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# ESTIMATION OF UNCERTAINTY IN THE DETERMINATION OF NITROGEN OXIDES EMISSIONS

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## Estimation of uncertainty in the determination of nitrogen oxides emissions

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**Abstract** This paper presents a methodology for estimation of uncertainty on a reference test method for the determination of nitrogen oxides concentration in gaseous emissions from stationary sources. As a first stage for identification of uncertainty sources, the test method is carefully reviewed in detail. Afterwards, these sources are quantified, bearing in mind its partial uncertainty, allowing the determination of the combined uncertainty and, finally, the expanded uncertainty. The calculation procedure was implemented into an excel calculation file. Using this file

and considering several numerical applications from real situations, uncertainties around  $15 \text{ mg/Nm}^3$  over determined concentrations of  $350 \text{ mg/Nm}^3$  of  $\text{NO}_x$  (expressed as  $\text{NO}_2$ ) were obtained.

**Keywords** Uncertainty · Gaseous effluents · Nitrogen oxides

### Introduction

Estimation of uncertainty is, nowadays, a critical issue regarding the expression and reporting of experimental measurements. As a matter of fact, this subject is a mandatory requirement for accredited laboratories, according to International Standard ISO 17025 [1].

As a commitment from several national accreditation bodies exists, stating that the estimation and reporting of results measured by accredited testing laboratories should be done on a routine basis from December 2005, this subject is of paramount importance [2].

Therefore, accredited testing laboratories are currently facing the need to estimate the uncertainty of the determination they perform [3], which is already a common practice for accredited metrology laboratories.

In what concerns metrology laboratories, specific standards and test methods make uncertainty estimation easier to perform, when compared to the measurements performed by most testing laboratories.

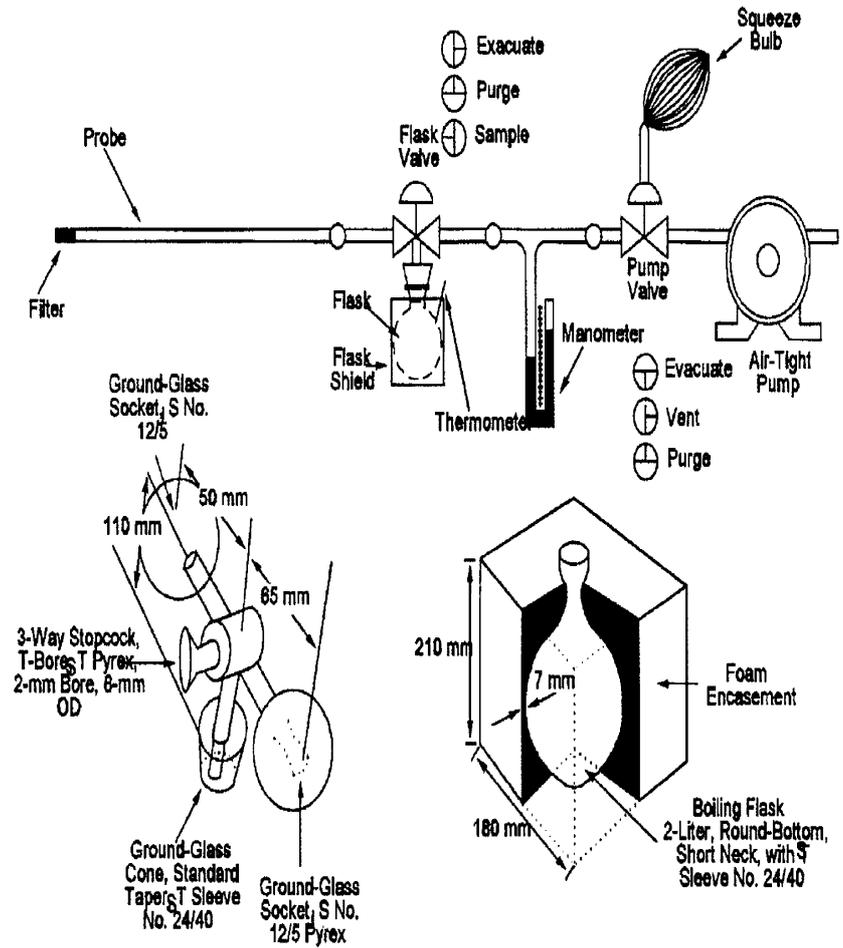
The estimation of uncertainty in test methods used by air quality laboratories is, somewhat, particularly difficult,

as it involves not only a laboratory procedure but also a sampling procedure [4].

This paper presents a methodology for estimation of uncertainty on a test method for the determination of nitrogen oxides concentration in gaseous emissions from stationary sources.

The significance of estimating uncertainty for stack sampling test methods should be pointed out [5]. In fact, the major objective of performing stack sampling tests is to evaluate the compliance of emitting sources with national and/or regional standards of performance for the industry [6]. Other objectives are related with the need to supply data for emission inventories and to declare the amount of emissions of certain specific pollutants, subjected to certain regulations, as it happens for carbon dioxide and other greenhouse gases. It becomes evident that, for any of these specific objectives, there is quite a clear need for an increased accuracy of the measured pollutant concentrations [5]. Therefore, where accuracy is a critical issue, uncertainty must be estimated and reported on a routine basis [7].

**Fig. 1** Schematic of sampling apparatus



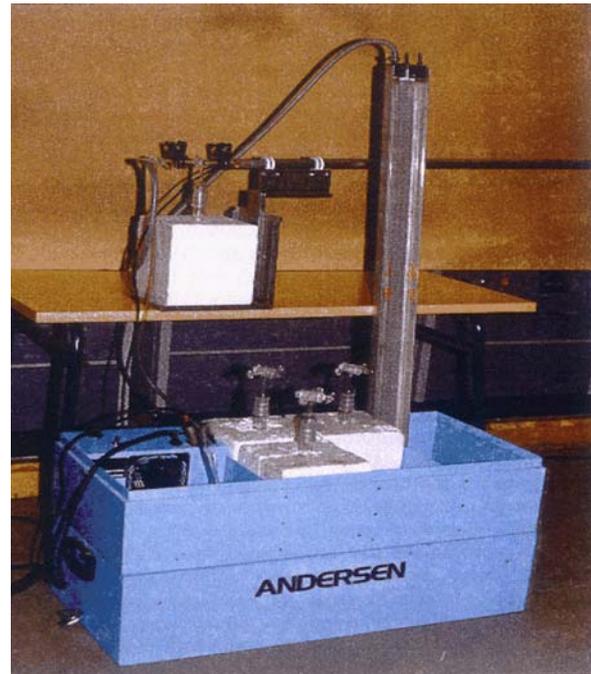
### Identification of uncertainty sources

#### Description of the sampling and analytical method

Prior to the estimation of uncertainty of any test method, it becomes necessary to examine in detail each and every method step and procedure, so that the sources of uncertainty can be duly identified [8]. Even if, at a later stage, one come to the conclusion that not every previously identified uncertainty source can be effectively quantified, it is recommended [9] to identify any and every sources of uncertainty.

The method under study [10] is a manual method, widely tested, being used currently as a reference method for stack sampling. According to this method, a grab sample is collected in an evacuated glass flask containing a dilute sulphuric acid–hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically, between 410 and 415 nm, using the phenoldisulphonic acid (PDS) procedure. The concentration of nitrogen oxides is expressed as nitrogen dioxide.

The method was developed for sampling concentrations of nitrogen oxides ranging from 2 to 400 mg in the collected samples. A schematic of the sampling equipment is presented in Fig. 1. Figure 2 shows the actual sampling equipment. The sampling equipment consists of:

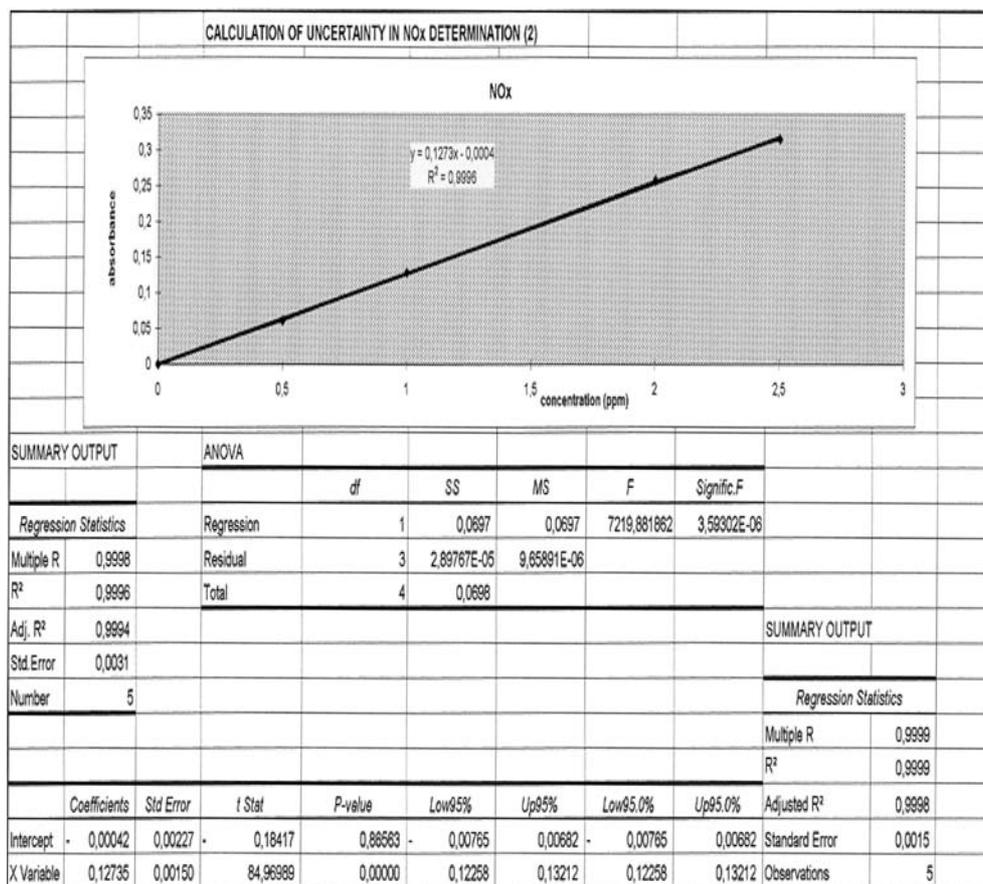


**Fig. 2** Aspect of sampling equipment

- (i) a borosilicate glass tubing probe, which is equipped with an in-stack glass wool filter to remove particulate



**Fig. 4** Worksheet 2 of 9 for calculation of uncertainty in Excel file



**Fig. 5** Worksheet 3 of 9 for calculation of uncertainty in Excel file

CALCULATION OF UNCERTAINTY IN NO <sub>x</sub> DETERMINATION (3)			
Uncertainty on calibration curve			
Slope	0,1273		
Intercept	0,0004	Uncertainty of calibration curve	0,0274
Number of standards	5		
Number of replicates	1		
Standard Error	0,0031		
Average y	0,1524		
Average x	1,2		
Yc (reading on measured sample)	0,215		
Sample concentration	1,725		
(xi-x average) <sup>2</sup>	4,3		

The spectrophotometer to be used should be a double-beam spectrophotometer, and a scanning procedure may be employed to determine the proper measuring of wavelength, scanning of the spectrum is done between 400 and

415 nm using a 200 µg NO<sub>2</sub> standard solution in the sample cell. When a peak is obtained, within this range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the



**Fig. 7** Worksheet 5 of 9 for calculation of uncertainty in Excel file

CALCULATION OF UNCERTAINTY IN NO <sub>x</sub> DETERMINATION (6)			
Dilution uncertainty			
Reading on equipment	1,725	Uncertainty of sample concentration	0,1102
Volume of flask with sample (cm <sup>3</sup> )	100		
	Uncertainty	0,1 cm <sup>3</sup>	
Volume of sample taken with pipette (cm <sup>3</sup> )	50		
	Uncertainty	0,05 cm <sup>3</sup>	
Volume of flask with previous solution (cm <sup>3</sup> )	100		
	Uncertainty	0,1 cm <sup>3</sup>	
Volume sample aliquot for preparing diluted reading standards (cm <sup>3</sup> )	10		
	Uncertainty	0,02 cm <sup>3</sup>	
Final volume with previous solution (cm <sup>3</sup> )	20		
	Uncertainty	0,04 cm <sup>3</sup>	
Sample concentration (ppm)	6,9		

the flask before sampling (mm Hg),  $P_f$ : final pressure in the flask after collection of the sample (mm Hg),  $T_i$ : initial temperature in the flask before sampling (K), and  $T_f$ : final temperature in the flask after collection of the sample (K).  $N$ , associated with  $m^3$ , means standard volume calculated at  $P = 760$  mm Hg and  $T = 273.15$  K.

The results are expressed in  $\text{mg}/\text{Nm}^3$  and at least one extra significant figure beyond that of the acquired data should be used. The significant figures are rounded off after final calculations [10].

#### Identification of uncertainty sources

From the description presented in Section “Description of the sampling and analytical method,” it is now possible to identify the major uncertainty sources related with both the sampling and analysis procedures. In fact, this identification was done by considering the variables present in the calculation formulae, that is, Eqs. (1) and (2).

#### Sampling

Relevant factors are the following: the collection flask volume, the temperature of the collection flask, the pressure of the collection flask, and the volume of the absorbing solution. Other factors such as the created vacuum in the pump and the dimensions of the glassware are not relevant for the uncertainty estimation, as they are not considered in the calculations [11].

#### Analysis

Relevant factors are the following: the volume of volumetric pipette and flasks used for dilution, the concentration

CALCULATION OF UNCERTAINTY IN NO <sub>x</sub> DETERMINATION (6)			
Combined uncertainty of sample concentration			
Uncertainty of sample concn.	0,11	Combined uncertainty	0,11 ppm
Uncertainty of calibration curve	0,03		
Precision uncertainty	0,00	Uncertainty in mg	0,01
		Concentration (mg)	0,69

**Fig. 8** Worksheet 6 of 9 for calculation of uncertainty in Excel file

of the standard solution of potassium nitrate and the calibration curve of the spectrophotometer. Other factors such as the operating wavelength of the spectrophotometer are not relevant for the uncertainty estimation, as they are not considered in the calculations [11].

#### Quantification of partial uncertainties

After the identification of uncertainty sources has been made, each associated uncertainty must be quantified so that a combined uncertainty can be obtained, based on the basic formulae for expression of results [11]. Considering the identified sources, it should be noted that some of them are associated with the use of measuring equipment that undergoes an external calibration. Those are the temperature gauge and the pressure gauge. External calibration

CALCULATION OF UNCERTAINTY IN NOx DETERMINATION (7)	
Uncertainty on the volume of sampling flask	
Sampling flask volume (cm <sup>3</sup> )	2,251,99
Final test pressure (mbar)	753,00
Initial test pressure (mbar)	52,50
Final test temperature (K)	288,70
Initial test temperature (K)	301,00
Volume of absorption solution (cm <sup>3</sup> )	25,00
Standard sampling volume (cm <sup>3</sup> )	1,946,90
Standard sampling volume (l)	1,95

Fig. 9 Worksheet 7 of 9 for calculation of uncertainty in Excel file

is done at metrological laboratories and each calibration has an uncertainty already expressed in each calibration certificate.

Regarding the volumetric glassware used for dilutions, each item is comprised within a tolerance class, with a characteristic uncertainty associated, presented in the manufacturer's specification. In fact, this procedure is approximated and the uncertainty associated with volumetric glassware could be estimated more accurately by performing repeatability tests [8]. However, if routine checks are made for the volumetric glassware used in the laboratory, as in this particular situation, the associated errors are limited and fairly acceptable for this estimate [11].

The calibration curve is determined by plotting absorbance measurements against its corresponding concentration. The analytical expression of this curve is obtained currently by linear regression using the least squares method and a statistical treatment that also estimates the correlation coefficient and the confidence interval, thus providing the corresponding uncertainty, as shown in Fig. 3, which is the printout of the first spreadsheet of an Excel file developed for this purpose.

From the identified sources only two other are now missing and can be easily estimated by performing repeatability measurements: the volume of the collecting flask and the concentration of the standard solution of potassium nitrate.

After all these individual uncertainties are estimated, the combined uncertainty can be estimated using the usual expressions [9] as follows:

- (a) when the analytical expression is:  $Z = X + Y$ , uncertainty  $U_c$  is given by:

$$U_c = \sqrt{(U_x/X)^2 + (U_y/Y)^2} \quad (3)$$

- (b) when the analytical expression is:  $Z = XY$ , uncertainty  $U_c$  is given by:

$$\frac{U_c}{Z} = \sqrt{(U_x/X)^2 + (U_y/Y)^2} \quad (4)$$

CALCULATION OF UNCERTAINTY IN NOx DETERMINATION (8)	
Uncertainty of sampling volume	
Volume of sampling flask (cm <sup>3</sup> )	2251,99
Uncertainty	8,14764
Final test pressure (mbar)	753
Uncertainty	1,3
Initial test pressure (mbar)	52,5
Uncertainty	1,3
Final test temperature (K)	288,7
Uncertainty	1,2
Initial test temperature (K)	301
Uncertainty	1,2
Absorbing solution volume (cm <sup>3</sup> )	25
Uncertainty	1
Standard sampling volume (cm <sup>3</sup> )	1,946,9004
Standard sampling volume (l)	1,9469

Fig. 10 Worksheet 8 of 9 for calculation of uncertainty in Excel file

CALCULATION OF UNCERTAINTY IN NOx DETERMINATION (9)	
Uncertainty of final result	
Sample concentration	0,68
Uncertainty	0,0114
Conversion factor to m <sup>3</sup>	1000
Standard sampling volume (l)	1,9469
Uncertainty	0,0123
Final result	354,4095
Final result	354 ± 13 mg/Nm <sup>3</sup>

Fig. 11 Worksheet 9 of 9 for calculation of uncertainty in Excel file

- (c) when repetitive measurements are made, uncertainty  $U_c$  is given by:

$$U_c = \frac{\sigma}{\sqrt{n}} \quad (5)$$

Where  $\sigma$  is the standard deviation of the measurements and  $n$  the number of measurements.

Considering all these contributions, the combined uncertainty can be estimated as well as the expanded uncertainty for a given tolerance interval.

Figures 4–11 present the other calculation worksheets of the developed Excel file, which considers a real numerical example.

Worksheets 6 (Fig. 8) and 9 (Fig. 11) sum up the combined uncertainties for each operation described previously as well as the uncertainty of the final result.

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## Conclusions

The methodology presented herewith is considered effective for estimating the uncertainty associated with the measurement of nitrogen oxides concentration in gaseous effluents by using the manual US EPA Method 7. The calculation procedure was implemented into an excel calculation file. Using this file and considering several numerical applications from real situations, uncertainties around 15 mg/Nm<sup>3</sup> over determined concentrations of 350 mg/Nm<sup>3</sup> of NO<sub>x</sub> (expressed as NO<sub>2</sub>) were obtained.

It should be noted that each time a different determination takes place, involving the use of different measuring equipment and/or any alteration of equipment such as volumetric glassware, uncertainty should be recalculated again following this methodology [11]. Therefore, it is recommended to have the sequence of calculations inserted in a worksheet (such as the one presented here) so that the individual uncertainty contributions can be inserted and, thus, obtain the proper combined uncertainty for the actual determination. This practice is now being adopted by accredited European laboratories involved in emission measurements [5].

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