

# Evaluation of the laboratory testing of ozone sensor systems

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## 1 Introduction

The performance characteristics of the ozone  $(O_3)$  sensors determined in our laboratory study were: accuracy (deviation from reference), linearity (coefficient of determination, slope, intercept; compared to reference), sensor stability (standard deviation of the sensor signal), between-sensor uncertainty, influence of temperature and relative humidity and cross-interference.

In total, the laboratory tests took 77 hours. Essential part of the testing schedule was the ramping experiment at constant temperature and relative humidity. During this experiment concentrations (NO<sub>2</sub>, O<sub>3</sub>) were kept constant for two hours followed by a stepwise change to another concentration level. For further details on the experimental setup, the reader is referred to <u>the test protocol</u>.

The VAQUUMs project started with the selection of a number of gas sensors (nitrogen dioxide and ozone) for the comparative testing (laboratory and field). The following sensor systems were finally chosen (Table 1):

NO <sub>2</sub>	O <sub>3</sub>	
Alphasense B43F	Aeroqual SM50	
Envea Cairclip NO <sub>2</sub>	Alphasense B431	
Citytech 3E50*	Citytech 3E1F*	
Membrapor C1	Envea Cairclip O3	
Membrapor C20	Membrapor C5	

Table 1 The list of NO<sub>2</sub>-sensors as selected in the VAQUUMS project

Note that no lab test results can be shown for the Citytech sensors. The sensors were not installed properly, due to a mistake by the VAQUUMS-team. Thus, no trustworthy data have been collected in the laboratory.

In this report we will discuss the results of the  $O_3$  sensors. First a summary is given, followed by a report per sensor type.



## 2 Summary: O<sub>3</sub>-sensors

At the beginning of the experiment, it appeared that not every  $O_3$  sensor copy operated satisfactorily. In the case of the ozone sensors, all the Envea Cairclip types measured without noticeable malfunctioning. For the remaining four sensor systems, at least one copy appeared unreliable (and therefore not included in the experiment).

During the ramping experiment all the sensor copies tracked reasonably well with the step changes in concentration (indicated by the reference instrument). As an example, see the results for the Envea Cairclip and Membrapor C5  $O_3$  sensors below in Figure 1.

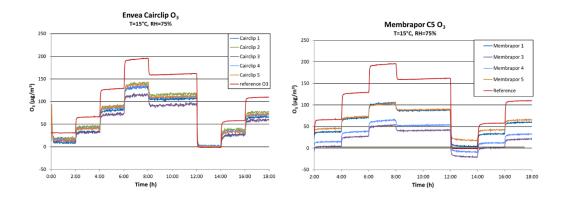
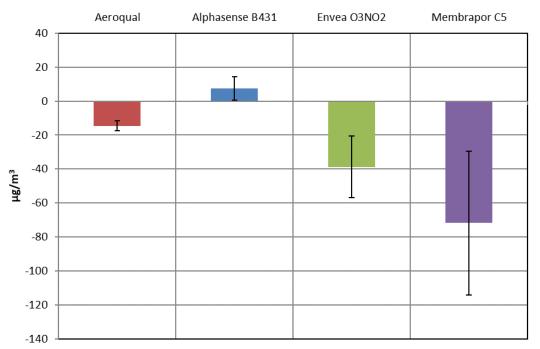


Figure 1 Examples of sensors' responses (Cairclip and Membrapor C5) during the O<sub>3</sub> ramping experiment compared to the reference instrument (indicated in red); time resolution is one minute

The **accuracy** of the different sensor systems (uncalibrated) is variable (Figure 2, average per sensor type). As a contrast to the NO<sub>2</sub> sensors, the O<sub>3</sub>-systems under- or overestimate the reference concentrations. The Aeroqual and Alphasense perform best (less than 20  $\mu$ g/m<sup>3</sup> difference) while the largest deviation is observed for the Membrapor C5; here, every copy overestimates the reference value during the testing. Clearly, the need for (additional) calibration is demonstrated.





#### Average deviation from reference



The evaluated O<sub>3</sub>-sensor systems all exhibit a high degree of **linearity** (typically  $r^2 > 0.9$ ) over the concentration range examined in this study (0-200 µg/m<sup>3</sup>). As can already be deduced from Figure 1, slopes and intercepts (largely) differ between systems (see Figur3 for examples and Table 2 for an overview of average linear regression coefficients per system).

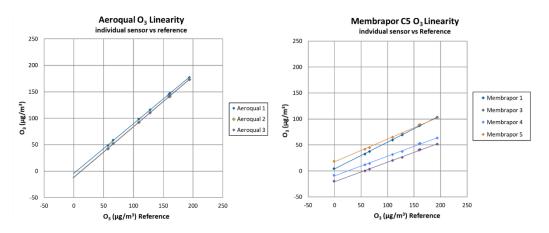






Table 2 Average linear regression coefficients per system

y = ax+b	а	b	n
Aeroqual	0.95	4,3	3
Alphasense B431	1.05	0	4
Envea Cairclip	0.63	-4	5
Membrapor C5	0.43	-2	4

Regression equations per sensor copy were applied for calibration of the sensor outcomes. After doing so, results of the ramping experiment look like in Figure 4 for the Cairclip and Membrapor C5 O<sub>3</sub>-sensors (as in Figure 1).

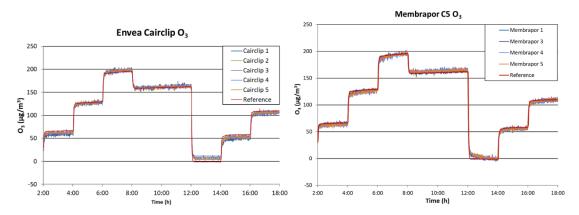
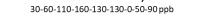


Figure 4 Examples of sensors' (Cairclip and Membrapor C5) responses in the ramping experiment after calibration; time resolution: one minute, reference indicated in red

Results of the sensor **stability** ('repeatability') are given in Figure 5 for all the available sensor copies and systems (as function of concentration level; after calibration). The Alphasense, and Aeroqual O<sub>3</sub> sensors perform best here: 1.0, and 1.5  $\mu$ g/m<sup>3</sup>, respectively, when averaged over the entire experiment. and by indicating relatively small differences between concentration levels. The Envea Cairclip and Membrapor C5 behave similar: 2.3  $\mu$ g/m<sup>3</sup> and 2.8  $\mu$ g/m<sup>3</sup>, but with larger differences between copies.



sensor stability



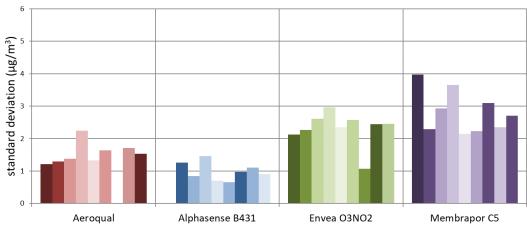
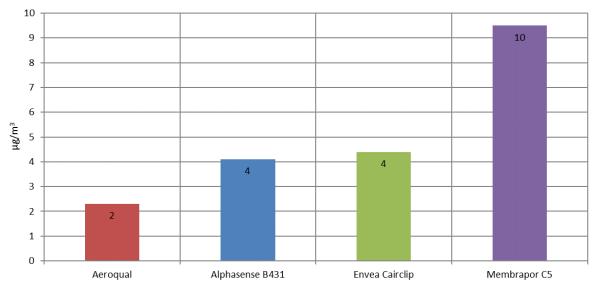


Figure 5 Standard deviations for the  $O_3$  sensors during the nine steady-state conditions of the ramping experiment

As a measure of the variation between copies of one O<sub>3</sub> sensor type the **between sensor uncertainty** (BSU) has been calculated (after calibration) and visualized in Figure 6 (for its definition *see link report*). Clearly, the Alphasense B431 performs best while the highest BSU is observed for the Membrapor C5.



#### Between sensor uncertainty

Figure 6 Between sensor uncertainty for each sensor system

The readings of chemical sensor  $O_3$  systems are influenced by (changes in) **relative humidity** (RH) and **temperature** (T). As RH and T in the atmosphere are highly (inversely) correlated, focus here is on the effect of a changing RH (from 50 to 60%) keeping T (15°C) and ambient concentrations (80 ppb) constant (Figure 7; uncalibrated data).



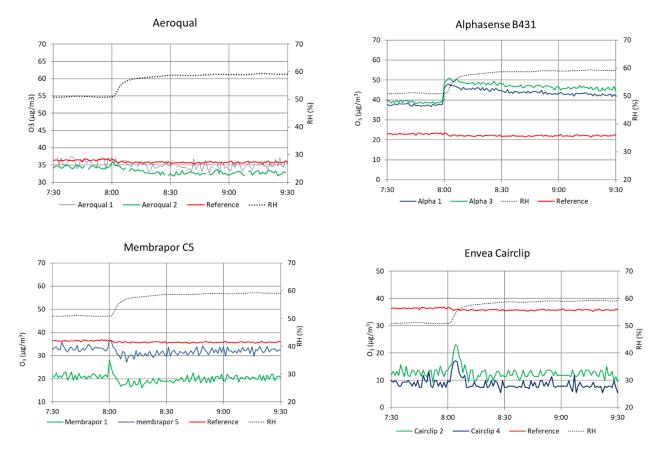


Figure 7 Responses of various O<sub>3</sub> sensors when increasing RH (at fixed T and O<sub>3</sub>)

All the  $O_3$ -sensors investigated here appear sensitive for changes in RH but in (very) different ways. In Figure 7 responses differ in magnitude, sign and duration (like is the case for the  $NO_2$ -sensors).

A direct comparison of the various systems is given in Figure 8. For two systems (Alphasense and Membrapor) a change in RH leads to higher measurement values. The Cairclip returns to the ambient level within 15 min; in the case of Membrapor this is roughly 1 hour. As in the case for NO<sub>2</sub>, the Alphasense does not return to the ambient level within two hours. The Aeroqual system indicates a rather small negative change in concentration but does not return to its original value. Deviations are larger for Cairclip and Membrapor but as noted earlier signals return to ambient level. In the case of the Alphasense and Aeroqual the deviations persist. Overall, due to the quick return to the original level the Membrapor perform best. In general, the sensor systems react more

sensitive for larger steps for RH, and at higher ambient T and  $O_3$ -concentration levels (leaving conclusions above unchanged).



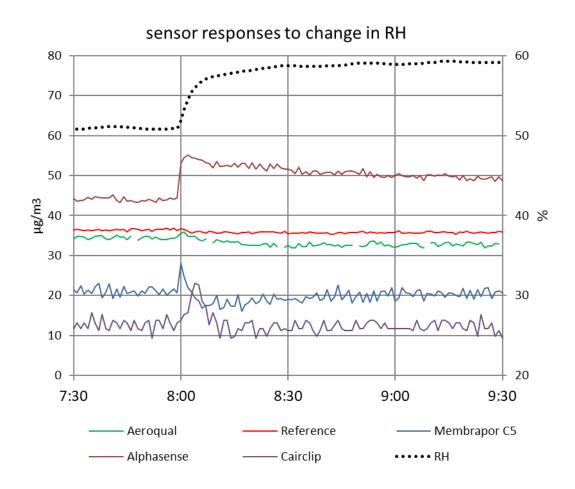


Figure 8 Responses of various O<sub>3</sub> sensors when increasing RH (at fixed T and O<sub>3</sub>)

To test the **cross sensitivity** (for NO<sub>2</sub>), the sensors in the exposure box were exposed to different levels at nonzero O<sub>3</sub> levels. Due to a technical failure, testing at zero O<sub>3</sub> levels could unfortunately not be carried out. The ratio O<sub>3</sub> sensor versus O<sub>3</sub> Reference has been estimated at different levels of O<sub>3</sub> and the average result per sensor type has been given in Figure 9 (and compared with the case that NO<sub>2</sub> is zero; uncalibrated data).



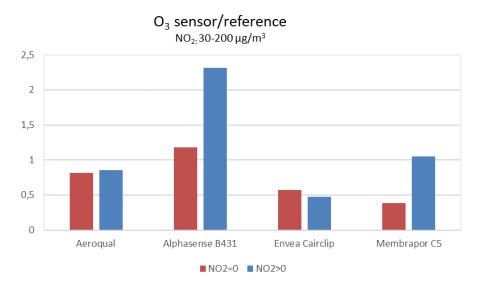


Figure 9 Ratios sensor vs Reference (per sensor) with NO<sub>2</sub>>0 and NO<sub>2</sub>=0

It is seen that every sensor type is influenced by the presence of NO<sub>2</sub> in various rates. The least affected are the Aeroqual and Cairclip while the Alphasense and Membrapor C5 are distorted most.

## 2.1 Remarks on laboratory experiment

- The examination via a characterized gas chamber and exposure box proves to be an adequate means for establishing basic behavioral properties of gas sensors. There was no direct evidence of gas phase interaction (reactivity) between exposure box and sensor systems that might have influenced results in the various stages of the tests. This indicates that the chamber and its supporting components (gas delivery system, environmental controls) were of sufficient quality.
- Characterization of the chamber and box prior to the testing (e.g., reference monitors
  response versus change in test atmosphere, stability of test atmosphere under static
  conditions, impact of changing environmental conditions upon reference monitors)
  ensured a reasonable evaluation of the devices under the testing scenarios. However,
  during one of the tests, at (very) high temperature and relative humidity, the gas tubing
  to the reference monitor showed indications of condensation effects that influenced the
  reading of the reference monitor (leaving the qualitative results of the susceptibility
  experiment unchanged).
- A comparison between the sensors' performances is not straightforward. Except for the Alphasense B34F and B431 it was unclear if the sensor system included built-in





calibration features. In order to obtain an equal 'level playing field' all the  $NO_2$  and  $O_3$  sensors were calibrated (simple linear regression) by using the data of the ramping experiment (for more information on this, see the performance summaries).

## 2.2 General remarks and recommendations

- All sensors appear to offer detection sensitivities in the low range with a stability (repeatability) within acceptable values. Such findings are encouraging for their potential applicability for citizen science and probably for professionally-performed.
- Of significance here is that the rise and lag times observed with the sensors are in good correspondence with the reference instrument (in the order of a few minutes). The sharp stair-step pattern of response in the graphical displays of the ramping experiment is an indication of how quickly most of the sensors respond. This indicates that such sensors also have a potential for use in non-static situations (movement with respect to spatial setting). However, the tests performed here were not of sufficient design to evaluate very short temporal impacts.
- Some positive and negative bias occurred when pollutant-free air was being supplied to the exposure box. Linked to the often high linearity of response, this is an indication that for the sensors tested, commonly used zero and span procedures might be replaced with simple collocation comparisons with reference monitors preferably in the users environmental setting.
- Some sensor copies provided for evaluation yielded no usable data and were discarded for the evaluations to proceed. This is an important finding: users need to ensure that their device has been calibrated or compared with ambient monitoring data from collocation trials before being used in data collections.
- This evaluation did not have the capability of examining long-term performance response characteristics (e.g., drift of signal over extended time periods, stability of response with respect to sensor lifetime). End users should perform at least one of the evaluation procedures described above on a reoccurring basis to ensure the operation status of their device.
- The evaluations performed here represent a first step in understanding how the low cost sensor compares to recognized reference specifications. The results were encouraging with respect to how well the devices performed for certain performance characteristics (e.g., linearity, stability).



• Additional testing, i.e. evaluation of sensors under true ambient conditions, will provide enhanced understanding of how well these sensors respond to changing environmental conditions and their applicability for various data collection scenarios.



## 3 Reports per sensor type: O<sub>3</sub> sensors

## 3.1 Tested parameters

The calculations carried out in the examination of the VAQUUMS sensor data sets are defined here:

## 1. linearity

Correlation of sensors (of one type) with reference equipment is calculated using orthogonal regression on the (average) concentrations of each step in the ramping experiment. To exclude irregular behaviour after changing the climate chamber conditions, the data for the first fifteen minutes of each step have been discarded. The calibration of sensors used the slope and intercept as determined in this analysis.

## 2. accuracy

The accuracy has been calculated as follows:

accuracy (%) = 
$$100 - \left(\frac{|\overline{\text{sensor}} - \overline{\text{reference}}|}{\overline{\text{reference}}}\right) * 100,$$

where sensor and reference indicate the average concentration levels as measured by the sensor and reference equipment in the ramping experiment.

## 3. stability during ramping experiment

The stability of a sensor or a set of sensors (of one type) is expressed by the standard deviation (SD) of the concentration datasets collected in the ramping experiment. The average standard deviation (SD<sub>average</sub>) for a set of *n* sensors is calculated by

$$SD_{average} = \sqrt{\sum_{i=1}^{n} \frac{SD_i^2}{n}}$$
.

The relative standard deviation (SD $_{\rm rel}$ ) is the standard deviation divided by the corresponding average concentration.

## 4. between sensor uncertainty

The variation between the various sensors (of one type) over a measurement period is given by the between-sensor uncertainty (BSU<sub>sensor</sub>):

$$\mathsf{BSU}_{\mathsf{sensor}} = \sqrt{\frac{\sum_{i=1}^{n} \sum_{j=1}^{k} (\mathsf{sensor}_{ij} - \mathsf{average}_{i})^2}{k(n-1)}},$$

with n the number of sensors and k the number of measurements. The BSU has been derived from 5-min averages derived from the ramping experiment.



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# Laboratory Evaluation Aeroqual SM50 O<sub>3</sub> sensor



Manufacturer: Aeroqual Link to website manufacturer

Link to test protocol



## 3.2 Aeroqual SM50 versus Reference

Three **Aeroqual SM50**  $O_3$  sensors were evaluated in the RIVM Testing Laboratory under controlled  $O_3$  concentrations, temperature and relative humidity. These sensors were also tested in the field (at the reference monitoring station in Borgerhout).

### <u>Aeroqual O<sub>3</sub></u>

- Electrochemical sensor
- Time resolution is 1 minute (mean value)
- Unit ID's: Aeroqual1, Aeroqual2, Aeroqual3; a fourth unit stopped producing data after half a day.

#### Reference instrument

- Thermo 49i UV photometric O<sub>3</sub> analyzer
- Time resolution: 1 minute

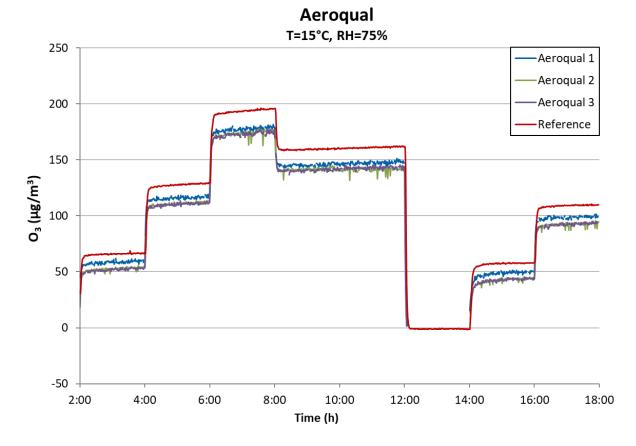


For the details about the laboratory protocol followed here, consult our <u>test protocol</u>.



## 3.2.1 Ramping experiment (T=15°C; RH=75%)

In the first test sensors were exposed to different concentration levels to check linearity, agreement between sensors and agreement with the reference.



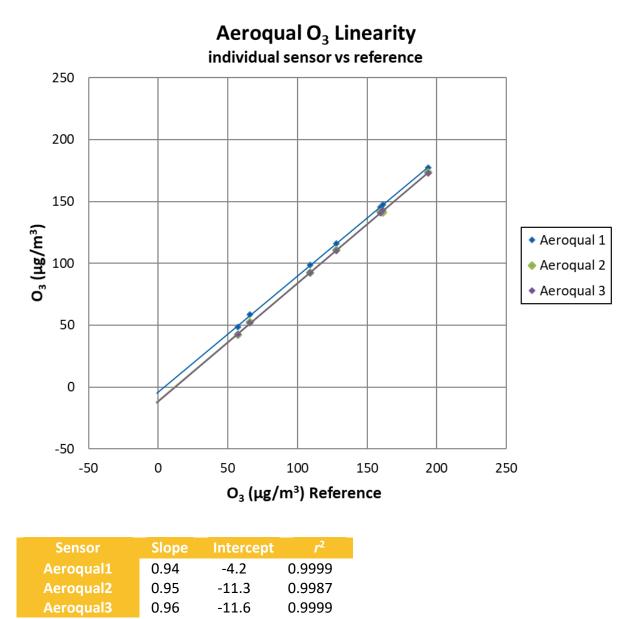
- The Aeroqual sensors followed the step changes in O<sub>3</sub> concentration (between 0 and 200  $\mu$ g/m<sup>3</sup>) reasonably. In comparison to the reference instrument all units underestimated the reference O<sub>3</sub> concentrations.
- During the baseline step, the sensor units produced no values and no baseline readings could be established.





#### 3.2.2 Linearity

Average concentrations per step were calculated and used for lineair regression (y=ax+b).

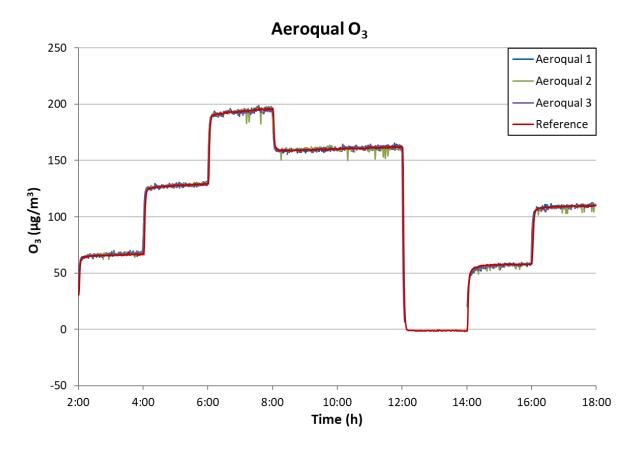


• All three units showed a very high correlation ( $r^2$ >0.99) with the corresponding reference data during this ramping experiment). The slopes in the regression equations were around 0.95; intercepts varied between -4.2 and -11.6 µg/m<sup>3</sup>.









• The slopes and intercepts calculated in the ramping experiment were used for a (simple) calibration of the sensor units. After applying such a procedure, all the units produced data that were (very) close to the levels measured by the Thermo reference instrument.





# 3.2.4 Accuracy

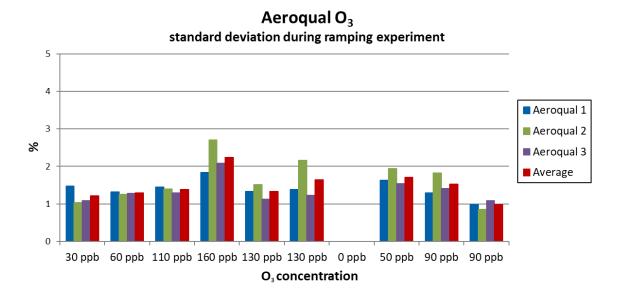
Reference mean (µg/m3)	Sensor mean (µg/m3)	Accuracy (%)
57	57	99
66	67	99
109	109	100
128	128	100
159	160	100
194	194	100

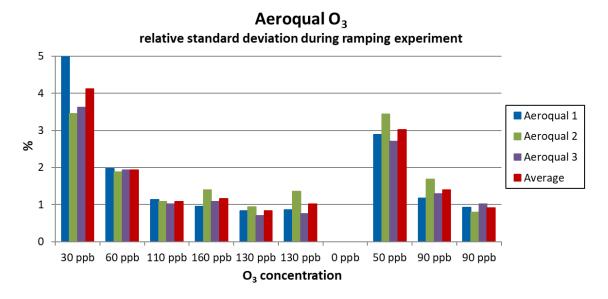
• After calibration, the sensors showed an accuracy very close to 100%.



## 3.2.5 Stability under steady-state conditions

Sensor stability is defined here as the standard deviation during each of the seven steadystate conditions of the ramping experiment (also see the Appendix). The standard deviation of the reference is 0.7  $\mu$ g/m<sup>3</sup> (range: 0.2-1.4  $\mu$ g/m<sup>3</sup>); relative standard deviation is 0.7 (0.3-1.3).





- In most cases, the standard deviations of the sensors' output were less than 2  $\mu$ g/m<sup>3</sup> (after calibration). There was no significant difference between the sensors.
- The relative standard deviations were less than 4% and depended on ambient O<sub>3</sub> concentrations. Since absolute SD's were quite constant, the RSD's were lower at higher concentration levels.





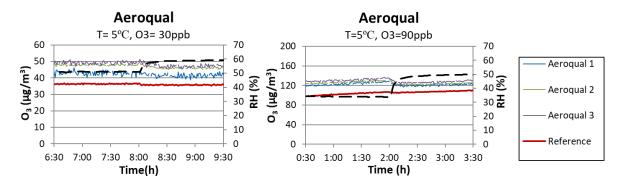
## 3.2.6 Between sensor uncertainty

• As a measure of the variation between sensors of one type the between sensor uncertainty (BSU) has been calculated. For this sensor the result was 2.3  $\mu$ g/m<sup>3</sup> (being the best result).



## 3.2.7 Influence of relative humidity

The readings of gas sensor systems are known to be affected by changes in meteorological parameters (RH, T). Here, the effect of a changing RH (at constant levels for temperature and concentration) is shown.

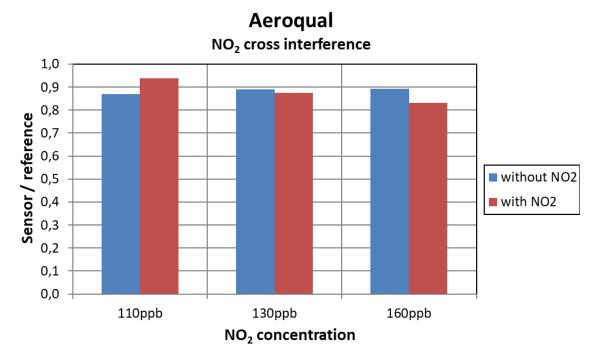


- Generally, a (rapid) increase in relative humidity resulted in slightly lower values produced by the sensors (at a constant level for NO<sub>2</sub>).
- The small decrease appeared systematic.



## 3.2.8 Cross sensitivity

To test the cross sensitivity, the sensors in the exposure box were exposed to different levels of  $NO_2$  at nonzero  $O_3$ -concentrations.



• A relatively small effect of interference was observed. The presence of NO<sub>2</sub> resulted in relatively minor changes in the sensor measurement values for O<sub>3</sub>.





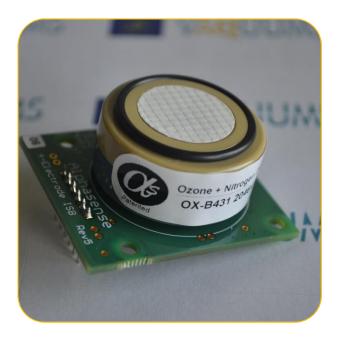
#### 3.2.9 Summary

- **Linearity of sensor response**: All sensor units show a very high correlation ( $r^2$ >0.99) compared to corresponding Thermo O<sub>3</sub> analyzer (between 0-220 µg/m<sup>3</sup> and after calibration).
- Accuracy: All the units indicate a very high accuracy compared to reference instrument (after calibration). Before calibration, the accuracies of individual sensors are between 80 and 87%.
- Stability: The standard deviations of the sensors' signals are less than 2 μg/m<sup>3</sup> (during stationary conditions over 2 hours) and appear independent of concentration level.
- Between-sensor uncertainty: The uncertainty between the sensors is 2.3 μg/m<sup>3</sup> (the best result).
- Effect of relative humidity and temperature: A rise in relative humidity only affects the sensor readings by showing a minor underestimation of the true values of O<sub>3</sub>.
- Cross sensitivity: A relatively small effect of interference is observed. The presence of NO<sub>2</sub> has a relatively small (systematic) effect on the sensor values for O<sub>3</sub>.
- Data recovery: The data recovery for the three units during this experiment is around 75% (for a measurement period of 80 hours in total).





# Laboratory Evaluation Alphasense B431 O<sub>x</sub> sensor



Manufacturer: Alphasense Link to website manufacturer

Link to test protocol



## 3.3 Alphasense B431 versus Reference

Four **Alphasense B431** O<sub>3</sub> sensors have been evaluated in the RIVM Testing Laboratory under controlled NO2 concentrations, temperature and relative humidity. In future, these sensors will also be tested in the field (at Borgerhout station)

## Alphasense B431

- Electrochemical sensors
- Time resolution: 1 minute
- Unit ID's : Alpha1, Alpha3, Alpha4, Alpha5; another device was left out during the study due to malfunctioning

#### Reference instrument

- Thermo 49i UV photometric O<sub>3</sub> analyzer
- Time resolution: 1 minute

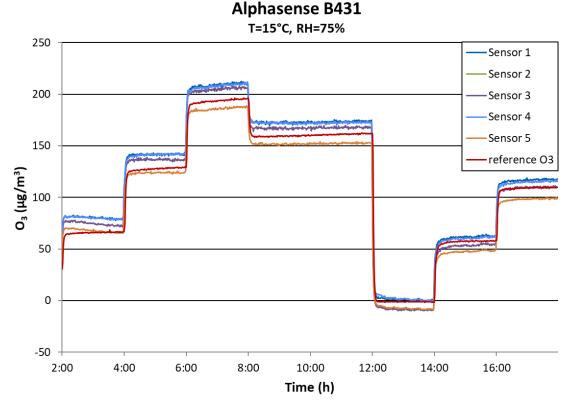


For the details about the laboratory protocol followed here, consult our <u>test protocol</u>.



## 3.3.1 Ramping experiment (T=15°C; RH=75%)

In the first test sensors were exposed to different concentration levels to check linearity, agreement between sensors and agreement with the reference.



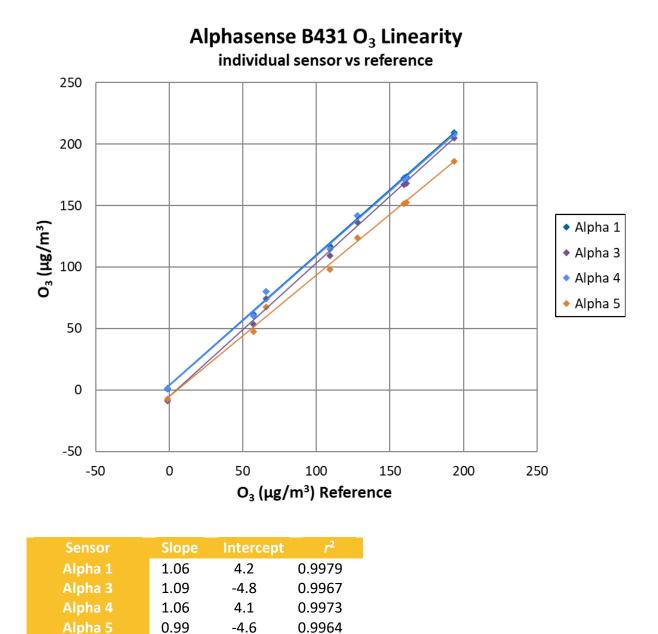
- The Alphasense sensors tracked well with the step changes in O<sub>3</sub> concentration (between 0 and 200  $\mu$ g/m<sup>3</sup>) measured by the Thermo reference analyzer. The various units over- or underestimated the O<sub>3</sub> reference concentrations.
- Two of the units (Alpha1, Alpha4) had baseline readings close to 0 μg/m<sup>3</sup> whereas
   Alpha3 and Alpha5 read around -8 μg/m<sup>3</sup>.





#### 3.3.2 Linearity

Average concentrations per step were calculated and used for lineair regression (y=ax+b).

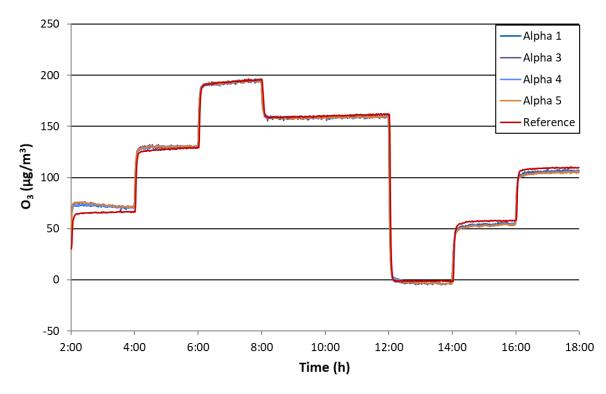


• All four units showed a very high correlation ( $r^2$ >0.99) with the corresponding reference data (derived from the ramping experiment). The slopes in the regression equations were close to one; intercepts varied between -4.8 and +4.2 µg/m<sup>3</sup>.





## 3.3.3 Ramping experiment after calibration



## Alphasense B431 O<sub>3</sub>

• The slopes and intercepts calculated in the linearity experiment were used for a (simple) calibration of the sensor units. After applying this procedure, the units produced data that were (very) close to the levels measured by the Thermo reference instrument.





# 3.3.4 Accuracy

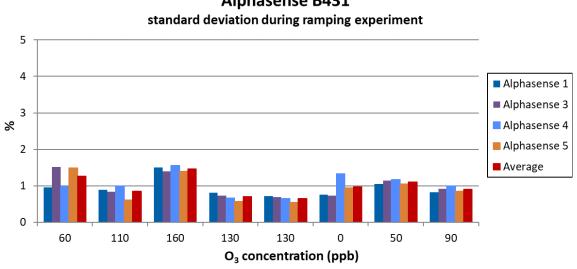
Reference mean (µg/m3)	Sensor mean (µg/m3)	Accuracy (%)
57	53	93
66	72	90
109	105	96
128	130	98
159	159	99
194	193	100

• After calibration, the sensors showed an accuracy between 90 and 100%.



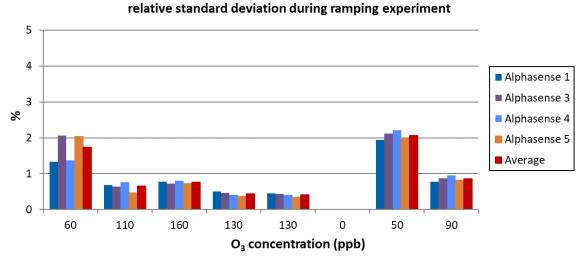
#### Stability under steady-state conditions 3.3.5

Sensor stability is defined here as the standard deviation during each of the seven steadystate conditions of the ramping experiment (also see the Appendix). The standard deviation of the reference is 0.7  $\mu$ g/m<sup>3</sup> (range: 0.2-1.4  $\mu$ g/m<sup>3</sup>); relative standard deviation is 0.7 (0.3-1.3).





## Alphasense B431



- The standard deviations of the sensors' output were less than 1.5  $\mu$ g/m<sup>3</sup> (after calibration). There was no dependence on the ambient O<sub>3</sub> level.
- The relative standard deviations were, in most cases, less than 2%. The performance was • better at higher concentration levels.





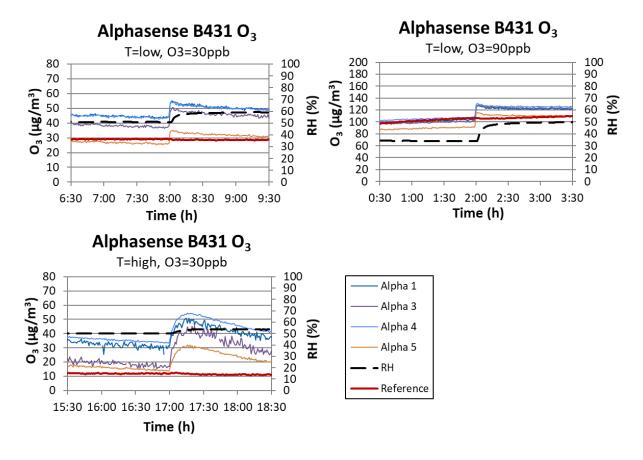
# 3.3.6 Between sensor uncertainty

• The calculated uncertainty between the sensors' data sets is 4.1  $\mu$ g/m<sup>3</sup> (slightly better than the average result).



## 3.3.7 Influence of relative humidity

The readings of gas sensor systems are known to be affected by changes in meteorological parameters (RH, T). Here, the effect of a changing RH (at constant levels for temperature and concentration) is shown.

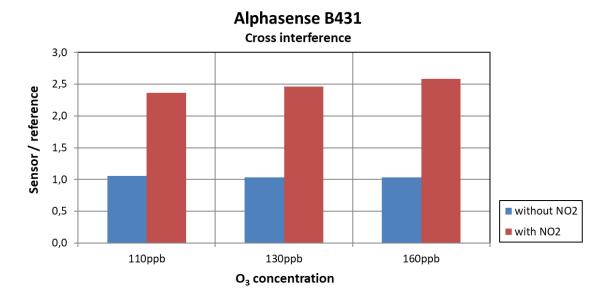


- Generally, a (rapid) increase in relative humidity resulted in a higher measurement value produced by the sensors (at a constant level for O<sub>3</sub>); the overestimation was larger at a higher temperature and ambient concentration of O<sub>3</sub>.
- This increase was followed by a rather slow decrease (lasting at least two hours) in the sensor signals.



## 3.3.8 Cross sensitivity

To test the cross sensitivity, the sensors in the exposure box were exposed to different levels of  $NO_2$  at nonzero  $O_3$ -concentrations.



• At various levels of ambient O<sub>3</sub> (100, 120, 150 ppb) the presence of NO<sub>2</sub> resulted in considerable higher values produced by the sensors for O<sub>3</sub> (20-40%)



#### 3.3.9 Summary

- Accuracy: All sensor units show an acceptable accuracy when compared to reference instrument (> 90%). On an individual basis, accuracies range from 89% to 94%.
- > **Linearity of sensor response**: All sensor units show a very high coefficient of determination ( $r^2$ >0.99) with the corresponding Thermo analyzer (measurements between 0-220 µg/m<sup>3</sup> and after calibration). Regression slopes are near to one.
- Stability: The standard deviations of the sensors' signals are less than 2 μg/m<sup>3</sup> (during stationary conditions over 2 hours) and appear independent of concentration level.
- **Between-sensor uncertainty**: The uncertainty between the sensors is  $4.1 \,\mu\text{g/m}^3$  (slightly better than the average).
- Effect of relative humidity and temperature: A rise in relative humidity affects the sensor readings. The resulting increase in the measured O<sub>3</sub> concentrations rises even more at higher temperatures and concentration levels.
- Cross sensitivity: The presence of NO<sub>2</sub> affects the operation of the sensors resulting in considerable higher concentration values for O<sub>3</sub>.
- Data recovery: In this study, the data recovery for every unit is 100% (for a measurement period of 77 hours in total).





### Laboratory Evaluation Envea Cairclip NO<sub>2</sub>/O<sub>3</sub> sensor



Manufacturer: Envea Link to website manufacturer Link to test protocol



### 3.4 Envea Caiclip NO<sub>2</sub>/O<sub>3</sub> versus Reference

Five **Envea Cairclip** sensors were evaluated in the RIVM Testing Laboratory under controlled O<sub>3</sub>concentrations, temperature and relative humidity. These sensors were also tested in the field (at the reference monitoring station in Borgerhout).

#### Envea Cairclip NO2/O3

- Electrochemical sensors
- Time resolution is 1 minute
- Unit IDs : Envea1, Envea2, Envea3, Envea4, Envea5

#### Reference instrument

- Thermo 49i UV photometric O<sub>3</sub> analyzer
- Time resolution: 1 minute

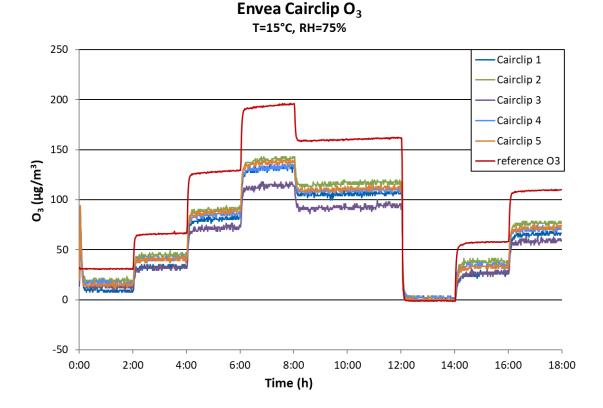


For the details about the laboratory protocol followed here, consult our <u>test protocol</u>.



### 3.4.1 Ramping experiment (T=15°C; RH=75%)

In the first test sensors were exposed to different concentration levels to check linearity, agreement between sensors and agreement with the reference.



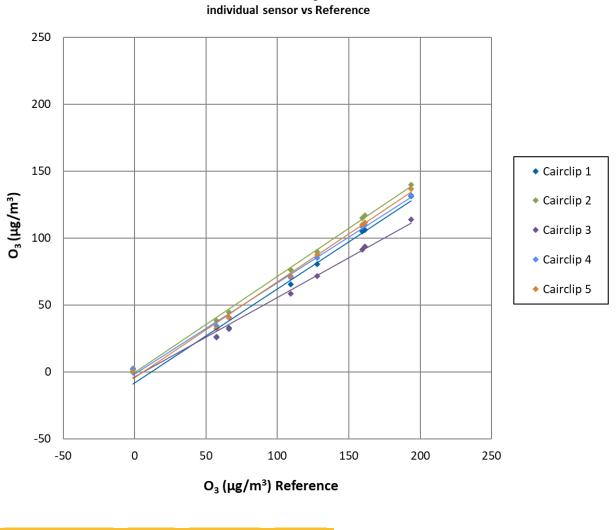
- The Envea sensors followed the step changes in  $O_3$  concentration (between 0 and 200  $\mu$ g/m<sup>3</sup>) rather well. In comparison to the reference instrument all units underestimated  $O_3$  reference concentrations
- The baseline readings of all units are very close to the reference baseline.





#### 3.4.2 Linearity

Average concentrations per step were calculated and used for lineair regression (y=ax+b).



### Envea Cairclip $O_3$ Linearity

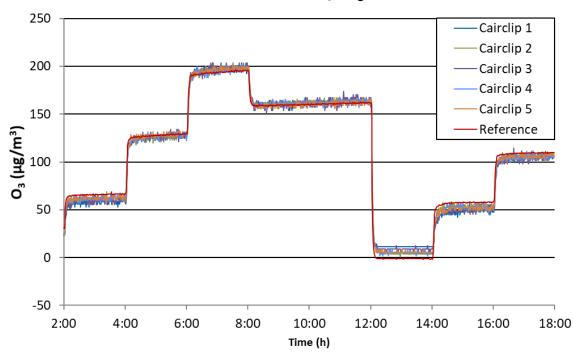
Sensor	Slope	Intercept	r <sup>2</sup>
Cairclip 1	0.70	-7.9	0.9885
Cairclip 2	0.72	0.72	0.9976
Cairclip 3	0.60	-3.4	0.9923
Cairclip 4	0.68	-1.4	0.9966
Cairclip 5	0.72	-4.0	0.9959

• All four units showed a very high correlation ( $r^2$ >0.99) with the corresponding reference data (derived from the ramping experiment). The slopes of the regression equations vary between 0.60 and 0.72 with intercepts relatively close to zero.









Envea Cairclip O<sub>3</sub>

• The slopes and intercepts calculated in the ramping experiment were used for a (simple) calibration of the sensor units. After applying this procedure, the units produced data that were (very) close to the levels measured by the Thermo reference instrument.





### 3.4.4 Accuracy

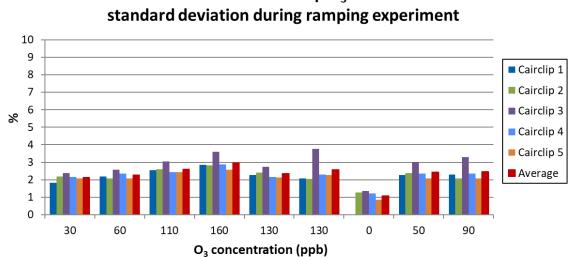
Reference mean (µg/m3)	Sensor mean (µg/m3)	Accuracy (%)
57	51	89
66	61	92
109	105	96
128	126	99
159	160	100
194	196	99

• After calibration, the sensors showed an accuracy between 89 and 100%.



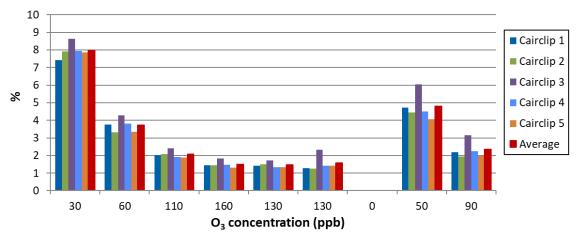
#### 3.4.5 Stability under steady-state conditions

Sensor stability is defined here as the standard deviation during each of the seven steadystate conditions of the ramping experiment (also see the Appendix). The standard deviation of the reference is 0.7  $\mu$ g/m<sup>3</sup> (range: 0.2-1.4  $\mu$ g/m<sup>3</sup>); relative standard deviation is 0.7 (0.3-1.3).



### Envea Cairclip O<sub>3</sub>

Envea Cairclip O<sub>3</sub> relative standard deviation during ramping experiment



- In most cases, the standard deviations of the sensors 'output' are less than  $3 \mu g/m^3$  (after • calibration). One unit (Cairclip 3) systematically owned the highest standard deviation during all steps.
- The relative standard deviations vary between 1% and 8% and depended on ambient concentration level.
- The relative standard deviations were less than 4% and depended on ambient  $O_3$ • concentrations. Since absolute SD's were quite constant, the RSD's were lower at higher concentration levels.





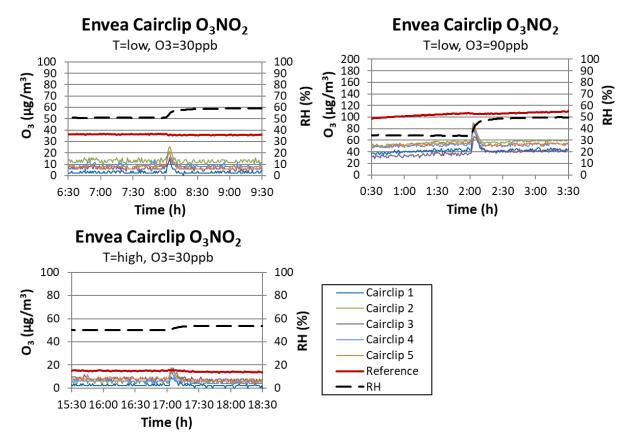
### 3.4.6 Between sensor uncertainty

• The calculated uncertainty between the sensors' data sets is 4.4  $\mu$ g/m<sup>3</sup> (an average result in this study).



### 3.4.7 Influence of relative humidity

The readings of gas sensor systems are known to be affected by changes in meteorological parameters (RH, T). Here, the effect of a changing RH (at constant levels for temperature and concentration) is shown.

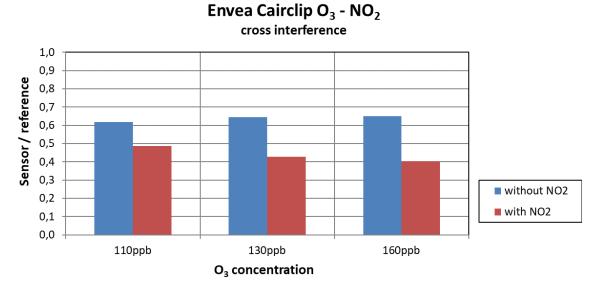


• Generally, a (rapid) increase in relative humidity resulted in a relatively small positive peak response followed by a gradual return to the original level within 15 minutes. There is no obvious dependence on ambient O<sub>3</sub> level or temperature.



### 3.4.8 Cross sensitivity

To test the cross sensitivity, the sensors in the exposure box were exposed to different levels of  $NO_2$  at nonzero  $O_3$ -concentrations.



• At various levels of ambient  $O_3$  (100, 120, 150 ppb) the presence of  $NO_2$  resulted in lower values produced in the sensor measurement values for  $O_3$  (+10-25%).





#### 3.4.9 Summary

- **Linearity of sensor response**: All sensor units show a very high correlation ( $r^2$ >0.99) compared to the corresponding Thermo analyzer O<sub>3</sub> measurements (between 0-220 µg/m<sup>3</sup> and after calibration).
- Accuracy: All sensor units show a reasonable accuracy when compared to reference instrument (>89%, after calibration). Before calibration, the individual accuracy can be as low as 55%.
- Stability: The standard deviations of the sensors' signals are generally less than 3 μg/m<sup>3</sup> (during stationary conditions over 2 hours) and appear independent of concentration level.
- Between-sensor uncertainty: The uncertainty between the sensors is 4.4 μg/m<sup>3</sup> (being an average result with five different types of sensors).
- Effect of relative humidity: A rise in relative humidity affects the sensor readings. The resulting (relatively) short peak in the measured O<sub>3</sub> concentrations disappears after some 15 min (and does not depend on ambient concentration level or temperature).
- Cross sensitivity: The presence of NO<sub>2</sub> affects the operation of the sensors resulting in lower concentration values for O<sub>3</sub>.
- Data recovery: In this study, the data recovery for every unit is 100% (for a measurement period of 77 hours in total).





### Laboratory Evaluation Membrapor C5 O<sub>3</sub> sensor



Manufacturer: Membrapor Link to website manufacturer Link to test protocol



### 3.5 Membrapor C5 O<sub>3</sub> versus Reference

Four **Membrapor C5** O<sub>3</sub> sensors were evaluated in the RIVM Testing Laboratory under controlled O<sub>3</sub>concentrations, temperature and relative humidity. These sensors were also tested in the field (at the reference monitoring station in Borgerhout).

#### Membrapor C5

- Electrochemical sensors
- Time resolution: 1 minute
- Unit IDs: Membrapor1, Membrapor3, Membrapor4, Membrapor5 ; one device was left out due to invalid data

#### Reference instrument

- Thermo 49i UV photometric O<sub>3</sub> analyzer
- Time resolution: 1 minute

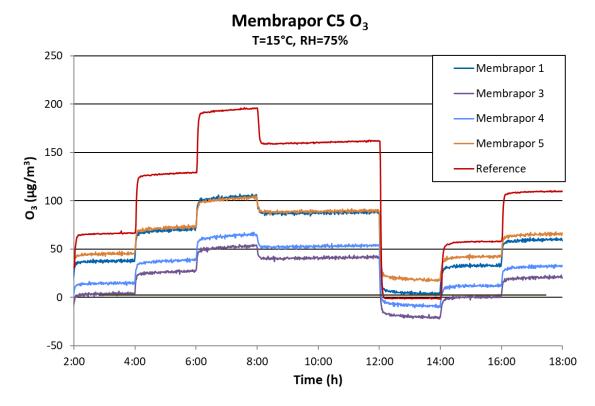


For the details about the laboratory protocol followed here, consult our test protocol.



### 3.5.1 Ramping experiment (T=15°C; RH=75%)

In the first test sensors were exposed to different concentration levels to check linearity, agreement between sensors and agreement with the reference.



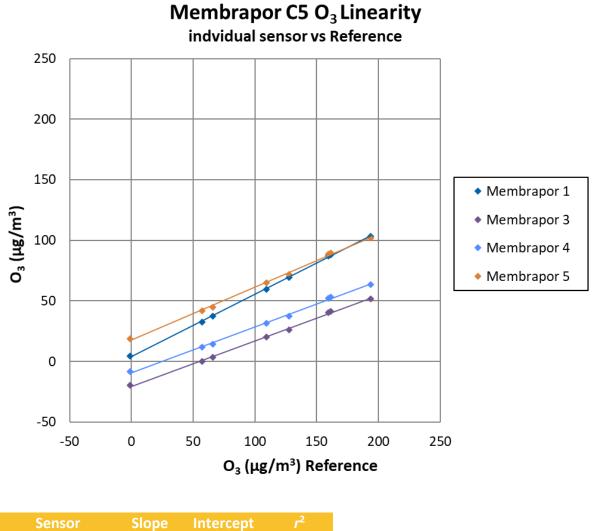
- The Membrapor sensors followed the step changes in  $O_3$  concentration (between 0 and 200  $\mu$ g/m<sup>3</sup>) rather well. In comparison to the reference instrument all units underestimated  $O_3$  reference concentrations
- The four units indicated baseline readings that varied between -20 (Membrapor3) and +18 (Membrapor5)  $\mu$ g/m<sup>3</sup>, respectively.





#### 3.5.2 Linearity

Average concentrations per step were calculated and used for lineair regression (y=ax+b).



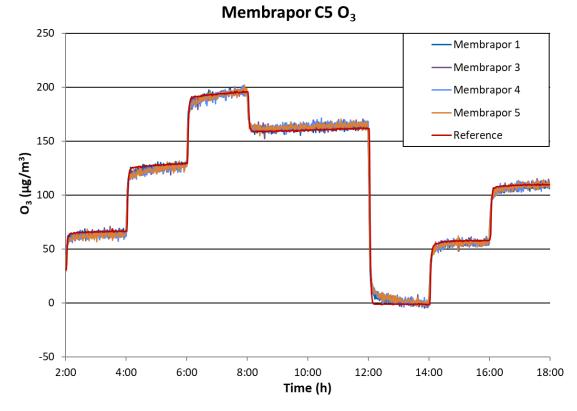
Sensor	Slope	Intercept	<b>r</b> <sup>2</sup>
Membrapor 1	0.52	4.1	0.9993
Membrapor 3	0.38	-20.5	0.9983
Membrapor 4	0.38	-9.2	0.9973
Membrapor 5	0.44	17.7	0.9977

• All four units showed a very high correlation ( $r^2$ >0.99) with the corresponding reference data (derived from the ramping experiment). The slopes of the regression equations vary between 0.38 and 0.52.









• The slopes and intercepts calculated in the ramping experiment were used for a (simple) calibration of the sensor units. After applying this procedure, procedure, the units produced data that were (very) close to the levels measured by the Thermo reference instrument.





### 3.5.4 Accuracy

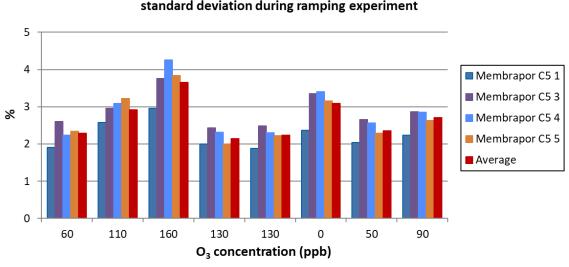
Reference mean (µg/m3)	Sensor mean (µg/m3)	Accuracy (%)
57	55	95
66	64	98
109	107	98
128	125	98
159	162	99
194	193	99

• After calibration, the sensors showed an accuracy above 95%.



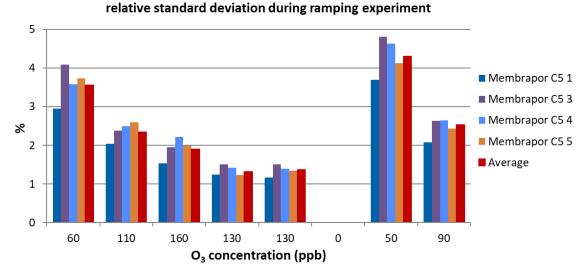
### 3.5.5 Stability under steady-state conditions

Sensor stability is defined here as the standard deviation during each of the seven steadystate conditions of the ramping experiment (also see the Appendix). The standard deviation of the reference is 0.7  $\mu$ g/m<sup>3</sup> (range: 0.2-1.4  $\mu$ g/m<sup>3</sup>); relative standard deviation is 0.7 (0.3-1.3).



### Membrapor C5 standard deviation during ramping experiment

### Membrapor C5



• In most cases, the standard deviations of the sensors' output were less than 4  $\mu$ g/m<sup>3</sup> (after calibration). Some units (Membrapor1) performed better than others (Membrapor3 and 4). There was some dependence on the ambient O<sub>3</sub> level.





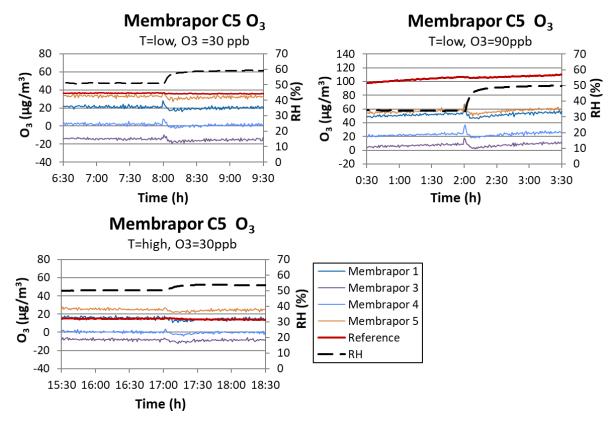
### 3.5.6 Between sensor uncertainty

• The calculated uncertainty between the sensors' data sets is 9.5  $\mu$ g/m<sup>3</sup> (which is the worst result in this study).



### 3.5.7 Influence of relative humidity

The readings of gas sensor systems are known to be affected by changes in meteorological parameters (RH, T). Here, the effect of a changing RH (at constant levels for temperature and concentration) is shown.

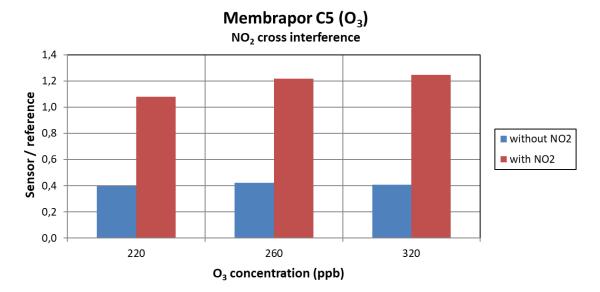


• A (rapid) increase in relative humidity resulted in a relatively small positive peak response quickly followed by a gradual return to the original level within an hour. There is some dependence on ambient O<sub>3</sub> level.



### 3.5.8 Cross sensitivity

To test the cross sensitivity, the sensors in the exposure box were exposed to different levels of  $NO_2$  at nonzero  $O_3$ -concentrations.



• At various levels of ambient O<sub>3</sub> (100, 120, 150 ppb) the presence of NO<sub>2</sub> resulted in (much) higher values produced in the sensor measurements for O<sub>3</sub>.





#### 3.5.9 Summary

- Linearity of sensor response: All sensor units show a very high correlation (r<sup>2</sup>>0.99) with the corresponding Thermo analyzer O3 measurements (between 0-220 µg/m<sup>3</sup> and after calibration).
- Accuracy: All sensor units show a high accuracy when compared to the reference instrument (>95%, after calibration). Before calibration, the individual accuracy can be as low as 20%.
- Stability: The standard deviations of the sensors' signals are less than 4 μg/m<sup>3</sup> (during stationary conditions over 2 hours) and appear independent of concentration level.
- **Between-sensor uncertainty**: The uncertainty between the sensors is 9.5  $\mu$ g/m<sup>3</sup>.
- Effect of relative humidity: A rise in relative humidity affects the sensor readings. The relatively small positive peak response is followed by a gradual return to the original level (within an hour).
- Data recovery: In this study, the data recovery for every unit is 100% (for a measurement period of 77 hours in total).

