

# **Test of the Boreal Gasfinder 2.0 for methane measurements and Vaisala AMT-100 sensor for ammonia measurements in animal houses**

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Report 295





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# Colophon

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## Abstract

Emissions from animal housings are modelled or measured. Modelling has to date a low precision, measuring is however costly. Reduction in costs can be achieved by using instruments that cheaper or less demanding in costs of maintenance, installation and calibration. The Boreal Gasfinder 2.0 Tunable Diode Laser (TDL) can potentially replace a gas chromatograph for measuring methane concentrations. The Vaisala AMT 100 sensor is far less costly than a  $\text{NO}_x$  monitor preceded by a converter. Both instruments were tested in a climate controlled room with variation in temperature, relative humidity,  $\text{CO}_2$  concentration,  $\text{CH}_4$  concentration and  $\text{NH}_3$  concentration. Final tests took place in a cow house under normal operating conditions. The Boreal TDL has an excellent linearity between 20-750 ppm.m  $\text{CH}_4$ . The relative accuracy is 2.3%. Path averaged concentrations are estimated 30% lower than the standard (GC). There is no influence of temperature or humidity detected on the signal. There is no interference from  $\text{CO}_2$  or  $\text{NH}_3$  on the signal. Tests in the cow house reveal that there is possibly saturation of the absorption wavelength at values larger than 2000 ppm.m  $\text{CH}_4$ . This would limit the path length in animal houses with concentrations up to 100 ppm to 20 m at maximum. The Vaisala sensor shows an accuracy larger than 20% as claimed by Vaisala. Results are much better when concentrations lower than 1 ppm  $\text{NH}_3$  are avoided as are situations with relative humidity larger than 90%. The linear range (taking the large standard deviation into account) extends only between 1 and 30 ppm  $\text{NH}_3$ . A larger range asks for calibration of the non linear response for concentrations between 30 and 100 ppm  $\text{NH}_3$ . The sensor is susceptible to the relative humidity and the concentration of  $\text{CO}_2$ . Changes in software and adding a preconcentration unit might improve the instrument for measuring in animal houses. The instrument can be used to for alarm monitoring, when demands in accuracy and precision are less than for emission monitoring.

Key words: ammonia, methane, sensor, tunable diode laser, TDL, interference, test, animal-house.



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# 1 Introduction

Gaseous emissions of agricultural activities got increasing attention after the mid eighties. Main emphasis was focussed on ammonia emissions after discovering their detrimental effect caused by deposition on terrestrial and aquatic ecosystems. In the nineties of last century, the issue of global warming emerged. Agriculture in the Netherlands is responsible for 91% of national ammonia emissions (134 kton per year), 44% of methane emissions (413 kton per year), 48% of nitrous oxide ( $\text{N}_2\text{O}$ ) emission (23 kton per year) and 20% of fine dust (PM-10) (9.5 kton per year) (Milieucompendium, 2003). So quantification of emissions of ammonia and greenhouse gases from agriculture and studies on mitigation of these emissions are important on a national scale. Early methods of quantifying emission relied on wet chemical analysis and passive analysis in conjunction with estimation of the ventilation rate. To date, emission measurements rely on converter- $\text{NO}_x$  monitor techniques, or opto-acoustic methods to measure ammonia emissions and direct measurements of greenhouse gases with a GC or off line sampling in evacuated canisters and subsequent analysis with GC (Mosquera *et al*, 2002).

Recent analysis of measuring protocols for agricultural emissions point to the need for emission measurements in more animal housings than in the past and larger intervals between the measurements at one site to avoid autocorrelation of the data (Hofschreuder *et al*, 2003). This approach asks for a flexible measuring set up, that is easily installed, low weight, and has minimum need for calibration. Low purchase and operating costs are also favourable. This study focuses on an alternative for GC analysis of methane, a technique, which is rather demanding on operating costs and maintenance.

Instruments based on a physical measuring principle have the potential to fulfil the requirements. Methods based on the use of powerful  $\text{CO}_2$  lasers have low detection limits, but are only commercial available for opto-acoustic  $\text{NH}_3$  measurements. Tunable diode lasers (TDL) in combination with White cells are used for many years but require liquid nitrogen cooling and much surveillance and are expensive. Fourier Transform InfraRed (FTIR) is expensive and DOAS is expensive and has too high detection levels for the mentioned gases. The Boreal Gasfinder (TDL) is an instrument that does not need liquid nitrogen for cooling and is easily set up. Open path detection of absorption offers path averaged concentrations without the need of multiple nozzle sampling lines. Set-up, maintenance and need for calibration are much smaller than for GC analysis of methane. Given this consideration a study was carried out to test the TDL for measuring methane. The objective was to assess its performance under practical conditions in animal housings.

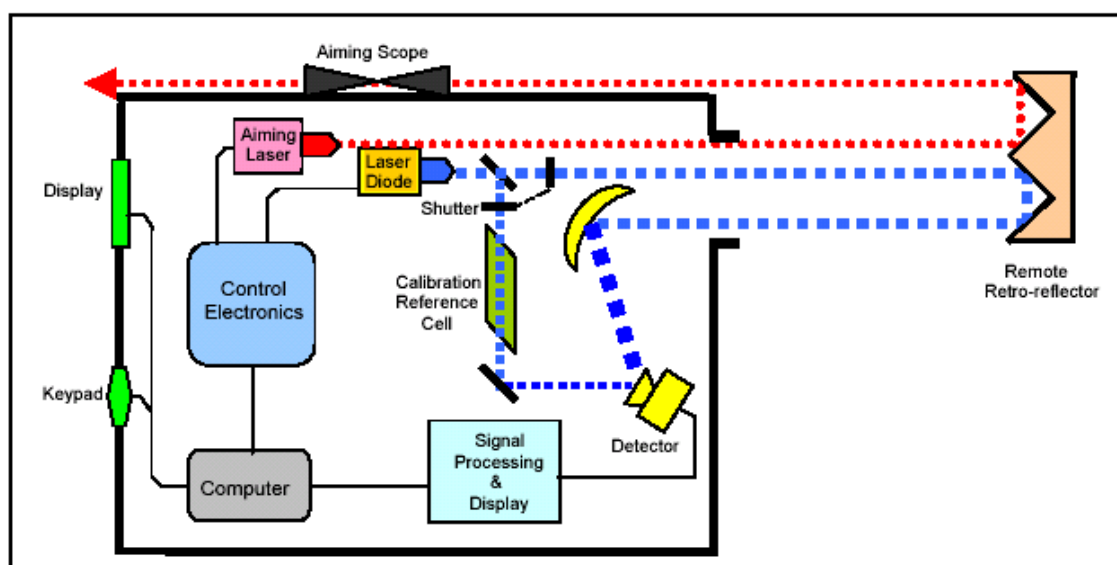
At the start of the experiments, a Vaisala AMT 100 ammonia sensor was kindly provided by the vendor. The sensor may provide a much cheaper and less complicated means of measuring ammonia concentrations in animal houses in the future. It was decided to test this instrument as well as  $\text{NH}_3$  concentrations were already provided for testing the possible interference on the TDL.



## 2 Methods

### 2.1 The Boreal Laser Inc. Gasfinder 2.0 TDL open path monitor

A scheme of the Boreal TDL is derived from the manual provided by the manufacturer and presented in figure 2.1.



**Figure 2.1** Diagram of the Boreal Gasfinder 2.0

The left part of the diagram contains the hardware (transmitter, receiver, computer and control facilities) in the temperature conditioned housing of the instrument. The right part represents the open path and the retroreflector. The choice of type of reflector is dependent on the desired optical path. Traffic tape is used for distances up to 10m, grey reflective tape and white reflective tape performed equally well for distances up to 30 m. For distances between 50 and 70 m one 1'' cornering cube is used. Other ranges were not met during the experiments.

The laser light emitted from the transceiver unit propagates through the experimental facilities or through the animal house to the retroreflector. There the light is returned and focused on a photodiode detector. Simultaneously a part of the laser beam is passed through a gas cell filled with a specified concentration of methane and led to the detector to provide a continuous calibration signal. The calibration signal is compared to factory settings. Proper functioning of the instrument is warranted when the signal is within a preset range. The light is emitted in a narrow spectrum around a dominant absorption line for  $\text{CH}_4$ . This spectrum has some wave form. The wave form of the light passing through the reference cell and the wave form the light received from the reflector are compared. With the same absorption by methane in the reference cell and in the atmosphere between transducer and mirror, the waveform on the receiver will be identical. Distortion of the wave form can be caused by much higher or much lower absorption by methane, interference of gases with absorption lines close to the absorption line for  $\text{CH}_4$  and light scattering on aerosols. This comparison of waveform is done using a statistical  $R^2$  test. The

higher  $R^2$  is, the more accurate the results are. Table 2.1 derived from the operation manual indicates the relation between  $R^2$  and accuracy.

**Table 2.1** Relation between  $R^2$  and accuracy for the Boreal Gasfinder, according to the manufacturer.

$R^2$	Reading accuracy
< 0.05	$\pm 100 \%$
0.1	$\pm 70 \%$
0.15	$\pm 50 \%$
0.3	$\pm 25 \%$
0.4	$\pm 20 \%$
0.5	$\pm 15 \%$
0.7	$\pm 10 \%$
0.9	$\pm 5 \%$
>0.95	$\pm 2 \%$

Overall influence of atmospheric conditions is accounted for by monitoring the light intensity.

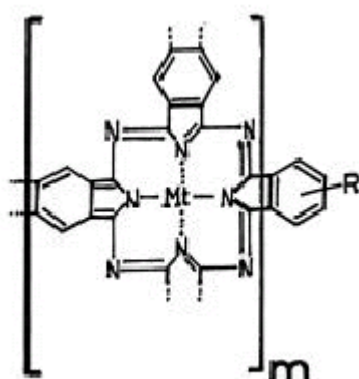
This intensity influences the amplitude of the wave but not the wave form.

The absorption of light by methane is related to the light intensity and the methane concentration according to Lambert-Beers law. The signal is converted into ppm.m or ppm (path average concentration) when the path length is inserted in the processor.

## 2.2 The Vaisala AMT 100 sensor

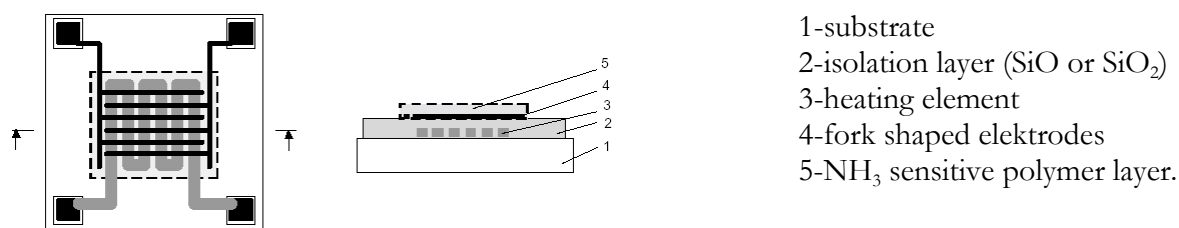
Vaisala developed a detector for measuring ammonia (Ammonicap) with a selected polymer coating to reach a specific response for ammonia. The polymer acts as a di-electrical layer of a capacitor. A change capacity (di-electrical constant) of the capacitor with the polymer caused by absorption of ammonia is measured. The characteristics of the polymer are not given.

Krutovertsev et al ([www.pnc.ru/conf/sensor99/sensor99PPc.pdf](http://www.pnc.ru/conf/sensor99/sensor99PPc.pdf)) provide information on a Russian patent, using phthalocyanine polymer with copper doping for this purpose. (see figure 2.2).



**Figure 2.2** Structure of the polymer layer for specific detection of  $\text{NO}_x$ ,  $\text{H}_2\text{S}$  and  $\text{NH}_3$ . The metal molecule Mt consists of Fe for  $\text{NO}_x$ , Ni+Cu for  $\text{H}_2\text{S}$ , and of Cu for  $\text{NH}_3$ . (Krutovertsev et al).

A scheme of the lay-out of a sensor is presented in figure 2.3. The Vaisala sensor may be different because change in capacity is measured instead of change in resistance.



**Figuur 2.3** Sensor design for a NH<sub>3</sub> sensor based on measuring the change in resistance on a chip.

The response of this type of sensor can be fast because of the short distance of diffusion for the gas. Based on this technology, which can be different from the Vaisala design, possible interference can be expected from polar molecules like H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub>S. Vaisala claims no interference for the AMT-100 sensor.

Technical specifications mention a warm up time of 3 minutes, a operation range of  $-40$ - $+60$  °C and 0-100 % Relative Humidity (non-condensing) and a measuring range of 0-100 ppm (this sensor) or 0-1000 ppm. The response time ( $t_{50}(0->1000 \text{ ppm})$ ) should be less than 90 seconds for the 0-1000 ppm sensor. This response time is not provided for the 0-100 ppm sensor but will probably be comparable to that of the 0-1000 ppm sensor.

## 2.3 Test design

Main goal of the test of the Boreal Gasfinder was to see if this instrument performed well in measuring path averaged concentrations of methane in animal houses. Variation of important gases and temperature and humidity within animal houses in the Netherlands are presented in table 2.2.

**Table 2.2** Range of gas concentrations (in ppm), temperature and humidity in Dutch animal housings

Component	Manure tank covered	Pig house mechanical ventilation	Cow house natural ventilation	Poultry mech/nat. ventilation
NH <sub>3</sub>	20-100	1-50	0.2-10	0.1-100
CH <sub>4</sub>	1,000-9,000	4-500	10-100	2.1-20
CO <sub>2</sub>	2,000-8,000	450-4,000	450-1,500	900-4,000
Temperature °C	-5- 35	10-30	5-30	10-30
Relative humidity	80-100	60-100	60-100	60-100

The goals of the experiment were:

- Compare the performance of the Boreal Gasfinder to the results of GC measurements of methane as a reference.
- Detect possible influences of temperature and humidity on the sensitivity of the instrument.
- Detect possible interference from  $\text{NH}_3$  and  $\text{CO}_2$  in the signal.

Detection of the influence of aerosol on the measurements would also be of interest, but were skipped because of limited funding.

From the statistical point of view a design of experiments with independent variation of all variables in a random sequence would be the best. Based on the available funds, it was decided to vary temperature and humidity independent from each other and from the gas concentrations. The gas concentrations were coupled as is strongly the case in the animal house, as they heavily depend on the ventilation rate. Patterns are however not totally coupled as they also depend on animal activity and feeding behaviour. An overview of target values for gas concentrations for the experiments is presented in table 2.3.

**Table 2.3** Target values for combinations of gas concentrations (ppm) in the experiments.

Component	K1	K2	K3	K4
$\text{CO}_2$	500	1.000	5.000	10.000
$\text{CH}_4$	5	10	50	100
$\text{NH}_3$	0,1	5	10	50

All combinations of gas concentrations were combined with all temperatures and all settings of relative humidity as presented in table 2.4.

**Table 2.4** Values for temperature and relative humidity independently set for all experiments.

Relative humidity	60%	80%	90%	95%
Temperature °C	5 °C	10 °C	20 °C	30 °C

The combinations made up a total of  $4 \times 4 \times 4 = 64$  experiments. After reaching equilibrium, each experiment lasted about 30 minutes.

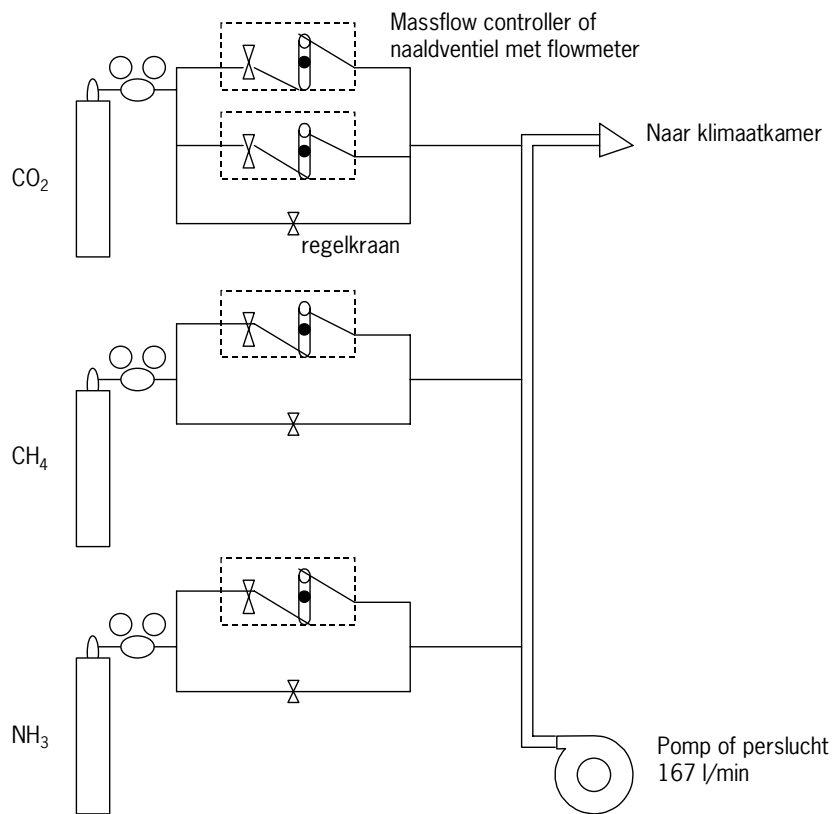
Main problem in using coupled concentration levels is, that interference of  $\text{NH}_3$  or  $\text{CO}_2$  or both on the methane signal can be detected, but not be attributed to the interfering gas. For that reason a small set of additional experiments was planned. In this set the methane concentration was set low (5 ppm) to see the maximum effect and the concentrations of  $\text{NH}_3$  and  $\text{CO}_2$  were set low (0.1 ppm) for  $\text{NH}_3$  and high (10,000 ppm) for  $\text{CO}_2$  or the other way around high (50ppm) for  $\text{NH}_3$  and low (500 ppm) for  $\text{CO}_2$  and both high (50 and 10,000 ppm). The temperature and relative humidity were set at 10 °C and 20 °C respectively 60% and 95%. This results in  $3 \times 2 \times 2 = 12$  additional experiments to detect a possible cause for interferences.

The results is a set of 76 experiments out of a set of 1024 possible combinations.

The ultimate test is in placing the instruments in a cow house. This was done during 5 days.

## 2.4 Experimental set-up

All experiments under controlled conditions were performed in a temperature and humidity controlled chamber of 4\*3\*3.5 m. The chamber was fitted with a heater, a cooler, steam injection and a fan that was running continuously to get uniform conditions in temperature humidity and concentrations. Gases were introduced from bottles of pure gas and controlled by means of pressure regulators and needle valves. The gas flow could be read from flow meters. Additional high throughput valves were added to shorten the time to get an equilibrium gas concentration when switching from low to higher concentrations. All gases were introduced in a flow of 167 lpm air, drawn from the building. Variations in background concentration of CH<sub>4</sub>, CO<sub>2</sub> and NH<sub>3</sub> did influence the concentrations in the chamber at low concentration levels. The design of the gas delivery system is presented in figure 2.4



**Figure 2.4** Gas delivery system for the experiments in the controlled chamber.

The actual system differed a little bit from this design. There was no second needle valve for CO<sub>2</sub> as the coarse valve was good enough to control CO<sub>2</sub> flows for the higher concentrations. The coarse valves for CH<sub>4</sub> and NH<sub>3</sub> were skipped as it appeared to be sufficient to fully open the needle valves to get higher flows. The chamber was operated in over pressure, with an passive exhaust to ambient air. When switching to low concentrations the chamber was opened and a high capacity fan transported the air through a duct outside the building.

The concentration of methane in the chamber was measured by a gas chromatograph placed next to the chamber. The gas chromatograph was calibrated two times with zero air and three calibration gases (60, 80 and 100 ppm) made by dilution out of one cylinder with high concentration  $\text{CH}_4$  calibration gas ( $205\text{ppm} \pm 4\text{ ppm}$ ).

The concentration of ammonia was determined by using a converter and  $\text{NO}_x$  monitor. The  $\text{NO}_x$  monitor was calibrated six times with zero air and NO calibration gas (40 ppm). The conversion efficiency of the converter was determined at 95% respectively 94 % for the two converters used during the experiment.

The concentration of  $\text{CO}_2$  was measured using a Licor  $\text{CO}_2$  monitor. The monitor was calibrated with zero gas and 1025 ppm  $\text{CO}_2$ .

For concentration of  $\text{CO}_2$  higher than 3,000 ppm a dynamic dilution system with a calibrated dilution factor was used to keep concentrations within the measuring range of the instrument. A view of the experimental set up is presented in figure 2.5.



**Figure 2.5** Reference instruments for the experiments; Converter with  $\text{NO}_x$  monitor and data acquisition system (rack), gas chromatograph, air dilution system for  $\text{CO}_2$  monitor (next to GC) and  $\text{CO}_2$  monitor (just visible)

At the start of the experiments a chip based ammonia monitor was kindly provided by Vaisala. This monitor (Vaisala AMT100) was placed inside the chamber. Data from this sensor can be compared to those from the  $\text{NO}_x$  monitor. No additional experiments were planned to study cross sensitivity for this instrument.

The Boreal Gasfinder was placed in the controlled chamber with a diagonal path length of 4 m. White(/red) reflective traffic tape was used as a retroreflector providing light value readings of about 7,000-8,000 for this distance.

The Vaisala monitor and sensors for temperature and relative humidity (Rotronic) were attached to a chair inside the room (see figure 2.6). The Rotronic was calibrated prior to the experiments.





**Figure 2.6** Boreal TDL, Viasala ammonia sensor, Rotronic and pressure sensor inside the controlled chamber

After the experiments under controlled conditions the TDL and the GC were transported to experimental cattle farm de Marke (Gld) the Netherlands. This is an animal house with a length of 70 metres. The path of the TDL was next to the sampling line for gases. This sampling line was fitted with 6 nozzles to sample air at 0.5 lpm at regular distances from the animal house. The air was led through slightly heated tubing to the gas chromatograph. The concentration of ammonia was analysed by a converter  $\text{NO}_x$  monitor and the ventilation rate determined by a constant tracer injection method separately for other purposes. Wind speed and wind direction were measured as well. Detailed information on the continuous traditional measurements at this farm and information on the farm can be obtained from Koskamp, G.J *et al.* (2004). Time needed to obtain a suitable reflector for the path length of 70 m (1"cube) restricted the measurements to 5 days.

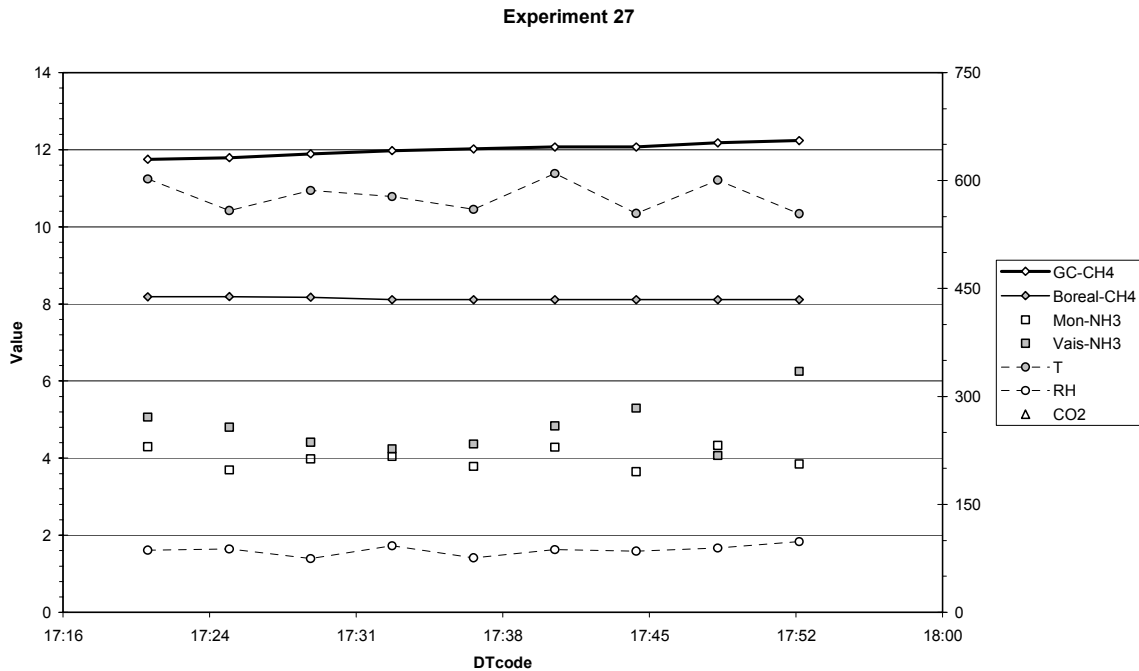


## 3 Results

### 3.1 Data handling

All data were processed according to this procedure;

- Determine the change in sensitivity of the reference instruments using the calibration data and make linear interpolations.
- Calculate the reference concentrations of the gases (ppm).
- Plot all concentrations and temperature and humidity in one plot, to see if equilibrium was reached and select the appropriate time interval for interpretation (see figure 3.1).
- Make a new data set for corrected and approved data. This dataset can be used for further analysis.



**Figure 3.1** Example of print of primary (corrected) data to examine suitability for interpretation.

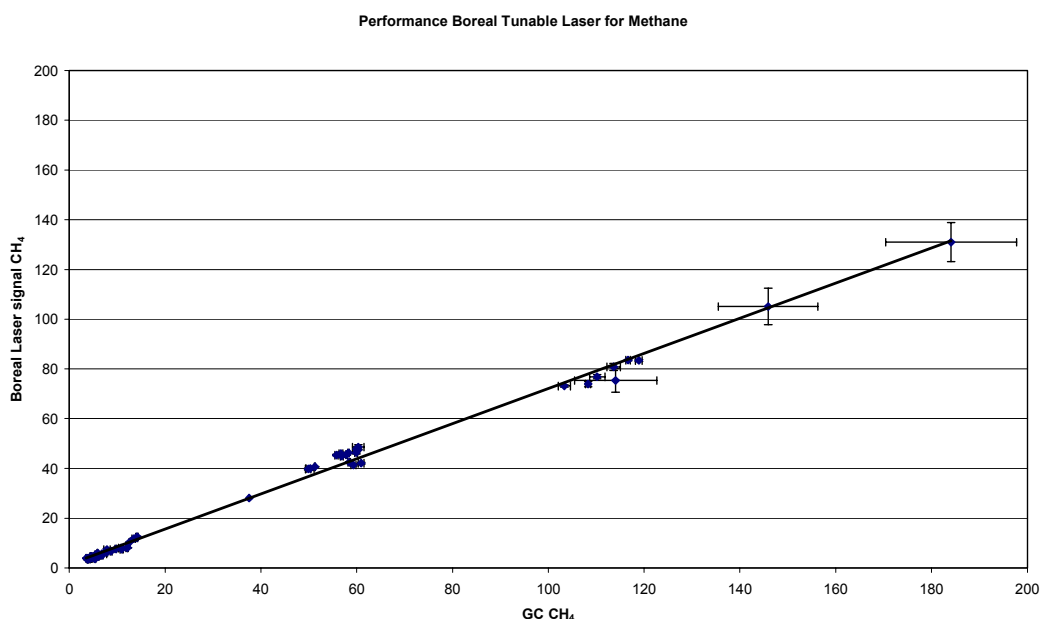
58 out of 76 experiments provided enough quality for interpretation. A reduction in number of experiments was caused by the pretty rough setting of the relative humidity. At normal temperature (10-20°C), the relative humidity was mainly determined by the actual temperature and relative humidity of incoming air and the temperature increase by heating or temperature drop by continuous cooling. Problems arose at high humidity and high temperature (30°C) as frequent steam injections were needed, resulting in large variations in relative humidity. The same holds for low temperature (5°C) with low water vapour capacity of the air). These variations in RH make the difference between 90% en 95% insignificant. The number of experiments, that can be used, is also reduced by the number of cases that stable concentrations are reached. One could argue that a steady change in concentration is good enough for interpretation, but there the difference in lag time and response time for the instruments enter the scene. We did not want to

add additional uncertainty because difference in response time. The number of data points for each experiment varies between 6 and 9 and is determined by the 4 minute measuring cycle of the gas chromatograph.

## 3.2 Results for the Boreal Gasfinder

### 3.2.1 Sensitivity to temperature, relative humidity and interfering gases.

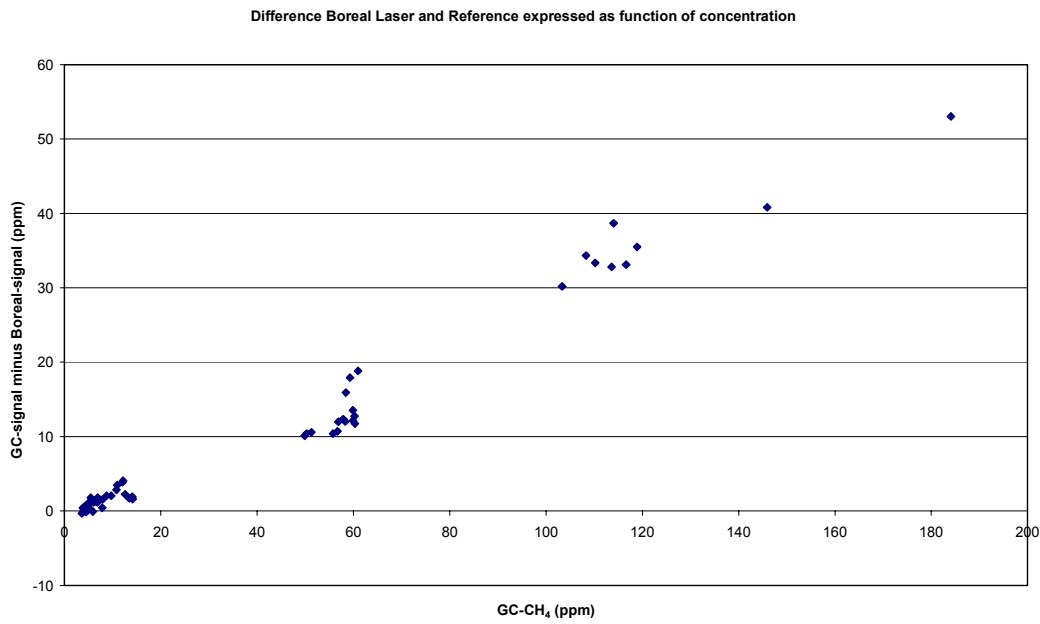
The first impression on the over all results of the instrument (all concentrations, temperatures and relative humidities) can be obtained by plotting all data in one graph. This is done in figure 3.2. All data of one experiment are grouped together as one data point. Uncertainty in concentration measured by the GC (1 sigma) is represented as a horizontal bar, for the concentration measured by the TDL as a vertical bar. Uncertainty is small for both measurements ( $<2.26$  respectively  $<2.27$  %) except for the high concentrations ( $>\pm 120$  ppm) where the concentration was not stable.



**Figure 3.2** Comparison of concentration measurement results for the GC (reference) and TDL for all experimental situations. Each experiment is represented by one data point.

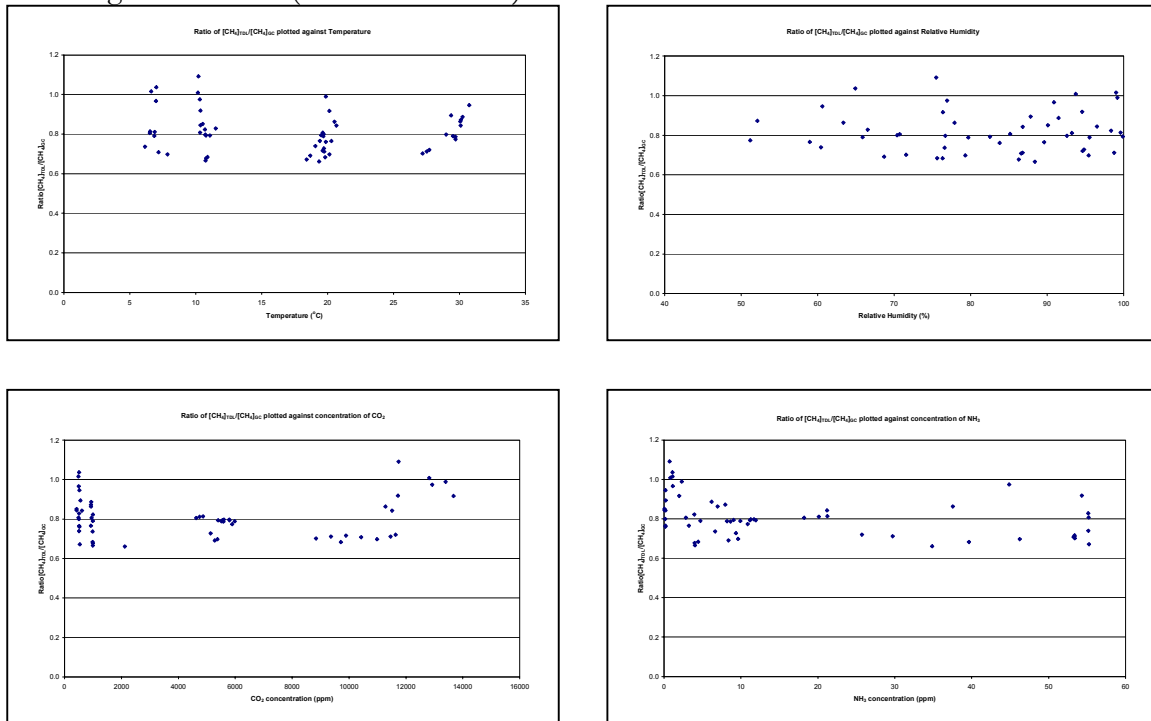
Figure 3.2 shows no outliers, that can be linked to certain experimental conditions like T, RH, or [NH<sub>3</sub>] or [CO<sub>2</sub>]. There is however a systematic difference, much larger than the overall measurement error of 3.2%, between GC and TDL represented by the regression line  $[\text{CH}_4]_{\text{TDL}} = 0.706[\text{CH}_4]_{\text{GC}} + 1.48$  ( $R^2 = 0.995$ )

This is confirmed by plotting the difference in measured concentration between GC and TDL against the concentration (see figure 3.3). There is obviously no a-linearity in this concentration interval for both instruments.



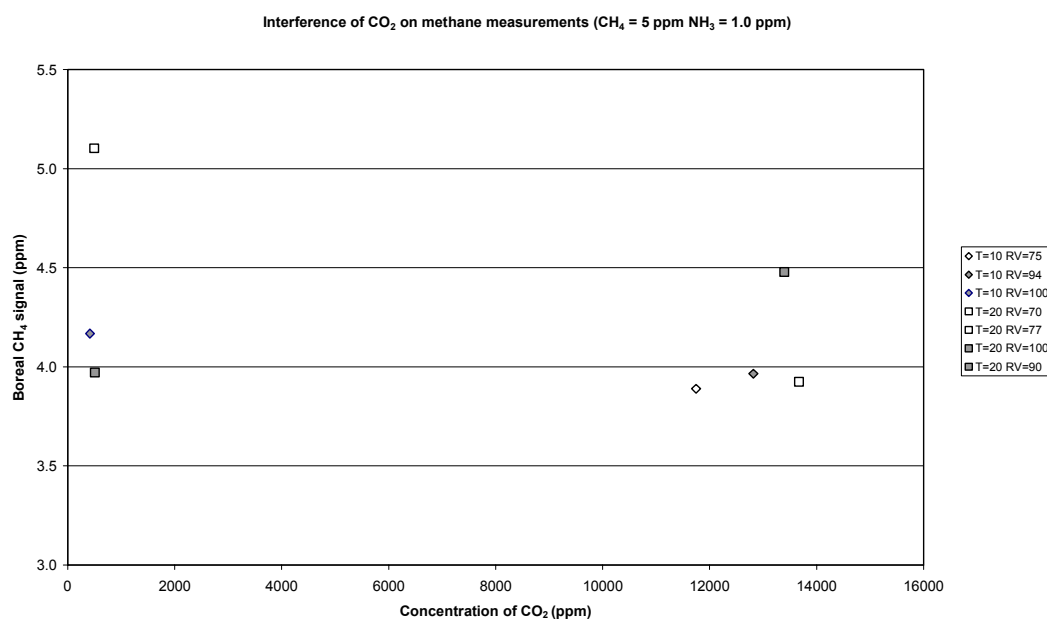
**Figure 3.3** Plot of GC signal minus TDL signal against concentration by GC.

The ratio of  $\text{CH}_4$  concentration measured by the TDL and measured by the GC is plotted against temperature, relative humidity,  $\text{NH}_3$  concentration and  $\text{CO}_2$  concentration. The standard deviation is about the same (9 %) for all plots and all values. There is no indication of influence of temperature, relative humidity,  $\text{NH}_3$  concentration and  $\text{CO}_2$  concentration on the TDL reading for methane (all less than 0.2%).



**Figure 3.4** The ratio of  $[\text{CH}_4]_{\text{TDL}}/[\text{CH}_4]_{\text{GC}}$  plotted against temperature, relative humidity,  $[\text{CO}_2]$  and  $[\text{NH}_3]$ .

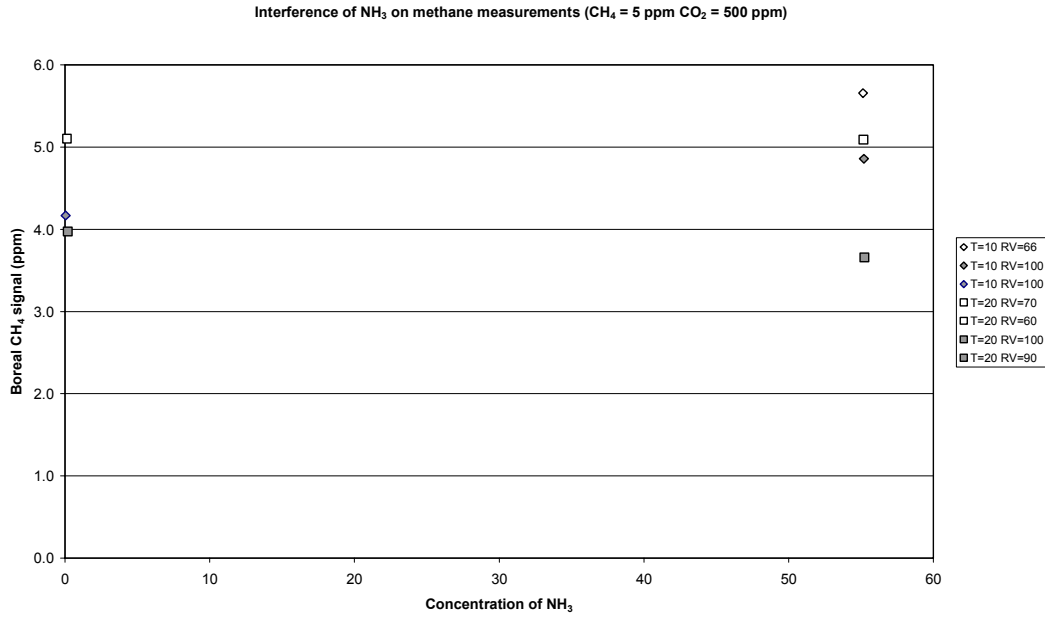
A drawback in the set-up of the experimental design is the simultaneous variation of all concentrations to certain levels between very low and very high. This is in agreement with the situation in an animal house and reduces the number of experiments, but hampers the detection of interference from a certain gas. Interference will show up in this design for all gasses although perhaps one gas may be responsible for the influence on instrument sensitivity. To detect this situation, the methane concentration was put at a low level (approximately 5 ppm) and the CO<sub>2</sub> and NH<sub>3</sub> concentration alternated between high for CO<sub>2</sub> (larger than 10,000 ppm) and low for NH<sub>3</sub> (1 ppm) or the other way around low for CO<sub>2</sub> (500 ppm) and high for NH<sub>3</sub> (50 ppm). Results for these experiments are shown in the figures 3.5 and 3.6.



**Figure 3.5** Interference of the CO<sub>2</sub> concentration on the signal of the Boreal TDL at about 5 ppm methane level.

The markers in figure 3.5 apply to about the same situation for temperature and humidity although humidity control was not accurate enough to reach the same settings for parallel experiments (see legend). As was already deduced from figure 3.4, no influence of CO<sub>2</sub> on the methane readings could be detected.

Figure 3.6 shows the same pattern for the influence of NH<sub>3</sub> on the methane readings of the Boreal TDL, no influence of NH<sub>3</sub>.



**Figure 3.6** Interference of the NH<sub>3</sub> concentration on the signal of the Boreal TDL at about 5 ppm methane level.

### 3.2.2 Detection limit, linearity, accuracy and precision.

The detection limit can be derived from the noise of the signal of the TDL. As we cannot guarantee constant parameters of the situation within the controlled chamber, we can only derive an overall noise level and related detection limit, which can be higher than the detection limit in a steady concentration. The noise level (1 stdv) of the signal at about 20 ppm.m is 0.6 ppm.m, resulting in a practical detection limit of 1.2 ppm.m (2 stdv). This level of 20 ppm.m is chosen (5 ppm with a path length of 4 m) because of the observation that at lower absorption rates the  $R^2$  value rapidly drops below 0.7 giving rise to an inaccuracy more than 10% (factory information) considered unacceptable for our purposes. This is reflected by the precision of the concentration readings being 3.3% at a concentration of 5 ppm and 2.3% for all measurements at a path length of 4 m. Myers *et al*, (2000) mention a detection limit of 0.29 ppm.m for an integration time of 1 minute and a path length of 2 m which is much lower but surprisingly 0.56 ppm.m for a 5 minute integration interval.

There are two types of linearity for the TDL. First is the range of a constant sensitivity. In our experiments there was no a-linearity observed in the range between 20 ppm.m and 740 ppm.m. This is in agreement with the observation of Myers *et al*, (2000) extending the range to 1000 ppm.m (500 ppm and 2 m path).

The second type of linearity is the dependence of the signal on source strength (determined by optical haze, light scattering, reflection of the mirror and dirty optics). We did not investigate this phenomenon but Myers *et al*, (2000) found no influence between 100% and 45%. This corresponds in our case with light value readings between 7,000 and 3,000.

The relative accuracy of the Gasfinder can be determined by calculating;

$$A = \frac{[CH_4]_{gasf} - [CH_4]_{ref}}{[CH_4]_{ref}} * 100$$

This relative accuracy is calculated to be 30%. This accuracy may be influenced by the way the gas chromatograph was calibrated. Calibration gases were made using an calibrated dilution apparatus , a bottle of CH<sub>4</sub> calibration gas of known concentration and point 5 Nitrogen dilution gas. A systematic difference in CH<sub>4</sub> concentration of the real concentration and the indicated concentration in the cylinder can give rise to systematic errors and influence the relative accuracy. The precision of the TDL and reference instruments is reported in percent RSD of all experiments. First step is calculation of the standard deviation of the sample;

$$\sigma = \left[ \frac{1}{n-1} \sum_{i=1}^n (C_i - \bar{C})^2 \right]^{0.5}$$

and than;

$$RSD = \left| \frac{\sigma}{\bar{C}} \right| * 100$$

The precision of the reference instruments in these experiments was 2.3% for the GC, 1.6% for the Licor CO<sub>2</sub> monitor and 6.2% for the converter-NO<sub>x</sub> monitor combination. The precision for the temperature measurements is 0.2 °C and for relative humidity 3.5 %. The larger fluctuations in the controlled chamber were due to pretty rough control equipment and not to the precision of T and RH sensors. The precision of the Boreal TDL over all measurements was 2.3%.

### 3.3 Results for the Vaisala NH<sub>3</sub> sensor

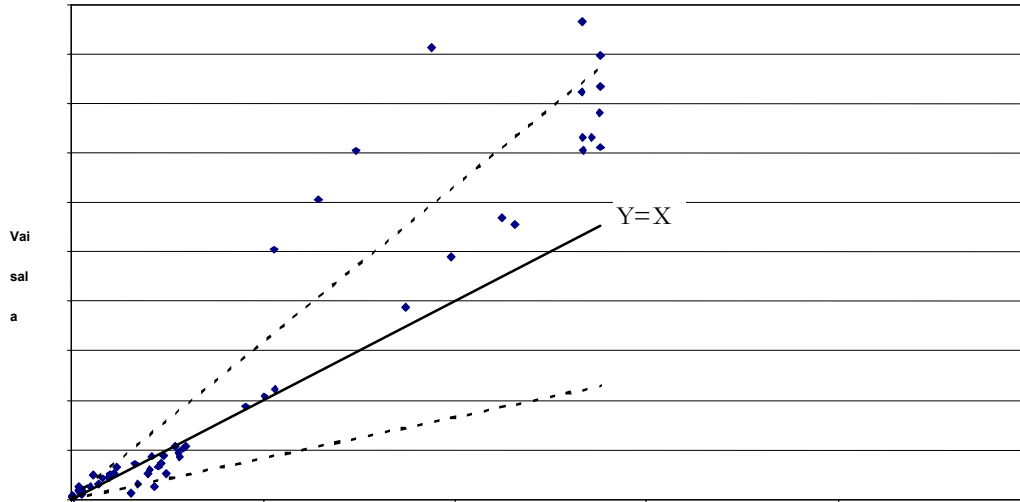
The experiments were designed to test the Boreal Gasfinder. Just before starting the experiments Vaisala offered the opportunity to test their NH<sub>3</sub> sensor as well. We welcomed this possibility very much as we were already applying different NH<sub>3</sub> concentrations, temperatures and relative humidities in the chamber. Additional experiments were not possible so we had to refrain from providing also an optimal design to test this sensor.

#### 3.3.1 Sensitivity to temperature, relative humidity and interfering gases.

The first impression on the over all results of the instrument (all concentrations, temperatures and relative humidities) can be obtained by plotting all data in one graph. This is done in figure 3.7

All data of one experiment are grouped together as one data point. Precision is less than in the methane measurements for both instruments (6.2% for the monitor versus resp. 18.5 % for the Vaisala sensor) based on the fluctuations in signal during a steady state concentration. The uncertainty for the monitor is much larger than normally encountered when doing NO<sub>x</sub> measurements. This variation is largely determined by the periodic insertion of steam in the controlled chamber, slightly influencing the NH<sub>3</sub> concentration.





**Figure 3.7** Comparison of concentration measurement results for the converter NO<sub>x</sub> monitor (reference) and Vaisala sensor for all experimental situations. Each experiment is represented by one data point.

Figure 3.7 shows the need for detailed analysis as a number of pronounced outliers can be seen. Not all outliers can be blamed to the smaller precision of the reference NO<sub>x</sub> monitor (6.2%) and smaller precision of the Vaisala sensor (18.5%) compared to that of the GC (2.3%) and TDL (2.3%) for the methane measurements. The overall precision of the comparison mounts up to 19.5% ( $\sqrt{18.5^2 + 6.2^2}$ ). One would expect 98% of measured values within an envelope of 41.5% and 158.5% ( $100\% \pm 3\sigma$ ) of the reference value as indicated by the solid 1:1 line and the dotted lines for the probability interval. Figure 3.7 shows that this is not the case.

The relation of reference NH<sub>3</sub> data and measured data for all experiments is represented by the regression line  $[\text{NH}_3]_{\text{Vais}} = 1.522[\text{NH}_3]_{\text{Mon}} - 2.08$  ( $R^2 = 0.912$ )

When we discard the values that are not within the probability interval, we obtain the relation;

$$[\text{NH}_3]_{\text{Vais}} = 1.419[\text{NH}_3]_{\text{Mon}} - 3.98 \quad (R^2 = 0.981) \text{ or;}$$

$$[\text{NH}_3]_{\text{Vais}} = 1.317[\text{NH}_3]_{\text{Mon}} \quad (R^2 = 0.972) \text{ when we force the line through the origin.}$$

These selected data and curves are shown in figure 3.8.

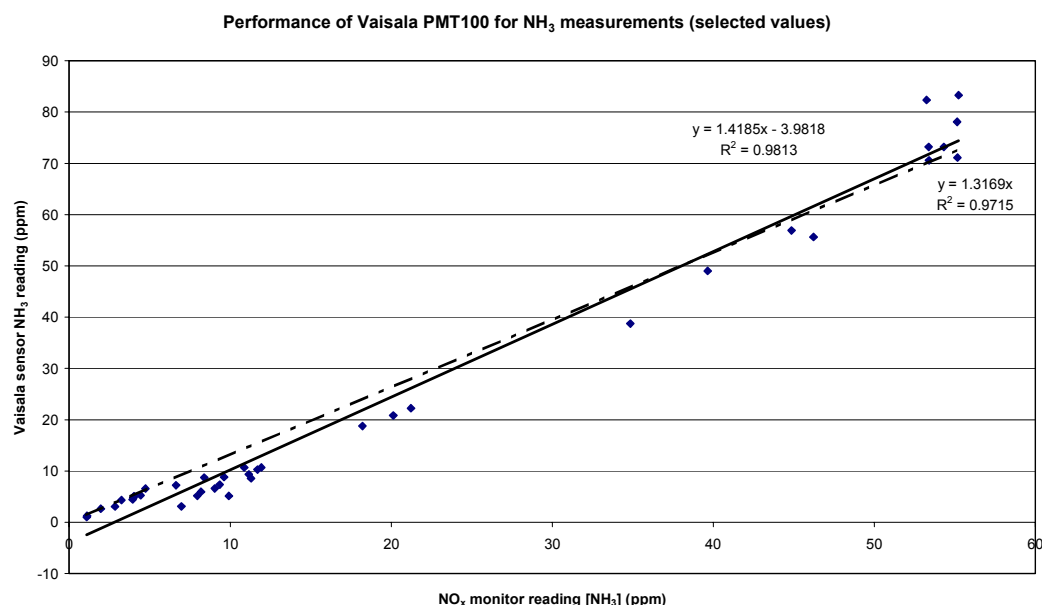
The interesting question is what do the non selected values have in common?

Table 3.1 illustrates the items that occur more than the average 25% per class;

Temperature	Humidity>90%	Condensation on sensor possible	[NH <sub>3</sub> ]< 1ppm	[CO <sub>2</sub> ]>10,000 ppm
No influence	55 % of values	35 % of values	50% of values	35% of values

**Table 3.1** Possible factors that influence sensor malfunctioning.

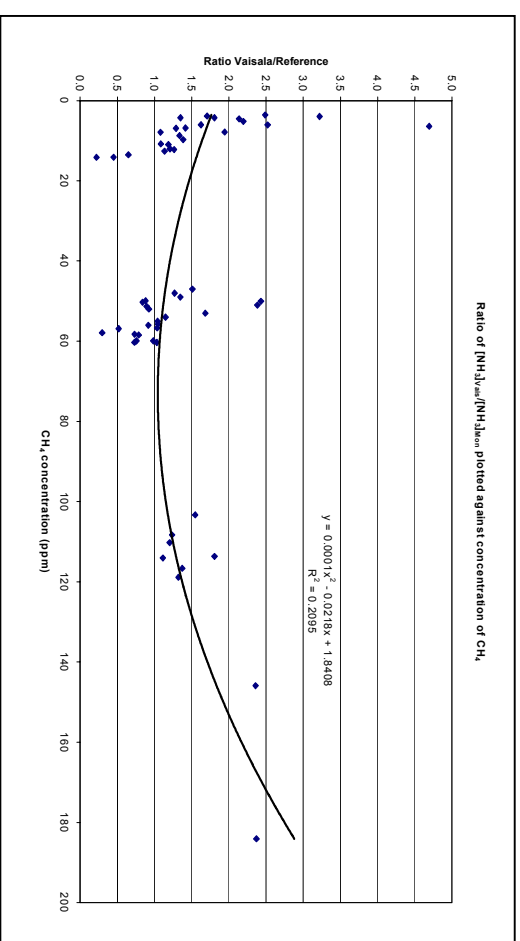
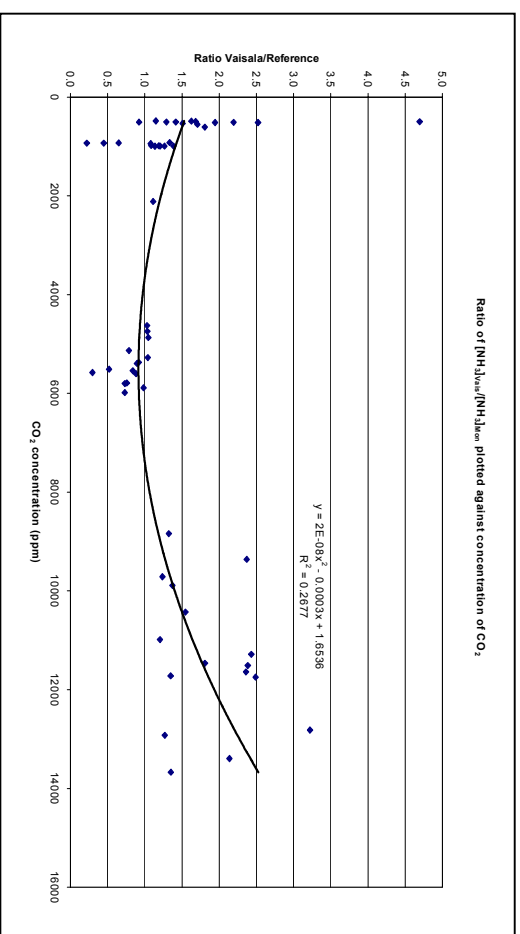
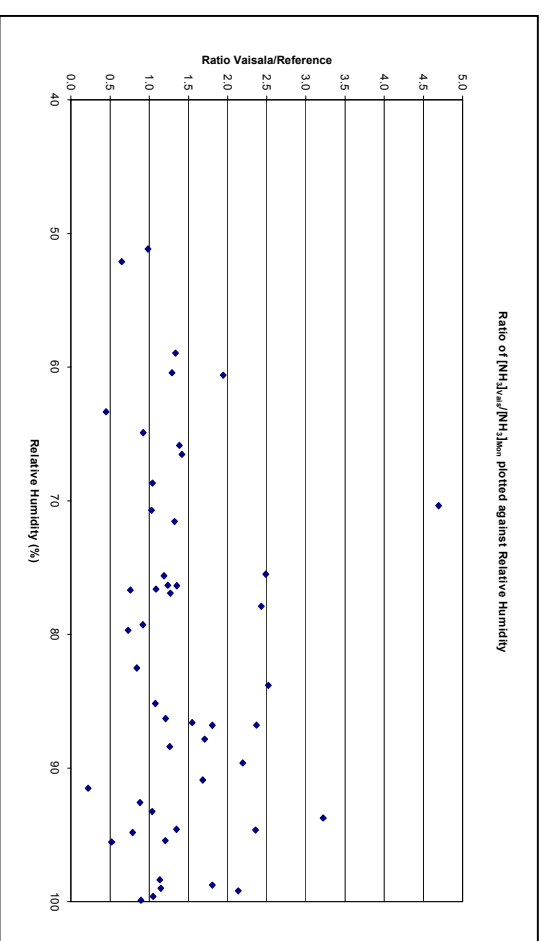
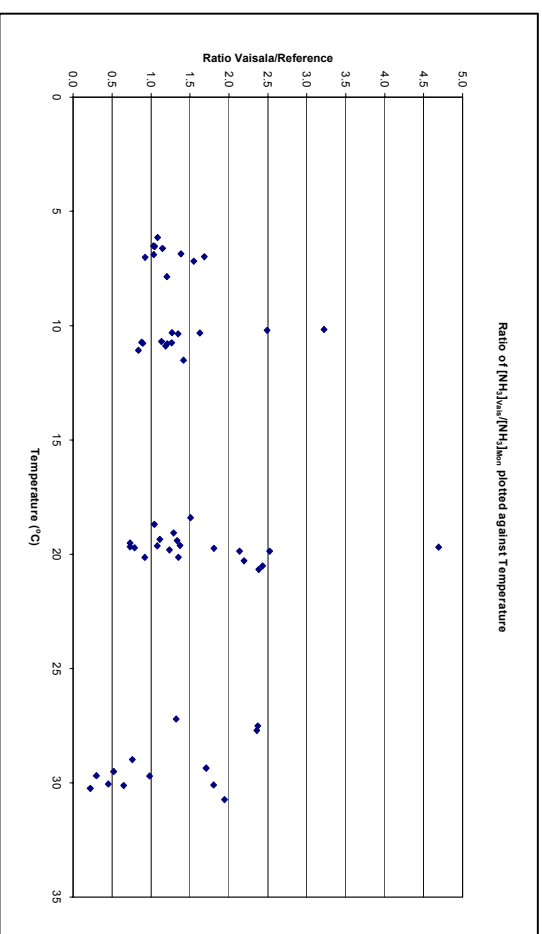
Combining humidity higher than 90% with concentrations of ammonia lower than 1 ppm covers 90% of the non selected data.



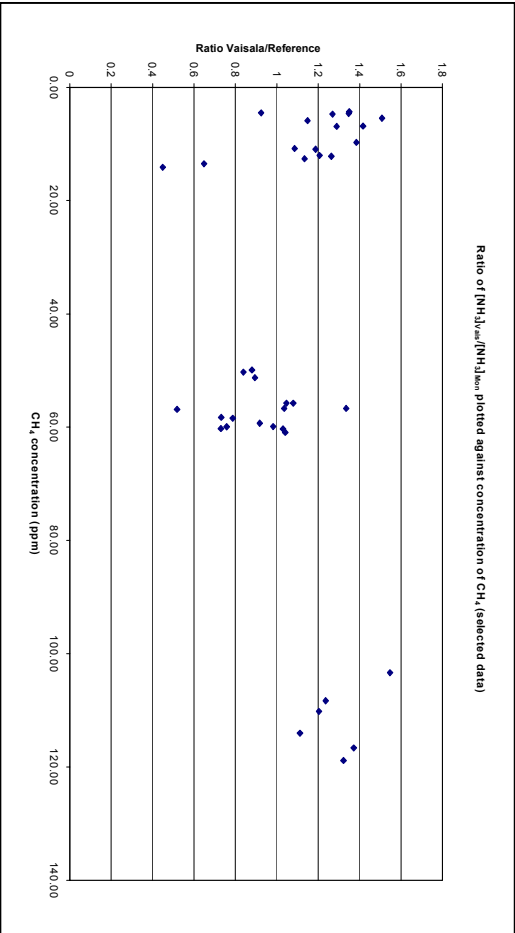
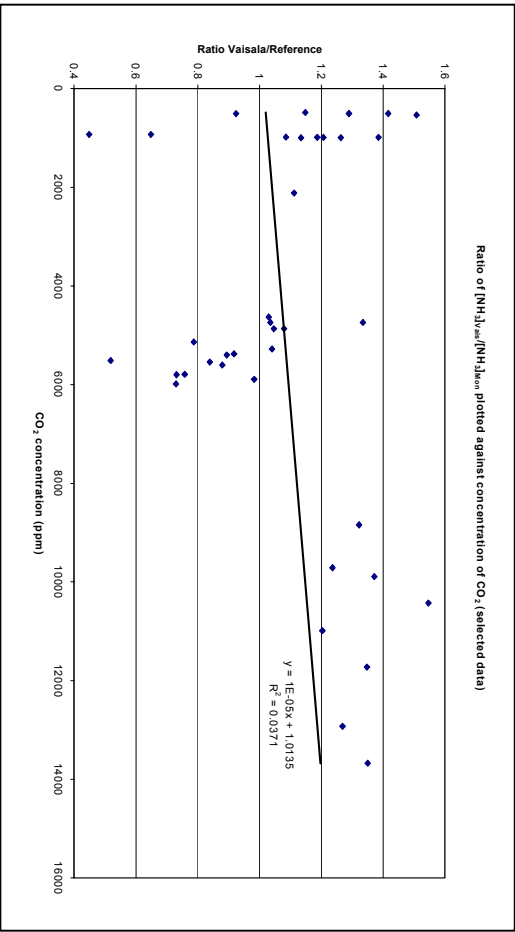
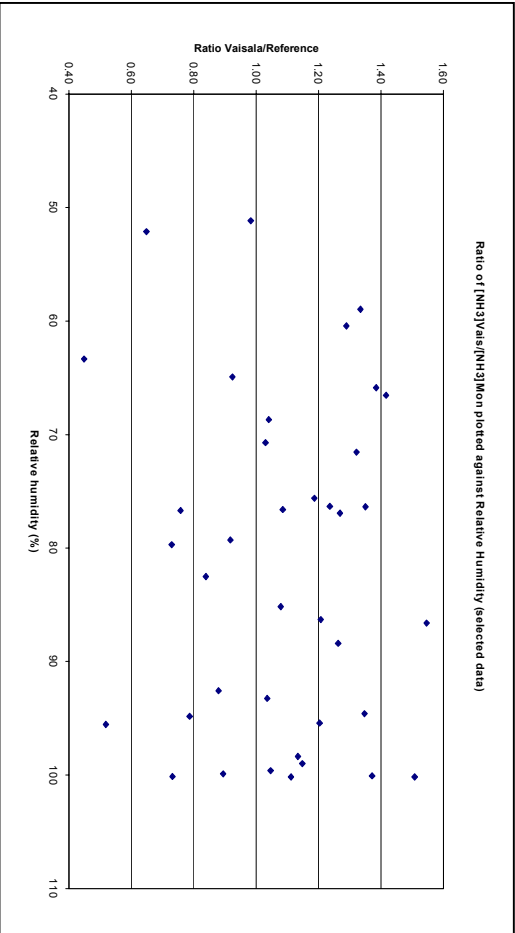
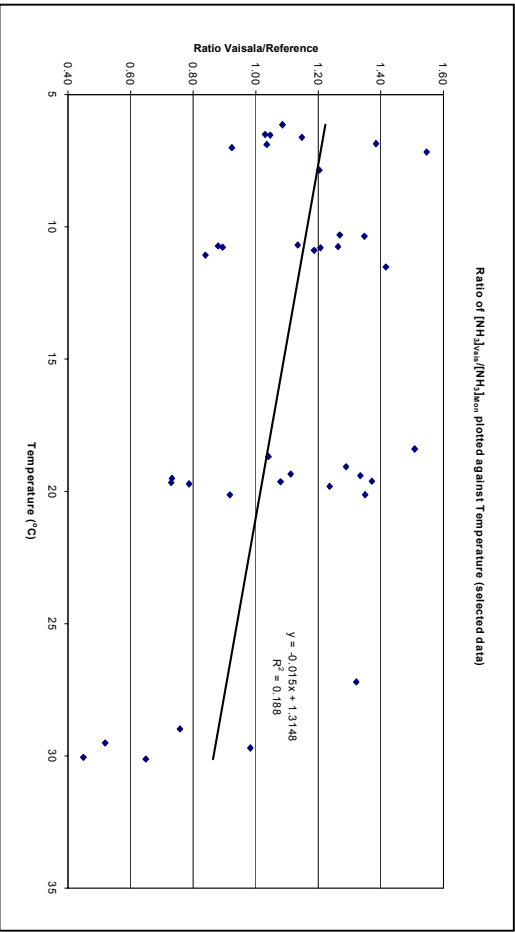
**Figure 3.8** Comparison of concentration measurement results for the converter NO<sub>x</sub> monitor (reference) and Vaisala sensor for selected situations. Each experiment is represented by one data point.

Non-selected and selected data are used to study interference. The non selected results are plotted in figure 3.9. For that graphs a correction was made by omitting the results of experiments 1 and 2 which resulted in very high  $[\text{NH}_3]_{\text{Vais}}/[\text{NH}_3]_{\text{Mon}}$  ratios of 12.9 and 14.8. The standard deviation of the results for the plots of the ratio  $[\text{NH}_3]_{\text{Vais}}/[\text{NH}_3]_{\text{Mon}}$  against temperature and humidity is larger than could be expected from the overall precision of about 20%. There is no indication of influence of temperature and perhaps a slight influence of relative humidity on the measured NH<sub>3</sub> concentration.

The lower graphs ( $[\text{NH}_3]_{\text{Vais}}/[\text{NH}_3]_{\text{Mon}}$  against  $[\text{CO}_2]$  and  $[\text{CH}_4]$ ) show a possible influence of the concentration of interfering gases on the signal of the Vaisala sensor. As explained in paragraph 3.2.1 the pattern will be comparable for the influence of both gases as determined by the experimental set-up. No additional experiments were performed to detect which of the two gases will be responsible for this interference. From the inert nature of CH<sub>4</sub> and the polarity of the CO<sub>2</sub> molecule and the sensitivity of the Vaisala sensor to changes in capacity of a coating on a chip it is probable that the interference stems from the CO<sub>2</sub> concentration. This adds to the conclusion on the outliers, where an imported part of outliers was related to high CO<sub>2</sub> concentrations. The selected data are used to study interference as well. The selected results are plotted in figure 3.10. One should of course expect no influence of temperature and slight influence of relative humidity, and CO<sub>2</sub> concentration as outliers were discarded. As explained before, the CH<sub>4</sub> effects will be parallel to the CO<sub>2</sub> effects.



**Figure 3.9** The ratio of  $[\text{NH}_3]_{\text{Vais}}/[\text{NH}_3]_{\text{Mon}}$  plotted against temperature, relative humidity,  $[\text{CO}_2]$  and  $[\text{CH}_4]$  for all experiments except experiments 1 and 2.



**Figure 3.10** The ratio of  $[NH_3]_{Vais}/[NH_3]_{Mon}$  plotted against temperature, relative humidity,  $[CO_2]$  and  $[CH_4]$  for selected data

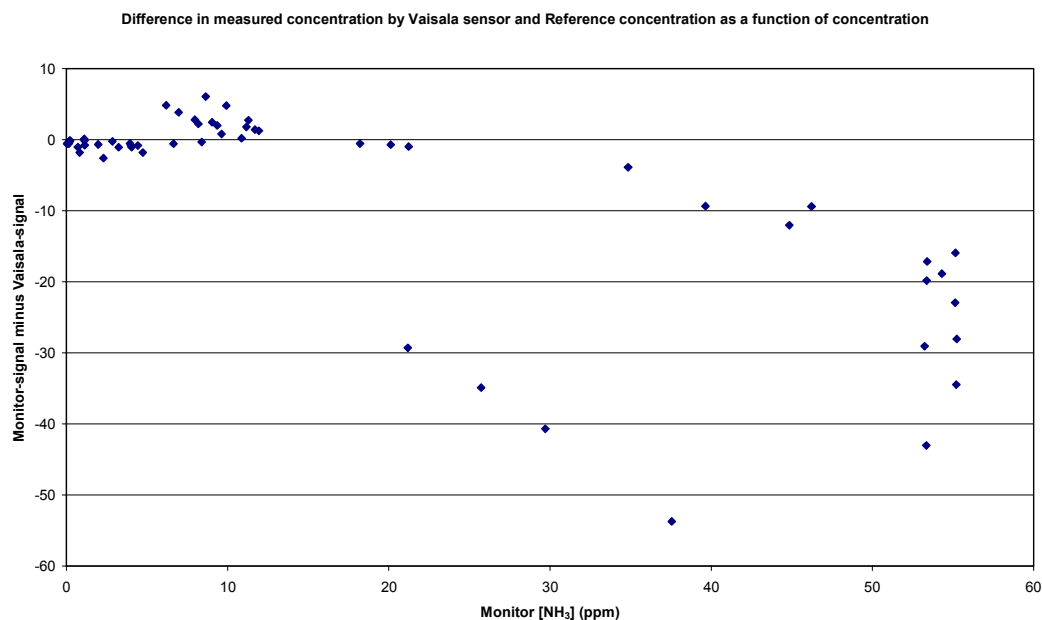
Figure 3.10 shows no relation between the ratio of measured and reference concentration and relative humidity and methane concentration. There is a tendency for a relation with temperature and CO<sub>2</sub> concentration though not significant.

### 3.3.2 Detection limit, linearity, accuracy and precision.

As no separate experiments were planned for the NH<sub>3</sub> sensor, no zero gas was introduced in the controlled chamber. The lowest concentrations of NH<sub>3</sub> were about 0.2 ppm. The standard deviation of the sensor is about 0.4 ppm at that level. This results in a lower limit of detection of 1 ppm.

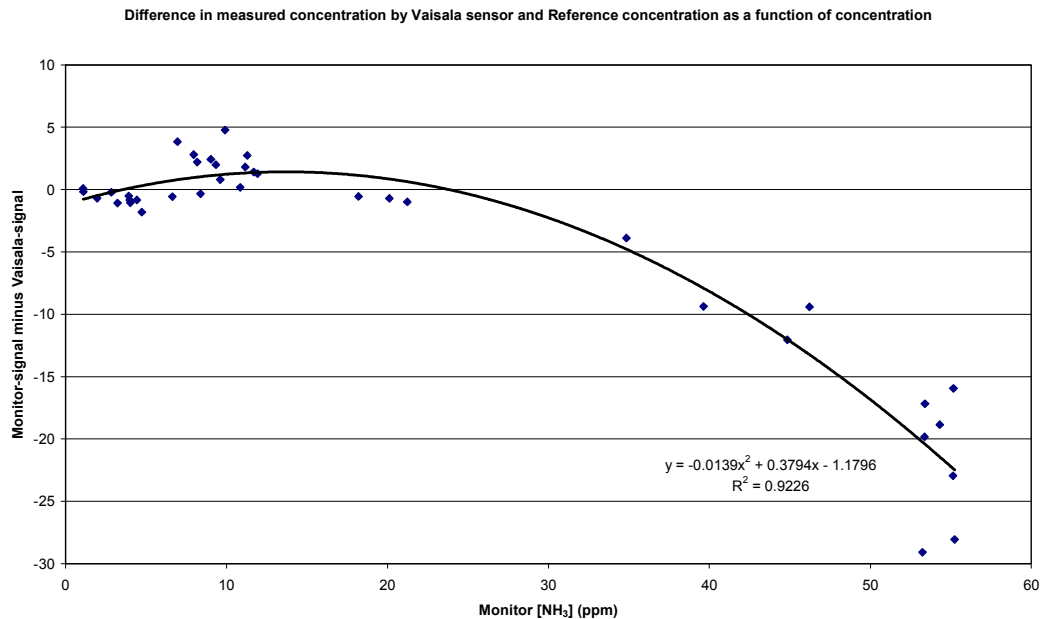
Figure 3.7 does not provide information on the linearity of the sensor. The pattern may however indicate a kind of hysteretic effect concerning the NH<sub>3</sub> concentration. One of the first thoughts would be, that the response time of the sensor is much longer than the time in the controlled cell to reach equilibrium (about 1/2 till 1.5 hours when concentrations are changed). We did not investigate the response time of the sensor, but the technical specifications indicate a  $t_{50}$  of less than 90 s for an increase of 0-1000 ppm NH<sub>3</sub>. No indication is given for the 0-100 ppm version of the sensor, but it might be a comparable response time. This means that the response time is not responsible for the spurious results. They have to be blamed to the influence of high humidity and high CO<sub>2</sub> concentrations as indicated before.

A plot of difference between the reference signal and the sensor sensor signal against the reference concentration gives an indication of linearity of the signal. The plot for all data (figure 3.11) indicates non linearity of the sensor.



**Figure 3.11** Difference in measured concentration of NH<sub>3</sub> by Vaisala sensor and converter-NO<sub>x</sub> monitor plotted against concentration.

Even when we plot the selected data, the indication of non-linearity persists as indicated in figure 3.12



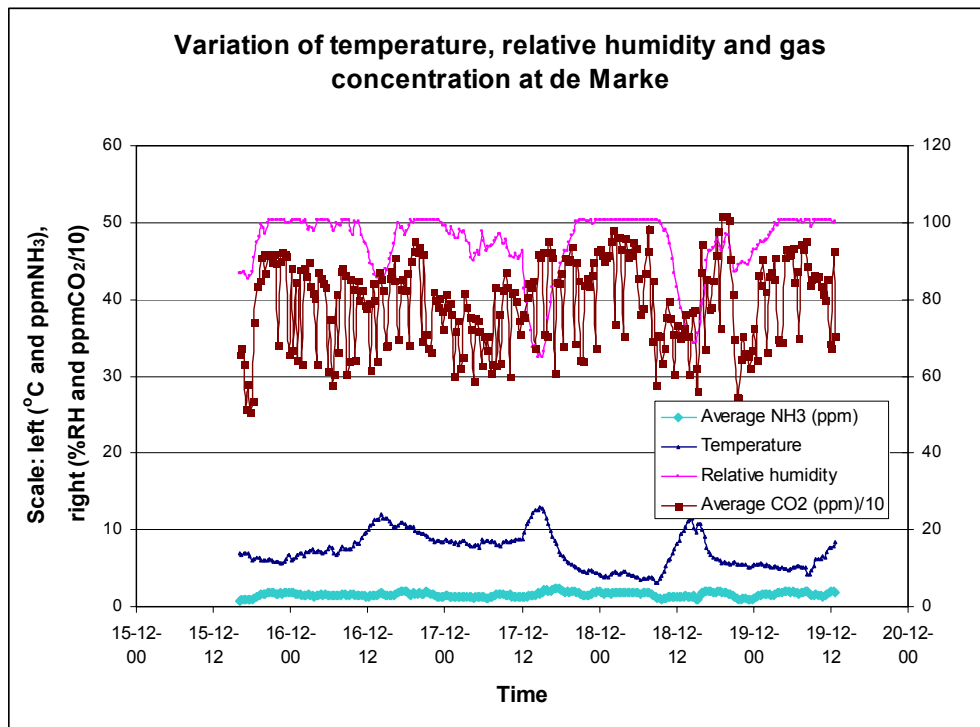
**Figure 3.12** Difference in measured concentration of NH<sub>3</sub> by Vaisala sensor and converter-NO<sub>x</sub> monitor plotted against concentration (selected data).

The accuracy of the sensor is (given the precision of 18.5%) correct within the range of 1-30 ppm (NH<sub>3</sub>) (selected data). For higher concentrations a non-linear calibration curve should be used. The overall precision of 18.5% (all data) is better than the 20% mentioned by Vaisala.

### 3.4 Performance of the Boreal TDL and the Vaisala NH<sub>3</sub> sensor in a cow house

Measurements in a cow house at the experimental farm de Marke took place between December 15 and December 19. The light path of the Boreal TDL was 70 m at a height of about 6 m from the floor and at about a distance of 1 m from the gas sampling line. The Vaisala sensor was placed in the middle of the cowhouse, 3 m above the floor (sampling tube about 6 m). Reference instruments were placed in a shelter outside of the animal house together with the data retrieval system. Data of the TDL and the ammonia sensor were transmitted by a RS232 transmitter-receiver unit, as the use of long cables would give rise to technical problems. All gases were led to the reference instruments by slightly heated and isolated tubing (to prevent condensation). The flow rate in the 1/4" tubing was kept constant using 6 capillaries at the entrance evenly spread over the length of the cowhouse at 0.5 liter per minute resulting in a residence time of about 30 sec and laminar flow. (T-piece and tubing to instruments in middle of the cow house).

Figure 3.13 presents an overview of the dynamics in ammonia concentration, CO<sub>2</sub> concentration, temperature and relative humidity as provided by the reference instruments.

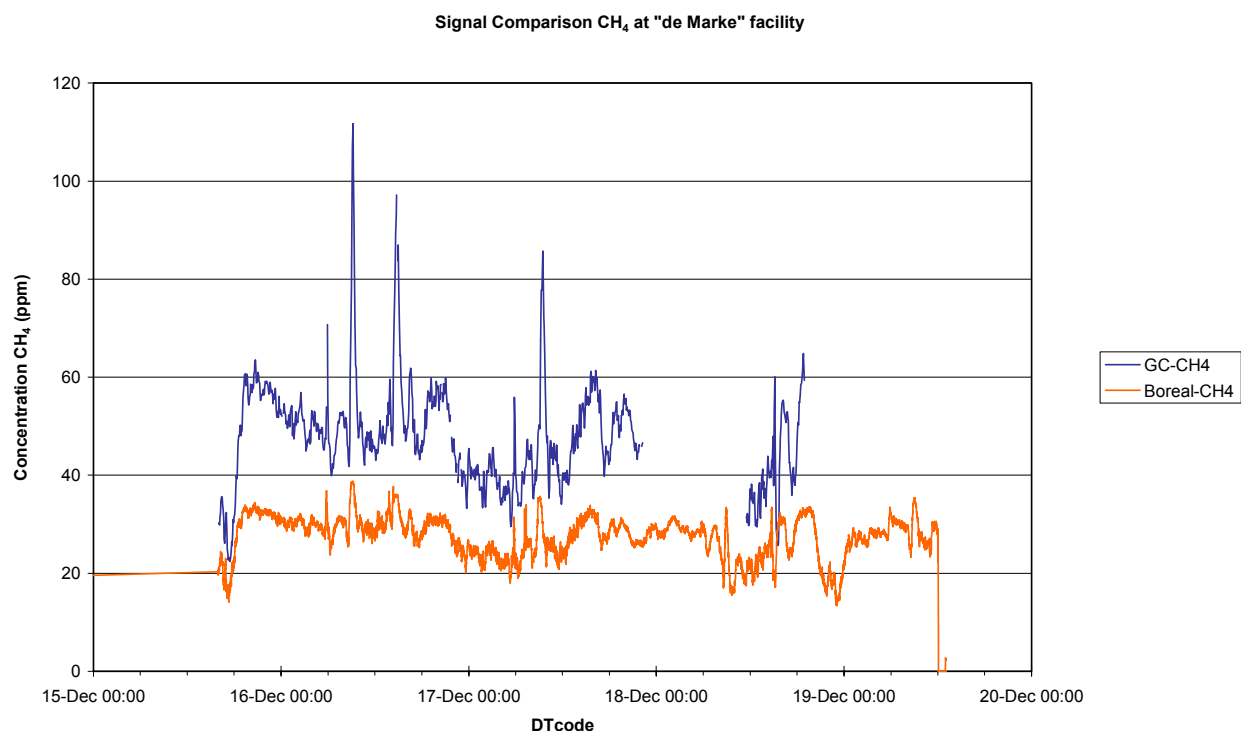


**Figure 3.13** Dynamics in ammonia concentration, CO<sub>2</sub> concentration, temperature and relative humidity in the cow house of De Marke from December 15 till 20.

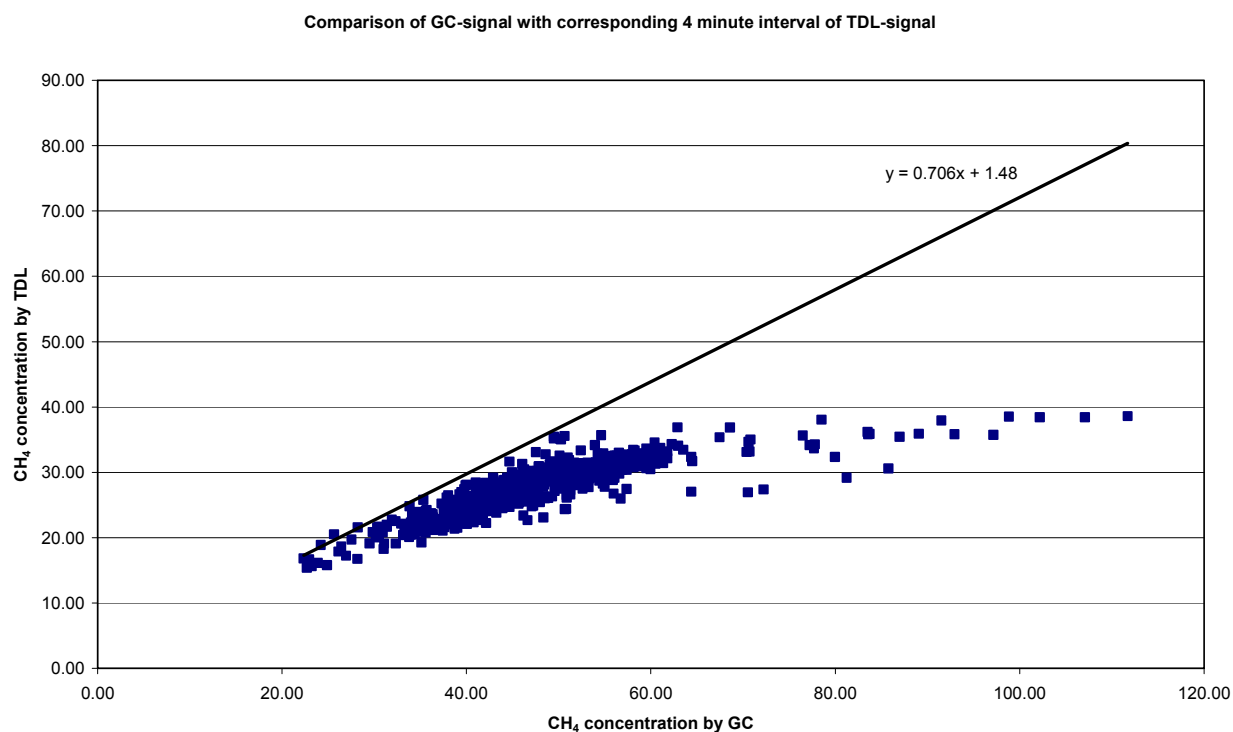
The temperature in the cow house is fluctuating because of large fluctuation in ambient temperature and opening and closing of curtains over the ventilation openings. This, together with variation in wind speed, accounts for variation in ventilation rate. Ventilation rate and activity of the animals determine the concentrations in the animal house. These concentrations are expected to be low because of a high ventilation rate and periodic cleaning of the floor by a manure scraper.

The methane concentration measured by the GC shows some distinct zero values caused by problems in integrating the peak area automatically. The period without methane values on December 18 was caused by malfunctioning of a relays switching the sampling pump on and off.

The relation between measuring results of the TDL and GC and between the Vaisala sensor and the converter NO<sub>x</sub> monitor are presented in figure 3.14 respectively 3.18. As could be expected from the experiments in the controlled chamber, the results of the TDL and GC have the same overall pattern. The GC shows more variation in accordance with instantaneous sampling from the sampling line. The number of inlet nozzles in the sampling line and the restricted mixing in the sampling line apparently delivers a fluctuating concentration to the GC. The TDL integrates over the whole path and has an averaging time of 30 seconds. Remarkable is the relation between GC and TDL signal, this relation differs from the observations in the controlled chamber (see figure 3.15).



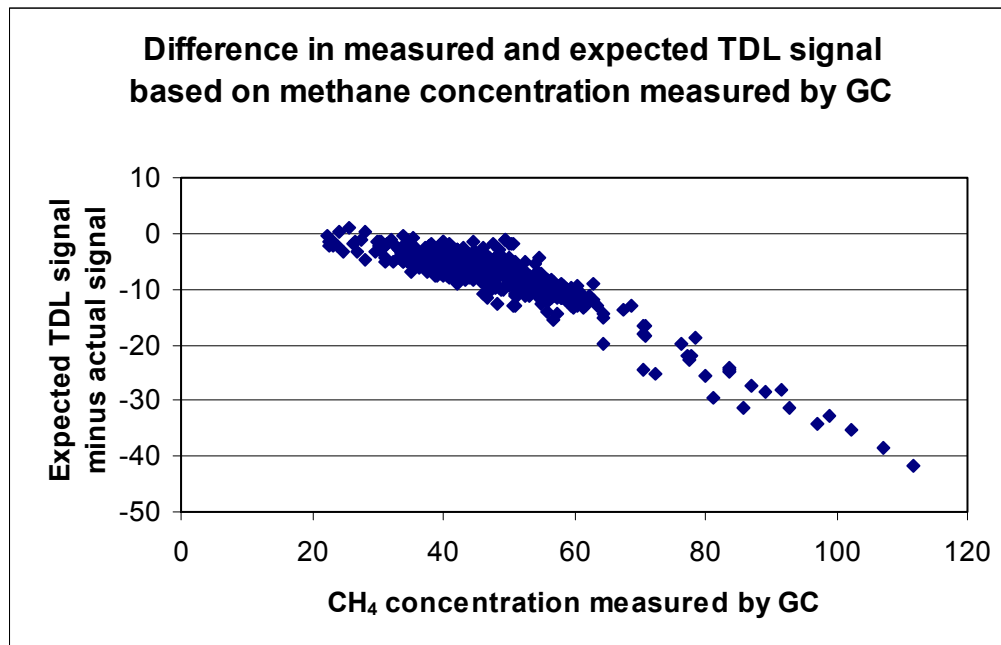
**Figure 3.14** Comparison of methane concentrations measured by GC and TDL at de Marke.



**Figure 3.15** Comparison of methane concentration measured by GC and concentration measured by TDL. Solid line represents expected curve based on experiments in controlled cell.



From figures 3.14 and 3.15 we learn that sudden peaks in concentration are not compensated by comparative dips in concentration. The sources in the animal house have a discontinuous character. As the peaks occur on a regular base between 9.00 and 10.00 am., the most probable source is a tractor entering the animal house for delivering food to the cows. These additional emissions are not well mixed in the sampling system (laminar flow). The TDL measures the average absorption over the whole length of the animal house and detects less strong peaks. Ventilation by outdoor air, lowering concentrations, was in this period a more steady situation. This may shift the concentrations measured by GC to a higher level than measured by TDL. When we maintain the intercept 1.48 from the relation  $[\text{CH}_4]_{\text{TDL}} = 0.706 [\text{CH}_4]_{\text{GC}} + 1.48$  unchanged (no observations of low concentrations in the animal house and tendency of the lower concentrations to be more close to the original relation), the new relation would read  $[\text{CH}_4]_{\text{TDL}} = 0.5c [\text{CH}_4]_{\text{GC}} + 1.48$  with the value of  $c$  between 0 and 6 depending on the weight that is given to the extreme GC values. The difference in measured and expected signal is dependent on the concentration level (see figure 3.16)



**Figure 3.16** Difference in expected TDL signal (based on the relation between TDL and GC from the controlled cell experiments) and measured signal at de Marke compared to methane concentration measured by GC.

This difference between GC and TDL is remarkable as the standard deviation of the concentration of the GC is 21.5% and TDL is 20.5% when the peaks are included and 17.1% resp. 16.4% when the peak values are excluded. Corresponding averages over this period are 48.6 ppm (GC) and 35.8 ppm (TDL) with-, or 47.4 ppm (GC) or 34.9 ppm (TDL) without peak values. This is well within the calibration range of the GC (see figure 3.17) . It is not clear if the TDL is also within its calibration range. The values for the controlled chamber ranged from 10-720 ppm.m. In de Marke the range is between 975-2,600 ppm.m.

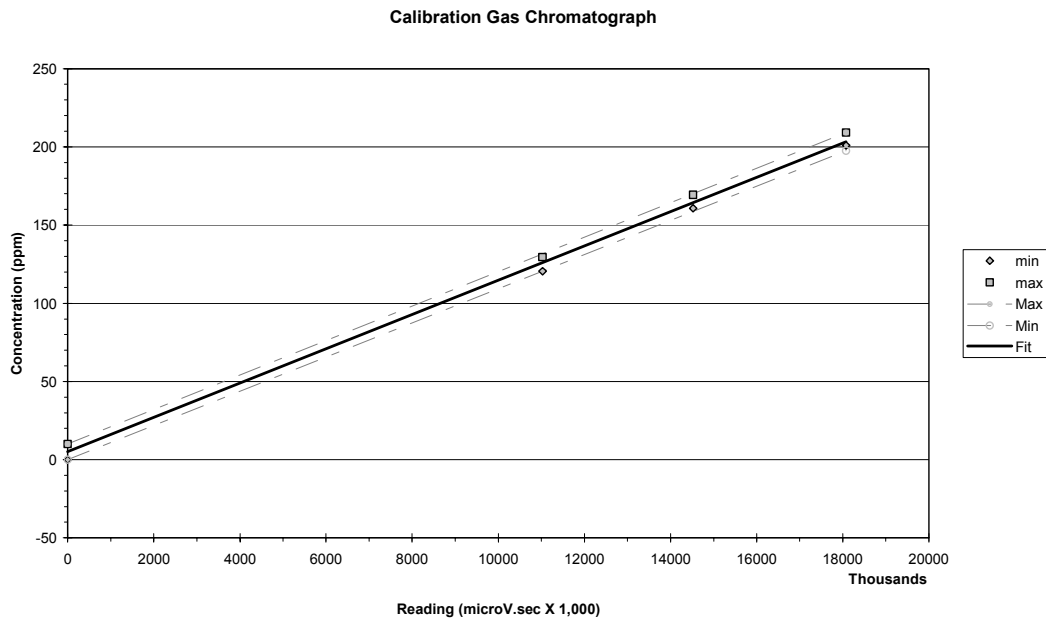


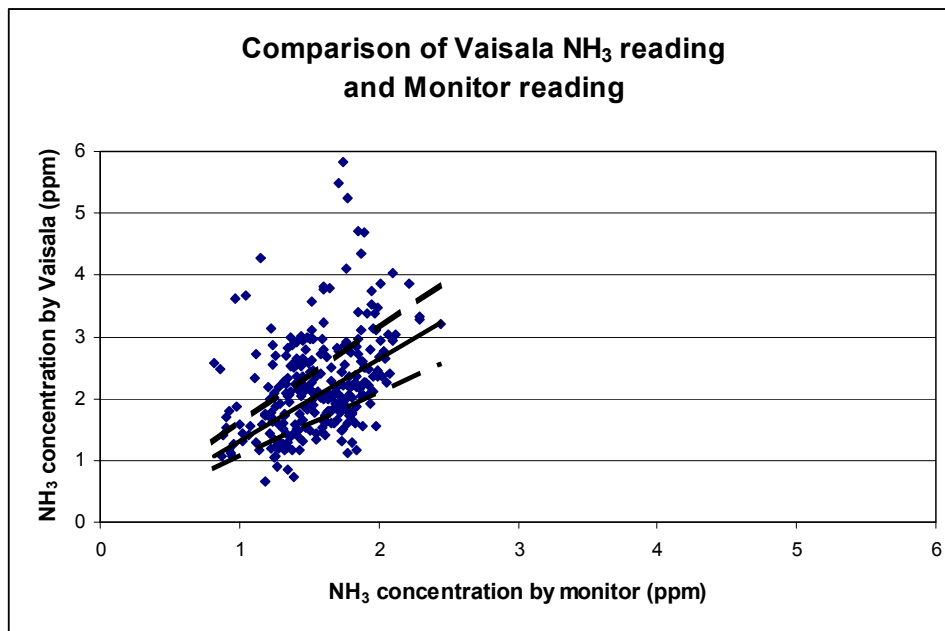
Figure 3.17 Calibration curve for Methane for GC. Min. and Max Values based on uncertainty in primary CH<sub>4</sub> standard and uncertainty in methane concentration of dilution gas (max 10 ppb).

Hypothesis for the deviant behaviour of the TDL are;

- Measurements outside the calibration range (?) of the TDL
- No correct absorption term for methane in the software of the instrument. This makes the signal dependant on concentration level, which is the case.
- No correct use of the entered (and measured) distance between source and mirror
- Not taking into account loss of intensity, due to spreading of the laser beam.
- Influence of aerosol on the signal.

These factors are dealt with in the discussion in chapter 4.

Data on the ammonia concentration are available on a time base of 20 minutes. The 4 minutes Vaisala measurements are averaged to the same time base. The relation between the two signals is presented in figure 3.17. The range in observed concentrations is small and close to the practical detection limit of 1 ppm NH<sub>3</sub>. There is no indication that the ratio of measured value by the Vaisala sensor and measured by the monitor differs from the regression line obtained in the controlled cell. The spread in concentration values is again larger than 20%.



**Figure 3.17** Comparison of Vaisala NH<sub>3</sub> reading and monitor reading in cow house de Marke. The regression line from selected values in the controlled cell and 20% variation interval from that line are inserted in the figure.



## 4 Discussion

The result of the comparison between Boreal Gasfinder TDL and the GC as a reference instrument in the controlled chamber leaves no doubt that the TDL is a well suited candidate for measuring methane in animal houses.

The precision of both instruments is the same (2.3%). No influence of temperature, relative humidity, CO<sub>2</sub> concentration and NH<sub>3</sub> concentration can be detected within the range of concentrations that normally are encountered in animal houses. The linearity is good between 20 ppm.m and 750 ppm.m and may extend to higher values that were not tested.

The accuracy remains an uncertain factor. The systematic difference between GC and TDL of 30% is large. It may stem from an incorrect rating of the primary calibration gas, calibration of the TDL or both. The reason for this discrepancy should be looked at. The good linearity and precision of the TDL make it possible to use a simple correction factor.

No investigations were performed on the influence of aerosols on instrument functioning. The air in animal houses is enriched in aerosols, especially in chicken barns. These aerosols will be to a large part in the middle size range 2-20 µm, about the same size of the wavelength of the infrared beam (not mentioned but probably close to the most used wavelength of 7.869 µm for methane). This means maximal optical effects. When absorption of infrared light on the aerosol or scatter do not effect the waveform, the effect of aerosol will be comparable to the reduction in light value from dirt on optics and mirror and have little influence on the signal for a transmission between 100% and 45% (Myers *et al*,2000). This needs further investigation.

The experiments in an animal house were less convincing for the TDL. The downward shift in sensitivity and the observed dependency of sensitivity on concentration both need an explanation.

In paragraph 3.4 some hypothetical factors are mentioned;

- Measurements outside the calibration range (?) of the TDL
- No correct absorption term for methane in the software of the instrument. This makes the signal dependant on concentration level, which is the case.
- No correct use of the entered (and measured) distance between source and mirror
- Not taking into account loss of intensity, due to spreading of the laser beam.
- Influence of aerosol on the signal.

It is a pity, that The Boreal manual provides so few information on signal processing. A not too clear explanation is provided in Appendix D (Explanation of R<sup>2</sup>) on waveform and reference waveform.

From theory of law of Lambert-Beer, the change in light intensity due to absorption will be;

$$I_{\lambda x} = I_{\lambda 0} \cdot e^{-kx}$$

As the light is reflected by a mirror, the path lenght for absorption is in fact 2 x (which is accounted for by the software. The mirror (plus guarding window) has a certain efficiency in returning the light (E<sub>refl</sub>).

$$I_{\lambda 2x} = E_{refl} \cdot I_{\lambda 0} \cdot e^{-k2x}$$

An additional factor is the divergence of the beam. The Technical note 02-3 by Boreal mentions a primary beam diameter of 2.5 mm and a divergence of 1.5 mrad. This leads to larger beam diameters at the reflector site (see table 4.1)

Table 4.1

Distance m	4	10	25	50	65	100	1000
Beam diam mm	8.5	17.5	40.0	77.5	100.0	152.5	1502.5

In the cattle house a 1" gold cube retroreflector was used. This means only partial reflection of the beam as the retroreflector is much smaller than the beam diameter of 10 cm at a distance of 65 m. The reduction in intensity is  $E_{diam}$ . When we assume uniform light intensity in the beam;

$$E_{diam} = \frac{A_{beam}}{A_{mirror}}, \text{ which may be a considerable light reduction as the area perpendicular to the}$$

beam scales with the square of the diameter.

This is turning the received light intensity to;

$$I_{\lambda 2x} = E_{diam} E_{rfl} I_{\lambda 0} e^{-k 2x}$$

The retroreflector directs the beam to the receiver. The light intensity, which is received depends strongly on the retroreflector. When a beam is returned by an omni directional mirror (so in a spherical volume) the received light intensity will be low.

$$E_{reic} = \frac{D^2}{4.x^2}$$

with; D = diameter of receiver and x = distance between receiver and reflector.

For reflection at a flat mirror (gold coated flat plate with surface reflection and no beam diffraction), the returned diameter of the beam would be twice that of the size at the mirror.

$$B = 2.5 + 2 \left( \frac{x}{1000} \cdot \sin(0.0015) \right)$$

Assuming uniform intensity, we get for a flat mirror;

$$E_{reic} = \frac{D^2}{16.B^2}$$

The reflection of traffic tape is perhaps somewhere between this two values for  $E_{reic}$ .

For a gold cube retroreflector the value of  $E_{reic}$  will be higher as the beam is actively directed to the receiver.

Soiling of transmitter, retroreflector and receiver window also gives attenuation of the beam with a factor  $E_{soil}$ .

The last attenuation factor is aerosol between transmitter and receiver. The attenuation is dependent on soil properties like size, refractive index, absorption of light etc resulting in  $E_{aer}$ .

In this way we end up with a received signal as a function of a couple of efficiencies;

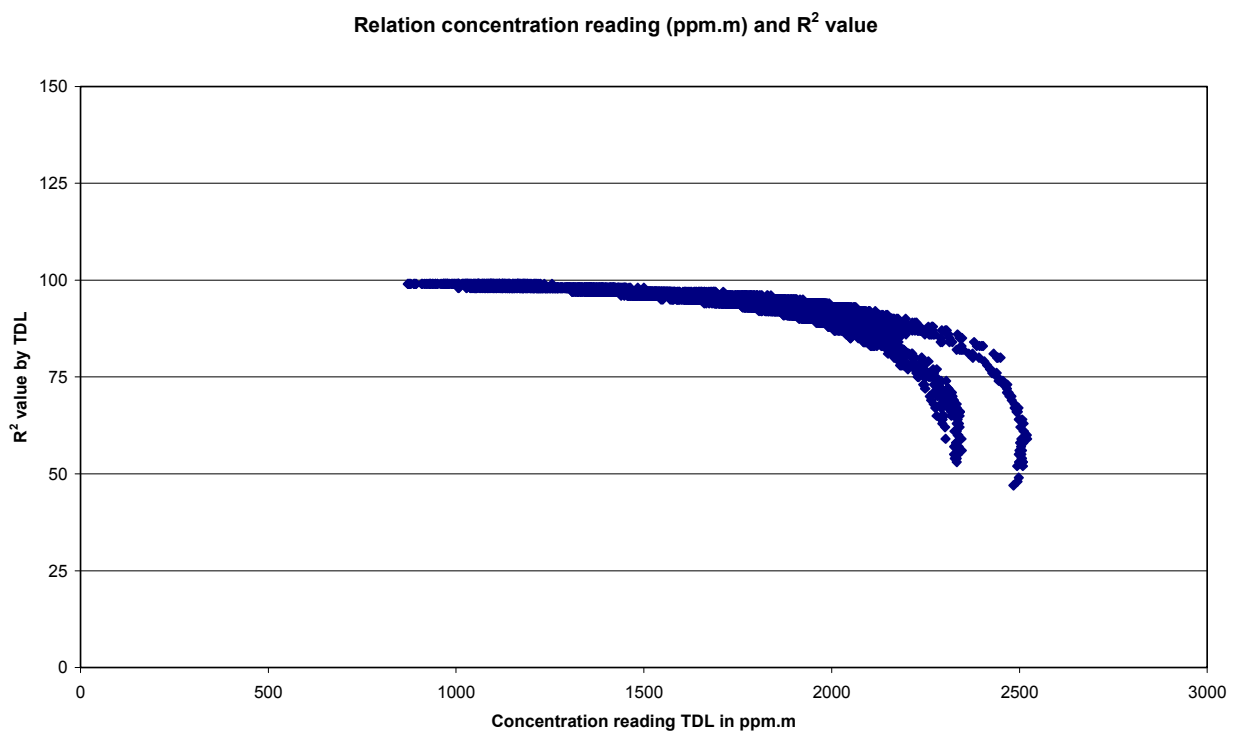
$$I_{\lambda 2x} = E_{diam} E_{rfl} E_{reic} E_{soil} E_{aer} I_{\lambda 0} e^{-k 2x}$$

The usual way to avoid of the need to determine all these factors is to a reference wavelength close to the absorption wavelength that has the same influence of all environmental factors except absorption by methane and use the intensity of that wavelength as a reference.

The use of a reference wavelength is not mentioned in the manual. When no reference wavelength is used it will be pretty clear, that the signal will be dependent on the geometry and environmental factors for the instrument. So there will be no unique calibration line for the TDL. When a reference wavelength is used, the most likely problem for this instrument will be a wavelength too close to the absorption line experiencing partial absorption, too far away from the absorption wavelength with other transmission characteristics (eg caused by aerosol scattering) or absorption of the reference line by other substances.

The cause for the systematic difference in calibration and concentration dependent deviation from the reference in the cow house remains unclear when no information is provided on signal processing.

Looking at instrument functioning, hardly no instrument errors were reported by the instrument. The light value remained almost constant at a level (average 8.677 stdv 1.134) indicating no severe blocking by aerosol or misalignment. Fluctuations in  $R^2$  value were much larger indicating signal processing problems.  $R^2$  was 0.95-0.99 for a large part of the time, but values between 0.90 and 0.95 were frequent and during the higher concentrations values dropped even to a level of 0.50. This is illustrated in figure 4.1



**Figure 4.1** Relation between integrated concentration over distance and  $R^2$  value for TDL

The crucial value of 2,000 relates to the product of ambient methane concentration times the maximum distance of 1000 m and may point to a saturation effect for the absorption. When this is the case, mentioning of a maximum in ppm.m instead of distance should be advised.

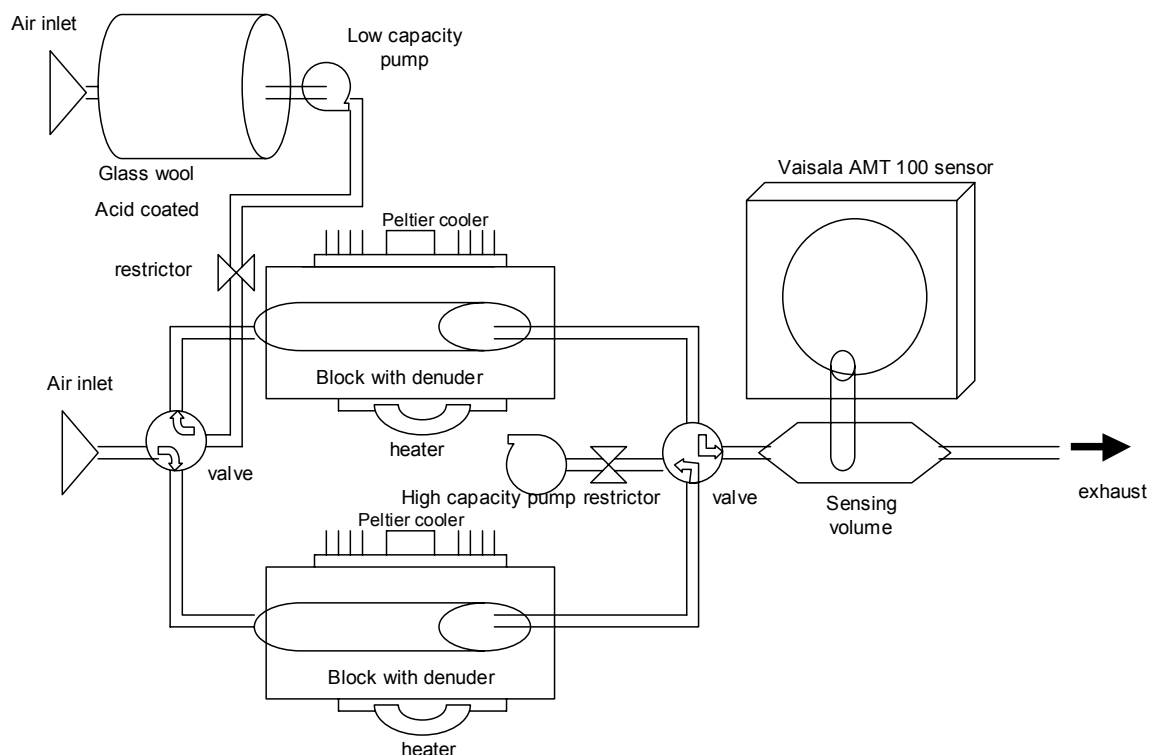
The findings on sensitivity of the Vaisala sensor to relative humidity and CO<sub>2</sub> concentration may lead to hesitation to introduce this instruments for measurements in animal houses. The limitation to concentrations larger than 1 ppm NH<sub>3</sub> limit the possible application to pig farms as concentrations of NH<sub>3</sub> in cow houses and chicken houses may be lower in an appreciable part of the time. Furthermore a calibration curve should be made before installing the instrument to account for non-linearity, especially at concentrations over 30 ppm. Experiments at the Marke show the problem of the detection limit and large spread in concentration values. Furthermore, the relative humidity was very close to or even 100% most of the time. The influence of relative humidity on sensor response was already demonstrated during the controlled room experiments. It should however be pointed out, that the ammonia concentration measured by the monitor come from a sampling system with six inlets at a height of about 6 m while the Vaisala sensor was placed at a height of 3 m in the middle of the cow house. The Vaisala sensor is closer to the sources of ammonia and may be prone to larger fluctuations in concentration. Therefore there should not be too much emphasis on figure 3.17.

The applicability for the Vaisala sensor for use in emission measurements (when combined with measurements of the ventilation rate) is negative for cattle housings. The sensor is however good enough for the work it was developed for, namely send a warning when concentrations reach a certain level. This is important for farmers, as too high concentrations of ammonia may lead to more infections of eyes and lungs for chicken and pigs and reduction of growth at levels of 25-50 ppm NH<sub>3</sub> is proven (Hofschreuder *et al*, 2004)

It is questionable to discard outliers and present selected data as is done in paragraph 3.3. The procedure however pointed in the direction of causes for extreme values (moist and CO<sub>2</sub>) and offered a view on the performance of the sensor when outliers could be prevented to occur. The CO<sub>2</sub> concentration used in the experiment went up to 12,000 ppm, the concentration in animal houses will most of the time be lower than 4,000 ppm. When we look at that range of concentrations and want to measure NH<sub>3</sub> concentration over 1 ppm, the influence will be minor (see figure 3.10).

A possible development for making the sensor applicable to low concentrations and at the same time get rid of the influence of high relative humidity or even condensing water vapour on the sensor would be the introduction of a pre-concentration step. Pre-concentration on a Tungsten oxide coated (Mennen *et al*, 1996) or Vanadium pent-oxide coated (Keuken *et al*, 1989) denuder has proven to be a reliable method. De-sorption should however be done at lower temperature as we want to get the ammonia from the ad-sorption layer and do not want it to be converted in NO<sub>x</sub>. A schematic diagram with two mini-denuders, timer, heating and cooling block, switching valves and sensor is presented in figure 4.2





**Figure 4.2** Schematic drawing of a pre-concentration unit for ammonia fitted with a Vaisala AMT 100 sensor

When the high capacity pump has a flow rate 4 times higher than the flow rate of the low capacity pump, the concentration factor is a factor of 4. The low flow rate of the de-sorption flow is kept low to have a higher concentration factor and accommodate for the slow response ( $T_{50} = 90$  s) for the Vaisala sensor. The block and coated denuder should preferably be made of the same material or material with the same coefficient of expansion. The Peltier cooling elements will work continuously, the heaters only when de-when if the system works, we end up with a low cost measuring system. The only drawback that will be left is the low precision of the system (18.5%), making the system more suitable for long term measurements, averaging out the variation in concentration.



## 5 Conclusions

Overall purpose of the experiments was to determine if a TDL could replace GC measurements for continuous monitoring concentration of methane in animal houses and evaluate the technical performance of an ammonia sensor based on a chip.

The versatility of the TDL gives it an advantage over the use of the traditional GC. The precision is the same, installation much quicker, there is no need for gas bottles or risk for explosions (GC needs  $H_2$  gas). Data handling may be as reliable and less complex as for a GC. Remote control of data may reduce the time spent for visiting the experimental sites.

An additional advantage is the possibility to use the TDL outdoors. This provides an integrated path measurement for mass balance measurements when combined to measurements of a vertical profile (Mosquera *et al*, 2002, Hofschreuder, 2002). In this way, emissions of manure dumps, manure lagoons, manure spreading and very open animal houses can be measured.

The tests for the Boreal TDL in a controlled chamber showed good linearity between 20-750 ppm.m, excellent accuracy (2.3%) and no influence of temperature, relative humidity,  $CO_2$  concentration and  $NH_3$  concentration on the methane reading. The only unsolved problem is the precision. This may be a calibration problem. Use of a calibration factor is possible.

The tests in a cow house were less convincing. Most probable cause for the not linear behaviour of the instrument is saturation of the absorption line for values larger than 2,000 ppm.m. This would limit the path length in animal houses with concentrations up to 100 ppm to 20 m at maximum.

A shorter distance than the wall to wall distance would ask for rigid frames within the animal house, which is a severe handicap in farm management or ask for a sampling line and a duct outside of the animal house for the laser path. The advantage of quick installation disappears in this configuration.

An alternative is the use of a TDL working at another wavelength with lower absorption cross section for  $CH_4$ . Disadvantage is the use of different instruments in animal housings and ambient air.

The Vaisala sensor shows a standard deviation in measuring values larger than 20% as claimed by Vaisala. Results are much better when concentrations lower than 1 ppm  $NH_3$  are avoided as are situations with relative humidity larger than 90%. The linear range (taking the large standard deviation into account) is only between 1 and 30 ppm  $NH_3$ . A larger range asks for calibration or modification of the sensor software. The sensor is susceptible to the relative humidity and the concentration of  $CO_2$ . Changes in software and adding a preconcentration unit might improve the instrument for measuring in animal houses. The instrument can be used to for alarm monitoring, when demands in accuracy and precision are less than for emission monitoring.



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## Summary

Emissions from animal housings are modelled or measured. Modelling has to date a low precision, measuring is however costly. Reduction in costs can be achieved by using instruments that are cheaper or less demanding in costs of maintenance, installation and calibration. The Boreal Gasfinder 2.0 Tunable Diode Laser (TDL) can potentially replace a gas chromatograph for measuring methane concentrations. The Vaisala AMT 100 sensor is far less costly than a  $\text{NO}_x$  monitor preceded by a converter. Both instruments were tested in a climate controlled room with variation in temperature, relative humidity,  $\text{CO}_2$  concentration,  $\text{CH}_4$  concentration and  $\text{NH}_3$  concentration. A large fan in the controlled room was used to get uniform concentrations for all gases. The room was kept at a slight overpressure to assure constant concentrations and minimum external influence. A calibrated GC was used as a standard for methane concentration measurements, a  $\text{NO}_x$  monitor with converter was used as a standard for ammonia.  $\text{CO}_2$  was measured by a Licor 6262, that was equipped with a calibrated dilution unit to measure concentration higher than 3,000 ppm. A Rotronic instrument was used to measure temperature and relative humidity. The TDL was placed at a height of 30 cm in the cell with the retroreflector at 4 m distance from the instrument. The Vaisala sensor was placed in the middle of the cell at 70 cm from the floor. Concentrations ranged from 5-120 ppm for  $\text{CH}_4$ , 0.2-50 ppm for  $\text{NH}_3$ , 500-10,000 ppm for  $\text{CO}_2$ . Temperature was varied (5, 10, 20 and 30 °C), as was relative humidity (55-100%).

The Boreal TDL showed an excellent linearity between 20-750 ppm.m  $\text{CH}_4$ . The relative accuracy is 2.3%. There is no influence of temperature or humidity detected on the signal. There is no interference from  $\text{CO}_2$  or  $\text{NH}_3$  on the signal. Precision is still an open question as there is a systematic difference between TDL concentration and reference concentration of 30%. The accuracy of the Vaisala sensor is larger than the 20% claimed by Vaisala. Results are much better when concentrations lower than 1 ppm  $\text{NH}_3$  are avoided as are situations with relative humidity larger than 90%. The linear range (taking the large standard deviation into account) extends only between 1 and 30 ppm  $\text{NH}_3$ . A larger range asks for calibration of the a-linear response for concentrations between 30 and 100 ppm  $\text{NH}_3$ . The sensor is susceptible to the relative humidity and the concentration of  $\text{CO}_2$ . Changes in software and adding a preconcentration unit might improve the instrument for measuring in animal houses. The instrument can be used to for alarm monitoring, when demands in accuracy and precision are less than for emission monitoring.

Final tests of both instruments took place in a cow house under normal operating conditions. Tests of the TDL in the cow house reveal that there is possibly saturation of the absorption wavelength at values larger than 2000 ppm.m  $\text{CH}_4$ . This would limit the path length in animal houses with concentrations up to 100 ppm to 20 m at maximum. Loss in sensitivity at larger values than 1,500-2,000 ppm.m  $\text{CH}_4$ , which is already reached at a level of 23 ppm at the used path length of 65 m make it impossible to use this instrument in cow houses. The use of an instrument functioning at a wavelength with less absorption cross section was not investigated.

The Vaisala sensor was exposed to ammonia concentrations close to the observed practical detection limit of 1 ppm  $\text{NH}_3$  in the cow house. The sensor was more close to the sources of ammonia and performed point measurements, that were compared to integrated measurements from a sampling line. This may account for the large spread in results compared to the reference concentration and makes the practical test less conclusive as the test in the controlled room.

Final conclusions with respect to the possibility to replace conventional measuring methods in animal houses are;

The Boreal TDL has great potential, but the linear range should be extended at least a factor of 2 up to 3,000 ppm.m  $\text{CH}_4$  or a less sensitive version of the instrument should be used.

The Vaisala AMT 100 sensor may be used for alarm monitoring with low precision. Precision for emission monitoring (in combination with determination of ventilation rate) may be improved by calibrating the a-linear response for concentrations over 30 ppm  $\text{NH}_3$  en adding a preconcentration unit.