Parameters affecting the measurement of nitrogen oxides in flames

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Abstract

A generally used sampling system for the measurement of nitrogen oxides in flames or process gases is being investigated, considering the main influencing parameters. Those are: Concentration of gas sample, temperature of heated pipe, volumetric flow rate and moisture of gas sample. The results show that the system has a reasonably good linear relationship between the sampled and the measured NO_x concentrations, and the temperature of the heated pipe plays only a minor role. At a small volumetric flow rate of gas sample, the measured concentrations of nitrogen oxides are lower than their entry concentrations to the sampling system, and moisture content of gas sample intensifies the decrease of measured concentrations significantly, even at a high volumetric flow rate of the gas sample. Further experiments show that NO and NO_2 in the gas sample are lost mainly in the cooler, due to physical and chemical absorption.

Introduction

Emissions of nitrogen oxides into the atmosphere have been increasing steadily in this century, which causes photochemical smog, acid rain precursors and destruction of ozone layer in the stratosphere, furthermore forest disease, health injury of human beings and global warming.

Most of NO_x-pollution in the atmosphere is being attributed to industrial and domestic combustion processes. Many efforts have been made to minimize NO_x-emissions from combustion processes[1-3], and to investigate the formation mechanism of NO_x[4-6]. However, those papers do not report on the parameters which could influence the measurement of NO_x. Actually, it is known that the measurement of NO_2 in combustion systems is difficult. Some efforts were made to simulate the conversion of NO to NO_2 in the sampling system[7-8]. Johnson et al.[8] even suspected that the NO_2 measured by a sampling system was formed from NO during the sampling process, rather than originating from the combustion system itself, whereas others[9-10] concluded that NO_2 was well produced in the flame gas.

In our work[11] it was noticed that some parameters such as volume flow rate, moisture etc. could significantly affect the value of NO_2 measured by the sampling system. During the investigation of small domestic combustion processes, only a quite low volume flow rate can be sampled in order to avoid disturbing the flame structure. Furthermore, depending on the conditions, a burnt gas always consists of about 15-18% moisture. Therefore, if the NO_2 formed during the combustion process is to be determined, possible systematic measuring errors in the sampling system have to be found out first.

Experiments

A generally used sampling system[12-13] for measuring gas concentrations in a burnt gas is shown in Fig.1.

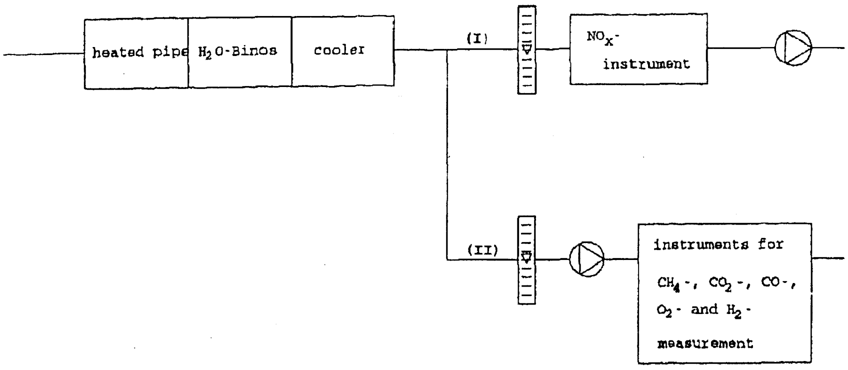

Fig. 1: Sampling system for gas concentration measurement

Burnt gas, containing mainly C_nH_m, CO_2, H_2O, O_2, CO and H_2 in the percent-range and NO_x in the ppm-range, is sucked through a heated pipe, a H_2O-Binos and a cooler, where the water is cooled down and thus separated from the gas sample. In the flow chart(Fig.1) this separation is necessary for further measurement of other components. After the cooler the moisture in the gas sample is lower than 1% at a volume flow rate of 13.5 l/h. Pipeline(I) and (II) are for concentation measurement of NO_x in the ppm-range, and of other gas components in the percent-range, respectively. The heated pipe is used to keep the temperature of the gas sample higher than its dew point, until its moisture content has been determined in the H_2O-Binos.

The most commonly used instrument to determine NO_x-levels is a converter/-chemiluminescent detector[14], which measures emission intensity of light radiation by the following reaction, accompanied by chemiluminescence:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu \tag{1}$$

This light radiation intensity is measured in a wavelength-range of 600 - 3000 nm, with a maximal intensity at about 1200 nm. By surplus of O_3, this radiation intensity is proportional to the NO-amount in the gas sample.

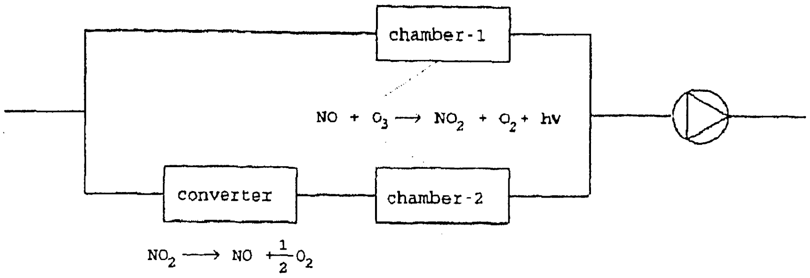

Fig. 2: Measuring Scheme of NO- and NO_2-Concentrations in the NO_x-instrument

According to Fig.2 the gas sample bifurcates into two flows. One stream passes directly chamber-1 where reaction (1) takes place, and from this the NO-level in the gas sample is being determined; the other stream first enters into a converter where NO_2-molecules are being converted into NO, and then all the NO is measured in chamber-2. This measured value is therefore the total value of NO_x, which is the sum of NO and NO_2, i.e. $[NO_2]=[NO_x]-[NO]$.

In this paper, the discussion is restricted to the measurement of nitrogen oxides, so the pipeline II in Fig.1 is closed.

In order to know NO- and NO_2-concentrations in the sampled gas exactly, standard calibration gas bottles of NO-N_2 and NO_2-air are adopted to produce the entry gas by diluting down to the needed NO- and NO_2-concentrations. In this work, the following parameters were to be investigated:

-- concentration of gas sample
-- temperature of heated pipe
-- volume flow rate of gas sample
-- H_2O-concentration in gas sample
-- location of the gas sample entrance

Results and discussions

For the sake of comparing the results under different conditions conveniently, a system-efficiency η and a transformation-degree η' have been introduced. Their definitions are as follows:

$$\eta\,(NO_i) = \frac{[NO_i]_{measured}}{[NO_i]_{input}} \qquad (i=1,2,x)$$

and

$$\eta'\,(NO_i) = \frac{[NO_i]_{measured} - [NO_i]_{input}}{[NO_x]_{input} - [NO_i]_{input}} \qquad (i=1,2)$$

where,

$[NO_i]_{measured}$: the measured NO_i concentration;
$[NO_i]_{input}$: the NO_i concentration in the sampled gasstream;
$[NO_x]_{input}$: the sum of NO and NO_2 concentrations in the sampled gasstream.

It is clear that a high system-efficiency $\eta(NO_i)$ and a low transformation-degree $\eta'(NO_i)$ are desired. The former may be lowered down because of many factors, which are being investigated in this paper. The latter describes conversion of part of the component which does not jet exist in the sampled gas but is being formed in the sampling system. The transformation-degree is only meaningful if the entry gas consists of only NO-O_2-N_2 or NO_2-O_2-N_2 molecules, that is, $[NO_x]=[NO]$ or $[NO_x]=[NO_2]$, respectively. In case that both NO- and NO_2-molecules are present in the sampled gas, the satuation is complex because this transformation-degree is coupled with the system-efficiency. In any case, however, the transformation-degree is negligibly small in comparison with the system-efficiency.

(1) Influence of NO_x concentration in the gas sample

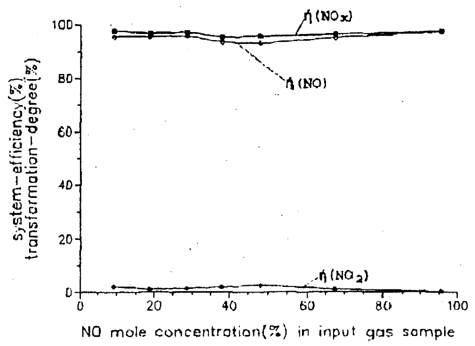

Fig.3: Influence of NO concentration

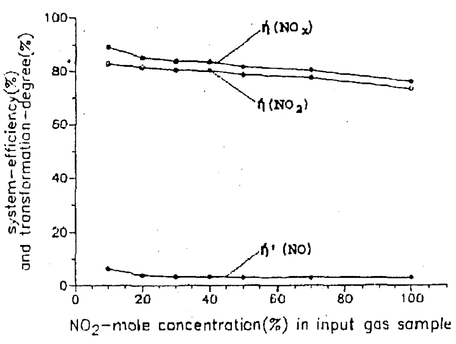

Fig.4: Influence of NO_2 concentration

Figs.3 and 4 show the influence of the entry concentration of NO and NO_2 on the system-efficiency and the transformation-degree, respectively. The results indicate that the system-efficiencies $\eta(NO)$ and $\eta(NO_2)$ are independent of the concentrations, and the transformationdegrees $\eta'(NO)$ and $\eta'(NO_2)$ are lower than 4%. This means that there exists a relatively good linear relationship between the measured and the probe entry concentrations in the sampling system, although the measured $\eta(NO_2)$ goes slightly down as the entry NO_2 concentration is increased. It is also noticeable that $\eta(NO)$ is greater than 95%, whereas $\eta(NO_2)$ reaches only about 80%. This phenomenon is going to be discussed later.

(2) Influence of the temperature of the heated pipe

As mentioned above, the temperature of the heated pipe is kept at above 80°C to prevent condensation of water from the gas sample. In the experiments[11-12], the gas sample flows through a 1.5 meter long heated pipe at a volume flow rate of 13.5 l/h. Its temperature is controlled at about 110 - 150°C.

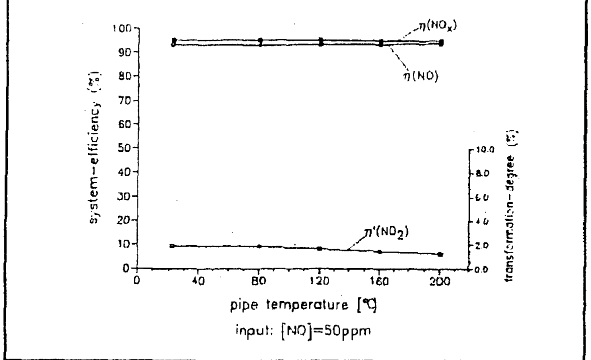

Fig.5: Influence of pipe temperature at $[NO]_{input} \approx 50ppm$

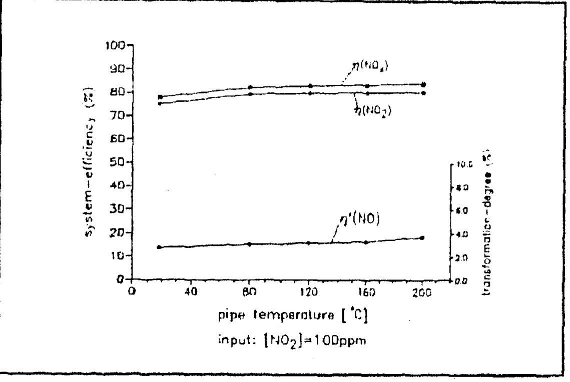

Fig.6: Influence of pipe temperature at $[NO_2]_{input} \approx 100ppm$

Figs.5 and 6 show the influence of pipe temperature on the system-efficiency and the transformation-degree. The data in Fig.5 were obtained with entry gas concentrations of $[NO]=48.2ppm$, $[O_2]=10.5\%$ and $[N_2]=89.5\%$. The measured $\eta(NO)$ is high and constant, and $\eta'(NO_2)$ is as small as negligible. The entry gas concentrations for Fig.6 were $[NO_2]=94.6ppm$, $[O_2]=4\%$ and $[N_2]=96\%$. It can be seen that $\eta'(NO)$ rises slightly as the pipe temperature increases. The formation of NO can be explained by reaction (2) because of the high N_2-content and a relatively large amount of NO_2 in the system:

$$\frac{1}{2}N_2+NO_2 \rightarrow 2NO \tag{2}$$

Reaction (2) is an endothermal reaction. As the temperature rises, the reaction shifts to the direction of NO-formation.

Comparing Fig.5 with Fig.6 it can be concluded that the NO-efficiency $\eta(NO)$ is higher than

95%, whereas the NO_2-efficiency $\eta(NO_2)$ reaches only about 80%; $\eta'(NO)$ increases very slightly with temperature.

(3) Influence of the volume flow rate of the gas sample

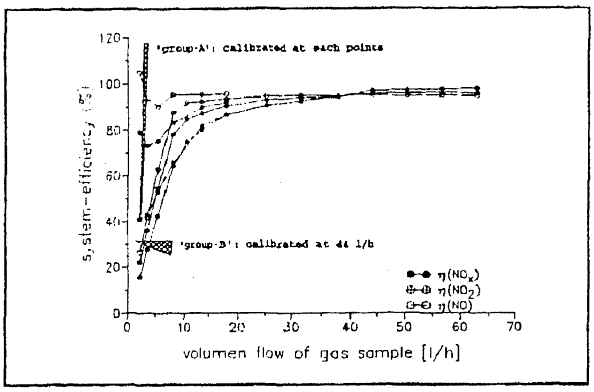

Fig.:7 Dependence of system-efficiency on the volume flow rate of gas sample with two calibration ways

Fig. 7 shows the influence of the volume flow rate on the system-efficiencies. In group-B the NO_x-instrument was calibrated at a volume flow rate of 44 l/h. Its efficiencies decrease strongly as the volume flow rate of the measured gas gets lower than 18 l/h. In group-A the NO_x-instrument was calibrated at each point. Nevertheless, the efficiencies of the measuring system are still low, and $\eta(NO_2)$ is always lower than $\eta(NO)$.

At a volume flow rate of 13.5 l/h the efficiency of this sampling system amounts to $\eta(NO)=92\%$ and $\eta(NO_2)=80\%$. Those efficiencies are in agreement with Figs.3 to 6 above.

For checking purpose, another NO_x-instrument (instrument-2) was applied, which can only be used if the volume flow rate of the gas sample is higher than 37 l/h. There is almost a complete efficiency of $\eta(NO)>98\%$ with instrument-2 (Fig.8).

From Figs.7 and 8 it can be seen that both NO_x-instruments have a high system-efficiency when the volume flow rate of the gas sample is higher than 37 l/h.

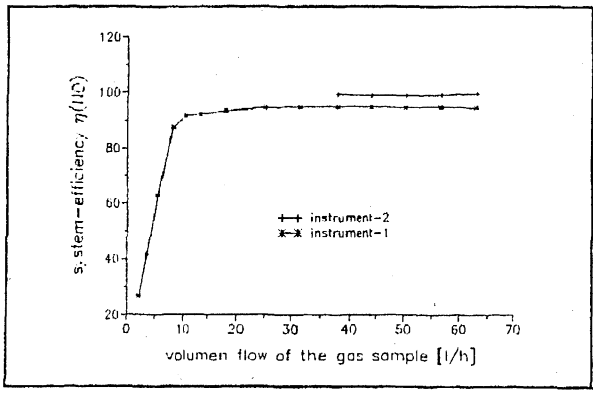

Fig.8: Comparing two instruments with regard to the influence of the volume flow rate of the gas sample

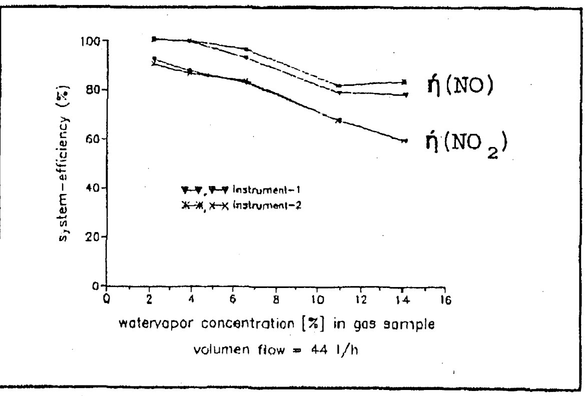

Fig.9: Comparing two instruments with regard to the influence of moisture content in the gas sample

Fig.9 shows further that even at a high volume flow rate of 44 l/h, moisture in the gas sample lowers down the system-efficiencies η(NO) and η(NO_2) very significantly.

(4) Influence of moisture in the gas sample

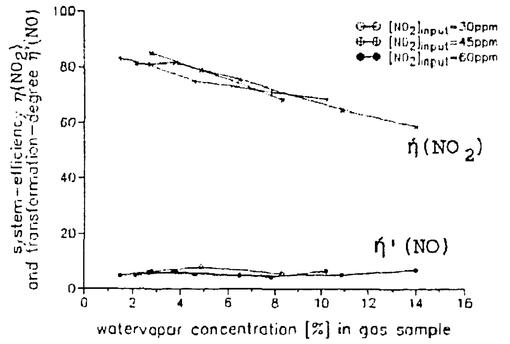

Fig.10: Influence of moisture in decreasing the system-efficiency of NO_2

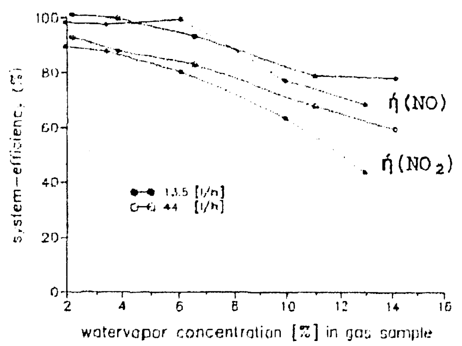

Fig.11: Influence of moisture and volume flow rate in decreasing the system-efficiencies

Fig.10 confirmed that the moisture in the gas sample decreases significantly the system-efficiency η(NO_2): The higher the moisture content in the gas sample, the lower the system-efficiency η(NO_2). Furthermore, Fig.11 shows that η(NO_2) decreases stronger than η(NO) does as the moisture content in the gas sample increases, and the system-efficiencies η(NO) and η(NO_2) decrease stronger at a smaller volume flow rate of the gas sample. That means, in the presence of moisture, compared to the NO-molecules, the NO_2-molecules are much more affected as regards decreasing of the system-efficiency. The longer the contact time of H_2O-molecules with the NO- and NO_2-molecules in the sampling system, the lower the system-efficiencies η(NO) and η(NO_2).

All these properties are in good agreement with the high water affinities of NO and NO_2. The former has a solubility of 7.34cc per 100 gram water at 0°C, and the latter decomposes in the waterphase[15]. The smaller the volume flow rate of the gas sample, the longer the contacting time in the cooler between them, and the lower the η(NO) and η(NO_2).

(5) Influence of the location of sample entrance

Further experiments were performed to find out where the NO- and NO_2-molecules get absorbed, destructed or converted inside the sampling system. A calibrated gas sample with [NO] $\approx$ 60ppm and [NO_2] $\approx$ 40ppm is fed to the system at different positions ("H"-, "C"- and "R"-entry)(Fig.12). In this comparison the system-efficiencies η(NO), η(NO_2) and η(NO_x) are still referred to the ratio of the measured and the sampled concentrations, but the 'system' here is shorter in case using "C"- and "R"-entry.

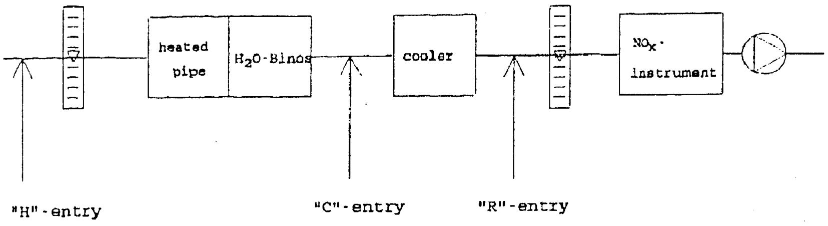

Fig. 12: Flowsheet for gas entry at different position of the sampling system

Tab. 1: Reduction of NO and NO_2 when feeding the gas sample at different positions to the sampling system

	η(NO) %	η(NO_2) %	η(NO_x) %
at 44 l/h:			
"R"-entry	100.5	99.0	99.8
"C"-entry	97.9	98.4	97.7
"H"-entry	95.5	93.7	94.7
at 13.5 l/h:			
"R"-entry	99.7	99.7	99.6
"C"-entry	96.3	84.6	91.5
"H"-entry	95.3	81.7	89.7

The results in Tab. 1 show that at the high volume flow rate of 44 l/h the η(NO), η(NO_2) and η(NO_x) are high enough; but at the volume flow rate of 13.5 l/h there is a considerable loss of NO_2 in the cooler (η(NO_2) = 84.6%), and also there are some losses in the heated pipe and H_2O-Binos where the temperature is held at 300°C.

Moreover, it was also noticed during the experiments that the pipeline material itself, its degree of absorptive saturation with the measuring gas, and the presence of condensate in the cooler exert important effects upon the system-efficiency. Silicon or PVC material is not suitable for the measurement of nitrogen oxides, as indicated already in the handbook of the instrument[14]. If a new Teflon pipe is used, the system will render accurate data only after it is saturated by the measuring gas. If there is already some condensate in the cooler, and if the metal plates for heat exchange in the cooler have a water film layer, this causes a lower $\eta(NO_2)$ and a higher $\eta'(NO)$, since there is some conversion of NO_2 to NO. The NO may be formed by the reactions:

$$2NO_2 \rightleftharpoons N_2O_4 \tag{3}$$

$$N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2 \tag{4}$$

$$3HNO_2 \rightleftharpoons 2NO + H_2O + HNO_3 \tag{5}$$

Reaction(3)[16] becomes effective when the temperature is lower than 100°C. Reactions(4) and (5)[17] take place at the interface of gas and liquid. The greater the interface area, the more NO is being formed from NO_2, and the higher the $\eta'(NO)$.

In view of all those influencing factors it should be stated, that all the data reported here were measured with saturated PTFE/stainless steel pipelines. The sampled gas was always dry except for the data group exhibiting the influence of moisture content, where a small amount of water may have been present in the cooler during the measurement.

Conclusions

It can be concluded that the sampling system used exhibits a fairly good linear relationship between the measured and the sampled NO_x values in the concentration range up to 100ppm. Influence of the temperature of the heated pipe is negligible. In the case of high NO_2-concentration, and with a large amount of N_2 in the gas sample, the endothermal reaction (2) may take place. Nevertheless, the transformation-degree of NO_2 to NO, $\eta'(NO)$, is still lower than 4%.

The system-efficiency $\eta(NO_i)$ is an important factor and must be taken into account. It is high for NO ($\eta(NO) > 92\%$), and relatively low for NO_2 ($\eta(NO_2) \approx 80\%$). This low system-efficiecy for NO_2 is associated with the volume flow rate of the gas sample. At a high volume flow rate of 37 l/h or more, $\eta(NO_2)$ reaches about 94%. Tab.1 shows that at the volume flow rate of only 13.5 l/h, the reducing effect on $\eta(NO_2)$ takes place mainly inside the cooler due to absorption in condensed phase.

If the gas sample contains higher water vapor concentration, not only $\eta(NO_2)$ but also $\eta(NO)$ decreases even at a high volume flow rate. The higher the moisture content in the gas sample, the lower the $\eta(NO_2)$ and $\eta(NO)$. $\eta(NO_2)$ decreases, however, stronger than $\eta(NO)$ does. This observation is to be explained by the high water affinity of NO and NO_2. NO is physically solved in water, and NO_2 is chemically absorbed, probably through the reactions (3,4,5) and due to the integral reaction equation:

$$NO_2 + \frac{1}{3}H_2O \rightarrow \frac{1}{3}NO + \frac{2}{3}HNO_3 \qquad (6)$$

One mole NO_2 forms through reaction (6) only 1/3 mole NO. This is one reason why measured NO_x-values ($[NO_x]=[NO]+[NO_2]$) was found always lower than the sampled NO_x-concentraion. If the moisture content in the gas sample is about 18% as for near-stoichiometric combustion of methane with air, $\eta(NO_2)$ is only about 50% for 44 l/h flow rate and 30% for 13.5 l/h, respectively, according to an extrapolation from Fig.11. Also from Fig.11 $\eta(NO)$ can be extrapolated to 72% and 60% at the volume flow rate of 44 l/h and 13.5 l/h, respectively. Hence, the correction factors to be applied depend on the sampling system, mainly the type of the cooler and the volume flow rate through the sampling line.

Another solution to the problem is, as suggested in some literature, to use hot tubing direct to the converter, without water condensation before. However, because of the presence of watervapor in the measuring chamber of the NO_x-analyser, certain correction factor must also be used. This correction factor is about -1.5%/%H_2O for both chambers in Fig. 2, i.e. it refers to both $\eta(NO)$ and $\eta(NO_2)$. It also differs from instrument to instrument[13-14].

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