EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Environment and Sustainability
Physical and Chemical Exposure Unit
I-21020 Ispra (VA) Italy

Uncertainty of NO_2 Measurements by Chemiluminescence: A Case Study at the JRC AIRMON Station and Discussion of the Quality Objective of the NO_2 European Directive

Michel Gerboles, Diana Rembges,
Claude Brun, Fritz Lagler

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Summary:

The European directive 99/30/CE, brought into force the 31 March 1999, regulates the monitoring of nitrogen dioxide (NO_2) ambient concentrations. The Directive states that the reference method for the NO_2 monitoring is the chemiluminescence method. The Directive gives a data quality objective of 15 % for the accuracy of continuous monitoring.

In general the bottom up approach, based on the measurement of certified reference materials, is used to evaluate the measurement uncertainty. This is not a complete approach: so is the inter - comparison method where some statistical parameters like repeatability, reproducibility and calibration bias can be assessed.

The implementation of the Guide for the expression of Uncertainty of measurement (GUM) method, advised by the Directive, is rather difficult since it requires a large data pool. However, it allows studying the relative influence of all possible sources to the uncertainty budget. While, some data are given by the manufacturer of the analyser others such as linearity, converter efficiency determination, sampling line losses evaluation, certified reference material data and expected level of interference require laboratory and field experiments.

The extent of NO_2 uncertainty is mainly dependent on the level of *NO* concentration and is decreased by the level of *NOx* concentration and the correlation between *NOx* and *NO*. Furthermore, the uncertainty budget reveals that the contribution of the uncertainty of calibration standard, of linearity, converter efficiency and calibration checks to the overall uncertainty is less important than the contribution of interference mainly humidity and *PAN*.

The relative expanded uncertainty of NO_2 hourly average may be rather high with maximum bigger than 50 % for NO_2 concentration of 40 $\mu g/m^3$. Nevertheless, for the hourly limit value of the European directive, 200 $\mu g/m^3$, the data quality objective (expanded uncertainty lower than 15 %) is ensured. On the contrary, for the limit value of the annual average, 40 $\mu g/m^3$, the data quality objective is not met in the unlikely case of annual *NO* average over 50 *ppb*. By correcting for the humidity and *PAN* interference the data quality objective is ensured because the relative expanded uncertainty becomes lower than 15 %.

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Abstract:

The European Directive 99/30/CE, gives a data quality objective of 15 % for the accuracy of NO_2 continuous monitoring. This paper describes the implementation of the Guide for the Expression of Uncertainty of Measurements method (GUM) and gives an example of uncertainty calculation taking into account all components of uncertainty. The relative influence of all possible sources to the uncertainty budget is evaluated and recommendation about which ones should be monitored is given. Finally the ability of the chemiluminescence method to meet the data quality objective of the European Directive is discussed.

Aknowlegdement:

The authors wish to thank Dr. Theo Hafkensheid of the Dutch Measurement Institute (NMI) for his support and for assuring that it was worth carrying out this uncertainty evaluation.

Glossary of symbols :

Quantity	Unit	Definition
$[NO_2]$	*ppb*	Corrected concentration of nitrogen dioxide
$[NO_X]$	*ppb*	Corrected concentration of nitrogen oxides
$[NO]$	*ppb*	Corrected concentration of nitrogen monoxide
eff	%	NO_2 to NO converter efficiency
$b_0(NOx)$	*ppb*	Intercept of calibration curve for NOx
$b_1(NOx)$		Slope of calibration curve for NOx
$R(NO_X)$	*ppb*	Monitor response to a test sample for NOx
$Span(NO_X)$	*ppb*	Reference value of span (cylinder) for NOx
$Zero(NO_X)$	*ppb*	Reference value of zero air for NOx
$R(Span(NO_X))$	*ppb*	Analyser response to span for NOx
$R(Zero(NO_X))$	*ppb*	Analyser response to zero air for NOx
$b_0(NO)$	*ppb*	Intercept of calibration curve for NO
$b_1(NO)$		Slope of calibration curve for NO
$R(NO)$	*ppb*	Monitor response to a test sample for NO
$Span(NO)$	*ppb*	Reference value of span (cylinder) for NO
$Zero(NO)$	*ppb*	Reference value of zero air for NO
$R(Span(NO))$	*ppb*	Analyser response to span for NO
$R(Zero(NO))$	*ppb*	Analyser response to zero air for NO
$er(x,y)$	*ppb*	Correlation coefficient of variables x and y.
k		Coverage factor ($k = 2$)
$u_c(x)$	*ppb*	Combined uncertainty of variable x
$u(x)$	*ppb*	Standard uncertainty of variable x
$U(x)$	*ppb*	Expanded uncertainty of variable x

Uncertainty of NO_2 measurements by chemiluminescence : A case study at the JRC AIRMON station and discussion of the quality objective of the NO_2 European Directive

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Introduction

The European directive 99/30/CE, brought into force the 31 March 1999, regulates the monitoring of nitrogen dioxide (NO_2) ambient concentrations[1]. This Directive gives a data quality objective of 15 % for the accuracy of continuous monitoring. The objective is intended for individual measurement and not only for yearly average. The Directive also states that the reference method for the NO_2 monitoring is the chemiluminescence[2] method and that the evaluation of the accuracy shall be conducted according to the Guide for the Expression of Uncertainty[3] (GUM) and/or ISO 5725[4].

However, the implementation of the GUM method is rather difficult since a lot of tests and other information are needed. The implementation has not been described so far. In general the bottom up approach, based on the measurement of certified reference materials, is used instead of the evaluation of all the independent influence factors. This is an easier but not complete approach. In addition, several alternative methods are available for the evaluation of the uncertainty of measurement. Hereafter the available methods are listed:

- Guide for the Expression of Uncertainty[3] (GUM): it provides a general method for the evaluation of the uncertainty based on the elaboration of a model laying for the measurement principle,
- ISO 5725-2[4]: this method is limited to the evaluation of trueness and precision through inter-laboratory measurement, in particular using this method the traceability of the evaluation of uncertainty to national/international cannot be ensured. This standard is well suited for the determination of repeatability and reproducibility of a method instead of evaluating the uncertainty of individual measurements.
- ISO 13752[5]: this method allows the evaluation of uncertainty of field measurements provided that a reference method is implemented in the field. The "candidate method" is then compared to the reference method in order to derive its uncertainty. This standard may be used as a method validation tool. However, it is not convenient for routine monitoring since a reference method complementing to the normal chemiluminescence method is rarely available in field measurements.
- ISO 6143[6]: this standard is derived from GUM, complemented by modelling of the calibration function by application of the generalised least square technique. This method requires more reference data than the ones available in the field. It is generally implemented at National laboratory of Metrology level for supplying high quality certified reference material and is not applied for routine field measurements.
- Finally it is worth mentioning that historically, uncertainty was evaluated for a whole method regardless of the range of concentration by comparison to an independent reference method by applying the NIOSH criteria: Bias ± 2 CV (coefficient of variation). This method gives an uncertainty for the whole concentration range without studying any influence of any parameter. This coarse evaluation has the main disadvantage that the uncertainty figure cannot be compared to uncertainty calculated by one of the previous method.

Even if it was not implemented so far, it appears that from the list of methods of evaluation of uncertainty listed above the only valid one is the GUM method because of its general application. After a brief description of the GUM method, an example will be given for the determination of the uncertainty of the nitrogen dioxide at the Air Monitoring Station (AIRMON) of the Environment institute of the Joint Research Centre in Ispra. The relative influence of all possible sources to the uncertainty budget is evaluated and recommendation about which ones should be monitored is given. Finally the ability of the chemiluminescence method to meet the data quality objective of the European Directive is assessed.

The JRC-AIRMON station participates in network like the Co - Operative Programme for Monitoring and Evaluation of the Long - Range Transmission of Air Pollutants in Europe (EMEP) and the Global Atmospheric Watch (GAW, WMO). Apart from these activities, AIRMON is intended as a station for the development and implementation of new measurement techniques. It is associated with the European Reference Laboratory of Air Pollution (ERLAP), an accredited Laboratory for the monitoring of ambient and synthetic mixture of sulphur dioxide (SO_2), ozone O_3 and NO/NO_2. AIRMON relies on certified standards supplied by ERLAP.

ERLAP is the reference laboratory for atmospheric pollution serving the European Commission. One of its activities is to maintain European standards for the calibration of NO_2 and SO_2 methods of analysis. ERLAP has chosen the permeation method[7] evaluated by gravimetry to produce reference standards for both NO_2 and SO_2 methods, but uses the static volumetric method[8] to cross check the permeation method.

The GUM method for calculating uncertainty

In general, an analytical measurement provides only an estimation of the value of a determinant, and must be accompanied by a quantitative statement of the uncertainty attached to the estimate.

In 1993, ISO published a guide to the expression of uncertainty (revised in 1995), in which each component contributing to the uncertainty of a measurement is attributed an estimated uncertainty, termed standard uncertainty (u_i), equal to the positive square root of the estimated variance u_i^2. The contribution of each component is calculated according to the model equation on which the measurement is based. The uncertainty associated with a measurement generally consists of several components, which may be grouped into two categories:

A Those which are evaluated by statistical methods.

B Those which are evaluated by other means.

Type A evaluation of uncertainty may be based on any valid statistical method for treating data like for example, calculating the standard deviation of the mean of a series of independent observations, using the method of least squares to fit a curve or carrying out an analysis of variance ANOVA to quantify random effects.

Type B evaluation of standard uncertainty is usually based on scientific judgement and may make use of all available relevant information, including: previously measured data, available information concerning the behaviour and properties of materials and instruments involved, manufacturer's specifications, calibration data and other available information. As an example of Type B evaluation, consider an input quantity X_i whose value is estimated from an assumed rectangular probability distribution with lower limit a- and upper limit a+. In this case the input estimate is usually expressed by:

$$x_i = (a_+ + a_-)/2 \quad (1)$$

and the standard uncertainty associated with x_i is :

$$u(x_i) = a/\sqrt{3} \text{ where } a = (a_+ - a_-)/2 \quad (2)$$

Combined standard uncertainty

The combined standard uncertainty of a measured value (u_c) is assumed to correspond to the estimated standard deviation of the result. It is derived from the model equation by combining individual standard uncertainties u_i, which may arise either from type A or type B evaluations. The method is often referred to as the law of propagation of uncertainty, and is expressed as:

$$u_c^2 = \sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2\sum_{1}^{N-1}\sum_{i+1}^{N}\frac{\partial f}{\partial x_i}\frac{\partial f}{\partial x_j}u(x_i)u(x_j)r(x_i,x_j) \quad (3)$$

The partial derivatives are referred to as sensitivity coefficients. $r(x_i, x_j)$ is the estimated correlation coefficient between x_i and x_j. It is assumed that corrections have been applied to compensate for each

systematic effect which significantly influences the measured value, and that every effort has been made to identify such effects.

Expanded uncertainty

An expression of uncertainty, which defines the limits associated with a measured value y within which the value Y is confidently believed to lie is often required. The measure of uncertainty intended to meet this requirement is termed the expanded uncertainty, suggested symbol U, and is obtained by multiplying $u_c(y)$ by a coverage factor, suggested symbol k. Thus $U = k\ u_c(y)$ and is confidently believed that $y\text{-}U \leq Y \leq y+U$, which is commonly written $Y = y \pm U$. In general, the value of the coverage factor k is chosen on the basis of the desired level of confidence to be associated with the interval defined by $U = k\ u_c$. Typically k is in the range 2 to 3. When the normal distribution applies, $U = 2\ u_c$ defines an interval having a level of confidence of approximately 95 percent and which is consistent with current international practice.

Principle of measurement of a chemiluminescent monitor

General principles

The NO_2 analyser by the chemiluminescence method is based on the reaction of nitric oxide (NO) and ozone (O_3) which produces a characteristic luminescence with intensity linearly proportional to the concentration of NO according to the reaction:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu \quad (4)$$

A photo-multiplier measures the infrared light emission due to the excitation of NO_2 molecule when its energy level falls down to a lower energy state. Nitrogen dioxide (NO_2) must first be transformed into NO before it can be measured using the reaction of chemiluminescence. NO_2 is converted to NO by molybdenum NO_2-to-NO converter. A simplified measurement scheme is given in Figure 1.

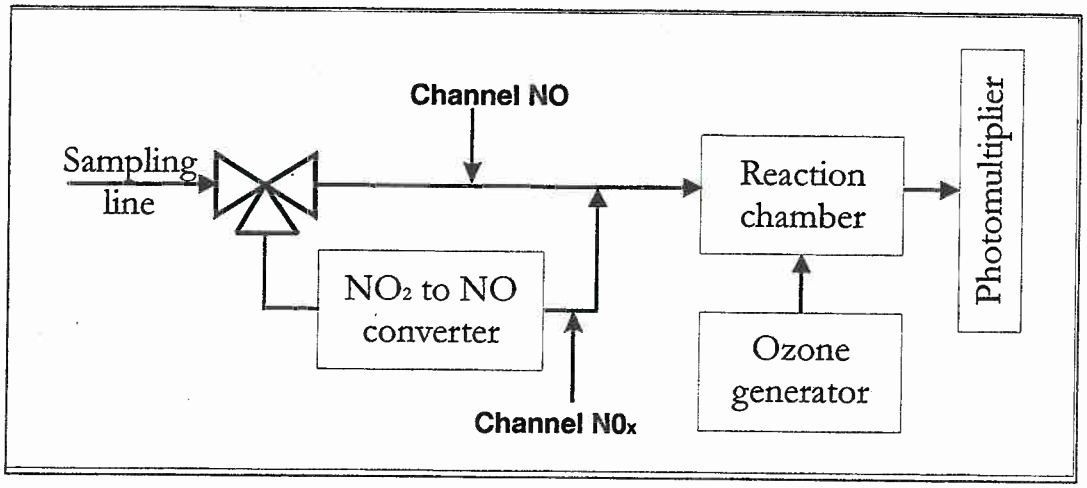


Figure 1: Diagram of a NO_2 analyser by the chemiluminescence method

Elaboration of the model equations

The first step towards calculation of uncertainty is the set up of the model equation describing the principle of measurement. As said previously, NO_2-chemiluminescence monitor measures alternatively NO_2 concentration and the sum of NO and NO_2 concentration (the so-called NO_X) when

the air sample passes through the NO_2-to NO converter. The NO_2 concentration is deduced by subtracting NO from the NO_X concentration. This leads to the following model equation:

$$[NO_2] = \frac{[NO_x] - [NO]}{eff} \quad (5)$$

Where [NOx] and [NO] are the NO concentrations in the NOx and NO channels of the analyser, *eff* is NO_2 to NO converter efficiency.

$[NO_2]$ combined uncertainty $u_c(NO2)$ is obtained by applying Eq. 3 on Eq. 5. The formula is:

$$u_c^2(NO_2) = \left(\frac{1}{eff}\right)^2 u^2(NO_x) + \left(\frac{-1}{eff}\right)^2 u^2(NO) + \left(-\frac{[NO_X] - [NO]}{eff^2}\right)^2 u^2(eff) + 2\left(-\frac{[NO_x] - [NO]}{eff^3} u(NO_x - NO)\, u(eff)\, r(NO_x - NO, eff) - \frac{1}{eff^2} u(NO_x)\, u(NO)\, r(NO_x, NO)\right) \quad (6)$$

The standard uncertainty of $[NO_X]$, [NO] and of the converter efficiency must be previously determined in order to compute $u_c(NO_2)$. The correlation between these three variables is also needed. The last term of Eq. 6 includes first the correlation between the converter efficiency and (NOx-NO) and second between [NOx] and [NO]. [NOx] and [NO] are both correlated by their chemical origin and by the method of measurement (same photo - multiplicator and pneumatic system in the analyser). The evaluation of the converter efficiency is carried out by means of Gas Phase Titration[2] (GPT).

Generally, an analyser at a field monitoring stations is calibrated with zero air and a span standard for example a certified cylinder (see Figure 2). Seen that the chemiluminescence method produces a beam whose intensity is linearly proportional to the NO concentration, $[NO_X]$ and $[NO]$ can be calculated according to their linear calibration (see Figure 2), with the following intermediary equations.

$$[NO_x] = b_0(NO_x) + b_1(NO_x).R(NO_x) \quad (7)$$

$$[NO] = b_0(NO) + b_1(NO)\, R(NO) \quad (8)$$

Where $b_0(NOx)$ is the Intercept of calibration curve for *NOx*, $b_1(NOx)$ is the Slope of calibration curve for *NOx* and $R(NO_X)$ is the Monitor response to a test sample for *NOx*. The same notation is used for the *NO* channel of the analyser. The standard uncertainty for *NO* (similar equation for NO_X) is calculated by applying Eq. 3 on Eq. 7 and 8, which gives for *NO*:

$$u^2(NO) = u^2(b_0(NO)) + R(NO)^2\, u^2(b_1(NO)) + b_1^2\, u^2(R(NO)) + 2R(NO)\, u(b_0(NO))\, u(b_1(NO))\, r(b_0(NO), b_1(NO)) \quad (9)$$

b_0 and b_1 are computed for *NO* (similar equation for NO_X) with two pairs of values noted *Span/R(Span) and Zero/R(Zero)*:

$$b_1 = \frac{Span - Zero}{R(Span) - R(Zero)} \quad (10)$$

$$b_0 = \frac{Zero.R(Span) - Span.R(Zero)}{R(Span) - R(Zero)} \quad (11)$$

Where: $Span(NO_X)$ is the Reference value of span (cylinder) for NOx, $Zero(NO_X)$ is Reference value of zero air for NOx, $R(Span(NO_X))$ is the Analyser response to Span(NOx) and $R(Zero(NO_X))$ is the analyser response to *Zero*(NOx). The same notation is used for the NO channel of the analyser.

The standard uncertainties for b_0 and b_1 (both for [NO] and $[NO_X]$) are calculated from the following equations:

$$u^2(b_1) = \frac{u^2(Span) + u^2(Zero)}{\left(R(Span) - R(Zero)\right)^2} + \left(\frac{Span - Zero}{\left(R(Span) - R(Zero)\right)^2}\right)^2 \left(u^2(R(Span) + u^2(R(Zero)\right) \quad (12)$$

$$u^2(b_0) = \frac{R(Zero)^2\left(u^2(Span) + b_1^2\, u^2(R(Span))\right) + R(Span)^2\left(u^2(Zero) + b_1^2\, u^2(R(Zero))\right)}{\left(R(Span) - R(Zero)\right)^2} \quad (13)$$

In Eq. 9, the correlation between b_0 and b_1 is included. The correlation between b_0 and b_1 can be estimated by repeatedly modifying the values of *Zero*, *Span*, *R(Span)* and *R(Zero)* by their estimated standard uncertainty (*Span* + u(*Span*) then *Span* – u(*Span*), *Zero* + u(*Zero*) …). For each modification of any variable a new pair of b_0 and b_1 will be computed. Finally, the correlation between the b_0 and b_1 sets of will be calculated.

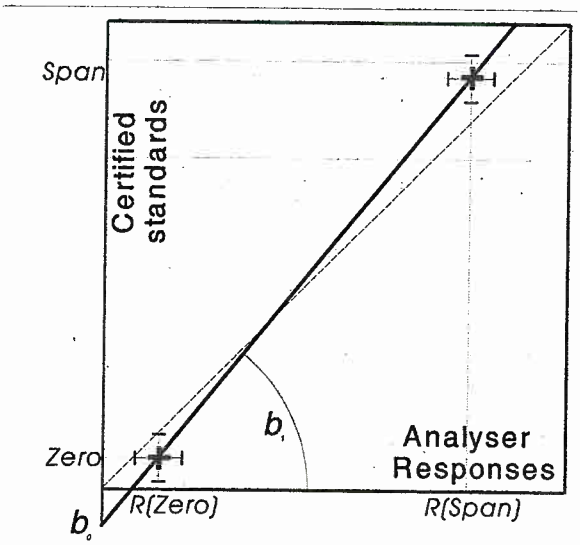


Figure 2: Calibration of an analyser with certified materials and zero air

Uncertainty budget

The different uncertainty sources and their influence on the nitrogen dioxide uncertainty are best analysed by visualising them in a cause and effect diagram (See Figure 3).

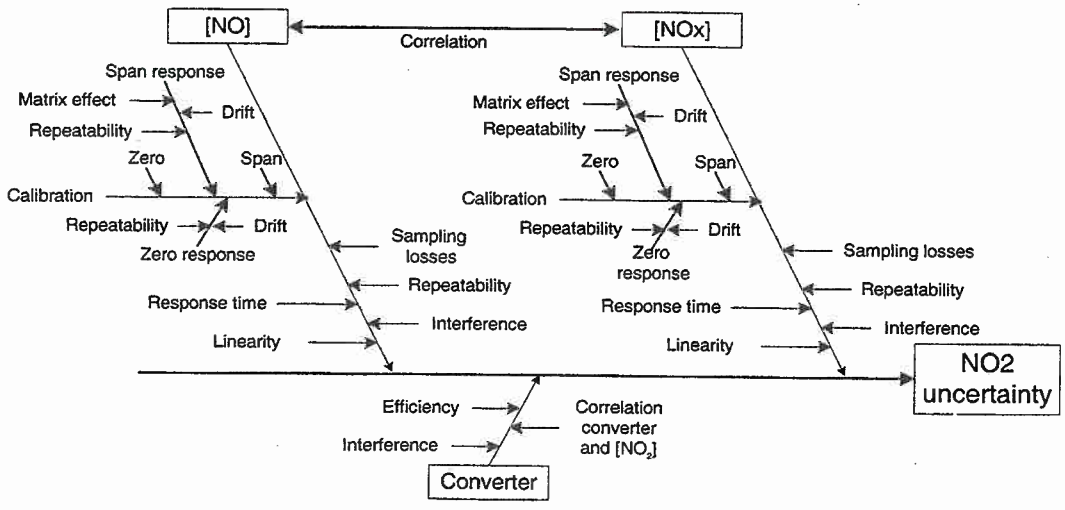


Figure 3: Cause and effect diagram for the nitrogen dioxide uncertainty

The calculation of uncertainty for nitrogen dioxide is carried out for the measurements of AIRMON at Ispra in 1999. The NOx analyser is a Thermo environmental model 42 C .

eff:

The converter efficiency is evaluated carrying out a yearly multi-point gas-phase titration (GPT). On 31 August 1999, the GPT report of the chemiluminescent analyser shows a converter efficiency of 99.7 ± 0.2 % (the quoted value being the standard deviation of the effciencies). Results are given in appendix 1. The GPT is carried out with an excess of NO and a stable level for *NOx*. The coefficient of correlation between $[NO_2]$ and the converter efficiency is r = - 0.864, a highly significant value .

$R(NO_X)$ and R(NO):

The standard uncertainties of *NO* and *NOx* consist of several components:

Analyser repeatability: the value given by the manufacturer is ± 0.4 *ppb* (expressed as standard deviation) in the typical range of ambient measurements. However, it is not possible to distinguish more than 1 *ppb* on the display of the analyser for concentration range higher than 100 *ppb*. Assuming a rectangular distribution between –1 to 1 *ppb*, the standard uncertainty is set to 0.6 *ppb*.

Analyser response time: AIRMON is a semi-rural location where the variability of concentration level is very small. No effect of response time is taken into account. This would include the photomultiplier measurement delay due to the one chamber measurement.

Analyser linearity : the manufacturer claims ± 1% of full scale (250 *ppb* = 2.5 *ppb*). A linearity check is yearly-performed (see appendix 2) with 11 points tested in the range 0-1000 *ppb*. The standard uncertainty due to the analyser linearity is 0.5 *ppb*.

Sampling line losses: during the comparison between the AIR MONITORING station and the ERLAP mobile laboratory (see Appendix 4) it was shown that losses in the sampling line at AIR MON were lower than 0.5 % of the measured *[NO]* and *[NOx]*. This evaluation would have also evidenced, if present, the bias due to the absorption of NO_2 by acid/base reaction on the inlet filter in presence of high relative humidity. Such absorption was not evidenced.

Two types of *interference* may occur: first the restriction of chemiluminescence intensity by competing third body quenching reactions at the reaction chamber step and second the bias due to the conversion of nitrogen-containing species to *NO* taking place into the NO_2-to-*NO* converter. The first type of interference produces both *NO* and *NOx* bias while the second one only affects the *NOx* signal.

Matthews *et al.*[9] reported that among H_2O, O_2, CO_2, *CO*, *Ar*, H_2, the major quenching effect is due to H_2O, CO_2, H_2, and hydrocarbure with high H/C ratio, molecules found near combustion plant which are not likely to be present at the JRC-AIRMON station a semi-rural site. On the other hand, the performances of the Thermo Environmental model 42 was evaluated by several laboratories[10,11,12,13]. Tatry *et al.* showed that for this analyser, among H_2O, O_2, CO_2, *CO*, *Ar*, H_2 third body molecules, only H_2O should be taken into account seen their relative effect and the observed ambient concentration. The same author reports a decrease of signal of - 4.5 % with a rise from 0 to 50 % of relative humidity at $[NO]$ = 300 *ppb*. Nodop *et al.*[12] reports a decrease of -3 % with initial $[NO_2]$ of 40 ppb for a rise of relative humidity from 0 to 50 % while for a rise of relative humidity from 0 to 80 %, the decrease is - 6 % with initial $[NO_2]$ of 40 ppb. Finally, the quenching effect of water vapour was shown[11] to be clearly identical for *NO* and *NOx* (relative humidity has no effect on $[NO_2]$), to be nearly 0 % for relative humidity from 0% to 50% and then linearly decreases to –5 % for relative humidity from 50 to 90 %.

It is difficult to draw a conclusion from these experimental results because the decrease of concentration is sensitive to the absolute density of water vapour rather than to the relative humidity[14]. Appendix 3 shows some experiments that confirm the linear relationship between absolute humidity increase and concentration decrease. Moreover the results shows that the efficiency of conversion is not affected by humidity and that for a constant absolute humidity, the *NO* relative decrease is constant whatever the *NO* concentration.. The AIRMON sampling line is heated over 50 °C to avoid condensation in the sampling line. However, this warming should not modify the absolute humidity in the reaction cell which is temperature controlled at 43 °C. In fact, the observed linear dependence in Figure 10 suggests that NO_2 concentration should be corrected for the absolute humidity in the air like the GUM method advises. However it is generally not the case, so that an uncertainty contribution should be evaluated. Figure 4 gives the plot of the annual distribution of hourly absolute humidity and

allows associating an uncertainty distribution to the concentration decrease. The best-fitted distribution could be a trapezoidal distribution. It is assumed that the input value is equally distributed over 0 to –8 % and a shape factor of 5/9. Then the standard uncertainty due to humidity is the sum of the bias of (-4 %) and the trapezoidal distribution. One may argue that the effect of humidity on *NO* will be subtracted to the one on NOx. This is true since *NOx* and *NO* are highly correlated (see hereafter). Anyhow this correlation is taken into account in Eq. 6.

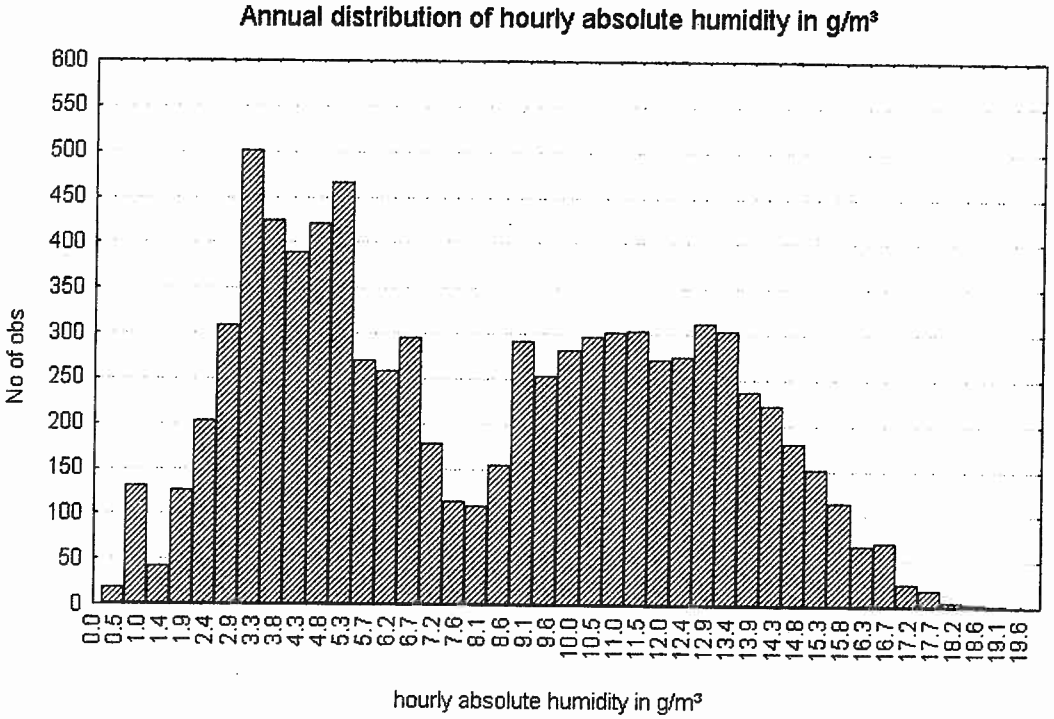


Figure 4: Annual hourly distribution of absolute humidity at the AIRMON station in 1999

Regarding the conversion of N-species, it was initially reported in the literature that HNO_3 (100 %) and HNO_2[12,14] (100 %), *HCN* (68%), CH_3NH_2 (82 %) and NH_3[15] (86 %) are converted to *NO*. Grosjean[16] *et al.* also showed a quantitative conversion to *NO* for *PAN*, methyl nitrate and other alkyl nitrate. The subsequent evaluations of performance of the analyser invalidated the possible conversion of NH_3[10,12]. Measurements of HNO_2[17] carried out by means of Differential Optical Absorption Spectroscopy (DOAS) at AIRMON showed that apart from the rare peak concentrations, $[HNO_2]$ was within 1 ppb, a lower concentration than the uncertainty of measurement. Subsequent measurements by denuder technique (seeappendix 5) gives the HNO_2 measurement extent and showed very low concentrations for HNO_3. Furthermore ambient levels of *HCN*, and CH_3NH_2 must be low and it is not necessary to take into account these compounds. Routine measurements of *PAN* were performed at the AIRMON station[18] between 1992 and 1995 by gas chromatography (see Appendix 6). A summarise of these is given in Table 1. It was decide that the standard uncertainty due to these interferents will be, a part from their bias represented by the average concentrations, the difference between the maximum and their average concentration associated to a triangular distribution.

Interference	Average Concentration	*Max*
PAN (1992-1995)	1.0 *ppb* (mean of monthly average)	8.9 *ppb*
HNO_2 (2000)	0.5 *ppb* (mean of hourly average)	2.7 *ppb*
HNO_3 (2000)	0.2 *ppb* (mean of hourly average)	1.8 *ppb*

Table 1: Concentration of interference

Experiments were also conducted to evaluate the effect of H_2O, NH_3 and HNO_3 interference (see Appendix 7). The results shows that among H_2O, NH_3 and HNO_3, only humidity produces a significant interference. These results implies that NH_3 and HNO_3 are not included into the uncertainty budget

In conclusion, the variance of *R(NOx)* and *R(NO) are* the sum of repeatability, linearity, sampling line losses and effect of relative humidity variances. For the variance of $R(NO_X)$, the variances of the bias of HNO_2 and PAN are added. For [*NO*] = 130 *ppb* and [*NOx*] = 150 *ppb* the standard uncertainties are:

$$u(R(NOx)) = \sqrt{\begin{array}{l} 0.6^2 + 0.5^2 + (0.005*150)^2 + \dfrac{(0.04*150)^2\left(1+\frac{5}{9}\right)^2}{6} \\ +(0.04*150)^2 + 1.0^2 + 7.9^2/6 + 0.5^2 + 2.2^2/6 \end{array}} = 8.0\ ppb$$

$$u(R(NO)) = \sqrt{0.6^2 + 0.5^2 + (0.005*130)^2 + \frac{(0.04*130)^2\left(1+\frac{5}{9}\right)^2}{6} + (0.04*130)^2} = 6.2\ ppb$$

Span(NOx) and Span(NO):

A *NO* cylinder in nitrogen was used as working standard (cylinder manufactured by Messer Griesheim certified by the Central Laboratory of ERLAP [*NO*]=[*NOx*]=909.5 ± 6.4 *ppb k*=2). This cylinder was certified against the reference standard of the ERLAP laboratory (permeation oven cross-checked by the static volumetric method[19]). The uncertainty of the cylinder concentration is calculated by the direct comparison method described in ISO 6143[6]. A certificate was available showing uncertainty calculation.

Zero(NOx) and Zero(NO)

The zero air was produced by filtering ambient air with purafil/activated charcoal. Experience has shown that the deviation between the zero air obtained by purification on active charcoal and the zero air of the calibration bench of the ERLAP central laboratory is likely to be about 1 ppb. This result is also confirmed by the linearity check (see ***Appendix 2***). Without other information, a rectangular distribution is assumed leading to a standard uncertainty of 0.6 *ppb*.

R(Span(NOx)) and R(Span(NO)):

For the same reason as for the repeatability of $R(NO_X)$ and *R(NO)*, the standard uncertainty is 0.6 ppb.

Matrix effect: the analyser is calibrated using a NO standard in nitrogen, which is then used to monitor nitrogen oxides in ambient air. The two different matrixes could yield to a difference in the measurement due to quenching effect into the reaction chamber. However, it was verified that the difference between the response of the analyser to nitrogen and filtered ambient air is within 0.3 ppb a value, which is within the repeatability of the analyser. It is concluded that, since no matrix effect is evidenced nor expected, matrix effect is not taken in account.

Drift of calibration: the nitrogen oxides analyser of the Air Monitoring Station is calibrated once a month, the observed drift on the control chart for 1999 was never bigger than 7% and the most appropriate distribution is the triangular one. The ERLAP quality system states that no correction of data would be performed for a drift up to ±10%. If this would appear, a triangular distribution of the drift of 10% instead of 7% would be used since it is assumed that values near the limits are less likely than those near the middle value.

The variance of *R(Span(NOx))* and *R(Span(NO))* is the sum of repeatability and calibration drift variances:

$$u(R(Span(NOx))) = \sqrt{0.6^2 + \frac{(0.07*909.5)^2}{6}} = 26.0\ ppb$$

R(Zero(NOx)) and R(Zero(NO))

For the same reason as for the repeatability of $R((NO_X))$ and *R((NO))*, the standard uncertainty is 0.6 *ppb*.

	Value	u
Span	909.5	3.2
Zero	0	0.6
R(Span)	909.5	26
R(Zero)	0	0.8
	b1	b0
Span+u	1.0035	0
Span-u	0.9965	0
Zero+u	0.9993	0.6
Zero-u	1.0007	-0.6
R(Span)+u	0.9722	0
R(Span)-u	1.0294	0
R(Zero)+u	1.0009	-0.8
R(Zero)-u	0.9991	0.8
Correlation	-0.0380	

Table 2: Correlation between b_0 and b_1 both for NO and NOx (same values).

Discusion

Table 3 and Table 4 give the uncertainty budgets for high and low NO_2 concentration and according of the range of concentrations observed in Figure 5. The expanded uncertainty calculated as two times (k = 2) the combined uncertainty ranges from 35 % at [NO_2] of 20 *ppb* to 13 % for 100 *ppb*.

Since it is difficult to describe the whole range of possible uncertainty in two tables and in particular because this uncertainty is dependent on the NO/NOx balance, the relative expanded uncertainty was plotted as a contour map of [*NOx*] and [*NO*] (see Figure 6). This contour map was obtained by calculation of the expanded uncertainty as explained before for a matrix of *NO* and *NOx* concentration from 0 to 150 ppb with a step increase of 2.5 ppb. For relative uncertainty over 30 %, the contours are rather parallel to the [NO_2] distribution. Then smaller isocurves are curved according to the increase of NO concentrations. This is due to the NO_2 calculation : a difference between *NOx* and *NO* which leads to identical NO_2 concentration having bigger uncertainty when *NO* concentrations are bigger.

Along the isocurve for 15 % of relative expanded uncertainty (the data quality objective of the daughter directive on individual measurements), it is observed that this requirement is not met for NO_2 concentration lower than 50 to 80 ppb according to the NOx/NO balance.

Some components were studied or taken into account but did not show significant contribution to the expanded uncertainty: efficiency of NO_2-to-*NO* converter, repeatability and linearity of the analyser, sampling line losses, reference value for working standard and zero. Moreover among the correlation which were included in the uncertainty budget, the one between [NO_2]/converter efficiency and the one between the slope/intercept of the calibration function can be neglected. The only significant one is the correlation between [*NOx*] and [*NO*] which serve to strongly decrease the expanded uncertainty (in particular the effect of interference).

By observing each uncertainty component in Table 3 and Table 4, one may note that the major component, both for low and high NO_2 concentrations, is the response on the *NOx* channel of the analyser. The response on the NO channel may be important when *NO* concentration is similar to the *NOx* one. Among the sources of uncertainties for the response on the *NOx* channel, the quenching effect of humidity is the main source at high concentration while at low concentration it is the molecules converted to N-species, PAN being the major interference. The second more important source of uncertainty is either the response signal of the analyser to the working standard *R(Span(NOx))* and *R(Span(NO))* and in particular the observed drift of the analyser if high concentration of *NOx* and/or *NO* are present either the quenching effect of humidity on the *NO* channel if sufficient *NO* is present.

Quantity	Value unit	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution to u_c	Contribution to
$[NO_X]$	150 ppb	9.1	1.003	9.2	$u_c(NO_2)$
$[NO]$	50 ppb	3.0	-1.003	-3.1	
eff	99.7%	0.2%	-100.6	-0.20	
$r(NO_2,eff)$	-0.86	0.019	-101	3.4	
$r(NO,NOx)$	0.94	27.8	-1.01	-52.6	
$b_0(NOx)$	0.00 ppb	1.0	1	1.0	$u(NOx)$
$b_1(NOx)$	1.00	0.03	150	4.3	
$R(NO_X)$	150 ppb	8.0	1.00	8.0	
$r(b_1, b_0(NOx))$	-0.038	0.0	150	-0.3	
$Span(NO_X)$	909.5 ppb	3.2			$u(b_0(NOx))$ and $u(b_1(NOx))$
$Zero(NO_X)$	0 ppb	0.6			
$R(Span(NO_X))$	909.5 ppb	26.0			
$R(Zero(NO_X))$	0 ppb	0.8			
$b_1(NO)$	0.00	1.0	1	1.0	$u(NO)$
$b_0(NO)$	1.00 ppb	0.03	50	1.4	
$R(NO)$	50 ppb	2.5	-1	-2.5	
$r(b_1, b_0(NO))$	-0.038	0.0	50	-0.1	
$Span(NO)$	909.5 ppb	3.2			$u(b_0(NO))$ and $u(b_1(NO))$
$Zero(NO)$	0 ppb	0.6			
$R(Span(NO))$	909.5 ppb	26.0			
$R(Zero(NO))$	0 ppb	0.8			
$[NO_2]$	100.3			6.6	

Table 3: Uncertainty table for high concentration of nitrogen dioxide (100 ppb, U=13.2%):

Quantity	Value unit	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution	Contribution to
$[NO_X]$	150 ppb	9.1	1.003	9.2	$u_c(NO_2)$
$[NO]$	130 ppb	7.3	-1.003	-7.3	
eff	99.7%	0.2%	-20.1	-0.04	
$r(NO_2,eff)$	-0.86	0.023	-20	0.8	
$r(NO,NOx)$	0.94	66.8	-1.01	-126.4	
$b_0(NOx)$	0.00 ppb	1.0	1	1.0	$u(NOx)$
$b_1(NOx)$	1.00	0.03	150	4.3	
$R(NO_X)$	150 ppb	8.0	1.00	8.0	
$r(b_1, b_0(NOx))$	-0.038	0.0	150	-0.3	
$Span(NO_X)$	909.5 ppb	3.2			$u(b_0(NOx))$ and $u(b_1(NOx))$
$Zero(NO_X)$	0 ppb	0.6			
$R(Span(NO_X))$	909.5 ppb	26.0			
$R(Zero(NO_X))$	0 ppb	0.8			
$b_1(NO)$	0.00	1.0	1	1.0	$u(NO)$
$b_0(NO)$	1.00 ppb	0.03	130	3.7	
$R(NO)$	130 ppb	6.2	-1	-6.2	
$r(b_1, b_0(NO))$	-0.038	0.0	130	-0.2	
$Span(NO)$	909.5 ppb	3.2			$u(b_0(NO))$ and $u(b_1(NO))$
$Zero(NO)$	0 ppb	0.6			
$R(Span(NO))$	909.5 ppb	26.0			
$R(Zero(NO))$	0 ppb	0.8			
$[NO_2]$	20.1 ppb			3.5	

Table 4: Uncertainty budget for low concentration of nitrogen dioxide (20 ppb, U = 34.8 %)

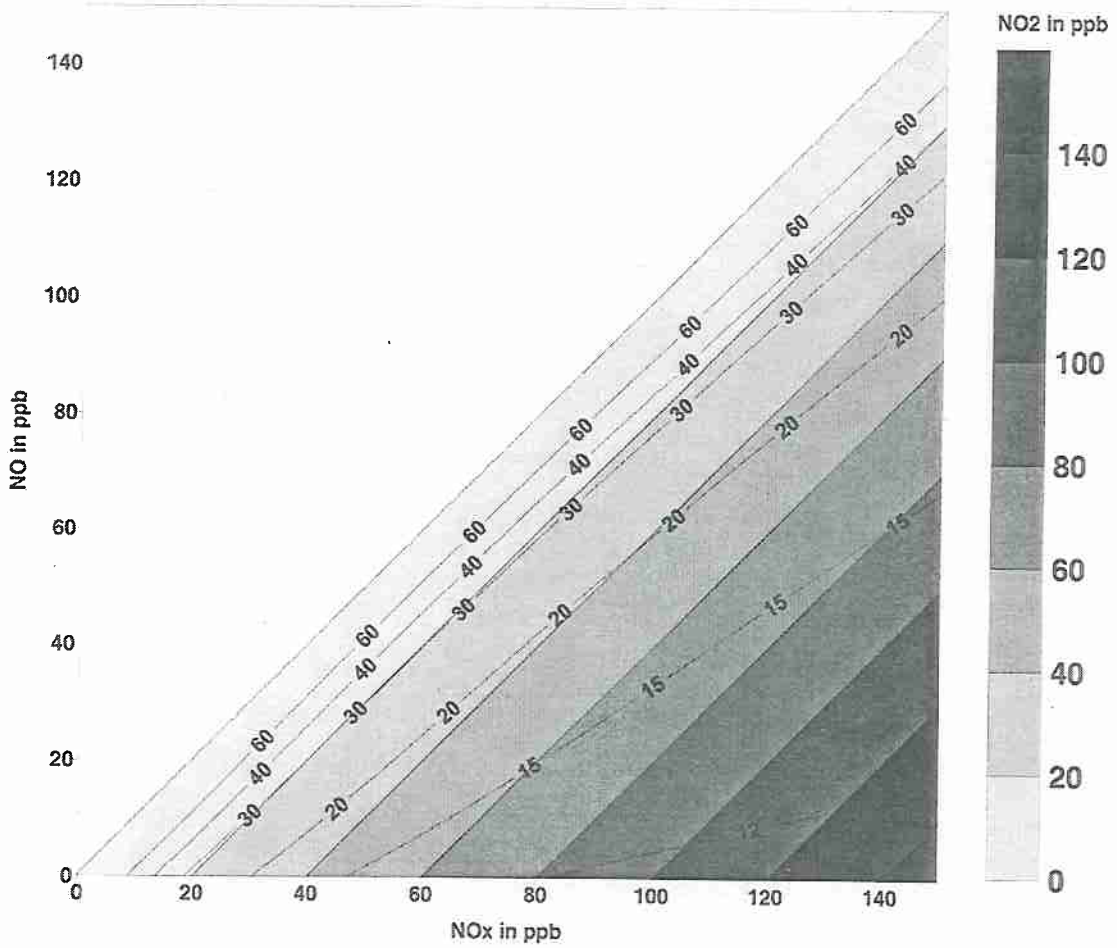


Figure 6: Isocurves of NO_2 relative expanded uncertainty in percent according to NOx and NO concentration. [NO_2] is represented by the grey color scale.

Recently a great deal of effort has been put on the certificate of calibration for the working standard. In particular in the framework of accreditation and in order to make sure that the traceability chain of measurement is not broken, certificate of standards showing a stamp of an organistation within the multilateral agreement of standards and a very small uncertainty became a must. However by rising the standard uncertainty from 0.3 to 5% for the certificate of calibration of the span at high concentration (Table 3), the relative expanded uncertainty would change from 13.2 to 13.4 % while at low concentration (Table 4), the relative expanded uncertainty would change from 34.8 to 35.5 %. Obviously the uncertainty of the standard is not within the major problem to tackle at once.

About the sampling line losses, which are very low at the AIRMON station, greater values are sometime observed and could modify the uncertainty value. An extended quality control of 40 European station monitoring ambient NO_2 was performed in 1995 by ERLAP. This study[20] showed that more than 95% of the station have a sampling line losses lower than 4% for NO_2. At higly polluted sites the NO_2 to NO converter efficiency may be increased and it is not to observe However, in the case of worse efficiency of conversion (98 ± 2 %) then the correlation between [NO_2] and the converter efficiency may become a more significant positive correlation.

In order to easily draw conclusion from the non - linear model equations, a partial factorial design was carried out to study the influence of parameters on the expanded uncertainty according to the table given in Appendix 8. From the following figure, it appears *that* NO_2 uncertainty is ruled by the balance *NOx/NO*, *NO* being the most important parameter to increase the uncertainty while *NOx* is the one which decreases it. The correlation between those two strongly allows decreasing the uncertainty and must be taken into consideration. Among the rest of components, the interference from humidity and PAN are significant. In particular the presence of nitrous acid, the uncertainty on span, on the converter efficiency are irrelevant.

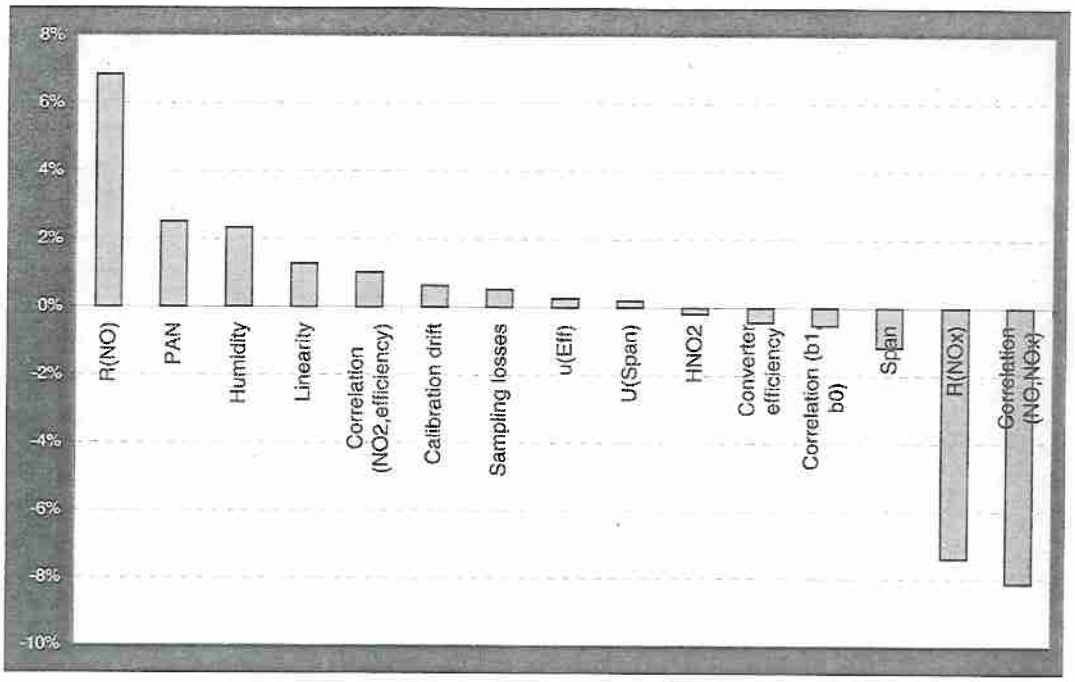


Figure 7: Relative influence of the components of uncertainty

Another point is that the AIRMON station does not report individual measurements but hourly averages of individual measurements. Hourly averages may be considered as the average of 15 measurements since a time response of 4 minutes was previously established[12] for chemiluminesence. It is inviting to consider the uncertainty of hourly average as the one of 15 independent individual measurements. This would allow to reduce the combined uncertainty by square root of 15 (see eq. 3). However, 15 consecutive measurements within one hour are correlated by the same span drift, interference, *NOx/NO* balance... The only parameters that are going to be reduced by a factor of square root of 15 are : the repeatability and partially the linearity error. However, both these components are low so that the uncertainty for hourly average will be similar to the values given in Figure 6. Anyhow, one may observe in Figure 6 that for the hourly average limit value of the European directive, which is larger than 100 ppb, the uncertainty is always smaller than the quality objective target of 15 %.

For the yearly average limit value of the European directive which is larger 20 ppb, here many components of the uncertainty may be neglected: span drift, repeatability, linearity and only the bias due to the interference of *PAN*, humidity and HNO_2 should be considered and not their distribution versus time. However the possibility of missing data should be considered. It was showed[21]. that using daily NO_2 series, the profiles of the error in determining the annual average against the number of random weekly samplings gives a standard uncertainty of about 1% when data capture is larger than 75 % as indicated by the European Directive. A new contour map is plotted for the yearly average uncertainties in Figure 8 which shows that 15 % of uncertainty may not be always respected in case of *NO* concentration bigger than 50 *ppb* as a yearly average. In fact, the study of interference shows that systematic bias is produced in the NO_2 measurements by the presence of humidity, *PAN* and HNO_2 A good implementation of the GUM requires that the bias should be corrected for respecting the assumption of normal distribution and not treated as a source of uncertainty like it is done in this paper. These corrections would ensure a NO_2 uncertainty about 5 % at 20 ppb.

Appendix 4 gives an example of the use of expanded uncertainty in a quality control check.

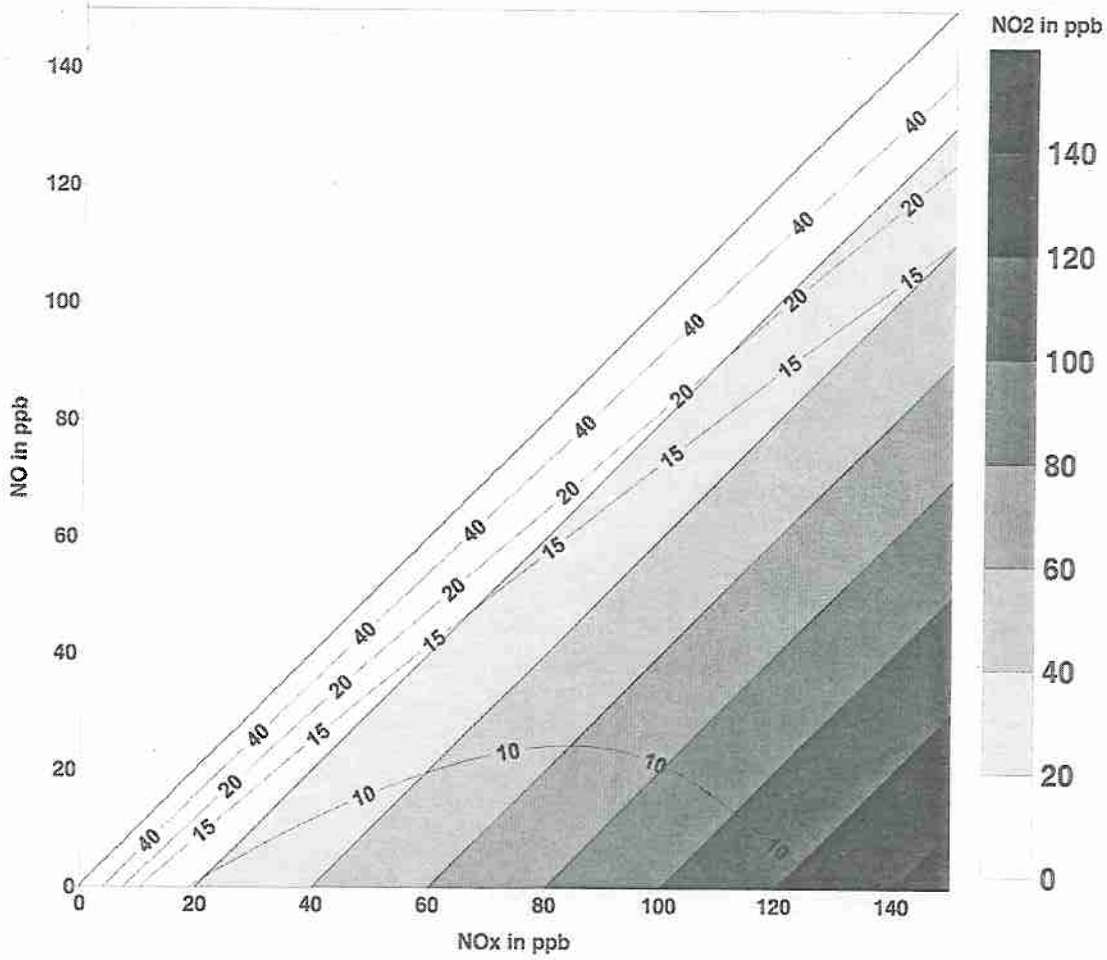


Figure 8: Isocurves of NO_2 relative expanded uncertainty in percent for yearly average according to NOx and NO concentration. [NO_2] is represented by the grey color scale

Conclusions

The GUM method for the evaluation of uncertainty for ambient NO_2 monitoring was applied at the JRC-AIRMON Station. The methodology is the most complete method to determine the components which affect the accuracy of NO_2 measurements. Although the model designed for the calculation of uncertainty is rather simple, the method of evaluation requires a large data pool. While, some data are given by the manufacturer of the analyser others such as linearity, converter efficiency determination, sampling line losses evaluation, certified reference material data and expected level of interference require laboratory and field experiments:

The extent of NO_2 uncertainty is mainly dependent on the level of *NO* concentration and is decreased by the level of *NOx* concentration and the correlation between *NOx* and *NO*. Furthermore, the uncertainty budget reveals that the contribution of the uncertainty of calibration standard, of linearity, converter efficiency and calibration checks to the overall uncertainty is less important than the contribution of interference mainly humidity and *PAN*. Perhaps less effort than the one nowadays implemented at the field-monitoring stations should be dedicated to the metrological parameters and more to the control or correction of interference.

The uncertainty of NO_2 hourly average could be rather high with maximum bigger than 50 % for NO_2 concentration of 40 $\mu g/m^3$. In fact, 15% of expanded uncertainty is only guaranty for NO_2 concentration larger than 60 *ppb*. Nevertheless, for the hourly limit value of the European directive, 200 $\mu g/m^3$, the data quality objective (expanded uncertainty lower than 15 %) is ensured. On the contrary, for the limit value of the annual average, 40 $\mu g/m^3$, the data quality objective is not met in the unlikely case of annual *NO* average over 50 *ppb*. By correcting for the humidity and *PAN* interference the data quality objective is ensured because the relative expanded uncertainty becomes lower than 15 %.

It is difficult to conclude on the level of uncertainty for all possible situations and, as the GUM states, it is more advisable to perform a calculation rather than to rely on this general conclusion.

Appendix 1: Gas phase titration

Steps	NO	NOx	NO2	O3	Eff
Zero Air	0	0	0	0	
NO Injection	777	787	10	0	
NO Injection + 1st injection O3	629	787	158	0	100.1%
Zero Air - Ozone	0	1	1	149	
NO Injection	779	789	10	0	
NO Injection + 2nd injection O3	481	788	307	0	99.8%
Zero Air - Ozone	0	1	1	298	
NO Injection	781	790	9	0	
NO Injection + 3rd injection O3	326	788	462	1	99.7%
Zero Air - Ozone	0	1	1	451	
NO Injection	781	790	9	0	
NO Injection + 4th injection O3	103	786	683	1	99.3%
Zero Air - Ozone	0	1	1	676	
NO Injection	781	791	10	0	
NO Injection + 5th injection O3	326	789	463	1	99.5%
Zero Air - Ozone	0	1	1	452	
NO Injection	782	792	10	0	
NO Injection + 6th injection O3	483	791	308	0	99.6%
Zero Air - Ozone	0	1	1	298	
NO Injection	782	793	10	0	
NO Injection + 7th injection O3	634	792	159	0	99.8%
Zero Air - Ozone	0	1	1	149	
Zero Air	0	0	0	0	

Eff = (NO_2f - NO_2i)/(NOf-NOi) *All measurements in ppb*

Table 5: Converter efficiencies and correlation coefficients determined by GasPhase Titration

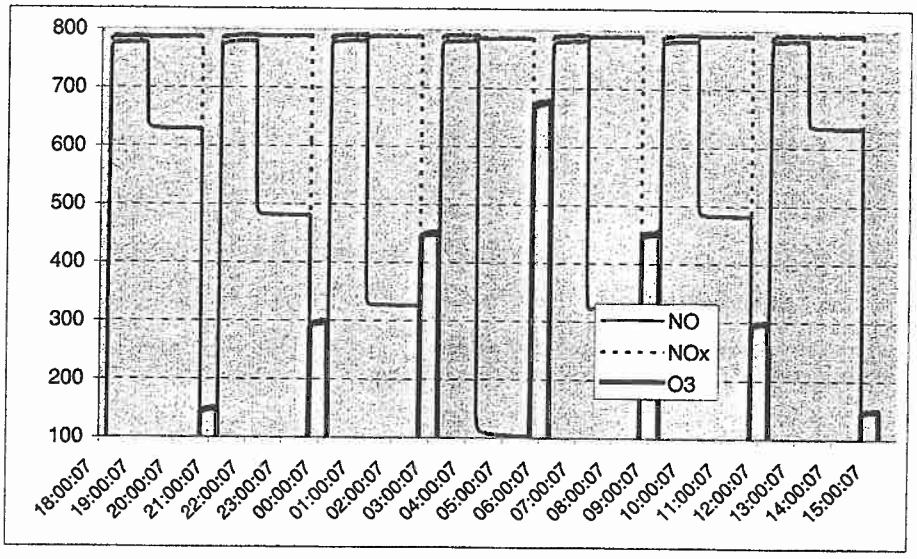


Figure 9: Gas phase titration: NO, NO_X and O_3 concentration versus time, raw results

Appendix 2: Check of Linearity of analyser

The linearity of the calibrated AIRMON analyser is checked against the reference analyser at several values of the concentration range. The outcome (see Table 6) of this check is an evaluation of the linearity deviation which is calculated by:

$$Linearity\ deviation = Analyser - reference$$

Step	Reference values	Analyser values	Linearity deviation
1	0.0	-0.7	0.7
2	200.0	201.2	-1.2
3	500.0	499.1	0.9
4	800.0	800.8	-0.9
5	500.0	499.0	1.0
6	200.0	201.8	-1.8
7	0.0	-0.6	0.6
8	200.0	201.6	-1.6
9	500.0	498.1	1.9
10	800.0	800.4	-0.4
11	0.0	-0.7	0.7

Table 6: Linearity deviations (in ppb)

The standard deviation of the linearity deviation between the reference value and the analyser value is 0.78 ppb. This is a common value obtained over the last 4 years. However this standard deviation includes both the linearity and the repeatability effects. Finally the standard uncertainty of the linearity effect is calculated by subtraction of variances:

$$s_{linearity} = \sqrt{s^2 - s^2_{repeatability}} = \sqrt{0.78^2 - 0.58^2} = 0.52\,ppb$$

Appendix 3: Effect of humidity on chemiluminescence analysers

In order to assess the influence of absolute humidity on the measurement of $[NO_2]$, two different analysers (Teco 42 C) were used. At the inlet of one of them, a "Permapure dryer" (Nafion dryer) able to totally dry the sampled air, was installed. A silicagel cartridge was used to confirm that the the air was totally dried since it did not turn to pinl color from its orginial blue color.

In the first experiment the concentration of *NO* and NO_2 was kept constant (50 *ppb* for *NO* and 150 *ppb* for NO_2) while humidity was changed (from 0% to 80% of relative humidity at 24 °C). The measurement of $[NO_2]$ was then performed in two ways: in a dry atmosphere and under a given amount of humidity. The measured values for NO_2, *NO* and *NOx* were then plotted as a function of the absolute humidity (see Figure 10). This figures clearly shows a linear relationship between the decrease in percent of nitrogen oxides and the absolute humidity (about 0.5 % for 1 g/m³).

In the second experiment, [*NOx*] and humidity were kept constant ([*NOx*]= 520 ppb and 58 % of relative humidity at 23 °C) while *NO* concentration was decrease and NO_2 increased accordingly. The results are given in Figure 11. The figure shows a constant *NOx* decrease (7.5 %) whatever the balance between *NO*/ NO_2, provided that the *NOx* concentration is constant, hence confirming that the water vapor has a quenching influence but does not affect the NO_2 to *NO* efficiency of conversion. The figure also shows a constant *NO* decrease (7.5 %) whatever the *NO* concentration.

The uncertainty on the relative decrease figure is about 3 % for a 1%-uncertainty of $[NO_2]$ of 500 *ppb*.

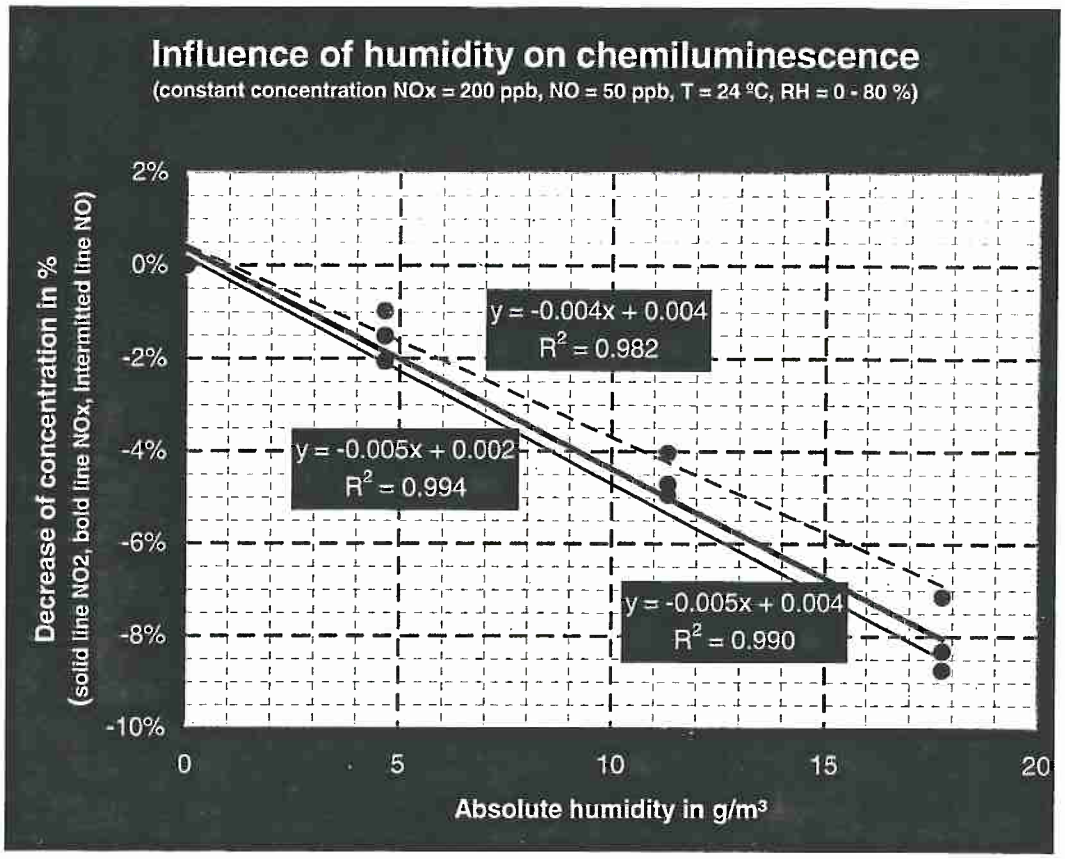


Figure 10: Decrease of [NOx] and [NO_2] as a function of absolute humidity (g/m3).

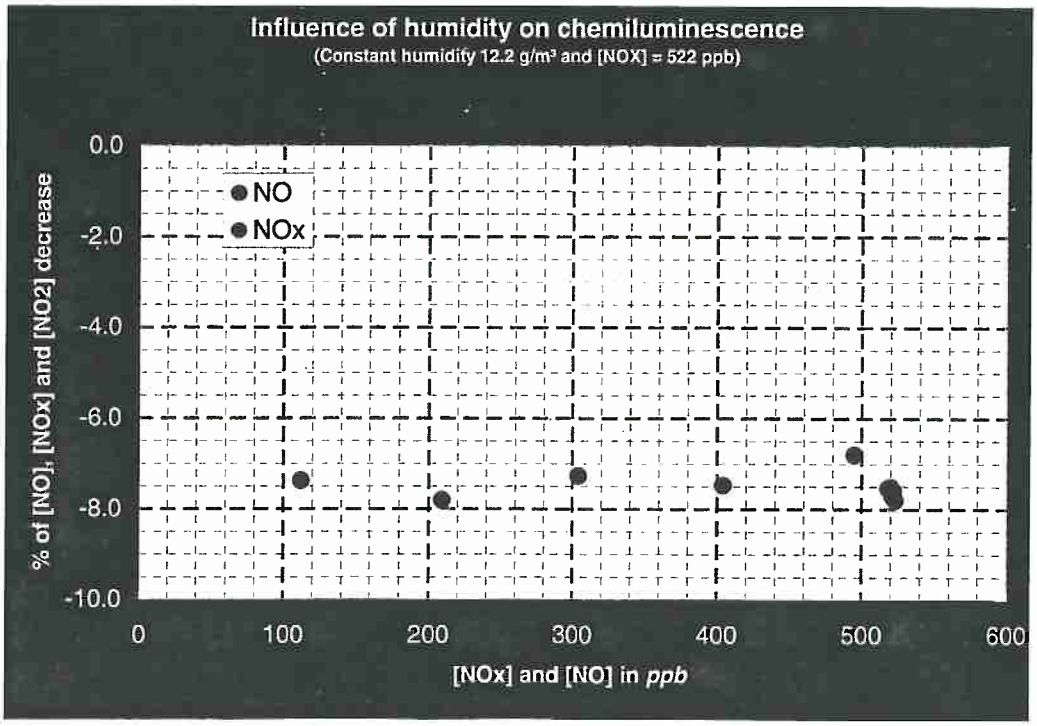


Figure 11: Decrease of concentration when the ratio [NO]/[NOx] is modified with constant [NOx]

Appendix 4: Evaluation of sample losses and confirmation of uncertainty

The mobile laboratory of ERLAP is equipped with a Test Atmosphere Generator (TAG). The TAG is a twin-level dynamic diluter designed to generate ambient concentrations of pollutants from gas cylinders of high-content pressurised mixtures. The first-step dilution uses mass flow controllers in order to perform dynamic dilutions of the gas cylinders of high-content pressurised mixtures with synthetic air (air quality: chromatography C air made up oxygen-nitrogen). The second step dilution uses a variable-flow turbine to dilute the first-step dilution with filtered/purified ambient air of the turbine so that a total flow of 160 l/min test –mixtures is injected into the sampling line of AIRMON trough a sampling hood. An ozone generator is added to the TAG in order to produce nitrogen dioxide by oxidation of the nitrogen monoxide supplied by gas cylinders of high-content pressurised mixtures. The test samples were generated in the TAG and injected in the sample hood through a 4-cm diameter teflon pipe.

The measurements of AIRMON are compared with the measurement of the mobile laboratory taken at the sample hood. Eventual losses in the EMEP station sample line are investigated.

The analysers of AIRMON were not specially calibrated for the comparison but were kept under normal calibration schedule (periodicity once a month). The AIRMON sample line was not specially cleaned for the test but the normal maintenance was observed.

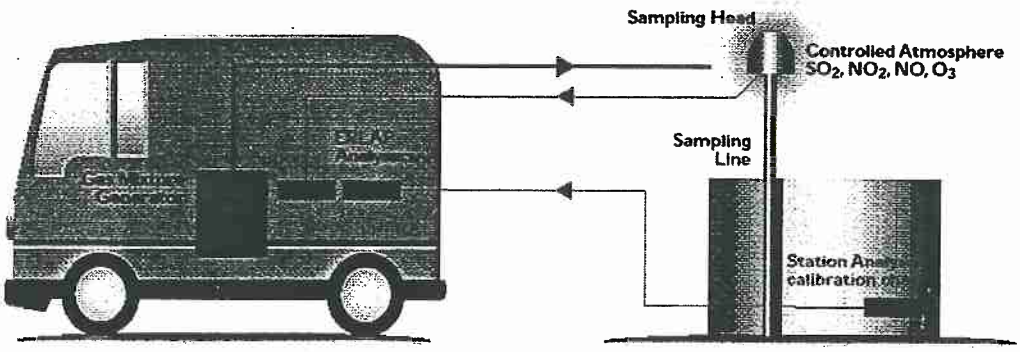


Figure 12: The Test Atmosphere generator implemented at AIRMON

Comparison procedure

Several comparisons, each one of half an hour duration were performed on 04/02/1999:

- NO: zero, about 30, 50, 85, 100 and 190 ppb *ppb*,
- NO_2: zero, about 20, 90 and 140 *ppb*.

Significant deviations are evidenced if the normalised deviation En is > 1 with:

$$En = \left| \frac{AIRMON - Mobile\ Lab}{\sqrt{U^2_{AIRMON} + U^2_{MobileLab}}} \right| \quad (15)$$

Results and associated uncertainty

The nitrogen oxides analyser of the EMEP sation under test was a Thermo Environment model TECO 42. This analyser uses the Cheminluminescent method of NOx determination.
The mobile laboratory of ERLAP was equipped with a Nitrogen oxides: Environnemnt SA model AC 31M with corresponding working standard (cylinder manufactured by Messer Griesheim code MG A7520 certified by ERLAP NO=NOx=195 ± 3 ppb)

Time	Mobile Laboratory NO	AIRMON NO	Mobile Laboratory NO2	AIRMON NO2	En NO	En NO_2
	ppb	ppb	ppb	ppb		
12:30-13:00	2 ± *4*	1 ± *4*	11 ± *7*	13 ± *7*	***0.18***	***0.20***
14:00-14:30	29 ± *4*	33 ± *4*	*25* ± *6*	23 ± *6*	***0.71***	***0.24***
15:00-15:30	85 ± *4*	89 ± *4*	*19* ± *7*	15 ± *7*	***0.71***	***0.40***
16:00-13:30	190 ± *6*	189 ± *6*	*4* ± *9*	14 ± *9*	***0.12***	***0.79***
17:00-17:30	53 ± *4*	54 ± *4*	*140* ± *8*	143 ± *8*	***0.18***	***0.24***
17:39-17:43	101 ± *5*	106 ± *5*	*90* ± *8*	93 ± *8*	***0.71***	***0.24***

Table 7: Comparison of AIRMON and mobile laboratory measurements with normalised deviation

Sampling line losses

No NOx losses in the EMEP station sampling line were observed by the mobile laboratory by simultaneously measuring at the sample hood and at the manifold ([NO]: 145 *ppb* at the hood and 144 *ppb* at the manifold, [NOx]: 194 *ppb* at the hood and 193 *ppb* at the manifold).

Conclusion

All the normalised deviation *En* being smaller or equal to 1, the results of the TAG comparison between AIRMON and the ERLAP mobile laboratory for nitrogen oxides in the range 0 to 200 ppb are compliant with the expectations (the evaluated uncertainties). Furthermore, it was shown that no absorption occurs in the station sampling line.

Appendix 5: Nitrous and nitric acid measurement at the AIRMON station

(Communication of Dr. J. P. Putaud of the Institute for Environment and Sustainability of the Joint Research Centre of Ispra)

Data	(ora	[HNO2] ppb	[HNO3 ppb
05-Apr-00	7		0.25
05-Apr-00	8		0.21
05-Apr-00	9		0.19
05-Apr-00	10		0.16
05-Apr-00	11		0.11
06-Apr-00	12		0.13
06-Apr-00	1		0.09
06-Apr-00	2		0.08
06-Apr-00	3		0.08
06-Apr-00	4		0.05
06-Apr-00	5		0.05
06-Apr-00	6		0.05
06-Apr-00	7		0.05
06-Apr-00	8		0.06
06-Apr-00	9		0.07
06-Apr-00	10		0.08
06-Apr-00	4		0.29
06-Apr-00	5		0.20
06-Apr-00	7		0.17
06-Apr-00	8		0.12
06-Apr-00	9		0.10
06-Apr-00	10		0.09
06-Apr-00	11		0.09
07-Apr-00	12		0.08
07-Apr-00	1		0.08
07-Apr-00	2		0.10
07-Apr-00	3		0.18
07-Apr-00	4		0.18
07-Apr-00	5		0.12
07-Apr-00	6		0.11
07-Apr-00	7		0.10
07-Apr-00	8		0.05
07-Apr-00	9		0.06
07-Apr-00	10		0.07
07-Apr-00	11		0.08
07-Apr-00	12		0.06
07-Apr-00	1		0.09
07-Apr-00	3		0.14
07-Apr-00	4		0.29
07-Apr-00	5		0.43
10-Apr-00	11		0.09
10-Apr-00	12		0.09
10-Apr-00	1		0.08
10-Apr-00	2		0.05
10-Apr-00	3		0.08
10-Apr-00	4		0.10
10-Apr-00	5		0.08
10-Apr-00	6		0.09
10-Apr-00	7		0.02
10-Apr-00	8		0.14
10-Apr-00	9		0.18
10-Apr-00	10		0.16
10-Apr-00	11		0.15
11-Apr-00	12		0.14
11-Apr-00	1		0.17
11-Apr-00	2		0.16
11-Apr-00	3		0.16
11-Apr-00	4		0.20
11-Apr-00	5		0.18
11-Apr-00	6		0.19
11-Apr-00	7		0.17
11-Apr-00	8		0.18
11-Apr-00	9		0.18
11-Apr-00	10		0.19
26-Apr-00	12	0.20	0.29
26-Apr-00	1	0.22	0.32
26-Apr-00	2	0.20	0.54
26-Apr-00	3	0.10	0.28
26-Apr-00	4	0.09	0.20
26-Apr-00	5	0.11	0.32
26-Apr-00	6	0.10	0.15
26-Apr-00	7	0.08	0.14
26-Apr-00	8	0.12	0.15
26-Apr-00	9	0.18	0.12
26-Apr-00	10	0.21	0.10
26-Apr-00	11	0.23	0.10
26-Apr-00	12	0.22	0.05
27-Apr-00	9	0.24	0.09
27-Apr-00	11	0.25	0.08
27-Apr-00	12	0.30	0.22

27-Apr-00	1	0.19	0.10
27-Apr-00	2	0.18	0.24
27-Apr-00	3	0.23	0.38
27-Apr-00	4	0.22	0.39
27-Apr-00	5	0.17	0.33
27-Apr-00	6	0.13	0.32
27-Apr-00	7	0.16	0.27
27-Apr-00	8	0.17	0.19
27-Apr-00	9	0.22	0.16
27-Apr-00	10	0.30	0.11
27-Apr-00	11	0.34	0.11
28-Apr-00	12	0.36	0.09
28-Apr-00	1	0.35	0.10
28-Apr-00	2	0.29	0.13
28-Apr-00	3	0.35	0.10
28-Apr-00	4	0.38	0.09
28-Apr-00	5	0.43	0.08
28-Apr-00	6	0.40	0.08
28-Apr-00	7	0.37	0.07
28-Apr-00	8	0.37	0.06
02-May-00	11	0.15	0.12
02-May-00	12	0.31	0.29
02-May-00	1	0.30	0.43
02-May-00	2	0.31	0.43
02-May-00	3	0.34	0.27
02-May-00	4	0.53	0.13
02-May-00	5	0.60	0.10
02-May-00	6	0.38	0.07
02-May-00	7	0.39	0.05
02-May-00	8	0.36	0.06
02-May-00	9	0.53	0.06
02-May-00	10	0.74	0.06
02-May-00	11	0.56	0.08
03-May-00	12	0.58	0.06
03-May-00	1	0.59	0.09
03-May-00	2	0.62	0.10
03-May-00	3	0.60	0.06
03-May-00	4	0.59	0.06
03-May-00	5	0.51	0.07
03-May-00	6	0.68	0.06
03-May-00	7	0.62	0.06
03-May-00	8	0.75	0.06
03-May-00	9	1.02	0.05
03-May-00	10	0.47	0.08
03-May-00	11	0.41	0.17
03-May-00	12	0.20	0.23
03-May-00	1	0.17	0.34
03-May-00	2	0.20	0.36
03-May-00	3	0.14	0.35
03-May-00	4	0.11	0.30
03-May-00	5	0.15	0.25
03-May-00	6	0.20	0.21
03-May-00	7	0.30	0.13
03-May-00	8	0.29	0.12
03-May-00	9	0.27	0.08
04-May-00	1	0.20	0.13
04-May-00	2	0.19	0.14
04-May-00	3	0.11	0.20
04-May-00	4	0.11	0.19
04-May-00	5	0.24	0.21
04-May-00	6	0.22	0.21
04-May-00	7	0.24	0.13
04-May-00	8	0.27	0.18
04-May-00	9	0.25	0.10
04-May-00	11	0.35	0.07
05-May-00	12	0.39	0.09
05-May-00	1	0.38	0.08
05-May-00	2	0.32	0.06
05-May-00	3	0.30	0.05
05-May-00	4	0.34	0.06
05-May-00	5	0.30	0.05
05-May-00	6	0.26	0.04
05-May-00	7	0.27	0.04
05-May-00	8	0.33	0.06
05-May-00	9	0.26	0.05
05-May-00	10	0.29	0.09
05-May-00	11	0.29	0.14
05-May-00	12	0.31	0.20
05-May-00	1	0.31	0.23
05-May-00	2	0.12	0.31
08-May-00	12	0.35	0.06
08-May-00	1	0.21	0.07

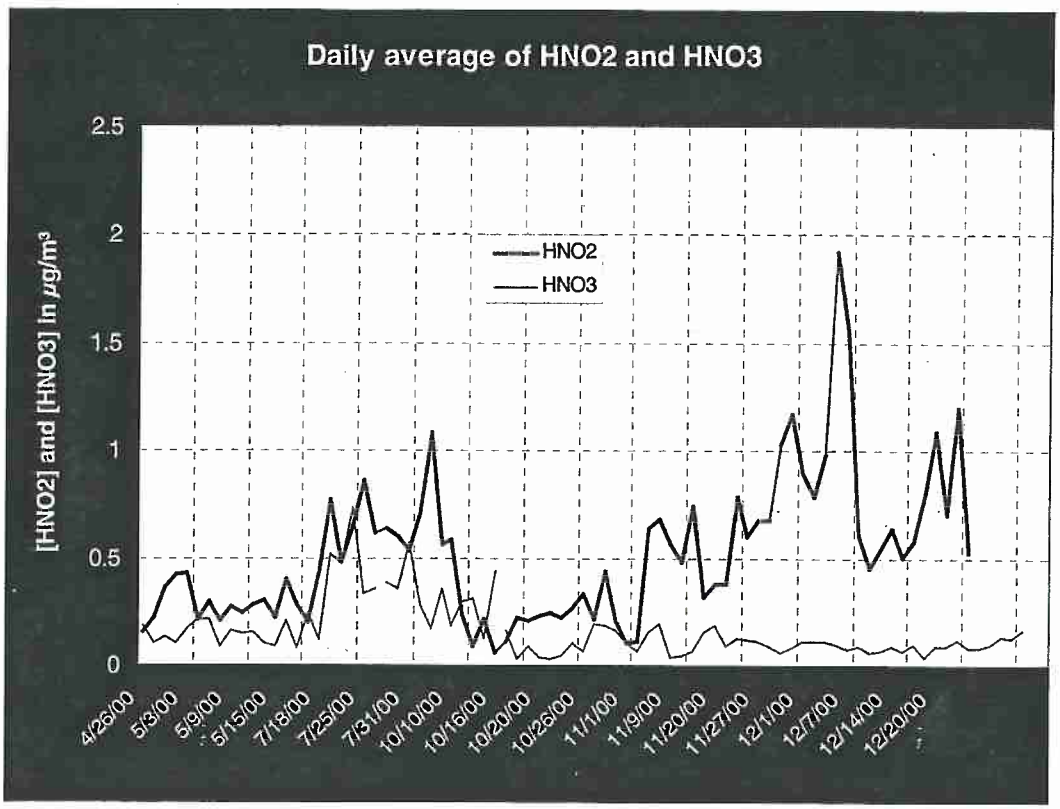
08-May-00	2	0.16	0.08
08-May-00	3	0.07	0.08
08-May-00	4	0.07	0.10
08-May-00	5	0.09	0.12
08-May-00	6	0.07	0.11
08-May-00	7	0.17	0.18
08-May-00	10	0.39	0.08
08-May-00	11	0.43	0.05
08-May-00	12	0.40	0.05
09-May-00	1	0.38	0.04
09-May-00	2	0.34	0.04
09-May-00	3	0.33	0.04
09-May-00	4	0.31	0.09
09-May-00	5	0.35	0.12
09-May-00	6	0.31	0.09
09-May-00	7	0.43	0.05
09-May-00	8	0.54	0.41
09-May-00	9	0.39	0.05
09-May-00	10	0.20	0.09
09-May-00	11	0.15	0.11
09-May-00	12	0.14	0.18
09-May-00	1	0.17	0.30
09-May-00	2	0.19	0.49
09-May-00	3	0.24	0.59
09-May-00	4	0.25	0.68
09-May-00	5	0.18	0.49
09-May-00	6	0.18	0.19
09-May-00	7	0.33	0.12
09-May-00	8	0.25	0.10
09-May-00	11	0.17	0.08
10-May-00	12	0.26	0.05
10-May-00	1	0.18	0.08
10-May-00	2	0.28	0.05
10-May-00	3	0.24	0.07
10-May-00	4	0.27	0.05
10-May-00	5	0.23	0.05
10-May-00	6	0.18	0.04
10-May-00	7	0.06	0.03
10-May-00	8	0.14	0.03
10-May-00	9	0.15	0.03
10-May-00	10	0.17	0.03
10-May-00	11	0.11	0.03
10-May-00	12	0.07	0.04
10-May-00	3	0.22	0.19
10-May-00	4	0.14	0.16
10-May-00	5	0.21	0.14
10-May-00	6	0.16	0.15
10-May-00	7	0.27	0.12
10-May-00	8	0.33	0.16
10-May-00	9	0.39	0.15
10-May-00	10	0.54	0.10
10-May-00	11	0.49	0.11
10-May-00	12	0.51	0.10
11-May-00	1	0.46	0.11
11-May-00	2	0.42	0.08
11-May-00	3	0.38	0.11
11-May-00	4	0.37	0.07
11-May-00	5	0.33	0.08
11-May-00	6	0.35	0.08
11-May-00	7	0.34	0.05
11-May-00	8	0.38	0.05
11-May-00	9	0.26	0.07
11-May-00	10	0.29	0.09
11-May-00	11	0.36	0.16
11-May-00	12	0.18	0.31
11-May-00	1	0.22	0.47
11-May-00	2	0.17	0.44
11-May-00	3	0.23	0.60
11-May-00	4	0.22	0.77
11-May-00	5	0.18	0.54
11-May-00	6	0.16	0.34
11-May-00	7	0.13	0.33
11-May-00	8	0.14	0.30
11-May-00	9	0.18	0.24
11-May-00	10	0.32	0.17
11-May-00	11	0.34	0.18
12-May-00	12	0.37	0.15
12-May-00	1	0.38	0.15
12-May-00	2	0.33	0.11
12-May-00	3	0.27	0.14
12-May-00	4	0.33	0.21
12-May-00	5	0.36	0.12

12-May-00	6	0.34	0.10
12-May-00	7	0.33	0.09
12-May-00	8	0.31	0.09
12-May-00	9	0.19	0.09
12-May-00	10	0.11	0.07
15-May-00	10	0.42	0.25
15-May-00	11	0.28	0.32
15-May-00	12	0.18	0.44
15-May-00	1	0.14	0.54
15-May-00	2	0.15	0.61
15-May-00	3	0.09	0.75
15-May-00	4	0.09	0.88
15-May-00	5	0.08	0.82
15-May-00	6	0.08	0.82
15-May-00	7	0.16	0.83
15-May-00	8	0.21	0.48
15-May-00	9	0.46	0.29
15-May-00	10	0.34	0.18
15-May-00	11	0.44	0.10
16-May-00	12	0.28	0.12
16-May-00	1	0.42	0.12
16-May-00	2	0.43	0.10
16-May-00	3	0.50	0.09
16-May-00	4	0.50	0.09
16-May-00	5	0.53	0.10
16-May-00	6	0.46	0.08
16-May-00	7	0.45	0.12
16-May-00	8	0.46	0.14
16-May-00	9	0.36	0.20
16-May-00	10	0.34	0.27
16-May-00	11	0.39	0.34
16-May-00	3		0.99
16-May-00	4	0.24	1.26
16-May-00	5	0.23	1.48
16-May-00	6	0.24	1.42
16-May-00	8	0.22	1.07
16-May-00	9	0.40	0.71
16-May-00	10	0.66	0.47
16-May-00	11	0.54	0.34
17-May-00	12	0.47	0.27
17-May-00	4	0.59	0.39
17-May-00	5	0.34	0.25
17-May-00	6	0.32	0.17
17-May-00	8	0.28	0.21
17-May-00	9	0.17	0.31
17-May-00	10		0.43
17-May-00	11	0.24	0.54
17-May-00	12	0.31	0.94
17-May-00	1	0.36	1.44
17-May-00	2	0.26	1.82
17-May-00	3	0.20	1.82
17-May-00	4	0.21	1.42
17-May-00	5	0.09	0.81
17-May-00	11	0.12	0.24
18-May-00	12	0.06	0.23
18-May-00	1	0.06	0.20
18-May-00	2	0.06	0.20
18-May-00	3	0.11	0.18
18-May-00	4	0.28	0.16
18-May-00	5	0.28	0.14
18-May-00	6	0.27	0.14
18-May-00	7	0.31	0.13
18-May-00	8	0.33	0.14
18-May-00	9	0.16	0.18
18-May-00	10	0.23	0.29
18-May-00	11	0.28	0.53
18-May-00	12	0.17	0.77
18-May-00	1	0.15	0.82
18-May-00	2	0.23	0.70
18-May-00	3	0.33	0.54
18-May-00	4	0.12	0.40
18-Jul-00	11	0.70	0.18
18-Jul-00	12	0.95	0.22
18-Jul-00	1	0.41	0.38
18-Jul-00	2	0.47	0.70
18-Jul-00	3	0.35	0.72
18-Jul-00	4	0.08	0.72
18-Jul-00	5	0.24	0.58
18-Jul-00	6	0.26	0.43
18-Jul-00	7	0.28	0.27
18-Jul-00	8	0.32	0.20
18-Jul-00	9	0.58	0.10

18-Jul-00	10	0.56	0.10	26-Jul-00	10	0.73	0.16	10-Oct-00	4	0.70	0.23	19-Oct-00	12	0.27	0.05
18-Jul-00	11	0.46	0.07	26-Jul-00	11	0.67	0.12	10-Oct-00	5	0.62	0.26	19-Oct-00	1	0.15	0.04
19-Jul-00	12	1.07	0.45	27-Jul-00	12	0.61	0.11	10-Oct-00	6	0.47	0.19	19-Oct-00	2	0.17	0.03
19-Jul-00	1	1.15	0.30	27-Jul-00	1	0.55	0.10	10-Oct-00	7	0.29	0.18	19-Oct-00	3	0.16	0.01
19-Jul-00	2	1.21	0.14	27-Jul-00	2	0.49	0.08	10-Oct-00	8	0.24	0.11	19-Oct-00	4	0.06	0.00
19-Jul-00	3	1.11	0.20	27-Jul-00	3	0.50	0.08	10-Oct-00	9	0.24	0.10	19-Oct-00	5	0.04	0.00
19-Jul-00	4	0.95	0.06	27-Jul-00	4	0.44	0.07	10-Oct-00	11	0.23	0.00	19-Oct-00	6	0.04	0.00
19-Jul-00	5	0.86	0.05	27-Jul-00	5	0.39	0.07	11-Oct-00	12	0.22	0.00	19-Oct-00	7	0.04	0.00
19-Jul-00	6	0.87	0.05	27-Jul-00	6	0.44	0.06	11-Oct-00	1	0.19	0.00	19-Oct-00	8	0.05	0.00
19-Jul-00	9	1.25	0.16	27-Jul-00	7	0.41	0.05	11-Oct-00	2	0.24	0.00	19-Oct-00	9	0.16	0.00
19-Jul-00	10	1.22	0.16	27-Jul-00	8	0.39	0.06	11-Oct-00	3	0.25	0.00	19-Oct-00	10	0.25	0.04
19-Jul-00	11	1.03	0.26	27-Jul-00	11	0.68	0.22	11-Oct-00	4	0.27	0.00	19-Oct-00	11	0.22	0.04
19-Jul-00	12	0.98	0.38	27-Jul-00	12	0.68	0.29	11-Oct-00	5	0.29	0.00	19-Oct-00	12	0.11	0.05
19-Jul-00	1	0.91	0.53	27-Jul-00	1	0.74	0.39	11-Oct-00	6	0.35	0.00	19-Oct-00	1	0.15	0.08
19-Jul-00	2	0.47	0.73	27-Jul-00	2	0.72	0.55	11-Oct-00	7	0.35	0.00	19-Oct-00	2	0.16	0.13
19-Jul-00	3	0.33	0.81	27-Jul-00	3	0.71	0.66	11-Oct-00	8	0.42	0.00	19-Oct-00	3	0.19	0.15
19-Jul-00	4	0.14	0.71	27-Jul-00	4	0.69	0.68	11-Oct-00	9	0.39	0.00	19-Oct-00	4	0.22	0.15
19-Jul-00	5	-0.04	0.69	27-Jul-00	5	0.70	0.73	11-Oct-00	8	0.09	0.08	19-Oct-00	5	0.25	0.13
19-Jul-00	6	0.17	0.61	27-Jul-00	6	0.75	0.74	11-Oct-00	9	0.09	0.11	19-Oct-00	6	0.27	0.13
19-Jul-00	7	0.15	0.56	27-Jul-00	7	0.68	0.76	11-Oct-00	10	0.10	0.08	19-Oct-00	7	0.30	0.14
19-Jul-00	8	0.31	0.47	27-Jul-00	8	0.67	0.72	11-Oct-00	11	0.10	0.11	19-Oct-00	8	0.33	0.12
19-Jul-00	9	0.49	0.32	27-Jul-00	9	1.05	0.51	12-Oct-00	12	0.11	0.07	19-Oct-00	9	0.36	0.10
19-Jul-00	10	0.83	0.33	27-Jul-00	10	0.89	0.47	12-Oct-00	1	0.09	0.14	19-Oct-00	10	0.43	0.08
19-Jul-00	11	1.44	0.50	27-Jul-00	11	0.83	0.36	12-Oct-00	2	0.08	0.08	19-Oct-00	11	0.39	0.06
20-Jul-00	12	1.68	0.65	28-Jul-00	12	0.71	0.30	12-Oct-00	3	0.08	0.10	19-Oct-00	12	0.38	0.05
20-Jul-00	1	1.24	0.49	28-Jul-00	1	0.61	0.25	12-Oct-00	4	0.09	0.05	20-Oct-00	1	0.26	0.05
20-Jul-00	2	0.89	0.25	28-Jul-00	2	0.61	0.23	13-Oct-00	10	0.13	0.04	20-Oct-00	2	0.22	0.05
20-Jul-00	3	0.44	0.38	28-Jul-00	3	0.59	0.20	13-Oct-00	11	0.16	0.04	20-Oct-00	3	0.21	0.04
20-Jul-00	4	0.03	0.17	28-Jul-00	4	0.66	0.18	13-Oct-00	12	0.19		20-Oct-00	4	0.25	0.05
20-Jul-00	5	0.16	0.71	28-Jul-00	5	0.73	0.15	13-Oct-00	1	0.25	0.04	20-Oct-00	5	0.15	0.04
20-Jul-00	6	0.36	0.12	28-Jul-00	6	0.72	0.13	13-Oct-00	2	0.27	0.04	20-Oct-00	6	0.09	0.03
20-Jul-00	7	0.34	0.05	28-Jul-00	7	0.66	0.12	13-Oct-00	3	0.28	0.05	20-Oct-00	7	0.06	0.03
20-Jul-00	8	0.27	0.04	28-Jul-00	8	0.71	0.12	16-Oct-00	2	0.00	0.00	20-Oct-00	8	0.10	0.03
20-Jul-00	9	0.62	-0.06	28-Jul-00	11	0.54	0.16	16-Oct-00	3	0.04	0.00	20-Oct-00	9	0.23	0.04
20-Jul-00	10	0.35	-0.03	28-Jul-00	12	0.45	0.22	16-Oct-00	4	0.10	0.00	20-Oct-00	10	0.25	0.07
20-Jul-00	11	0.33	-0.01	28-Jul-00	1	0.39	0.26	16-Oct-00	5	0.08	0.00	20-Oct-00	11	0.08	0.06
20-Jul-00	12	0.19	0.05	28-Jul-00	2	0.45	0.19	16-Oct-00	6	0.07	0.00	20-Oct-00	12	0.19	0.12
20-Jul-00	3	-0.02	0.76	28-Jul-00	3	0.54	0.14	16-Oct-00	7	0.06	0.04	20-Oct-00	1	0.18	0.13
20-Jul-00	4	0.24	0.77	31-Jul-00	11	0.45	0.11	16-Oct-00	8	0.07	0.05	20-Oct-00	2	0.20	0.21
20-Jul-00	5	0.15	0.86	31-Jul-00	12	0.45	0.12	16-Oct-00	9	0.06	0.08	20-Oct-00	3	0.25	0.39
20-Jul-00	6	0.07	0.90	31-Jul-00	1	0.48	0.22	16-Oct-00	10	0.07	0.07	20-Oct-00	4	0.28	0.65
20-Jul-00	9	0.44	0.35	31-Jul-00	2	0.47	0.34	16-Oct-00	11	0.05	0.08	20-Oct-00	5	0.31	0.69
20-Jul-00	10	0.66	0.37	31-Jul-00	3	0.44	0.39	17-Oct-00	12	0.04	0.07	20-Oct-00	6	0.37	0.60
20-Jul-00	11	1.16	0.39	31-Jul-00	4	0.42	0.47	17-Oct-00	1	0.03	0.06	20-Oct-00	7	0.43	0.33
21-Jul-00	12	1.34	0.25	31-Jul-00	5	0.46	0.43	17-Oct-00	2	0.03	0.05	20-Oct-00	8	0.50	0.25
21-Jul-00	1	1.16	0.40	31-Jul-00	8	0.50	0.38	17-Oct-00	3	0.01	0.01	23-Oct-00	12	0.16	0.08
21-Jul-00	2	1.24	0.42	31-Jul-00	9	0.65	0.27	17-Oct-00	4	0.00	0.00	23-Oct-00	1	0.15	0.11
21-Jul-00	3	1.24	0.32	31-Jul-00	10	0.72	0.30	17-Oct-00	5	0.00	0.00	23-Oct-00	2	0.15	0.17
21-Jul-00	4	1.36	0.46	31-Jul-00	11	0.86	0.26	17-Oct-00	6	0.00	0.00	23-Oct-00	3	0.15	0.28
21-Jul-00	5	1.33	0.58	01-Aug-00	12	0.94	0.18	17-Oct-00	7	0.00	0.00	23-Oct-00	4	0.14	0.37
21-Jul-00	6	1.30	0.35	01-Aug-00	1	0.89	0.15	17-Oct-00	8	0.00	0.00	23-Oct-00	5	0.13	0.35
21-Jul-00	9	0.47	0.05	01-Aug-00	2	0.76	0.13	17-Oct-00	9	0.04	0.00	23-Oct-00	6	0.18	0.26
21-Jul-00	10	0.33	0.13	01-Aug-00	3	0.69	0.10	17-Oct-00	10	0.05	0.03	23-Oct-00	7	0.30	0.18
21-Jul-00	11	0.40	0.26	01-Aug-00	4	0.70	0.10	17-Oct-00	11	0.05	0.03	23-Oct-00	8	0.41	0.16
21-Jul-00	12	0.29	0.39	01-Aug-00	5	0.68	0.07	17-Oct-00	12	0.08	0.04	23-Oct-00	9	0.40	0.13
21-Jul-00	1	0.18	0.65	01-Aug-00	6	0.67	0.06	17-Oct-00	1	0.08	0.05	23-Oct-00	10	0.32	0.11
21-Jul-00	2	0.15	0.93	01-Aug-00	7	0.68	0.06	17-Oct-00	2	0.09	0.06	23-Oct-00	11	0.42	0.10
21-Jul-00	3	0.16	1.11	01-Aug-00	8	0.69	0.07	17-Oct-00	3	0.15	0.06	23-Oct-00	12	0.30	0.11
21-Jul-00	4	-0.06	1.22	01-Aug-00	9	0.64	0.17	17-Oct-00	4	0.14	0.09	24-Oct-00	1	0.32	0.08
21-Jul-00	5	0.05	1.22	01-Aug-00	10	0.44	0.37	17-Oct-00	5	0.14	0.13	24-Oct-00	2	0.27	0.07
21-Jul-00	6	0.01	0.98	01-Aug-00	11	0.66	0.26	17-Oct-00	6	0.19	0.10	24-Oct-00	3	0.18	0.06
25-Jul-00	1	0.96	0.26	01-Aug-00	12	0.73	0.27	17-Oct-00	7	0.28	0.10	24-Oct-00	4	0.13	0.05
25-Jul-00	2	0.97	0.29	01-Aug-00	1	0.69	0.32	17-Oct-00	8	0.27	0.07	24-Oct-00	5	0.12	0.04
25-Jul-00	3	0.86	0.46	01-Aug-00	2	0.58	0.46	17-Oct-00	9	0.33	0.08	24-Oct-00	6	0.10	0.03
25-Jul-00	4	0.94	0.48	01-Aug-00	3	0.51	0.47	17-Oct-00	10	0.37	0.05	24-Oct-00	7	0.09	0.03
25-Jul-00	5	0.82	0.39	01-Aug-00	4	0.61	0.63	17-Oct-00	11	0.30	0.04	24-Oct-00	8	0.09	0.03
25-Jul-00	6	0.82	0.30	01-Aug-00	5	0.50	0.57	18-Oct-00	12	0.31	0.04	24-Oct-00	9	0.16	0.03
25-Jul-00	9	0.91	0.18	01-Aug-00	6	0.53	0.68	18-Oct-00	1	0.29	0.05	24-Oct-00	10	0.19	0.04
25-Jul-00	10	0.76	0.10	01-Aug-00	7	0.56	0.61	18-Oct-00	2	0.26	0.05	24-Oct-00	11	0.17	0.05
25-Jul-00	11	0.70	0.05	01-Aug-00	8	0.55	0.53	18-Oct-00	3	0.29	0.04	24-Oct-00	12	0.14	0.07
26-Jul-00	12	0.72	0.04	01-Aug-00	9	0.79	0.41	18-Oct-00	4	0.17	0.05	24-Oct-00	1	0.13	0.12
26-Jul-00	1	0.68	0.03	01-Aug-00	10	1.06	0.39	18-Oct-00	5	0.14	0.05	24-Oct-00	2	0.13	0.33
26-Jul-00	2	0.70	0.02	01-Aug-00	11	1.07	0.38	18-Oct-00	6	0.12	0.05	24-Oct-00	3	0.13	0.58
26-Jul-00	3	0.70	0.01	01-Aug-00	12	1.14	0.29	18-Oct-00	7	0.10	0.05	24-Oct-00	4	0.11	0.62
26-Jul-00	4	0.66	0.02	02-Aug-00	9	1.08	0.13	18-Oct-00	8	0.12	0.04	24-Oct-00	5	0.11	0.50
26-Jul-00	5	0.67	0.01	09-Oct-00	2	0.19	0.30	18-Oct-00	9	0.15	0.04	24-Oct-00	6	0.20	0.29
26-Jul-00	6	0.68	0.02	09-Oct-00	3	0.21	0.42	18-Oct-00	11	0.05	0.04	24-Oct-00	7	0.45	0.18
26-Jul-00	7	0.72	0.01	09-Oct-00	4	0.20	0.48	18-Oct-00	12	0.12	0.08	24-Oct-00	8	0.45	0.14
26-Jul-00	11	0.59	0.08	09-Oct-00	5	0.31	0.77	18-Oct-00	1	0.15	0.13	24-Oct-00	9	0.40	0.11
26-Jul-00	12	0.70	0.19	09-Oct-00	6	0.53	0.70	18-Oct-00	2	0.14	0.16	24-Oct-00	10	0.40	0.11
26-Jul-00	1	0.67	0.29	09-Oct-00	7	0.60	0.54	18-Oct-00	3	0.15	0.25	24-Oct-00	11	0.57	0.12
26-Jul-00	2	0.50	0.30	09-Oct-00	8	0.82	0.33	18-Oct-00	4	0.16	0.34	25-Oct-00	12	0.46	0.13
26-Jul-00	3	0.47	0.39	09-Oct-00	9	0.99	0.32	18-Oct-00	5	0.14	0.31	25-Oct-00	1	0.29	0.11
26-Jul-00	4	0.44	0.42	09-Oct-00	10	0.93	0.26	18-Oct-00	6	0.41	0.17	25-Oct-00	2	0.30	0.11
26-Jul-00	5	0.48	0.37	09-Oct-00	11	0.83	0.23	18-Oct-00	7	0.32	0.15	25-Oct-00	3	0.23	0.11
26-Jul-00	6	0.47	0.33	10-Oct-00	12	1.02	0.17	18-Oct-00	8	0.34	0.11	25-Oct-00	4	0.19	0.10
26-Jul-00	7	0.48	0.31	10-Oct-00	1	0.94	0.17	18-Oct-00	9	0.36	0.09	25-Oct-00	5	0.22	0.09
26-Jul-00	8	0.49	0.26	10-Oct-00	2	0.87	0.18	18-Oct-00	10	0.43	0.08	25-Oct-00	6	0.23	0.09
26-Jul-00	9	0.74	0.18	10-Oct-00	3	0.80	0.19	18-Oct-00	11	0.42	0.06	25-Oct-00	7	0.17	0.10

25-Oct-00	8	0.26	0.08	01-Nov-00	11	0.37	0.10	10-Nov-00	11	0.54	0.08	22-Nov-00	3	0.19	0.14
25-Oct-00	9	0.30	0.08	02-Nov-00	12	0.34	0.09	10-Nov-00	12	0.29	0.08	22-Nov-00	4	0.31	0.13
25-Oct-00	11	0.10	0.09	02-Nov-00	1	0.28	0.09	10-Nov-00	1	0.30	0.09	22-Nov-00	5	0.75	0.15
25-Oct-00	12	0.14	0.09	02-Nov-00	2	0.26	0.08	10-Nov-00	2	0.27	0.19	22-Nov-00	6	0.99	0.14
25-Oct-00	1	0.12	0.10	02-Nov-00	3	0.15	0.08	10-Nov-00	3	0.21	0.32	22-Nov-00	7	1.22	0.13
25-Oct-00	2	0.14	0.11	02-Nov-00	4	0.09	0.07	10-Nov-00	4	0.19	0.38	22-Nov-00	8	1.18	0.11
25-Oct-00	3	0.16	0.13	02-Nov-00	5	0.09	0.07	10-Nov-00	5	0.22	0.31	22-Nov-00	9	1.56	0.12
25-Oct-00	4	0.19	0.14	02-Nov-00	6	0.08	0.08	10-Nov-00	6	0.42	0.16	22-Nov-00	10	1.74	0.11
25-Oct-00	5	0.22	0.14	02-Nov-00	7	0.07	0.09	10-Nov-00	7	0.60	0.11	22-Nov-00	11	2.15	0.10
25-Oct-00	6	0.30	0.10	02-Nov-00	8	0.08	0.07	10-Nov-00	8	0.85	0.09	23-Nov-00	12	1.62	0.10
25-Oct-00	7	0.28	0.11	02-Nov-00	9	0.10	0.05	15-Nov-00	11	0.38	0.23	23-Nov-00	1	1.26	0.10
25-Oct-00	8	0.36	0.09	02-Nov-00	10	0.06	0.05	15-Nov-00	12	0.37	0.08	23-Nov-00	2	1.93	0.09
25-Oct-00	9	0.55	0.09	02-Nov-00	11	0.05	0.05	15-Nov-00	1	0.32	0.11	23-Nov-00	3	0.78	0.15
25-Oct-00	10	0.59	0.09	02-Nov-00	12	0.04	0.05	15-Nov-00	2	0.26	0.12	23-Nov-00	4	0.57	0.12
25-Oct-00	11	0.40	0.08	02-Nov-00	1	0.04	0.04	15-Nov-00	3	0.30	0.15	23-Nov-00	5	0.32	0.17
26-Oct-00	12	0.32	0.07	02-Nov-00	2	0.04	0.05	15-Nov-00	4	0.48	0.15	23-Nov-00	6	0.18	0.13
26-Oct-00	1	0.31	0.06	02-Nov-00	3	0.05	0.05	15-Nov-00	8	1.06	0.09	23-Nov-00	7	0.11	0.13
26-Oct-00	2	0.39	0.07	02-Nov-00	4	0.07	0.07	15-Nov-00	9	1.45	0.12	23-Nov-00	8	0.10	0.10
26-Oct-00	3	0.29	0.05	02-Nov-00	5	0.08	0.07	15-Nov-00	10	1.49	0.10	23-Nov-00	9	0.11	0.08
26-Oct-00	4	0.32	0.05	02-Nov-00	6	0.09	0.07	15-Nov-00	11	1.29	0.08	23-Nov-00	10	0.13	0.05
26-Oct-00	5	0.26	0.05	07-Nov-00	11	0.26	0.11	16-Nov-00	12	0.96	0.07	23-Nov-00	11	0.10	0.09
26-Oct-00	6	0.26	0.05	07-Nov-00	12	0.29	0.17	16-Nov-00	1	0.71	0.06	27-Nov-00	12	0.24	0.05
26-Oct-00	7	0.20	0.04	07-Nov-00	2	0.25	0.21	16-Nov-00	2	0.44	0.23	27-Nov-00	3	0.06	0.11
26-Oct-00	8	0.31	0.05	07-Nov-00	3	0.29	0.18	16-Nov-00	3	0.41	0.14	27-Nov-00	4	0.19	0.12
26-Oct-00	9	0.33	0.04	07-Nov-00	4	0.32	0.19	16-Nov-00	4	0.34	0.23	27-Nov-00	5	0.23	0.15
26-Oct-00	5	0.31	0.11	07-Nov-00	5	0.58	0.22	16-Nov-00	5	0.25	0.17	27-Nov-00	6	0.26	0.18
26-Oct-00	6	0.29	0.10	07-Nov-00	6	0.71	0.21	16-Nov-00	6	0.23	0.17	27-Nov-00	7	0.40	0.20
26-Oct-00	7	0.39	0.10	07-Nov-00	7	0.94	0.17	16-Nov-00	7	0.28	0.18	27-Nov-00	8	0.65	0.17
26-Oct-00	8	0.47	0.09	07-Nov-00	8	1.21	0.07	16-Nov-00	8	0.23	0.17	27-Nov-00	9	0.75	0.06
26-Oct-00	9	0.44	0.09	07-Nov-00	9	0.99	0.09	16-Nov-00	9	0.24	0.10	27-Nov-00	10	1.50	0.06
26-Oct-00	10	0.43	0.08	07-Nov-00	10	1.05	0.11	16-Nov-00	10	0.26	0.09	27-Nov-00	11	1.82	0.06
26-Oct-00	11	0.34	0.08	07-Nov-00	11	0.77	0.10	16-Nov-00	11	0.21	0.09	27-Nov-00	12	1.35	0.06
27-Oct-00	12	0.32	0.07	08-Nov-00	12	0.80	0.13	16-Nov-00	12	0.31	0.08	28-Nov-00	1	1.07	0.05
27-Oct-00	1	0.33	0.06	08-Nov-00	1	0.82	0.13	16-Nov-00	1	0.32	0.08	28-Nov-00	2	1.02	0.04
27-Oct-00	2	0.26	0.05	08-Nov-00	2	0.78	0.09	16-Nov-00	2	0.20	0.07	28-Nov-00	3	0.98	0.07
27-Oct-00	3	0.20	0.05	08-Nov-00	3	0.66	0.13	16-Nov-00	3	0.11	0.06	28-Nov-00	4	0.79	0.05
27-Oct-00	4	0.18	0.04	08-Nov-00	4	0.62	0.11	16-Nov-00	4	0.18	0.07	28-Nov-00	5	0.81	0.05
27-Oct-00	5	0.22	0.04	08-Nov-00	5	0.57	0.08	16-Nov-00	5	0.23	0.07	28-Nov-00	6	0.75	0.03
27-Oct-00	6	0.16	0.03	08-Nov-00	6	0.60	0.09	16-Nov-00	6	0.21	0.04	28-Nov-00	7	0.75	0.03
27-Oct-00	7	0.13	0.03	08-Nov-00	7	0.48	0.08	20-Nov-00	12	0.44	0.13	28-Nov-00	8	0.66	0.03
27-Oct-00	8	0.13	0.03	08-Nov-00	8	0.42	0.06	20-Nov-00	1	0.43	0.08	28-Nov-00	9	0.65	0.03
27-Oct-00	9	0.19	0.03	08-Nov-00	9	0.58	0.06	20-Nov-00	2	0.60	0.07	28-Nov-00	10	0.79	0.03
27-Oct-00	10	0.20	0.03	08-Nov-00	10	0.66	0.05	20-Nov-00	3	0.63	0.07	28-Nov-00	11	0.78	0.05
27-Oct-00	2	0.10	0.28	08-Nov-00	1	0.32	0.30	20-Nov-00	4	0.58	0.08	28-Nov-00	12	0.33	0.19
27-Oct-00	3	0.12	0.38	08-Nov-00	2	0.39	0.39	20-Nov-00	5	0.31	0.10	28-Nov-00	2	0.15	0.22
27-Oct-00	4	0.14	0.49	08-Nov-00	3	0.37	0.38	20-Nov-00	6	0.34	0.10	28-Nov-00	3	0.18	0.25
27-Oct-00	5	0.20	0.39	08-Nov-00	4	0.41	0.55	20-Nov-00	7	0.38	0.10	28-Nov-00	4	0.19	0.24
27-Oct-00	6	0.33	0.29	08-Nov-00	5	0.41	0.46	20-Nov-00	9	0.29	0.07	28-Nov-00	5	0.20	0.29
27-Oct-00	7	0.42	0.36	08-Nov-00	6	0.81	0.28	20-Nov-00	10	0.29	0.05	28-Nov-00	6	0.30	0.24
30-Oct-00	3	0.88	0.25	08-Nov-00	7	0.89	0.17	20-Nov-00	11	0.15	0.10	28-Nov-00	7	0.74	0.16
30-Oct-00	4	0.58	0.22	08-Nov-00	8	0.95	0.13	20-Nov-00	12	0.10	0.10	28-Nov-00	8	0.94	0.13
30-Oct-00	5	0.56	0.20	08-Nov-00	9	1.05	0.13	21-Nov-00	1	0.08	0.08	28-Nov-00	9	1.02	0.11
30-Oct-00	6	0.51	0.20	08-Nov-00	10	1.11	0.11	21-Nov-00	2	0.12	0.04	28-Nov-00	11	1.10	0.02
30-Oct-00	7	0.38	0.21	08-Nov-00	11	1.14	0.12	21-Nov-00	3	0.12	0.04	29-Nov-00	12	1.23	0.05
30-Oct-00	8	0.34	0.21	08-Nov-00	12	0.94	0.20	21-Nov-00	4	0.14	0.04	29-Nov-00	1	1.19	0.05
30-Oct-00	9	0.33	0.19	09-Nov-00	1	0.82	0.16	21-Nov-00	5	0.16	0.07	29-Nov-00	2	1.55	0.06
30-Oct-00	10	0.23	0.16	09-Nov-00	2	0.65	0.17	21-Nov-00	6	0.17	0.05	29-Nov-00	3	1.72	0.05
30-Oct-00	11	0.12	0.12	09-Nov-00	3	0.60	0.16	21-Nov-00	7	0.24	0.04	29-Nov-00	4	1.40	0.05
31-Oct-00	12	0.08	0.09	09-Nov-00	4	0.56	0.11	21-Nov-00	8	0.26	0.03	29-Nov-00	5	1.42	0.04
31-Oct-00	1	0.06	0.07	09-Nov-00	5	0.62	0.14	21-Nov-00	9	0.35	0.03	29-Nov-00	6	1.11	0.03
31-Oct-00	9	0.16	0.07	09-Nov-00	6	0.66	0.09	21-Nov-00	10	0.39	0.03	29-Nov-00	7	0.99	0.05
31-Oct-00	10	0.08	0.04	09-Nov-00	7	0.59	0.10	21-Nov-00	11	0.30	0.04	29-Nov-00	8	1.08	0.03
31-Oct-00	11	0.07	0.04	09-Nov-00	8	0.73	0.09	21-Nov-00	12	0.12	0.06	29-Nov-00	9	0.96	0.03
31-Oct-00	12	0.27	0.06	09-Nov-00	9	0.74	0.07	21-Nov-00	1	0.12	0.07	29-Nov-00	10	1.08	0.05
31-Oct-00	1	0.38	0.02	09-Nov-00	10	0.62	0.08	21-Nov-00	2	0.13	0.09	29-Nov-00	11	1.10	0.15
31-Oct-00	2	0.44	0.06	09-Nov-00	11	0.68	0.10	21-Nov-00	3	0.18	0.11	29-Nov-00	12	0.74	0.15
31-Oct-00	3	0.69	0.02	09-Nov-00	12	0.20	0.13	21-Nov-00	4	0.20	0.13	29-Nov-00	1	0.44	0.16
31-Oct-00	4	0.58	0.03	09-Nov-00	1	0.26	0.16	21-Nov-00	5	0.24	0.10	29-Nov-00	2	0.31	0.20
31-Oct-00	5	0.78	0.02	09-Nov-00	2	0.15	0.07	21-Nov-00	6	0.33	0.09	29-Nov-00	3	0.32	0.19
31-Oct-00	6	0.12	0.04	09-Nov-00	3	0.17	0.09	21-Nov-00	7	0.67	0.07	29-Nov-00	4	0.40	0.16
31-Oct-00	7	0.02	0.03	09-Nov-00	4	0.16	0.10	21-Nov-00	8	0.95	0.04	29-Nov-00	5	0.36	0.17
31-Oct-00	8	0.02	0.06	09-Nov-00	5	0.24	0.08	21-Nov-00	9	1.05	0.04	29-Nov-00	6	0.76	0.19
31-Oct-00	9	0.00	0.00	09-Nov-00	6	0.39	0.05	21-Nov-00	10	1.34	0.04	29-Nov-00	7	0.95	0.13
31-Oct-00	10	0.00	0.00	09-Nov-00	7	0.55	0.03	21-Nov-00	11	1.09	0.04	29-Nov-00	8	1.12	0.10
31-Oct-00	11	0.00	0.00	09-Nov-00	8	0.75	0.05	22-Nov-00	12	0.94	0.03	29-Nov-00	9	1.35	0.08
31-Oct-00	12	0.00	0.00	09-Nov-00	9	0.80	0.04	22-Nov-00	1	0.99	0.04	29-Nov-00	10	1.49	0.08
01-Nov-00	1	0.00	0.00	09-Nov-00	10	0.96	0.04	22-Nov-00	2	0.74	0.05	29-Nov-00	11	1.74	0.08
01-Nov-00	2	0.00	0.00	09-Nov-00	11	0.92	0.03	22-Nov-00	3	0.63	0.05	30-Nov-00	12	1.66	0.07
01-Nov-00	3	0.01	0.00	09-Nov-00	12	0.79	0.04	22-Nov-00	4	0.69	0.03	30-Nov-00	1	1.48	0.05
01-Nov-00	4	0.03	0.02	10-Nov-00	1	0.82	0.04	22-Nov-00	5	0.54	0.06	30-Nov-00	2	1.52	0.06
01-Nov-00	5	0.02	0.00	10-Nov-00	2	0.77	0.04	22-Nov-00	6	0.49	0.04	30-Nov-00	3	1.40	0.06
01-Nov-00	6	0.00	0.00	10-Nov-00	3	0.75	0.04	22-Nov-00	7	0.61	0.03	30-Nov-00	4	1.33	0.05
01-Nov-00	8	0.03	0.00	10-Nov-00	4	0.67	0.04	22-Nov-00	8	0.43	0.02	30-Nov-00	5	1.10	0.04
01-Nov-00	9	0.03	0.00	10-Nov-00	5	0.53	0.06	22-Nov-00	9	0.46	0.02	30-Nov-00	6	0.96	0.04
01-Nov-00	10	0.04	0.05	10-Nov-00	6	0.51	0.11	22-Nov-00	10	0.63	0.02	30-Nov-00	7	0.92	0.04
01-Nov-00	11	0.05	0.10	10-Nov-00	7	0.33	0.14	22-Nov-00	11	0.78	0.09	30-Nov-00	8	0.78	0.03
01-Nov-00	8	0.21	0.12	10-Nov-00	8	0.30	0.14	22-Nov-00	12	0.43	0.09	30-Nov-00	9	0.75	0.03
01-Nov-00	9	0.29	0.11	10-Nov-00	9	0.46	0.06	22-Nov-00	1	0.29	0.10	30-Nov-00	10	1.04	0.04
01-Nov-00	10	0.35	0.11	10-Nov-00	10	0.66	0.05	22-Nov-00	2	0.19	0.13	30-Nov-00	11	1.02	0.08

30-Nov-00	6	0.66	0.17	06-Dec-00	10	2.22	0.08	13-Dec-00	10	0.52	0.07	19-Dec-00	4	0.96	0.05
30-Nov-00	7	0.76	0.16	06-Dec-00	11	2.01	0.09	13-Dec-00	11	0.49	0.07	19-Dec-00	5	1.03	0.05
30-Nov-00	8	0.94	0.12	06-Dec-00	4	1.43	0.15	13-Dec-00	12	0.33	0.09	19-Dec-00	6	1.04	0.05
30-Nov-00	9	1.37	0.11	06-Dec-00	5	1.02	0.12	13-Dec-00	1	0.27	0.10	19-Dec-00	7	0.94	0.05
30-Nov-00	10	1.34	0.08	06-Dec-00	6	1.26	0.11	13-Dec-00	2	0.19	0.10	19-Dec-00	8	0.79	0.05
30-Nov-00	11	1.63	0.08	06-Dec-00	7	1.28	0.10	13-Dec-00	3	0.16	0.14	19-Dec-00	9	0.76	0.04
30-Nov-00	12	1.66	0.07	06-Dec-00	8	1.81	0.09	13-Dec-00	4	0.20	0.13	19-Dec-00	10	0.99	0.06
01-Dec-00	1	1.42	0.07	06-Dec-00	9	1.29	0.09	13-Dec-00	5	0.32	0.13	19-Dec-00	11	0.72	0.10
01-Dec-00	2	1.42	0.06	06-Dec-00	10	0.84	0.10	13-Dec-00	6	0.48	0.12	19-Dec-00	12	0.50	0.14
01-Dec-00	3	1.16	0.05	06-Dec-00	11	1.41	0.08	13-Dec-00	7	0.68	0.11	19-Dec-00	1	0.45	0.13
01-Dec-00	4	1.08	0.05	07-Dec-00	12	2.15	0.07	13-Dec-00	8	0.61	0.10	19-Dec-00	2	0.27	0.10
01-Dec-00	5	0.91	0.04	07-Dec-00	1	2.16	0.07	13-Dec-00	9	0.94	0.09	19-Dec-00	6	0.28	0.14
01-Dec-00	6	0.81	0.04	07-Dec-00	2	1.89	0.07	13-Dec-00	10	0.94	0.08	19-Dec-00	7	0.44	0.14
01-Dec-00	7	0.89	0.04	07-Dec-00	3	1.78	0.07	13-Dec-00	11	1.10	0.09	19-Dec-00	8	0.60	0.13
01-Dec-00	8	0.81	0.04	07-Dec-00	4	1.51	0.06	14-Dec-00	12	0.88	0.09	19-Dec-00	9	0.80	0.09
01-Dec-00	9	0.84	0.04	07-Dec-00	5	2.08	0.06	14-Dec-00	10	0.54	0.05	19-Dec-00	10	0.90	0.08
01-Dec-00	10	0.97	0.05	07-Dec-00	6	1.34	0.06	14-Dec-00	11	0.39	0.06	19-Dec-00	11	0.91	0.07
01-Dec-00	11	0.71	0.06	07-Dec-00	7	0.86	0.06	14-Dec-00	12	0.33	0.09	19-Dec-00	12	1.04	0.07
01-Dec-00	12	0.76	0.11	07-Dec-00	8	0.86	0.06	14-Dec-00	1	0.35	0.09	20-Dec-00	1	1.06	0.06
01-Dec-00	1	0.72	0.15	07-Dec-00	9	1.21	0.06	14-Dec-00	2	0.38	0.11	20-Dec-00	2	1.24	0.08
01-Dec-00	2	0.72	0.21	07-Dec-00	10	1.27	0.07	14-Dec-00	3	0.47	0.11	20-Dec-00	3	1.16	0.07
01-Dec-00	3	0.45	0.17	11-Dec-00	12	0.32	0.06	14-Dec-00	4	0.44	0.10	20-Dec-00	4	1.22	0.06
01-Dec-00	4	0.66	0.26	11-Dec-00	1	0.37	0.09	14-Dec-00	5	0.59	0.10	20-Dec-00	5	1.08	0.06
04-Dec-00	2		0.05	11-Dec-00	2	0.32	0.12	14-Dec-00	6	0.75	0.09	20-Dec-00	6	1.16	0.06
04-Dec-00	3	0.35	0.07	11-Dec-00	3	0.28	0.12	14-Dec-00	7	1.34	0.10	20-Dec-00	7	1.08	0.06
04-Dec-00	4	0.25	0.06	11-Dec-00	4		0.17	14-Dec-00	8	0.90	0.11	20-Dec-00	8	0.93	0.06
04-Dec-00	5	0.37	0.09	11-Dec-00	5		0.15	14-Dec-00	9	0.68	0.11	20-Dec-00	9	1.01	0.06
04-Dec-00	6	0.46	0.09	11-Dec-00	6	0.52	0.13	14-Dec-00	10	0.85	0.09	20-Dec-00	10	1.20	0.07
04-Dec-00	7	0.78	0.06	11-Dec-00	7	0.58	0.10	14-Dec-00	11	0.65	0.10	20-Dec-00	11	1.15	0.08
04-Dec-00	8	0.91	0.06	11-Dec-00	8	0.87	0.09	15-Dec-00	12	1.04	0.10	20-Dec-00	12	1.21	0.10
04-Dec-00	9	1.18	0.04	11-Dec-00	9	0.87	0.08	15-Dec-00	1	0.81	0.11	20-Dec-00	1	1.11	0.17
04-Dec-00	10	1.63	0.04	11-Dec-00	10	0.82	0.07	15-Dec-00	2	0.64	0.12	20-Dec-00	2	0.93	0.18
04-Dec-00	11	1.15	0.03	11-Dec-00	11	0.81	0.06	15-Dec-00	3	0.80	0.10	20-Dec-00	3	0.84	0.32
05-Dec-00	12	1.21	0.04	11-Dec-00	12	0.92	0.06	15-Dec-00	4	0.90	0.08	21-Dec-00	12	0.25	0.05
05-Dec-00	1	1.02	0.04	12-Dec-00	1	0.87	0.05	15-Dec-00	5	0.69	0.09	21-Dec-00	1	0.73	0.07
05-Dec-00	2	0.95	0.03	12-Dec-00	2	0.93	0.05	15-Dec-00	6	0.55	0.09	21-Dec-00	2	0.71	0.15
05-Dec-00	3	1.11	0.03	12-Dec-00	3	0.88	0.05	15-Dec-00	7	0.63	0.08	21-Dec-00	3	0.66	0.16
05-Dec-00	4	0.85	0.03	12-Dec-00	4	0.67	0.03	15-Dec-00	8	0.76	0.08	21-Dec-00	4	0.64	0.15
05-Dec-00	5	0.78	0.02	12-Dec-00	5	0.57	0.03	15-Dec-00	9	0.86	0.09	21-Dec-00	5	0.49	0.16
05-Dec-00	6	0.42	0.00	12-Dec-00	6	0.58	0.03	15-Dec-00	10	0.89	0.10	21-Dec-00	6	0.56	0.17
05-Dec-00	7	0.45	0.00	12-Dec-00	7	0.44	0.03	15-Dec-00	11	0.59	0.13	21-Dec-00	7	0.67	0.15
05-Dec-00	8	0.46	0.00	12-Dec-00	8	0.41	0.03	15-Dec-00	12	0.34	0.16	21-Dec-00	8	0.78	0.15
05-Dec-00	9	0.38	0.00	12-Dec-00	9	0.37	0.03	15-Dec-00	1	0.27	0.20	21-Dec-00	9	0.86	0.15
05-Dec-00	10	0.59	0.00	12-Dec-00	10	0.45	0.03	15-Dec-00	2	0.22	0.21	21-Dec-00	10	0.96	0.13
05-Dec-00	11	0.65	0.06	12-Dec-00	11	0.31	0.03	15-Dec-00	3	0.29	0.21	21-Dec-00	11	1.14	0.12
05-Dec-00	12	0.42	0.07	12-Dec-00	12	0.24	0.03	15-Dec-00	4	0.14	0.21	22-Dec-00	12	1.39	0.11
05-Dec-00	1	0.31	0.08	12-Dec-00	1	0.22	0.05	15-Dec-00	5	0.04	0.10	22-Dec-00	1	1.45	0.12
05-Dec-00	2	0.31	0.11	12-Dec-00	2	0.18	0.06	15-Dec-00	6	0.07	0.10	22-Dec-00	2	1.50	0.13
05-Dec-00	3	0.23	0.11	12-Dec-00	3	0.16	0.07	15-Dec-00	7	0.07	0.10	22-Dec-00	3	1.59	0.12
05-Dec-00	4	0.25	0.13	12-Dec-00	4	0.17	0.06	15-Dec-00	8	0.09	0.10	22-Dec-00	4	1.71	0.11
05-Dec-00	5	1.00	0.17	12-Dec-00	5	0.20	0.05					22-Dec-00	5	1.72	0.10
05-Dec-00	6	1.62	0.13	12-Dec-00	6	0.28	0.03	18-Dec-00	12	0.16	0.04	22-Dec-00	6	1.60	0.09
05-Dec-00	7	1.99	0.12	12-Dec-00	7	0.40	0.03	18-Dec-00	1	0.25	0.06	22-Dec-00	7	1.84	0.10
05-Dec-00	8	2.16	0.11	12-Dec-00	8	0.60		18-Dec-00	2	0.20	0.08	22-Dec-00	8	1.69	0.09
05-Dec-00	9	2.00	0.09	12-Dec-00	9	0.45	0.03	18-Dec-00	3	0.21	0.09	22-Dec-00	9	1.83	0.09
05-Dec-00	10	1.97	0.08	12-Dec-00	10	0.45	0.03	18-Dec-00	4	0.16	0.11	22-Dec-00	10	1.67	0.08
05-Dec-00	11	2.38	0.08	12-Dec-00	11	0.51	0.03	18-Dec-00	5	0.29	0.12	22-Dec-00	12	0.55	0.10
06-Dec-00	12	2.35	0.08	13-Dec-00	12	0.53	0.03	18-Dec-00	6	0.43	0.12	22-Dec-00	1	0.53	0.12
06-Dec-00	1	2.51	0.07	13-Dec-00	1	0.62	0.03	18-Dec-00	7	0.56	0.08	22-Dec-00	2	0.47	0.18
06-Dec-00	2	2.37	0.07	13-Dec-00	2	0.74	0.07	18-Dec-00	8	0.80	0.07	22-Dec-00	3	0.33	0.20
06-Dec-00	3	2.52	0.07	13-Dec-00	3	0.50	0.07	18-Dec-00	9	0.99	0.07	22-Dec-00	4	0.27	0.21
06-Dec-00	4	2.71	0.08	13-Dec-00	4	0.55	0.06	18-Dec-00	10	1.22	0.08	22-Dec-00	5	0.39	0.18
06-Dec-00	5	2.62	0.07	13-Dec-00	5	0.64	0.07	18-Dec-00	11	1.19	0.08	22-Dec-00	6	0.69	0.15
06-Dec-00	6	2.27	0.07	13-Dec-00	6	0.68	0.07	18-Dec-00	12	1.03	0.07	22-Dec-00	7	1.02	0.13
06-Dec-00	7	2.40	0.08	13-Dec-00	7	0.58	0.07	19-Dec-00	1	0.98	0.06	22-Dec-00	8	1.39	0.12
06-Dec-00	8	2.12	0.07	13-Dec-00	8	0.50	0.07	19-Dec-00	2	1.06	0.05	22-Dec-00	9	1.37	0.12
06-Dec-00	9	1.98	0.06	13-Dec-00	9	0.46	0.07	19-Dec-00	3	1.17	0.06	22-Dec-00	10	1.46	0.12



Appendix 6: PAN Measurements in ppb at the AIRMON station

Monthly average	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1992					2.37	1.74	2.02	1.3	1.38	0.85	0.57	0.79
1993	0.76	1.77	1.92	1.27	1.33	0.74	0.75	0.61	0.49	0.35	0.47	0.33
1994	0.47	1.45	1.77	0.91	0.8	0.98	1.16	0.69	0.64	0.88	0.68	0.91
1995	0.58	0.87	1.37	1.27	1.23	0.87	1.17	0.74	0.43	0.69	0.53	0.65

Monthly mini	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1992					0.17	0.04	0.06	0.04	0.09	0.02	0.02	0.04
1993	0.09	0.13	0.31	0.39	0.24	0.01	0.07	0.06	0.02	0.03	0.04	0.04
1994	0.04	0.14	0.15	0.13	0.13	0.12	0.26	0.15	0.05	0.07	0.05	0.06
1995	0.09	0.04	0.1	0.04	0.13	0.04	0.2	0.03	0.01	0.01	0.03	0.04

Monthly maxi	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1992					9.59	7.59	10.3	6.02	7.22	4.69	3.36	3.67
1993	2.74	7.18	8.9	3.59	8.85	5.03	3.69	2.94	2.73	3.36	1.7	2.02
1994	2.44	6.43	7.22	3.36	4.53	5.97	3.93	2.33	2.79	6.47	2.37	3.01
1995	2.65	6.96	6.84	5.25	5.74	3.75	2.2	4.59	1.92	6.69	2.94	2.13

All values in ppb

Appendix 7: Evaluation of H_2O, NH_3 and HNO_3 interference on NO_2- to-NO converter efficiency

Experiments were also conducted to evaluate the effect of H_2O, NH_3 and HNO_3 interference using a full factorial design. H_2O was generated and controlled using saturation method while NH_3 and HNO_3 were generated by permeation method (permeation rate NH_3: 426 ng/min and HNO_3: 163ng/min of which 68% of nitric acid) as was the NO_2 (permeation rate 575 ng/min). The temperature of the experiment was 15.5 ± 1 °C. The results (see last column Table 8 the ratio between the calculated over the measured NO_2 concentration) shows that among H_2O, NH_3 and HNO_3 only humidity produces a significant interference even for high

ammonia concentration. This results is confirmed by the ANOVA table where the only probability over 5 % is one for H_2O.

	Components						Calculated concentrations				Measured	
Test	NO_2 Nl/min	Saturated air Nl/min	Water Nl/min	NH_3 Nl/min	HNO_3 Nl/min	Dry Air Nl/min	Humidity g/Nm³	NH_3 ppb	HNO_3 ppb	NO_2 ppb	NO_2 ppb	TECO II
1	0.223	1.283	0	0	0	2.007	0	0	0	79.8	78	0.98
2	0.223	1.283	0	0	0.231	2.007	0	0	10.5	74.9	75	1.00
3	0.223	1.283	0	0.335	0	2.007	0	145.9	0	72.9	74.5	1.02
4	0.223	1.283	0	0.335	0.231	2.007	0	137.6	9.7	68.8	71	1.03
5	0.223	1.283	0.035	0	0	0.777	12.3	0	0	121.0	81	0.67
6	0.223	1.283	0.035	0	0.231	0.777	11.2	0	15.5	110.0	89.8	0.82
7	0.223	1.283	0.035	0.335	0	0.777	10.8	160.6	0	105.7	92	0.87
8	0.223	1.283	0.035	0.335	0.231	0.777	9.9	147.7	13.7	97.3	94	0.97

Table 8: Theoretical concentrations according to flows and permeation rates

	Sum of Squares	Degrees of freedom	Mean Square	F	Probability
HNO_3	0.009800	1	0.009800	49	0.090
NH_3	0.022050	1	0.022050	110	0.060
H_2O	0.061250	1	0.061250	306	0.036
1 by 2	0.000450	1	0.000450	2.25	0.3743
1 by 3	0.006050	1	0.006050	30.3	0.1145
2 by 3	0.009800	1	0.009800	49.	0.0903
Error	0.000200	1	0.000200		
Total SS	0.109600	7			

Table 9: Analysis of variance of interference

Appendix 8: Study of the influence of the components of expanded uncerainty

R(NOx)	R(NO)	r(NO,NOx)	RH	r(NO2,eff)	Eff	u(Eff)	Span	U(Span)	r(b1, b0)	SpanDrift	Linearity	HNO_2	r	LOSSES	PAN		U%	U	NO_2
60	10	NO	NO	NO	98%	0.2%	200	1%	NO	2%	2.5	YES	2	4.0%	NO	1	24.6%	12.3	51.0
60	10	NO	NO	YES	99.7%	2.0%	200	5%	YES	10%	2.5	NO	0.6	0.5%	YES	1	26.5%	13.2	50.2
60	10	NO	YES	NO	98%	2.0%	900	1%	YES	10%	0.5	YES	0.6	0.5%	YES	1	22.4%	5.7	51.0
60	10	NO	YES	YES	99.7%	0.2%	900	5%	NO	2%	0.5	NO	2	4.0%	NO	1	23.2%	11.6	50.2
60	10	YES	NO	NO	99.70%	0.2%	900	5%	NO	10%	0.5	NO	0.6	0.5%	YES	1	12.7%	6.4	50.2
60	10	YES	NO	YES	98%	2.0%	900	1%	YES	2%	0.5	YES	2	4.0%	NO	1	13.9%	7	51.0
60	10	YES	YES	NO	99.7%	2.0%	200	5%	YES	2%	2.5	NO	2	4.0%	NO	1	9.5%	4.8	50.2
60	10	YES	YES	YES	98%	0.2%	200	1%	NO	10%	2.5	YES	0.6	0.5%	YES	1	14.1%	7.2	51.0
60	40	NO	NO	NO	98%	0.2%	900	5%	YES	2%	0.5	NO	2	0.5%	YES	1	54.4%	5.5	20.4
60	40	NO	NO	YES	99.7%	2.0%	900	1%	NO	10%	0.5	YES	0.6	4.0%	NO	1	49.7%	10	20.1
60	40	NO	YES	NO	98%	2.0%	200	5%	NO	10%	2.5	NO	0.6	4.0%	NO	1	67.1%	13.8	20.4
60	40	NO	YES	YES	99.7%	0.2%	200	1%	YES	2%	2.5	YES	2	0.5%	YES	1	71.8%	14.4	20.1
60	40	YES	NO	NO	99.7%	0.2%	200	1%	YES	10%	2.5	YES	0.6	4.0%	NO	1	16.7%	3.4	20.1
60	40	YES	NO	YES	98%	2.0%	200	5%	NO	2%	2.5	NO	2	0.5%	YES	1	30.2%	6.2	20.4
60	40	YES	YES	NO	99.7%	2.0%	900	1%	NO	2%	0.5	YES	2	0.5%	YES	1	24.7%	5	20.1
60	40	YES	YES	YES	98%	0.2%	900	5%	YES	10%	0.5	NO	0.6	4.0%	NO	1	20.4%	4.2	20.4
110	10	NO	NO	NO	99.7%	2.0%	200	1%	NO	2%	0.5	NO	0.6	4.0%	YES	1	12.6%	12.6	100.3
110	10	NO	NO	YES	98%	0.2%	200	5%	YES	10%	0.5	YES	2	0.5%	NO	1	12.8%	13.2	102.0
110	10	NO	YES	NO	99.7%	0.2%	900	1%	YES	10%	2.5	NO	2	0.5%	NO	1	17.5%	17.6	100.3
110	10	NO	YES	YES	98%	2.0%	900	5%	NO	2%	2.5	YES	0.6	4.0%	YES	1	21.1%	21.4	102.0
110	10	YES	NO	NO	98%	2.0%	900	5%	NO	10%	2.5	YES	2	0.5%	NO	1	6.9%	7	102.0
110	10	YES	NO	YES	99.7%	0.2%	900	1%	YES	2%	2.5	NO	0.6	4.0%	YES	1	8.1%	8.2	100.3
110	10	YES	YES	NO	98%	0.2%	200	5%	YES	2%	0.5	YES	0.6	4.0%	YES	1	13.3%	13.6	102.0
110	10	YES	YES	YES	99.7%	2.0%	200	1%	NO	10%	0.5	NO	2	0.5%	NO	1	15.1%	15.2	100.3
110	40	NO	NO	NO	99.7%	2.0%	900	5%	YES	2%	2.5	YES	0.6	0.5%	NO	1	12.8%	9	70.2
110	40	NO	NO	YES	98%	0.2%	900	1%	NO	10%	2.5	NO	2	4.0%	YES	1	26.9%	19.2	71.4
110	40	NO	YES	NO	99.7%	0.2%	200	5%	NO	10%	0.5	YES	2	4.0%	YES	1	30.1%	21.2	70.2
110	40	NO	YES	YES	98%	2.0%	200	1%	YES	2%	0.5	NO	0.6	0.5%	NO	1	20.4%	14.6	71.4
110	40	YES	NO	NO	98%	2.0%	200	1%	YES	10%	0.5	NO	2	4.0%	YES	1	13.3%	9.4	71.4
110	40	YES	NO	YES	99.7%	0.2%	200	5%	NO	2%	0.5	YES	0.6	0.5%	NO	1	4.2%	3	70.2
110	40	YES	YES	NO	98%	0.2%	900	1%	NO	2%	2.5	NO	0.6	0.5%	NO	1	8.7%	6.2	71.4
110	40	YES	YES	YES	99.7%	2.0%	900	5%	YES	10%	2.5	YES	2	4.0%	YES	1	21.6%	15.2	70.2

All values in ppb unless indicated.

The expanded uncertainty is calculated according the equations given in "Elaboration of the model equations" and "uncerainty budget".

Bibliography

[1] EUROPEAN COUNCIL - Directive 1999/30/CE du conseil du 22 avril 1999 relative à la fixation de valeurs limites pour l'anhydride sulfureux, le dioxyde d'azote et les oxydes d'azote, les particules et le plomb dans l'air ambiant. L 163/41, Journal officiel des Communautés européennes, page 1, 1999.

[2] Norme internationale ISO 7996 :. "Qualité de l'air - Détermination des oxydes d'azote dans l'air ambiant - Méthode par chimiluminescence", 1985.

[3] GUIDE TO THE EXPRESSION OF UNCERTAINTY IN MEASUREMENT, International Organization for Standardization, 1995, ISBN 92-67-10188-9, Switzerland, 100 pg.

[4] ISO 5725, "Accuracy (trueness and precision) of measurement methods and results", International Organization for Standardization, 1994.

[5] ISO 13752, "Air Quality Assessment of uncertainty of a measurement method under field conditions using a second method as reference", International Organization for Standardization, 1998.

[6] ISO 6143, "Gas analysis – determination of the composition of calibration gas mixtures – comparison methods", ", International Organization for Standardization, 2001.

[7] Norme internationale ISO 6145-10. "Analyse des gaz - Préparation des mélanges de gaz pour étalonnage - Méthode par perméation". 2002.

[8] Norme internationale ISO 6144 . "Analyse des gaz - Préparation des mélanges de gaz pour étalonnage - Méthode volumétriques statique". 2002.

[99] R. D. Matthewa, R. F. Sawyer and R. W. Schefer, "Interferences in chemiluminescent measurements of NO and NO2 emissions from combustion systems", Env. Sci. and Technol., Vol. 11, n° 12, 1977.

[10] TATRY, V.GODET, Y., "Evaluation d'un analyseur d'oxydes d'azote NO, NO_2, NOx par chemiluminescence", Institut National de l'Environnement et des Risques INERIS, 1994.

[11] "Bericht über die Eignungsprüfung des immissionsmeβgerätes für stickoxide – Modell TE 42, Fa. Thermo Instrument Systems Gmbh. Testbericht – Nr. 17. September 1993", Eigungsprüfung, UmweltBundesAmt.

[12] Nodop, K., Rudolf, W., Hanssen, J. E., "NOx Monitors – Performance characteristics including interfering test within EMEP", R. Ballaman, R. gehrig, I. M. Kvalvaagnes, J. Schaug (eds) (1993), EMEP, Workshop on measurments of nitrogen-containing compounds, Les Diablerets, Switzerland, June 1993, EMEP/CCC-Report 1/93, Norvegian Institute for Air Research

[13] Troch, W., "Technische Evaluatie van 7 chemiluminescentie – NO/Nox monitoren", Dossier VMM/LA/GI/93/06, Vlaamse Milieumaatschappij, 1994.

[14] Winner A. M., Peters, J. F., Smith, J: P. and Pitts, J. N. Jr (1974), "Response of commercial Chemiluminescent NO-NO2 analysers to other nitrogen-containing compounds", Env. Sci. Technol. 8, 1118-1121.

[15] R. D. Matthewa, R. F. Sawyer and R. W. Schefer, "Interferences in chemiluminescent measurements of NO and NO2 emissions from combustion systems", Env. Sci. and Technol., Vol. 11, n° 12, 1977.

[16] Grosjean, D. and Harrison J. (1985b), "Response of chemiluminescent analysers and ultraviolt ozone analysers to organic air pollutant", Env. Sci. Technol. 19, 862-865.

[17] Notholt, J., Hjorth, J., Raes, F., "Formation of HNO2 on aerosol surfaces during foggy periods in the presence of NO and NO2", Atmospheric Environment, vol. 26A, page 211-217, 1992.

[18] Rembges, D., Duane, M., Hjorth, J.L., Bloem, J.J., Zaaiman, W., Larsen, B.R. "*PAN and Air Quality in Northern Italy (Ispra) Diurnal and Long-Term Trends*". 8th European Symposium "A Changing Atmosphere", EC, IGAC, EIPO, EUROTRAC, 17-20 Sep. 2001, Torino (I) - ORA/POST 62268

[19] M.GERBOLES, E. DIAZ, A. NORIEGA, *"Uncertainty calculation and implementation of the static volumetric method for the preparation of NO and SO_2 standard gas mixtures"*, Journal of Accreditation and Quality Assurance, 1998 vol. 3, p 69-78.

[20] PAYRISSAT,M., GERBOLES,M., SIEJA,B., DE SAEGER,E. "Quality Assessment of Ambient NO, NO2 and SO2 Measurements in European Monitoring Networks", European Commission, EUR Report 17671 E.

[21] GERBOLES, M., "Relation between the number of samplings and the accuracy of the ambient NO_2 annual average determined by passive samplers" poster presented at *The International Conference Measuring Air Pollution by Diffusing Sampling Montplellier France 26 – 28 September 2001.*

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