

Determination of uncertainty of automated emission measuring systems under field conditions using a second method as a reference

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Abstract

This report presents a procedure to determine the uncertainty of an automated emission measuring system (AMS) by comparing the results with a second method (REF). The procedure determines the uncertainty of AMS by comparing the final concentration and emission results of AMS and REF. In this way, the data processing of the plant is included in the result evaluation.

This procedure assumes that the uncertainty of REF is known and determined in due form.

The uncertainty determination has been divided into two cases; varying and nearly constant concentration.

The suggested procedure calculates the uncertainty of AMS at the 95 % confidence level by a tabulated t-value. A minimum of three data pairs is required. However, a higher amount of data pairs is desirable, since a low amount of data pairs results in a higher uncertainty of AMS.

The uncertainty of AMS is valid only within the range of concentrations at which the tests were carried out.

Statistical data processing shows that the uncertainty of the reference method has a significant effect on the uncertainty of AMS, which always becomes larger than the uncertainty of REF. This should be taken into account when testing whether AMS fulfils the given uncertainty limits.

Practical details, concerning parallel measurements at the plant, and the costs of the measurement campaign, have been taken into account when suggesting alternative ways for implementing the comparative measurements.

Preface

This work was done on behalf of the Finnish Ministry of the Environment where the project supervisor was chief engineer Markku Hietamäki. The responsible director in VTT was senior research scientist Merja Tolvanen from VTT Chemical Technology and the project manager was research engineer Harri Puustinen from VTT Chemical Technology. Other project team members were research scientist Leena Aunela-Tapola and research scientist Tuula Vahlman and research scientist Kari Wellman from VTT Chemical Technology and senior research scientist Keijo Kovanen from VTT Building Technology (Chapter 6). The experience on using the automated emission monitoring systems of Ekokem Ltd was available through the expertise and help of the environmental protection manager Hannu Ukkonen. Also, the experience on carrying out the quality assurance system of AMS in practice in IVO Technology Centre was available through the expertise and help of technology manager Jukka Leskelä, senior research engineer Heikki Hoffrén, senior technician Seppo Tuomaala and senior engineer Georg Bergman who also commented on the uncertainty calculation.

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1 Introduction

Automated measuring systems (AMS) are utilised in Finland in growing numbers to produce data that is used to control how individual plants comply with the given emission limit values. Parallel measurements are typically used to verify that AMS produces reliable and representative data.

A question has been raised:

Is it possible to determinate the uncertainty of AMS, permanently installed in a plant, by comparing the results with a second method as a reference (REF) with known uncertainty?

Requirements concerning the evaluation of the uncertainty of AMS are currently under discussion in the EU as well as in the international community. The need for harmonising the procedure and setting up requirements is becoming evident through the increased use of AMS on the sites obliged to carry out emission control. Some EU directives, e.g. the Council Directive of the Incineration of Hazardous Waste 94/67/EC, already express requirements concerning the uncertainty limits of the results of AMS. The matter has been discussed in several forums such as CEN, ISO and national standardisation committees.

The authors of this report have observed that very little is discussed in the literature about *how* the test for determination of uncertainty should be carried out in order to guarantee the representativeness of the results. Also, the statistical methods suggested are not applicable, as such, in all cases. For instance, how should we manage the comparative results, if the measured concentrations are nearly constant and the regression method is not applicable?

This report aims at giving added value to the international discussion concerning determination of uncertainty for automated measuring systems by using a reference method. Comparison tests are paramount in the quality assurance of AMS, since exhaust gas conditions cannot be entirely simulated by calibration gases. The functional tests of AMS, which also are crucial, are excluded from this paper.

2 Background

Determination of uncertainty for automated emission measuring systems using a reference method means, in this report, a procedure in which the results of AMS are compared with the results of a method with known uncertainty by comparative emission measurement at a site where AMS is permanently installed. In the European standardisation the procedure has also been termed “calibration“. Usually “calibration“ requires that the uncertainty of the reference method is insignificant compared to the method under calibration. However, this is seldom the case in reference emission measurement methods.

Determination the accuracy of AMS by comparative measurement has been discussed at least in the following standards or drafts of standards:

- ISO 7935:1992. Stationary source emissions – Determination of the mass concentration of sulphur dioxide – Performance characteristics of automated measuring methods
- VDI 3950, part 1;1994. Calibration automatic emission measuring instruments
- ISO/FDIS 13752:1997. Air quality – Assessment of uncertainty of a measurement method under field conditions using a second method as a reference. (The reader is asked to pay attention to the current status of the document)

Relevant aspects of the above standards or drafts affecting the task of this report are pointed out in the following:

VDI 3950, part 1; 1994

- The statistical analysis is performed with the paired values obtained from parallel measurements. The results of AMS are treated in electrical units (mA), REF as mg/m^3 .
- At least 15 paired samples are required to determine the analytical function. In some special cases a lower number can be used.
- The analytical function is defined according to the results of the comparative measurement by regression analysis.
- Confidence and tolerance ranges are calculated.
- The calibration term comprises both *functional tests* and *comparative measurements*.
- Two alternatives: 1) the comparative tests are carried out directly as grid measurement by the reference method, 2) the point-related comparison tests are carried out first, then completed by the grid measurement.
- Both linear and quadratic regression are included in the calculation.

- Constant standard deviation of AMS values is required to calculate the regression line
- In the calibration report, the procedures to determine the representativeness and the results are presented.

ISO/FDIS 13752:1997

- The statistical analysis is performed with the paired values obtained from parallel measurements by linear regression analysis. No repetitive measurements.
- Requires at least 30 pairs of measured values.
- The standard is especially intended for method validation (not e.g. to check the representativeness of AMS) since a requirement is stated that both methods should measure samples with insignificant difference in composition.
- It is required that the uncertainty of REF in the test environments is insignificant compared to AMS
- Linear relation is assumed between the results of REF and AMS. The regression analysis is performed, the procedure of which depends on whether the st.dev. of AMS is independent of the measured value of REF or whether the st.dev. of AMS is proportional to the measured value.
- Constant standard deviation of AMS value is not required. In the case of general variance model, iterative computations are required.
- The systematic error can be compensated by applying a correction. However, the uncertainty of the correction remains.
- An Excel-spreadsheet program is available.

Other relevant articles can be found in e.g. Jahnke, 1992.

Before going further in this presentation, the boundary conditions set in this study – partly also existing in the standards prescribed above - for determining the uncertainty for AMS by comparative measurements with a reference method, are specified:

1. The data of AMS is recorded for the comparison as concentration units, not e.g. as mA (i.e the uncertainty of the signal processing is included).
2. The internal quality assurance system of the AMS is considered as executed in due form.
3. The installation of AMS in terms of spatial representativeness is assumed to be considered but is, however, subject to evaluation.
4. The timing of the comparison test should be selected with consideration in terms of the maintenance cycle of the AMS.

5. The exhaust gas matrix is considered unsteady and therefore the results of the consecutive measurements of the AMS or the REF cannot be treated as repetitive samples.
6. The uncertainty of the reference method is known and it should preferably be considerably smaller than that of AMS.
7. The uncertainty obtained is valid only in the range where the comparison tests have been performed.
8. The number of the paired test samples has an influence on the uncertainty value of AMS.

3 Sampling techniques of automated measuring systems

Automated measuring systems (AMS) can mainly be divided into two types according to their sampling techniques:

- extractive methods
- non-extractive methods, known as in-situ or cross-duct measuring methods

In the extractive method, the *gas sample* is taken from one sampling point using probes of different design. The sample gas is first filtered and then either dried before analysis or analysed without gas-conditioning. In some methods sample gas is diluted before the analysis.

Concerning *the particle concentration* measurements the sample can be analysed without any pre-treatment, or it can be diluted and cooled before analysis.

The non-extractive method (in-situ) applies no sampling procedure. The gas components are detected by one point or by path measurement. The path measurement can be carried out using an optical or, alternatively, acoustic (e.g. velocity) line scanning across the duct or across a specific path in the duct.

4 Factors affecting the uncertainty of the reference method

In this chapter, factors of uncertainty for different types of methods used as reference methods are listed. Some factors may have an insignificant influence on the overall uncertainty, but nevertheless they are named here. The overall uncertainty of a reference method can be calculated using uncertainties of individual factors.

4.1 Manual method to determine the volume flow rate

Sources of uncertainties of volume flow rate are as follows.

1) Density of the gas in duct

1.1) Density of the dry gas in normal conditions

- volume proportion of the gas components (i.e. O₂, CO₂, CO, N₂) (see later)

1.2) Density of the wet gas in normal conditions

- density of the dry gas in normal conditions (see above)
- mass of the condensed water
 - repeatability/accuracy of the balance
 - resolution of the balance
 - non-linearity of the balance
 - handling losses of the sample (water) in the lines etc.
- volume of the dried sample gas in normal conditions
 - A. volume of the dried sample gas
 - accuracy of the gas meter
 - resolution of the gas meter
 - calibration
 - factor from calibration, when result not corrected according to the calibration
 - B. pressure of the gas in dry gas meter
 - calibration
 - reading accuracy
 - C. temperature of the gas in dry gas meter
 - accuracy of the thermometer
 - resolution of the thermometer
 - calibration
 - correction factor from calibration

1.3) Density of wet gas in the duct

- density of the wet gas in normal conditions (see above)
- gas pressure in the duct
 - A. atmospheric pressure
 - calibration
 - reading accuracy
 - B. over/under pressure in the duct
 - a) recording with micromanometer
 - accuracy of the micromanometer
 - non-linearity of the micromanometer
 - resolution of the micromanometer
 - calibration of the micromanometer
 - factor coming from the atmospheric temperature
 - factor coming from calibration, when result not corrected according to the calibration
 - b) recording with U-tube and tape measure
 - resolution of the tape measure
 - uncertainty of the tape measure
- gas temperature in the duct
 - accuracy of the thermometer
 - resolution of the thermometer
 - calibration
 - factor coming from calibration, when result not corrected according to the calibration

2) Velocity of wet gas in the duct (with Pitot-tube and micromanometer)

- coefficient of the Pitot-tube
- the density of the wet gas in the duct (see above)
- dynamic pressure (recording with micromanometer)
 - accuracy
 - non-linearity
 - resolution
 - calibration
 - factor coming from calibration, when result not corrected according to the calibration
 - atmospheric temperature
- turbulence in gas flow
- gradient velocity in the duct
- compressibility of the gas in the duct
- inclination of Pitot-tube

3) Volume flow rate of the gas in the duct

3.1) Volume flow rate of wet gas in the duct

- average gas velocity in the duct (see above)
- cross-section area of the duct
 - diameter of the duct

3.2) Volume flow rate of the wet gas in normal conditions

- volume flow rate of wet gas in the duct (see above)
- gas temperature in the duct (see above)
- gas pressure in the duct (see above)

3.3) Volume flow rate of the dry gas in normal conditions

- volume flow rate of the wet gas in normal conditions (see above)
- density of the dry gas in normal conditions (see above)
- mass ratio of water and dry gas in duct
 - mass of condensed water
 - volume of dried sample gas in normal conditions
 - volume proportion of the gas components (i.e. O₂, CO₂, CO, N₂) (see later)

4.2 Manual method to determine the dust concentration

Sources of uncertainties of dust concentration are as follows:

1) The mass of sampled particles

- repeatability/accuracy of the balance
- resolution of the balance
- non-linearity of the balance
- calibration
- factor coming from calibration, when result is not corrected according to the calibration
- handling losses (depositions onto the sampling probe)
- isokinetic sampling

2) The volume of dried sampled gas in normal conditions

- see above for the manual method to determine the volume flow rate/1.2)
density of the wet gas/volume of the dried sample gas in normal conditions.

4.3 Manual method to determine the concentration of gaseous compounds

Sources of uncertainties of concentration of gaseous compounds determined by the manual method are as follows:

1) The volume of dried sampled gas in normal conditions

- see above for the manual method to determine the volume flow rate/1.2 density of the wet gas/volume of the dried sample gas in normal conditions.

2) Samples

- effects of storage (time, temperature etc)
- effects of sample treatment

3) Analytical results

- break-through from absorbent/adsorbent
- uncertainty of the analysis

4.4 Continuous gas emission monitoring

Sources of uncertainties of concentration of gaseous compounds determined by a continuous method are as follows:

1) Calibration

- accuracy of calibration gas
- drift (zero/span)

1) Analyser

- noise
- detection limit
- non-linearity
- interfering components
- temperature/pressure effect (ambient conditions)
- accuracy
- repeatability

3) Recorder

- accuracy
- resolution

4) Sampling

- sampling line (length, leakages, reactions with sampling line's material)

- dilution
- effect of sample gas conditioning (drying)
- accuracy of determination of water content (see above: mass ratio of water and dry gas in duct)

In addition to the factors given above, the final uncertainty of the reference method is determined by taking into account the results of comparison measurements between other reference methods.

5 Relevant aspects on determination of uncertainty of AMS by comparison measurement

5.1 Introduction

Emission measurement is typically a combination of more than one type of measurement. At least the concentration of the component and the exhaust gas flow rate are determined separately. Emission control regulations are either focused on the *concentration* value (expressed in certain standard conditions) or on the *emission* value.

AMS typically measures the *concentration* of specific components. The flow rate of the exhaust gas is measured or determined separately.

In the case where the uncertainty is calculated only for the *concentration* value, the parallel measurement with AMS is adequate. In the case where the uncertainty determination is needed for the *emission*, the flue gas flow rate must also be determined during the comparison measurements. In this case, the emission result of the plant - incorporating terms of concentration value by AMS and flue gas flow rate - is compared with the corresponding emission result of REF. Due to the nature of the determination, the emission value possesses higher uncertainty than the concentration value.

5.2 Implementation of the tests

In this Chapter, practical aspects concerning the implementation of the comparative measurements are presented briefly.

5.2.1 Sampling level

Before the comparison tests the expected concentrations of the flue gas should be examined.

When selecting the sampling level for parallel measurements with AMS, the REF chooses a level that is preferably as near as possible to the level AMS measures. In the case where such arrangement is difficult, the measurements of AMS and REF can also be carried out on different levels, provided that the concentrations are not altered e.g. by a control unit between the levels. To identify the profile of the gas stream in the sampling level, the velocity, temperature and O₂ can be measured

before starting the parallel tests. For normalising the measurement results O₂ shall be measured also throughout the parallel measurement test in the same measurement level with the REF.

5.2.2 Parallel measurements

A measurement by AMS is representative if the measured signal represents the average condition in the cross sectional area of the stack. The representativeness of the results of AMS installed in a certain location shall be investigated due to the spatial distribution of the measured objects across the duct. This can be evaluated with the aid of a method capable of performing a sc. grid measurement (REF). Figure 1 illustrates the alternatives for performing the comparative tests from the point of view of representativeness.

The number of the tests, the sampling time of each test and the number of the sampling points must be decided observing the following points:

- 1) Any needs for grid measurement (do concentrations have any significant spatial variations across the sampling level?). See Figure 1 for suggestion.
- 2) Adequate sampling time at each sampling point with regard to the response time of the methods.
- 3) The effect of the number of the paired samples on the uncertainty of AMS. This means that at a fixed confidence level, e.g. 95 %, with a small number of paired samples, a larger uncertainty for AMS is obtained compared to the uncertainty determined with a higher number of samples.

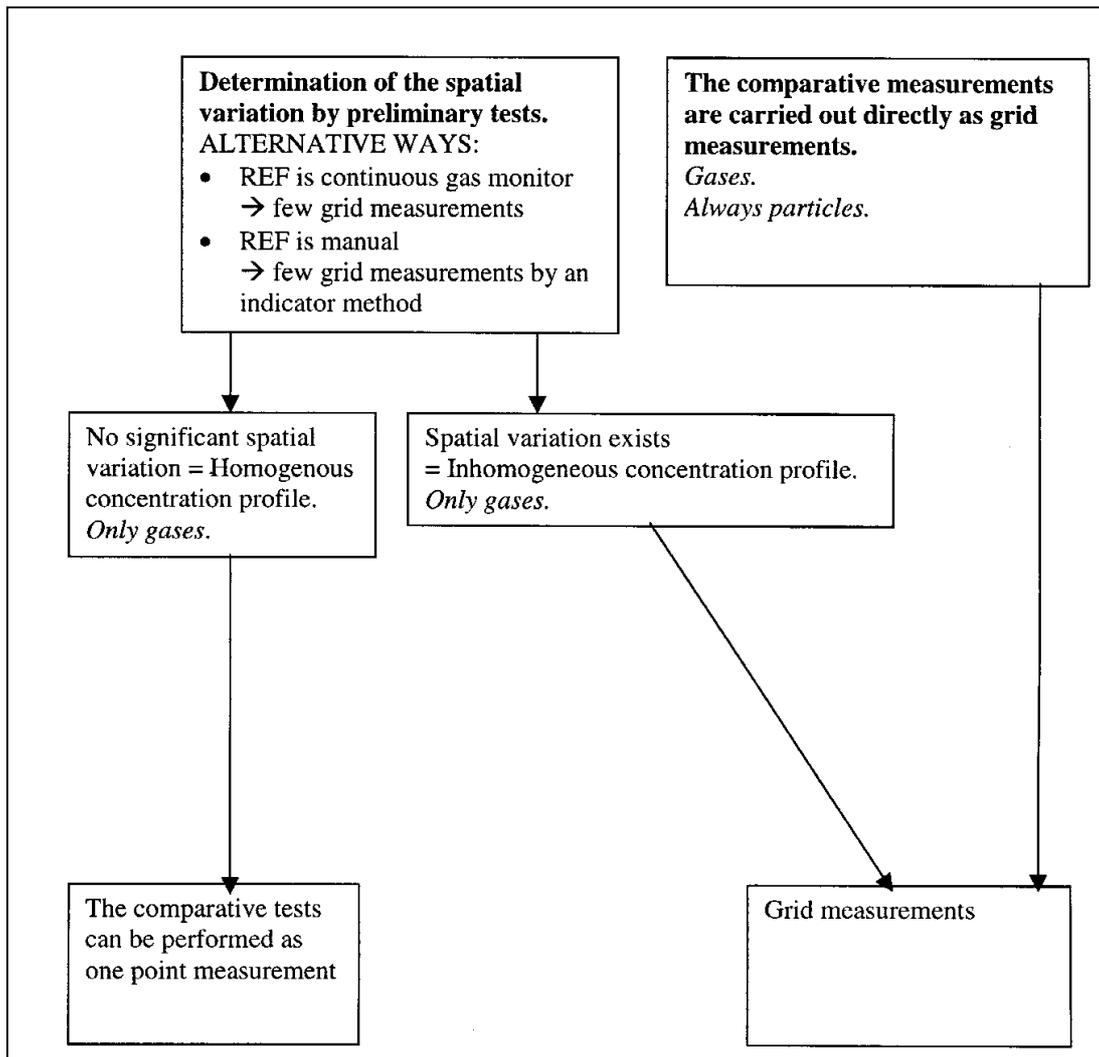


Figure 1. Alternative ways to perform the comparative tests from the viewpoint of the representativeness of the AMS

According to the suggestion presented in Figure 1, if there is no significant spatial variation, the comparative tests can be performed as one point measurement. If spatial variation exists, the comparative tests must be carried out as grid REF measurements.

It is also possible to determine the uncertainty of AMS by direct grid REF measurements.

In the case of extensive ducts where the grid measurements of REF is difficult to be carried out, the representativeness of AMS must be clarified in any cases in the report.

Notes:

- AMS and REF measurements must take place at the same time.
- When AMS measures dust concentration, the manual REF method shall perform the sampling isokinetically in each point.
- In special cases, such as batch processes, gases right after scrubbers or in ducts with air leakages, where the concentration and velocities of gas may vary significantly in the sampling level, the average concentration of the continuously monitoring REF is calculated by weighting the concentration of each sampling point with the ratios of velocities in the grid. In these particular cases all integral manual sampling methods should take samples isokinetically.

Suggestions of the number of paired samples vary quite a lot in different standards. For instance, in VDI 3950 at least 15 paired samples are required. In some special cases a lower number can be used. Both ISO/FDIS 13752 and ISO 7935 require at least 30 pairs of measured values. In this paper, the uncertainty of AMS is calculated at the 95 % confidence level by a tabulated t-value. Hence, the lower amount of data pairs results in higher uncertainty of AMS. The minimum of three data pairs is required.

5.2.3 Data processing for uncertainty determination

The results of AMS and REF will be processed as pairs representing the values of temporal correspondence. In the case of one point sampling with continuous analysers, the sampling time to determine the average concentration for paired samples is determined according to the shortest possible response data averages. When the grid measurement has been carried out with a continuous analyser as REF, the average of the concentration of the whole grid measurement is compared to the result of AMS, which is calculated as the average of exactly the same sampling period compared to the grid measurement (i.e. if the time needed to change the sampling port of REF method takes some minutes, this period is also taken away from the results of AMS in calculations).

In the case where concentration has large variations (e.g. <10...1000 ppm), the uncertainty can be determined separately for lower and higher concentration levels in statistical data processing. This is especially important in cases where the higher concentrations are close to the emission limit. The uncertainty of the continuous analyser is typically expressed as percentages of the measuring range (e.g. 1000 ppm), which means a higher relative value for low concentration.

5.3 Normalising the measurement results

If reference data and the data of AMS are determined in different exhaust gas conditions (dry/wet), the comparison of results shall be done after normalising the results to the same conditions. The normalising procedure depends on the final use of the results of AMS in an actual situation. If the aim is to determine the uncertainty of the result of AMS measured as such, the results of REF is normalised to correspond to the conditions of AMS results. In a situation where AMS gives a result which has to be normalised to different conditions for emission control purposes, it is appropriate to compare the results of AMS and REF only after normalising the results to the desired conditions. The cases are presented in Table 1.

Table 1. Cases of normalising the results.

AMS	REF	Final expression of the result	Comments
dry	dry	dry	Normalising not needed
dry	dry	wet	Both need normalising
dry	wet	dry	REF needs normalising
dry	wet	wet	AMS needs normalising
wet	wet	wet	Normalising not needed
wet	wet	dry	Both need normalising
wet	dry	wet	REF needs normalising
wet	dry	dry	AMS needs normalising

Always the one whose result is in a different condition from the “final result“ normalises its results according to the humidity measurement results. REF incorporates the uncertainty of determining the humidity in the expanded uncertainty of its results. A comparison is then made of the results in their final expression. When determining the humidity by REF, the homogeneity of the gas shall be taken into consideration.

In most cases, regulations demand that the concentrations must be presented in the dry gas phase in normal conditions ($p = 101,3 \text{ kPa}$, $t = 0 \text{ }^\circ\text{C}$).

5.4 The internal quality assurance system of AMS

Comparison measurements are carried out only periodically, e.g. once a year. The internal quality assurance system of AMS is important to ensure that the results of AMS are reliable also between comparison measurements. In the quality manual of the plant it is described which are those detailed activities of quality assurance system including responsibilities of the personnel, maintenance work and routines, calibrations etc. The whole measurement line from sampling to data processing is included in that process.

In the report the condition of AMS and the circumstances of the process must be described. For example, how often and when AMS has been calibrated, what was the calibration result and when has the last maintenance work been carried out etc. From the process conditions of the plant, the quality of the fuel, capacity of the plant and the parameters of the flue gas control should be known and reported.

5.5 Resource demands in the comparison measurement

A comparison measurement campaign includes planning, measurements at a site and reporting. Often it is necessary to visit the plant beforehand to ensure that technical conditions needed to perform the comparison measurements are met, etc.

The labour resource demands in a typical case involving one measurement place (i.e. the installation is done only once) are approximately as follows:

- comparison measurements in the field are carried out in two to three days including set up and unloading of equipment. In most cases at least two persons are needed.
- planning and reporting takes approximately one to two man-weeks, depending on the range of the measurement parameters.

6 Theory to determinate the uncertainty of AMS by comparative measurements

The uncertainty examination has been divided into two parts depending on the nature of the data. The concentrations of the paired samples can either be such that a linear regression is possible, or such that the concentrations are nearly constant. It is important to note that the uncertainty obtained is valid only within the range of concentrations at which the tests were carried out. In Appendix A, formulas of the spreadsheet form used in the statistical calculation of the uncertainty are given. In Appendix B, an example of a calculation procedure is given. The equations in this chapter are mainly from standards mentioned in References and from Dowdy & Wearden (1983).

6.1 Case of nearly constant concentration

In the case where measured concentrations by AMS and the reference method are nearly constant, as can be seen in Figure 2, and the samples are not independent, the matched-pair t-test can be used.

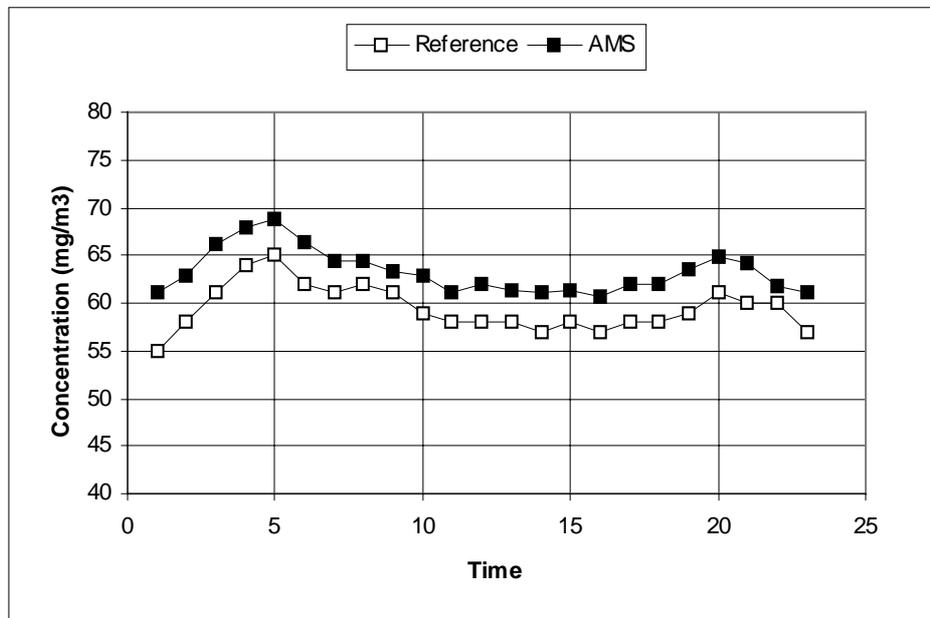


Figure 2. Example of a comparison measurement, where concentrations are nearly constant.

In order to check whether a significant systematic error is present, one must calculate the mean difference of the concentrations d_m using the formula

$$d_m = \frac{\sum d_i}{n}, \quad (1)$$

where d_i is the difference in the pairs of measured values
 n the number of comparing measurements.

The test statistic t in this case can be written as

$$t = \frac{d_m}{s_d / \sqrt{n}}, \quad (2)$$

where d_m is the mean difference
 s_d the standard deviation of differences d_i
 n the number of comparing measurements.

If the test statistic t is greater than the critical value of the t -distribution, then the error present is considered to be significant, Equation (3), and the systematic part of the uncertainty of AMS is $\Delta(\text{AMS}) = d_m$.

$$|t| \geq t_{\alpha, v}, \quad (3)$$

where t is the test statistic in Equation (2)
 $t_{\alpha, v}$ the critical value of the t -distribution
 α the risk level
 v the degree of freedom = $n-1$.

The standard deviation in Equation (2) has the formula

$$s_d = \sqrt{\frac{1}{n-1} \left[\sum_{i=1}^n d_i^2 - \frac{1}{n} \left(\sum_{i=1}^n d_i \right)^2 \right]}, \quad (4)$$

In comparing the random uncertainties of AMS and the reference method, an F distribution can be used. Then the test statistic F has a formula

$$F = \frac{s^2(AMS)}{s^2(REF)}, \quad (5)$$

where $s^2(AMS)$ is the variance of AMS values
 $s^2(REF)$ the variance of reference method values.

The difference in uncertainties is considered to be significant, if

$$F \geq F_{\alpha, n(AMS)-1, n(REF)-1} \quad \text{or} \quad F \leq F_{1-\alpha, n(AMS)-1, n(REF)-1} \quad (6)$$

where $F_{\alpha, n(AMS)-1, n(REF)-1}$ and $F_{1-\alpha, n(AMS)-1, n(REF)-1}$ are the critical values of the F-distribution. $n(AMS)$ and $n(REF)$ are the number of values of AMS and the reference method, respectively.

The uncertainty of AMS can be estimated at the confidence level of $1-\alpha$ by the formula

$$\frac{s^2(AMS)}{s^2(REF)} \frac{\sigma^2(REF)}{F_{\alpha/2, n(AMS)-1, n(REF)-1}} \leq \sigma^2(AMS) \leq \frac{s^2(AMS)}{s^2(REF)} \sigma^2(REF) F_{\alpha/2, n(REF)-1, n(AMS)-1}, \quad (7)$$

where $\sigma(REF)$ is	the uncertainty of the reference
method at	the confidence level of $1-\alpha$
$s^2(AMS)$	the variance of AMS values
$s^2(REF)$	the variance of reference method
	values
$F_{\alpha/2, n(AMS)-1, n(REF)-1}$	the critical value of the F-distribution
$F_{\alpha/2, n(REF)-1, n(AMS)-1}$	the critical value of the F-distribution.

The expanded, combined uncertainty of AMS at the confidence level of $1-\alpha$ can be calculated from

$$U = \sqrt{\sigma^2(AMS) + (t_{\alpha, v} \Delta(AMS))^2 + \sigma^2(REF)}, \quad (8)$$

where	$\sigma(\text{AMS})$ is	the random part of the uncertainty at the confidence level of $1-\alpha$
	$\Delta(\text{AMS})$	the systematic part of the uncertainty = d_m .
	$t_{\alpha, \nu}$	the critical value of the t-distribution
	α	the risk level
	ν	the degree of freedom = $n-1$
	$\sigma(\text{REF})$	the uncertainty of the reference method at the confidence level of $1-\alpha$.

6.2 Case of variable concentrations

In the case where the measured concentrations by AMS and the reference method have variable values, as can be seen in Figure 3, a regression analysis can be used.

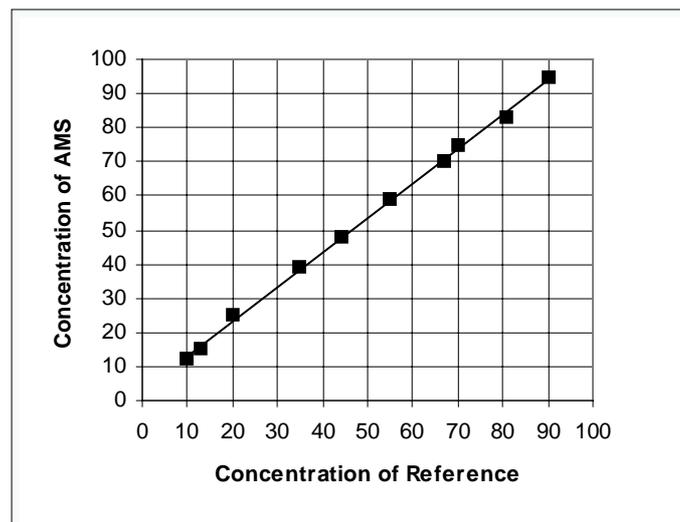


Figure 3. Example of a comparison measurement, where concentrations have low and high values.

The linear relationship between the pairs of values x_i and y_i to be compared has the following formula

$$Y = a + bx, \quad (9)$$

where	Y is	predicted value of y
	y	measured concentration value of AMS
	x	measured concentration value of the reference method

a, b parameters.

The method of least squares is used to calculate parameters a and b in Equation (9). Then the slope b has the formula

$$b = \frac{S_{xy}}{S_{xx}}, \quad (10)$$

where S_{xx} can be written as

$$S_{xx} = \sum x^2 - \frac{(\sum x)^2}{n}, \quad (11)$$

and S_{xy} can be written as

$$S_{xy} = \sum xy - \frac{(\sum x)(\sum y)}{n}. \quad (12)$$

The intercept a in Equation (9) has the formula

$$a = y_m - bx_m, \quad (13)$$

where y_m is average of y values
 x_m average of x values
b slope in Equation (10).

The following conditions are required to calculate the regression line:

1. The x values are measured with negligible error.
2. For each x value there is a normal distribution of y values.
3. The distribution of y for each x has the same variance.
4. The expected values of y for each x lie on a straight line.

Another way to express these conditions is to say that the variables satisfy the model

$$y = \alpha + \beta x + \varepsilon \quad (14)$$

in which the ϵ 's are normally distributed with a mean of 0 and a variance of σ^2 , and the ϵ 's are independent of the x 's and independent of each other.

One can test for violations of these assumptions by an examination of the residual $e = y - Y$ that result from fitting the least squares line to the sample data.

Linearity can be checked by plotting the residuals against the predicted values. A random scatter about a horizontal line at $e = 0$ reflects a linear relationship. A systematic plot that has some pattern reflects a nonlinear relationship, or another independent variable is affecting y .

Equality of variances can be checked by plotting the residuals against the predicted values or the independent variable x . A horizontal band of points reflects equal variances, whereas a fan-shaped distribution reflects variances that depend on the magnitude of x .

Another way to check the equality of variances is as follows:

- take n_1 measurement pairs from the upper end of the measurement range and n_2 pairs from the lower end

- compute the statistic

$$F = \frac{\frac{1}{(n_1 - 1)} \left(\sum_{i=1}^{n_1} (y_i - Y_i)^2 \right)}{\frac{1}{(n_2 - 1)} \left(\sum_{i=1}^{n_2} (y_i - Y_i)^2 \right)}, \quad (15)$$

where Y_i is the predicted value of y .

- Equality of variances can be considered, if F does not exceed the tabulated value $F_{1-\alpha, n1-1, n2-1}$ of the F-distribution for the one-sided test.

The regression model assumes independence of the ϵ 's. This means that the random error in one observation does not affect the random error in another observation. If the observations have a natural sequence in time or space, the lack of independence is called autocorrelation. Diagnosis is difficult, but this kind of dependence can sometimes be detected by plotting the residuals e against the time order or the spatial order of the observations.

If it is possible to reject the case, where slope $b = 0$, then prediction from the least-squares line is appropriate. Prediction may be done only for values of x within the range of the collected data. Extrapolation outside of that range is not reliable.

In order to check whether the intercept a in Equation (9) is significantly different from the ideal values of 0, the test statistic

$$t = \frac{a}{s_{yx} \sqrt{\frac{1}{n} + \frac{x_m^2}{S_{xx}}}}, \quad (16)$$

is used, where x_m is the average of x values, S_{xx} is given in Equation (11) and s_{yx} has the formula

$$s_{yx} = \sqrt{\frac{\sum_i (y_i - Y_i)^2}{n-2}}, \quad (17)$$

where Y_i is the predicted value of y_i . If the test statistic t in Equation (16) is greater than the critical value of the t -distribution, Equation (18), then the intercept a in Equation (9) differs significantly from the value of 0.

$$|t| \geq t_{\alpha, v}, \quad (18)$$

where

t	is	the test statistic in Equation (16)
$t_{\alpha, v}$		the critical value of the t -distribution
α		the risk level
v		the degree of freedom = $n-2$.

In order to check whether the slope b in Equation (9) is significantly different from the ideal values of 1, the test statistic

$$t = \frac{b-1}{s_{yx} / \sqrt{S_{xx}}}, \quad (19)$$

is used, where s_{yx} is given in Equation (17) and S_{xx} in Equation (11). If the test statistic t in Equation (19) is greater than the critical value of the t -distribution, Equation (20), then the slope b differs significantly from the value of 1.

$$|t| \geq t_{\alpha, v}, \quad (20)$$

where	t is	the test statistic in Equation (16)
	$t_{\alpha,v}$	the critical value of the t-distribution
	α	the risk level
	v	the degree of freedom = $n-2$.

The systematic error of AMS can be calculated as

$$\Delta y = a + (b - 1)x . \quad (21)$$

Sometimes there are situations, where the range of concentrations is so narrow that Equations (18) and (20) show no significance of corrections. However, there obviously is a clear systematic difference between the values of AMS and the reference. In such case, if desired, the systematic error of AMS will be included in the expanded uncertainty of AMS.

The random part of the uncertainty of AMS can be given as

$$\sigma(\text{AMS}) = \sqrt{\frac{\sum_i (y_i - Y_i)^2}{n - 2}} , \quad (22)$$

where Y_i is the predicted value of y_i .

The expanded, combined uncertainty of AMS can be calculated from

$$U = \sqrt{t^2_{\alpha,v} (\sigma^2(\text{AMS}) + \Delta y^2) + \sigma^2(\text{REF})} , \quad (23)$$

where	$\sigma(\text{AMS})$ is	the random part of the uncertainty
	Δy	the systematic part of the uncertainty.
	$t_{\alpha,v}$	the critical value of the t-distribution
	α	the risk level
	v	the degree of freedom = $n-2$
	$\sigma(\text{REF})$	uncertainty of the reference method at the confidence level of $1-\alpha$.

As an example the uncertainty of AMS in equation (23) has been calculated at the confidence level of 95 % in Appendix B.

7 Conclusions

In this report a procedure to determine the uncertainty of AMS by comparing the results with a second method is presented. The procedure determines the uncertainty of AMS in comparing the final concentration and emission results of AMS and REF. In this way the data processing of the plant is included in the result evaluation, which differs from those procedures where only raw data of AMS is considered. The uncertainty determination has been divided into two cases, for varying and for nearly constant concentration.

The suggested procedure calculates the uncertainty of AMS at the 95 % confidence level by a tabulated t-value. The minimum of three data pairs is required. However, higher amount of data pairs is desirable, since low amount of data pairs results in higher uncertainty of AMS.

It is important to note that the uncertainty is valid only within the range of concentrations at which the tests were carried out.

Statistical data processing shows that the uncertainty of the reference method has significant effect on the uncertainty of AMS, which becomes always larger than the uncertainty of REF. This should be taken into account when testing, whether AMS fulfils the given uncertainty limits.

Practical details concerning parallel measurements at the plant and the costs of the measurement campaign have been taken into account when suggesting alternative ways for implementing the comparative measurements. It is intended that in most cases a single measurement campaign on site should be carried out in one or two days to get enough data for the uncertainty determination.

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Formulae of the spreadsheet form

The table shows the calculations of the regression and uncertainty functions in a spreadsheet program based on Microsoft Excel ® Version 7.0.

Table 1. Formulae of the spreadsheet form

Cell	Content
G6	=IF(ISNUMBER(B46);COUNT(B46:B2029);"")
G7	=IF(G36="NO";IF(ISNUMBER(B46);AVERAGE(D46:D2029);"");"")
G8	=IF(G36="NO";IF(ISNUMBER(B46);STDEV(D46:D2029);"");"")
G9	=IF(G36="NO";IF(ISNUMBER(B46);G7/(G8/SQRT(G6));"");"")
G10	=IF(G36="NO";IF(ISNUMBER(B46);TINV(0,05;G6-1);"");"")
G11	=IF(G36="NO";IF(ISNUMBER(B46);IF(ABS(G9)>G10;"YES";"NO");"");"")
G12	=IF(ISNUMBER(B46);AVERAGE(B46:B2029);"")
G13	=IF(ISNUMBER(B46);AVERAGE(C46:C2029);"")
G14	=IF(G36="NO";IF(ISNUMBER(B46);STDEV(B46:B2029);"");"")
G15	=IF(G36="NO";IF(ISNUMBER(B46);STDEV(C46:C2029);"");"")
G16	=IF(G36="NO";IF(ISNUMBER(B46);G15^2/G14^2;"");"")
G17	=IF(G36="NO";IF(ISNUMBER(B46);FINV(0,05;G6-1;G6-1);"");"")
G18	=IF(G36="NO";IF(ISNUMBER(B46);FINV(0,95;G6-1;G6-1);"");"")
G19	=IF(G36="NO";IF(ISNUMBER(B46);FINV(0,025;G6-1;G6-1);"");"")
G20	=IF(G36="NO";IF(ISNUMBER(B46);FINV(0,025;G6-1;G6-1);"");"")
D8	=IF(G36="NO";IF(G11="YES";G7;0);"")
D11	=IF(G36="NO";IF(ISNUMBER(D5);SQRT(G15^2/G14^2*(D5)^2/G19); SQRT(G15^2/G14^2*(D6/100*G12)^2/G19));"")
D12	=IF(G36="NO";IF(ISNUMBER(D5);SQRT(G15^2/G14^2*(D5)^2*G20); SQRT(G15^2/G14^2*(D6/100*G12)^2*G20));"")
D13	=IF(G36="NO";AVERAGE(D11:D12);"")
D15	=IF(G36="NO";IF(ISNUMBER(D5);IF(OR(D9="YES";D9="yes");SQRT(D5^2+ D13^2);SQRT(D5^2+(G10*D8)^2+D13^2));IF(OR(D9="YES";D9="yes");SQRT((D6/100*G12)^2+D13^2);SQRT((D6/100*G12)^2+(G10*D8)^2+D13^2)));"")
D18	=IF(G36="NO";IF(OR(G16>=G17;G16<=G18);"YES";"NO");"")
G24	=IF(G36="YES";IF(ISNUMBER(B46);INTERCEPT(C46:C2029;B46:B2029);"");"")
G25	=IF(ISNUMBER(B46);SLOPE(C46:C2029;B46:B2029);"")
G27	=IF(ISNUMBER(G24);G24/G34/SQRT(1/G6+G12^2/G31);"")
G28	=IF(ISNUMBER(G24);IF(OR(ABS(G27)=G35;ABS(G27)>G35);"YES";"NO");"")

G29	=IF(ISNUMBER(G24);(G25-1)/(G34/SQRT(G31));"")
G30	=IF(ISNUMBER(G24);IF(OR(ABS(G29)=G35;ABS(G29)>G35);"YES";"NO");"")
G31	=IF(ISNUMBER(B46);SUMSQ(B46:B2029)-(SUM(B46:B2029))^2/G6;"")
G32	=IF(ISNUMBER(B46);SUMSQ(C46:C2029)-(SUM(C46:C2029))^2/G6;"")
G33	=IF(ISNUMBER(B46);G25*G31;"")
G34	=IF(ISNUMBER(B46);SQRT((G32-G33^2/G31)/(G6-2));"")
G35	=IF(ISNUMBER(B46);TINV(0,05;G6-2);"")
G36	=IF(ISNUMBER(B46);IF(OR(ABS(G25/(G34/SQRT(G31)))=G35;ABS(G25/(G34/SQRT(G31)))>G35);"YES";"NO");"")IF(ISNUMBER(B46);IF(OR(ABS(G25/(G34/SQRT(G31)))=G35;ABS(G25/(G34/SQRT(G31)))>G35);"YES";"NO");"")
D25	=IF(G36="YES";IF(OR(G28="YES";G30="YES");AVERAGE(I46:I2029);0);"")
D27	=IF(G36="YES";IF(OR(D26="NO";D26="no");D25;IF(OR(G28="YES";G30="YES");AVERAGE(J46:J2029);D25);"")
D29	=IF(G36="YES";SQRT(SUMSQ(F46:F2029)/(G6-2));"")
D32	=IF(G36="YES";IF(ISNUMBER(D5);SQRT(G35^2*(D29^2+D27^2)+D5^2);SQRT(G35^2*(D29^2+D27^2)+(D6/100*G12)^2));"")
J28	=IF(G36="YES";IF(G6>=20;(SUMSQ(INDIRECT(ADDRESS(G6+41;8)):INDIRECT(ADDRESS(G6+45;8)))/4)/(SUMSQ(H46:H50)/4);"Too few observations");"")
J29	=IF(G36="YES";IF(G6>=20;FINV(0,95;4;4);"");"")
J30	=IF(G36="YES";IF(G6>=20;IF(J28>J29;"NO";"YES");"");"")
D46	=IF(ISNUMBER(B46);C46-B46;"")
E46	=IF(\$G\$36="YES";IF(ISNUMBER(B46);\$G\$24+\$G\$25*B46;"");"")
F46	=IF(\$G\$36="YES";IF(ISNUMBER(B46);C46-E46;"");"")
I46	=IF(\$G\$36="YES";IF(ISNUMBER(B46);\$G\$24+(\$G\$25-1)*B46;"");"")
J46	=IF(ISNUMBER(B46);IF(OR(\$D\$26="YES";\$D\$26="yes");\$G\$34*SQRT(1/\$G\$6+(B46-\$G\$12)^2/\$G\$31);0);"")

