on the measuring result, but depending on which answer they choose, different uncertainties will be estimated. Based on this it was decided to write a report describing the problems, and if possible to give a proposal for an alternative procedure to estimate the uncertainty based on results collected in the field.

[2] ISO 14956 also describe that this result shall be divided with the square root of 3, because the uncertainty source is given as a maximum value. This is important for the calculation, but less important for the argumentation in this paper.

3. Proposed procedure.

3.1 General.

When the procedure was developed the starting point was, the zero and span reading, because they are normally performed in a typical measuring situation before and after each measuring campaign (or in the beginning and the end of each measuring day). It seems as very useful information but the question was if it could fit into a GUM/QUAM approach for uncertainty budgeting.

The difference of the readings before and after a measuring campaign express the average drift during measurements, and may be corrected for, and the variation of the differences expresses the typical stability of the instrument, and therefore it includes all the uncertainties related to the measuring situation. In the view to cause and effect diagrams, this approach corresponds to estimating the uncertainty of one branch in such a diagram (e.g. m(KHP) in figure 2).

The mathematics are:

For each measuring campaign calculate: $\Delta_i = x_{before} - x_{after}$

For a large number of measurements calculate the average drift by $$D = \frac{\sum_{i=1}^{n} \Delta_i}{n}$$

At this stage an important quality control parameter is calculated. If the value D is significant different from zero, then there is something wrong in the measuring procedure – normally it is because the warm up time of the instrument has been to short.

The standard deviation is calculated by: $$s(\Delta_i) = \sqrt{\frac{\sum_{i=1}^{n} (\Delta_i - D)^2}{n - 1}}$$

This value represents the uncertainty contribution from several sources. Looking at the list in section 2.1, it replaces the uncertainty from

- Reproducibility standard deviation
- Instability
- Pressure dependence (ambient and stack pressure)
- Temperature dependence (ambient and stack temperature)
- Losses in sample line and other instabilities in sampling line
- Variations in power supply
- Leakage

The consequence is that the measured uncertainty only has to be combined with the remaining three uncertainty sources.

- Non-linearity
- Interfering components – includes also possible chemical reaction at sampling filter
- Uncertainty of calibration gasses

3.2 Verification.

In order to verify if the proposed method result in uncertainties differing from the GUM approach given in ISO 14956 a small investigation was made. A traditional uncertainty budget was made for a NO_x-monitor used for regular measurements, and data for drift using calibration gasses at two different concentration levels were used as well.

The results are summarised in table 1.

Unit: ppm	Example 1		Example 2		Example 3	
Conditions						
Calibration gas concentration	880		200		880	
Measured concentration	220		220		850	
Uncertainties	Trad.	New	Trad.	New	Trad.	New
Field uncertainty	2,4	3,2	2,4	4,1	9,0	10,0
Linearity and interferences	6,4	6,4	6,4	6,4	6,4	6,4
Calibration gas	10,2	10,2	2,3	2,3	10,2	10,2
Combined uncertainty	12,2	12,4	7,2	7,9	15,0	15,6
Expanded uncertainty (relative)	11 %	11 %	7 %	7 %	4 %	4 %

Table 1: Examples on uncertainty calculations according to ISO 14956 and the measurements on site.

Looking only at the expanded uncertainties, there is no difference between the two methods described in this paper. But a close reading will demonstrate, that the uncertainty sources linearity, interferences and calibration gasses are the same in both situations.

Never the less the conclusion is, that there might be a difference in what is called field uncertainty in table 1, but that difference is not significant on the expanded uncertainty.

3.3 Enlargements

The standard deviation of the differences also express the “noise around zero”, in other words the information can be used to determine the detection limit of the instrument under field conditions. It is found, that the most reasonable way of calculating the detection limit is given in the formula below:

$$\text{Detection limit} = |D| + 3 \cdot s(\Delta_i)$$

The same formula for calculation of the detection limit is used in European standards (e.g. EN 13211:2001), while other standards may prescribe the use of factor 10 instead of factor 3 in the formula. It was decided to use the factor 3, because the detection limit is determined under field conditions. The factor 10 is normally used in connection with determination in the laboratory.

Working with the proposed procedure for uncertainty determination using field data, it became clear, that the determination were done only at zero level and span level. The studied concentration might be between those levels.

It was anticipated that the uncertainty is proportional to the measured value, and the uncertainty at an other level than zero and span can be determined by linear interpolation using the measured uncertainty at zero and span level. The formula used is:

$$u_{meas} = u_{zero} + \left[\frac{u_{span} - u_{zero}}{c_{cal.gas}} \cdot c_{meas} \right]$$

where u_{meas} is the uncertainty at the measured concentration
u_{zero} is the uncertainty at zero level determined in the field
u_{span} is the uncertainty at span level determined in the field
$c_{cal\ gas}$ is the concentration of calibration gas used.
C_{meas} is the concentration measured.

During the work special problem with lack of fit (or lack of linearity) occurred. Almost every instrument have a lack of fit of "less than 2% of range"[3], which in many situations are very high. The most serious example is CO, where many instruments have a range of 0 – 1000 mg/m^3, because concentrations up to 850 mg/m^3 has to be measured. The uncertainty from lack of fit is then 11,5 mg/m^3, which corresponds to 23 % of the emission limit value for waste incinerators (50 mg/m^3).

Since the impact from each uncertainty source is calculated from each sources through a sensitivity factor and the difference between the calibration situation and the measuring situation, then it is reasonable to calculate the impact from the lack of fit relative to the difference between the measured concentration and the concentration of the calibration gas (if the same concentration is measured in the flue gas as the calibration gas has, then the impact from lack of fit becomes zero, which seems reasonable).

To calculate the impact from lack of fit, the following formula is proposed.

$$u_{lin} = \frac{\frac{B_{lin}}{FS} \cdot (c_{cal} - c_{meas})}{\sqrt{3}}$$

where u_{lin} is the resulting impact on the combined uncertainty from lack of fit
B_{lin} is the sensitivity factor from lack of fit (e.g. 2% of full scale)
FS is full scale
c_{cal} is the concentration of the calibration gas
c_{meas} is the measured concentration in the gas

4. Discussion.

The major disadvantage using the proposed method is, that the measuring institute don't get detailed information about each individual possible major uncertainty source measuring with the specific instrument, because several uncertainty source is added and measured as one value only. The first calculations of uncertainty budgets using the principle, although they are few, demonstrate that the major uncertainty source often are others than those contributing to the field uncertainty determined by zero and span readings.

It can be jeopardised whether the proposed method are in line with ISO 14956, because that method foresee that all uncertainty sources has to be identified. The proposed method does not. It is although quite clear, that the method is in line with QUAM, because that document does allow that several uncertainty sources are put into groups, as long as the uncertainty from the whole group can be determined. Please note, that QUAM is a document that many accreditation bodies refers to when auditing measuring institutes.

The proposed method has several advantages, especially from a practical point of view. The major advantage is, that many problems with getting information about the instrument is remove, and especially the problem of extrapolating from laboratory test to field conditions is removed.

The method is relatively simple to use, and since it is based on reading produced by each individual measuring institute, the uncertainty from the field will express the quality of the specific institute. In this way an institute with low quality procedures and instruments will be penalised with a bigger uncertainty, than those with good procedures and instruments. The procedures given in ISO14956 will only distinguish between instruments, and do not take the additional procedures into account in the uncertainty budgeting.

Examples are seen where laboratories uses ISO14956 as basis for the uncertainty budget, and

[3] This very used value is probably due to the fact, that the requirement to lack of fit in German legislation is 2%, and therefore it is not necessary to specify a better performance.

others for determination of the detection limit, which is then calculated as $\text{Detection limit} = |D| + 10 \cdot s(\Delta_i)$.
Where the standard deviation is determined by e.g. 30 zero readings over a short time period – e.g. 1-2 hour. This results normally in a very low detection limit compared to the uncertainty. A consequence is that the measuring institute theoretically can measure 1 mg/m^3 CO with an uncertainty of $\pm$15 mg/m^3. This has caused some problems for the institute explaining such a measuring result for their costumers.

Because the method is relative simple – at least compared to ISO14956 – it is believed that it will be used in practise, especially because it is based on the institutes own readings, not something read in a manual, and it solves the problem of a reasonable link between detection limit and the actual uncertainty.

5. Conclusion.

This paper gives a proposal for a procedure to determine some essential uncertainty sources in methods based on online instrument used in the field. The procedure replaces a long list of uncertainty sources, which normally is determined in a laboratory and then extrapolated to field conditions.

The procedure proposed is rather simple to use, and it is based on the zero and span readings the measuring institutes do before and after each measuring campaign. Even though it can be jeopardised whether the method is fully in line with the existing standardised procedures, it is assumed it is easier to use, and based on actual readings in the field, during different measuring campaigns. And as a consequence it is likely to believe that it will be used – also in small measuring companies.

The method also includes a proposal for determining the detection limit of the instrumental method, based on the field reading, which might be more realistic than a detection limit determined in the laboratory.

Other uncertainty sources have to be added to the uncertainty determined in the field. One is lack of fit, which has shown to cause many problems, due to the way the suppliers of the instruments gives this information. The paper includes a proposal to overcome this problem.

References

[1] EN ISO 14956:2002 “Air quality – Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty”

[2] ENV 13005:1995 “Guide to the expression of uncertainty in measurements”.

[3] EURACHEM/CITAC Guide: Quantifying Uncertainty in Analytical Measurement (QUAM). Second edition. 2000.