

Performance Evaluation of Amperometric Sensors for the Monitoring of O₃ and NO₂ in Ambient Air at ppb-Level

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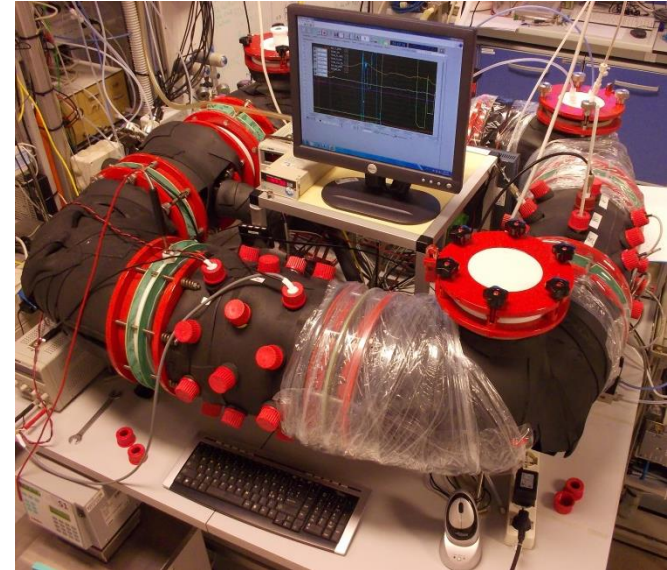
²Institute for applied Physics, CSIC, Madrid, Spain, manuel.alexandre@gmail.com

Eurosensors XXIX, Freiburg, Germany Sep. 6-9
2015 - COST Action TD1105 EuNetAir OPEN
SESSION



Lab. performance evaluation

- response time
 - calibration
 - repeatability
 - short and long term drifts,
 - matrix effect.
 - cross sensitivities from gaseous compounds
 - hysteresis
 - effect of temperature and humidity
-
- measurement uncertainty estimated from the laboratory tests →
Comparison with the Data Quality Objectives of the European Directive for
Air Quality



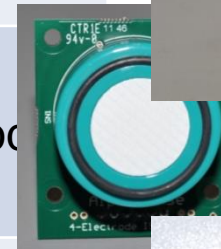
Data Quality Objectives (DQO) of the European Air Quality Directive

Uncertainty for	O ₃	NO ₂ /NO/NO _x
Limit values, ppb	60 (8hrs)	100 (1hr), 20 (1 year)
fixed measurements	15 %	15 %
indicative measurements	30 %	25 %



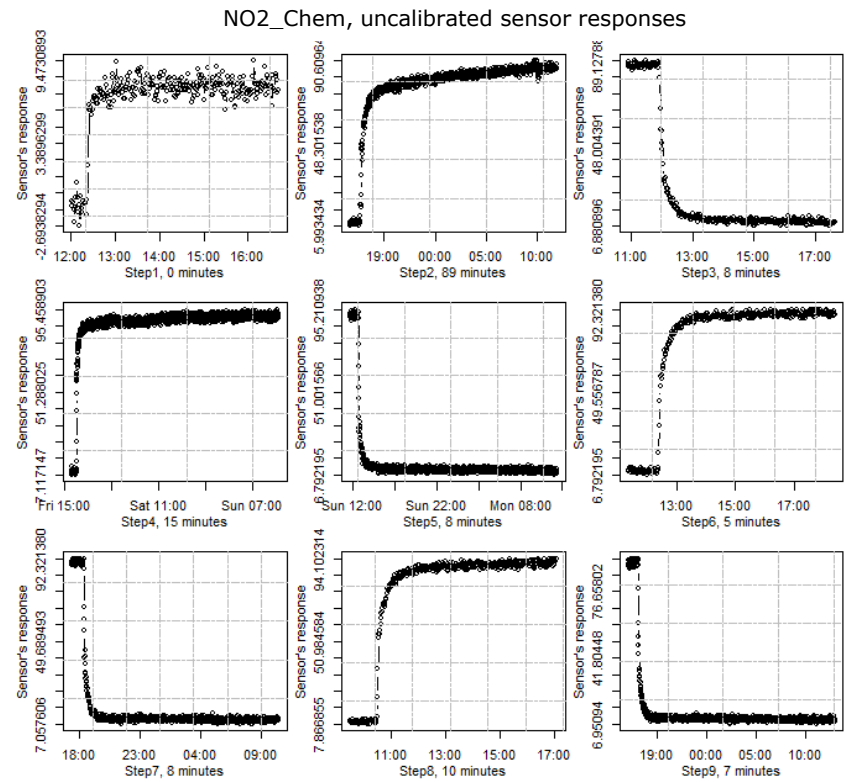
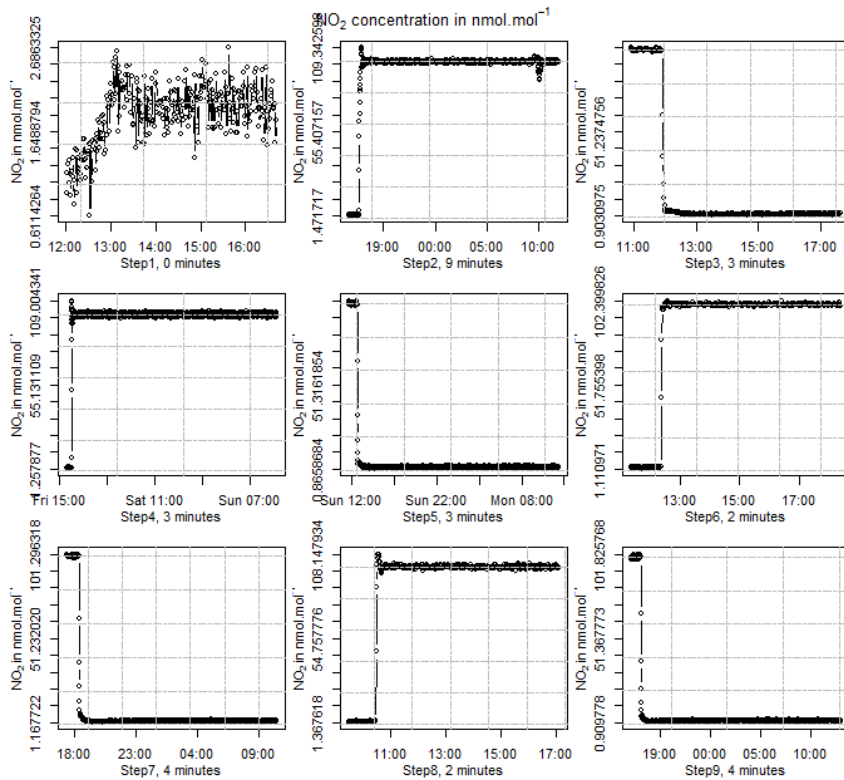
Amperometric sensors under tests

Manufacturers	Model	Type
CairPol – FR (Membrapor – CH)	NO ₂ /O ₃ sensors (CairClip NO ₂ /O ₃), (based on O3/M-5)	3 electrodes
	NO ₂ sensor (CairClip NO ₂) (based on O3/M-5 + filter)	
αSense - UK	O ₃ sensor (O3B4), ISB, issue 4	4 electrodes
	NO ₂ sensors (NO2B4), ISB, issue 4	
Citytech – UK (Sensoric –DE)	O ₃ sensor (O3-3E1F) – sensoric evaluation board	3 electrodes
	NO ₂ sensors (NO2-3E50) – sensoric evaluation board	

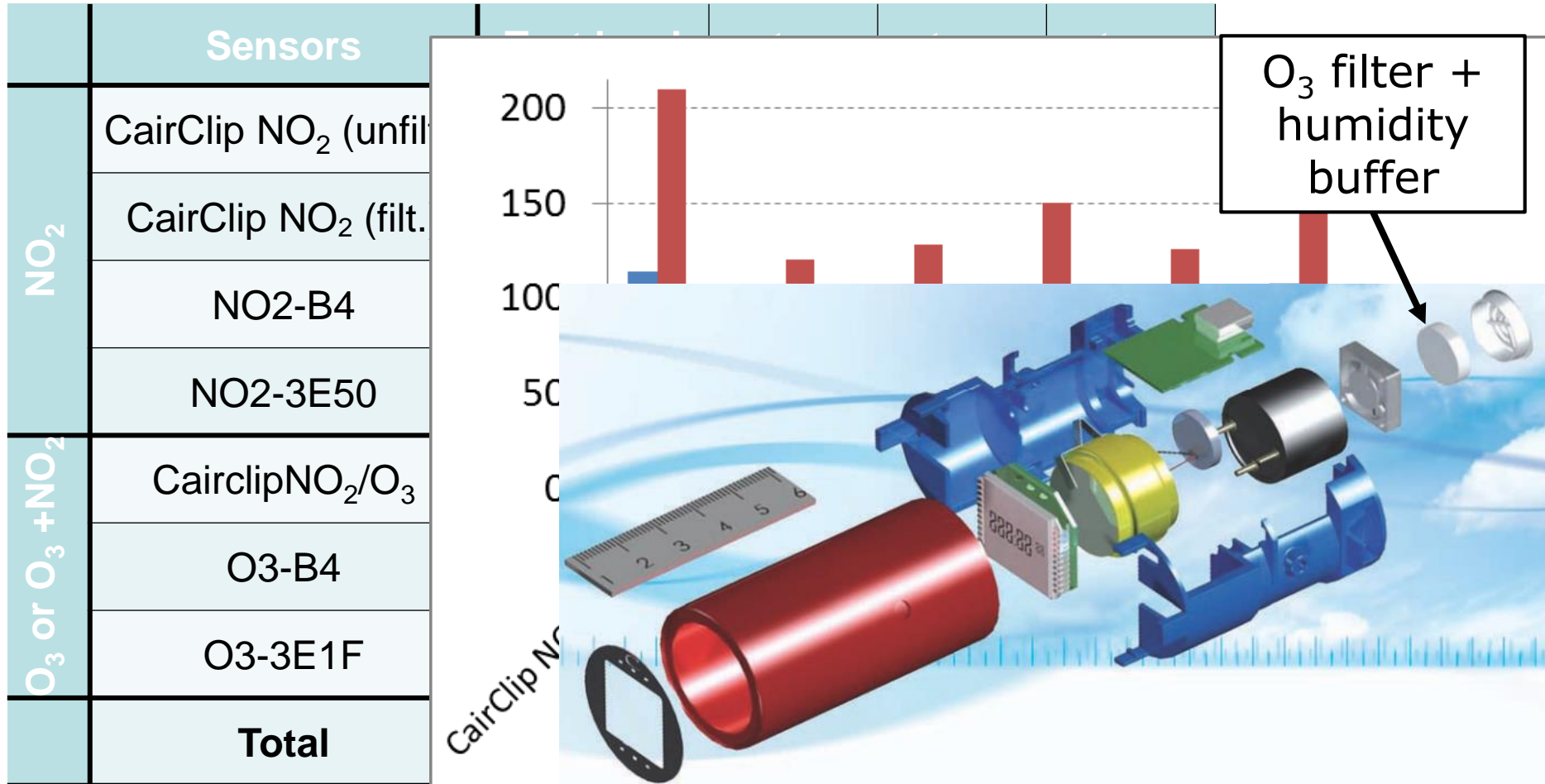


Metrological parameters

1 – Response Time



Response time:



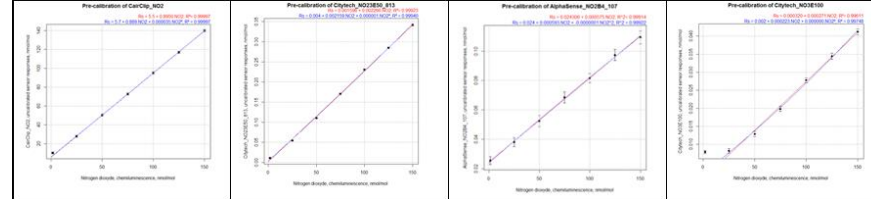


European Commission

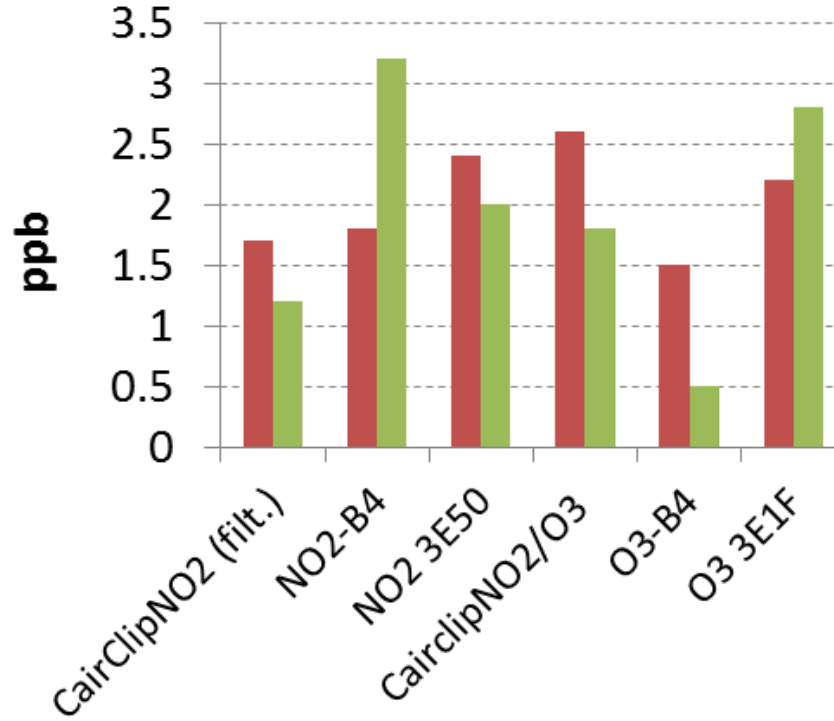
calibration:

R²: coefficient of determination

NO₂



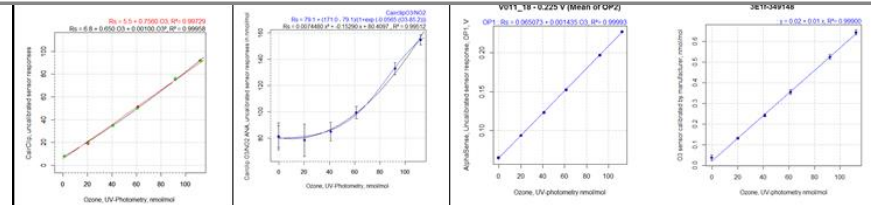
	Sensors	Model
NO ₂	CairClipNO ₂ (filt.)	Linear
	NO2-B4	Linear
	NO2 3E50	Linear
O ₃ or O ₃ +NO ₂	CairclipNO ₂ /O ₃	Parabolic Linear
	O3-B4	Linear
	O3 3E1F	Linear



■ Lack of fit, ppb
■ Max residual, ppb

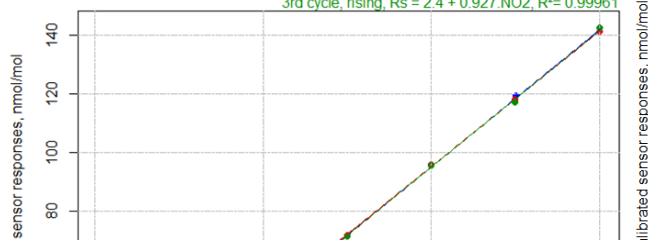
O₃

Joint Research Centre

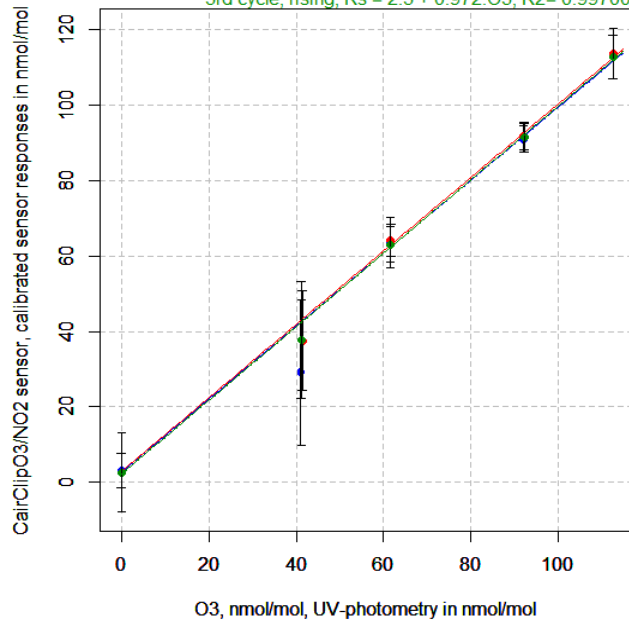


Hysteresis (NO₂ - O₃)

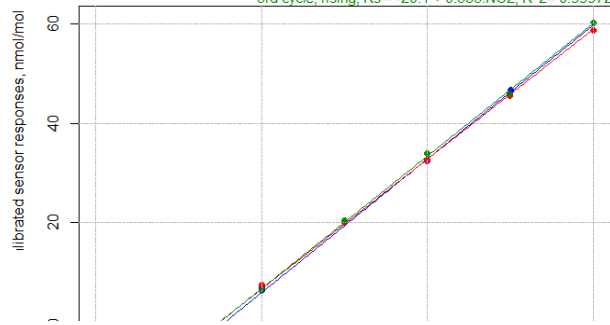
1st cycle, rising, $R_s = 1.9 + 0.932 \cdot \text{NO}_2$, $R^2 = 0.99972$
 2nd cycle, falling, $R_s = 3.2 + 0.920 \cdot \text{NO}_2$, $R^2 = 0.99992$
 3rd cycle, rising, $R_s = 2.4 + 0.927 \cdot \text{NO}_2$, $R^2 = 0.99961$



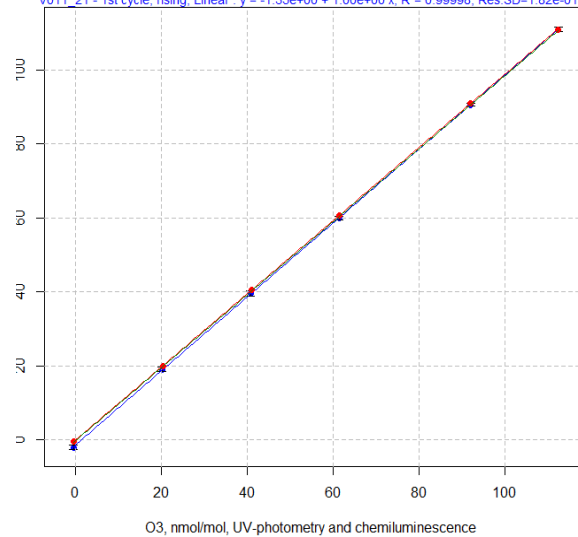
1st cycle, rising, $R_s = 2.8 + 0.965 \cdot \text{O}_3$, $R^2 = 0.99784$
 2nd cycle, falling, $R_s = 3.0 + 0.972 \cdot \text{O}_3$, $R^2 = 0.99700$
 3rd cycle, rising, $R_s = 2.3 + 0.972 \cdot \text{O}_3$, $R^2 = 0.99700$



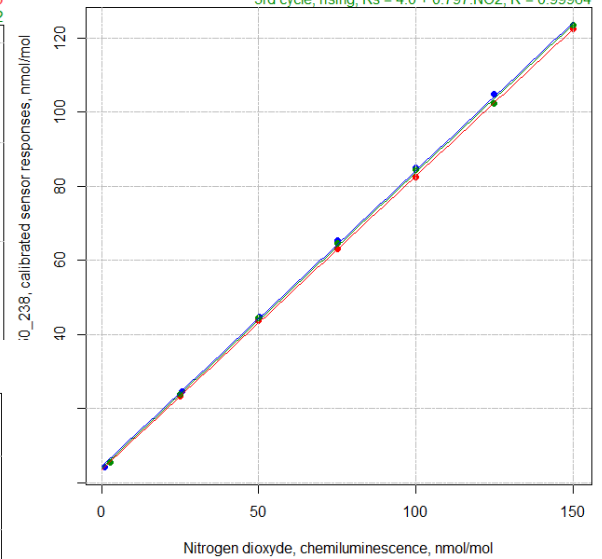
1st cycle, rising, $R_s = -21.2 + 0.540 \cdot \text{NO}_2$, $R^2 = 0.99891$
 2nd cycle, falling, $R_s = -19.6 + 0.524 \cdot \text{NO}_2$, $R^2 = 0.99970$
 3rd cycle, rising, $R_s = -20.1 + 0.535 \cdot \text{NO}_2$, $R^2 = 0.99972$



V011_21 - 3rd cycle, rising, Linear: $y = -2.33e-01 + 9.88e-01 x$, $R^2 = 0.99998$, Res.SD=1.78e-01
 V011_21 - 2nd cycle, falling, Linear: $y = -4.92e-02 + 9.90e-01 x$, $R^2 = 0.99999$, Res.SD=1.38e-01
 V011_21 - 1st cycle, rising, Linear: $y = -1.35e+00 + 1.00e+00 x$, $R^2 = 0.99998$, Res.SD=1.82e-01

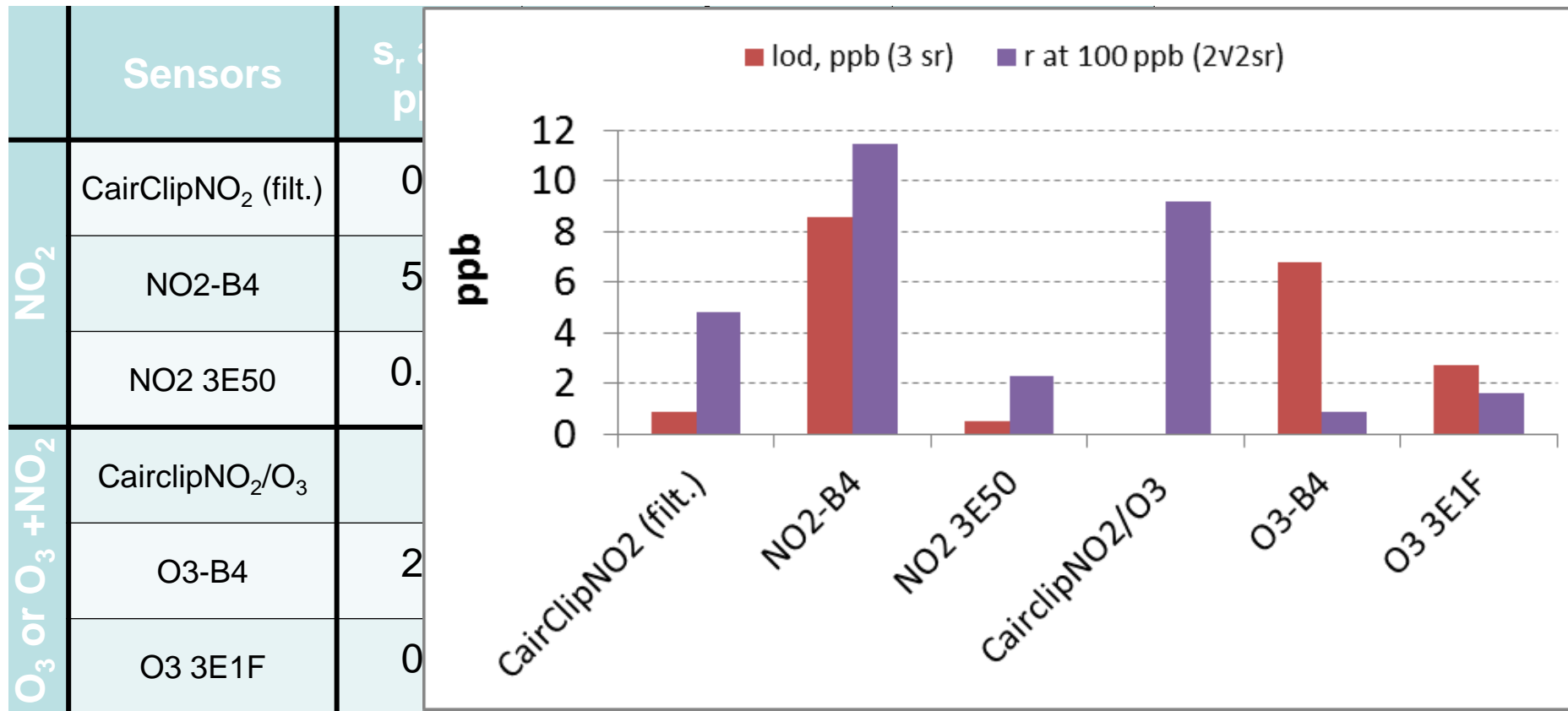


1st cycle, rising, $R_s = 4.5 + 0.797 \cdot \text{NO}_2$, $R^2 = 0.99945$
 2nd cycle, falling, $R_s = 3.6 + 0.792 \cdot \text{NO}_2$, $R^2 = 0.99994$
 3rd cycle, rising, $R_s = 4.0 + 0.797 \cdot \text{NO}_2$, $R^2 = 0.99964$



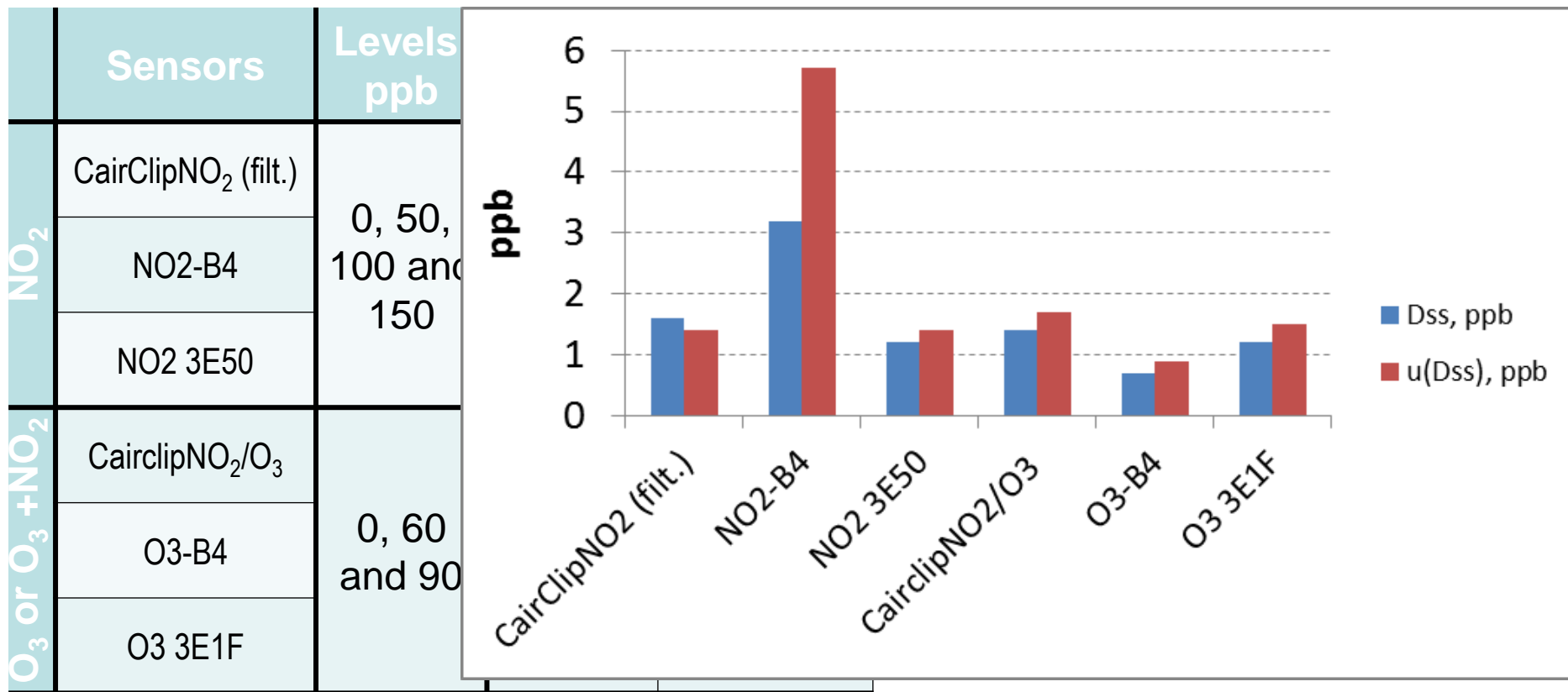
Limit of detection and repeatability:

based on repetition of 60 minute values



Short term drift:

replicated hourly values every 24 hours and at several levels

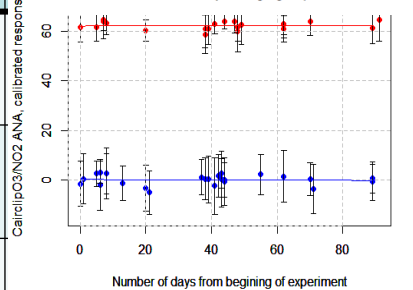
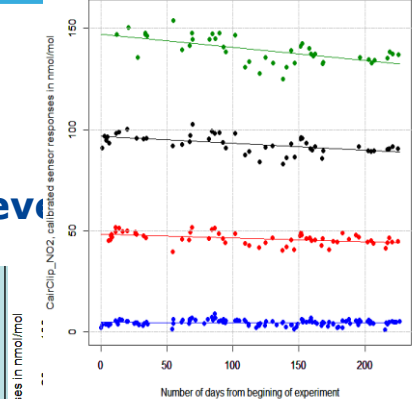




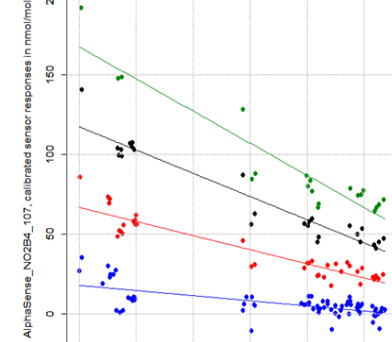
Long term drift: Tests every 15 days at several levels

	Sensors	DIs, ppb/day	
NO ₂	CairClipNO ₂ (filt.)	≤ -0.065	
	NO2-B4	≤ -0.497	
	NO2 3E50	≤ -0.196	
O ₃ or O ₃ +NO ₂	CairclipNO ₂ /O ₃	≤ 0.011	≤ 1.7
	O3-B4	≤ 0.016	≤ 3.0
	O3 3E1F	≤ 0.142	≤ 5.8

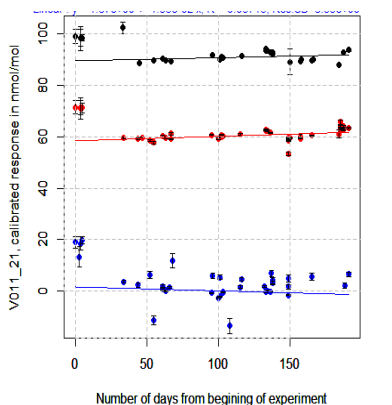
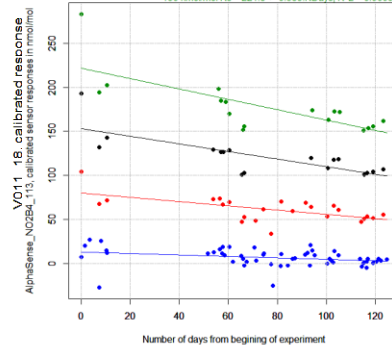
0 nmol/mol Rs = 4.7 + -0.0008 NDays, R²= 0.00172
 50 nmol/mol Rs = 48.4 + -0.019 NDays, R²= 0.20583
 100 nmol/mol Rs = 96.7 + -0.034 NDays, R²= 0.29623
 150 nmol/mol Rs = 147.1 + -0.065 NDays, R²= 0.36928



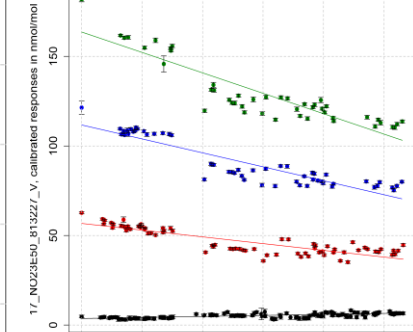
0 nmol/mol Rs = 17.8 + -0.0643 NDays, R²= 0.43923
 50 nmol/mol Rs = 66.9 + -0.177 NDays, R²= 0.85974
 100 nmol/mol Rs = 117.6 + -0.292 NDays, R²= 0.91746
 150 nmol/mol Rs = 167.8 + -0.404 NDays, R²= 0.87477



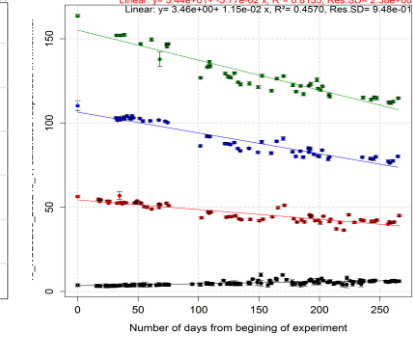
0 nmol/mol Rs = 13.1 + -0.0835 NDays, R²= 0.08653
 50 nmol/mol Rs = 80.0 + -0.242 NDays, R²= 0.37644
 100 nmol/mol Rs = 153.2 + -0.432 NDays, R²= 0.59657
 150 nmol/mol Rs = 221.8 + -0.589 NDays, R²= 0.56034



Linear: y = 1.64e+02 - 2.28e-01 x, R²= 0.8088, Res SD= 7.94e+00
 Linear: y = 1.12e+02 - 1.56e-01 x, R²= 0.8214, Res SD= 5.43e+00
 Linear: y = 5.68e+01 - 7.51e-02 x, R²= 0.7389, Res SD= 3.69e+00
 Linear: y = 3.67e+00 + 1.14e-02 x, R²= 0.5092, Res SD= 9.08e-01



Linear: y = 1.85e+02 - 1.78e-01 x, R²= 0.8874, Res SD= 4.50e+00
 Linear: y = 1.06e+02 - 1.24e-01 x, R²= 0.8960, Res SD= 3.11e+00
 Linear: y = 5.44e+01 - 5.77e-02 x, R²= 0.8155, Res SD= 2.38e+00
 Linear: y = 3.46e+00 + 1.15e-02 x, R²= 0.4570, Res SD= 9.48e-01



NO₂

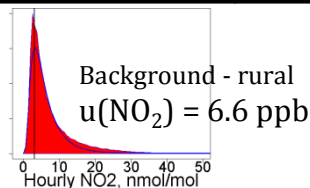
O₃

Gaseous interfering compounds:

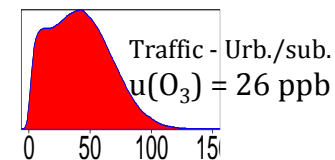
Sensitivity coefficients (ppb/ppb or ppb/ppm) / Uncertainty in ppb

	Sensors	O ₃ / NO ₂	NO	CO	CO ₂	NH ₃
NO ₂	CairClipNO ₂ (filt.)	-0.010 / 0.3 (O ₃)	-0.007 / 0.3	-0.001 / 0.5	0.009 / 0.3	-0.032 / 1.2
	NO2-B4	1.5 / 39 (O ₃)	-0.032 / 0.2	-0.0013 / 0.4	-0.042 / 1.2	-0.089 / 2.3
	NO2 3E50	1.5 / 37 (O ₃)	-0.058 / 0.4	-0.0016 / 0.5	-0.013 / 0.3	-0.11 / 2.9
O ₃ or O ₃ +NO ₂	CairclipNO ₂ /O ₃	0.84 / 5.5 (NO ₂)	0.006 / 0.1	0.070 / 0.1	-0.00006/<0.1	-0.01 / 1.0
	O3-B4	0.92 / 6.1 (NO ₂)	-0.042 / 0.3	-0.066 / 0.2	0.0002 / <0.1	0.00025 / <0.1
	O3 3E1F	0.76 / 5.0 (NO ₂)	-0.011 / 0.1	0.00007 / 0.0	0.0035 / 0.1	0.0016 / 0.1

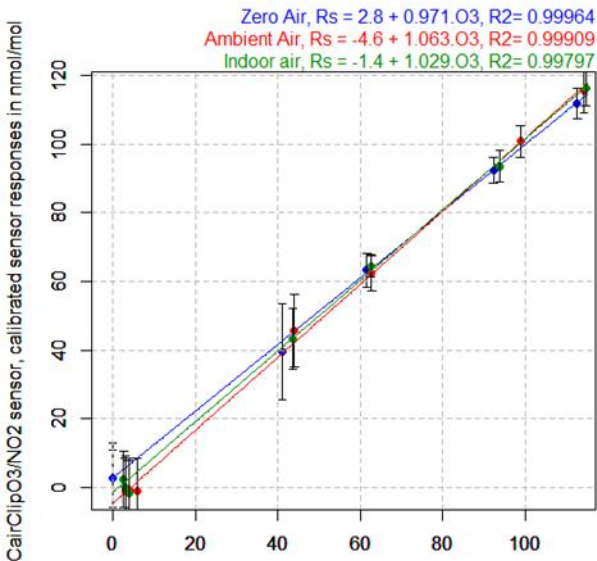
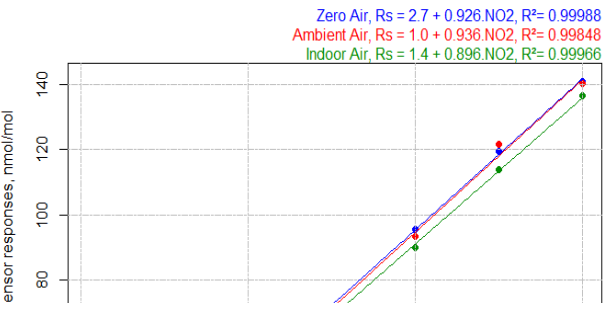
U = sensitivity coeff. X



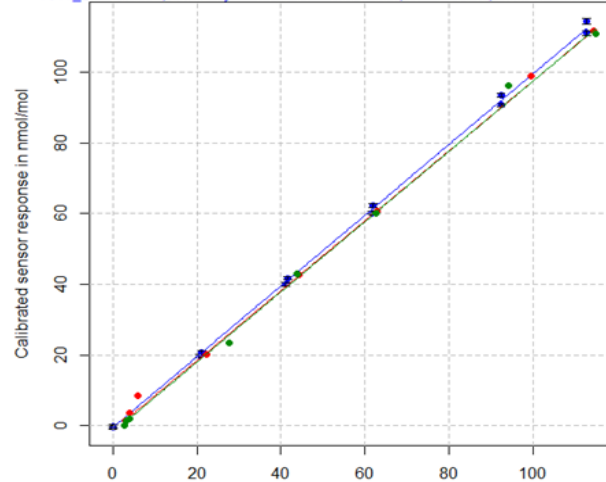
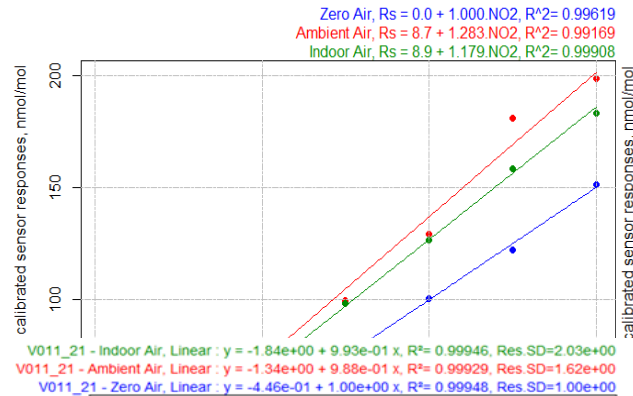
or



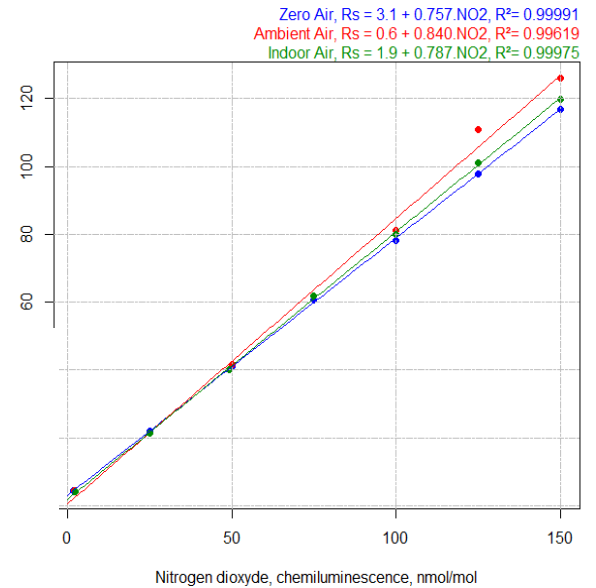
Air composition (NO₂ - O₃)



O₃ + 84 % NO₂, nmol/mol, UV-photometry and chemiluminescence



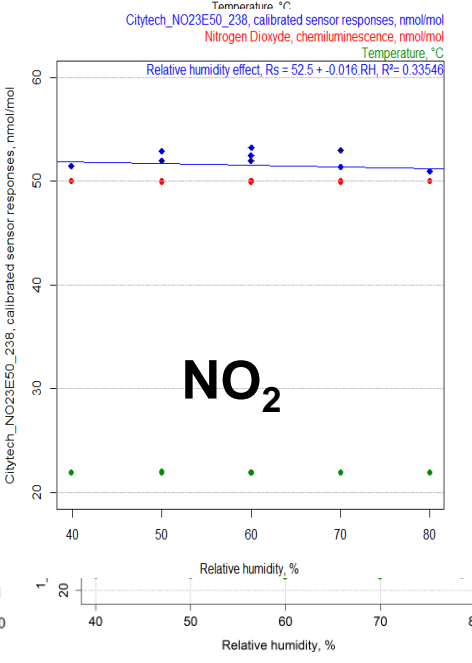
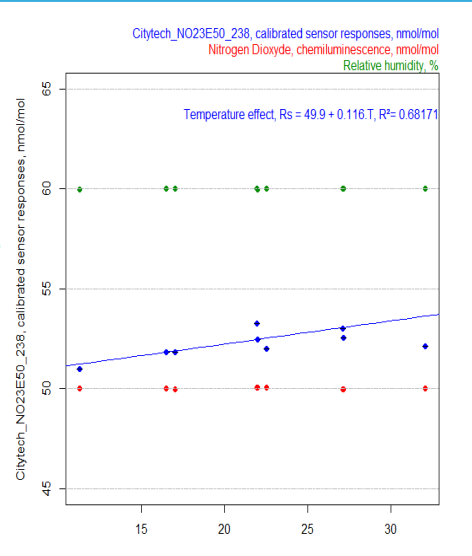
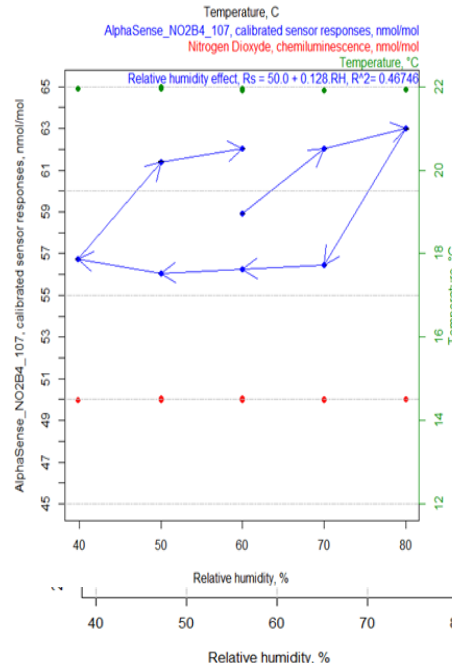
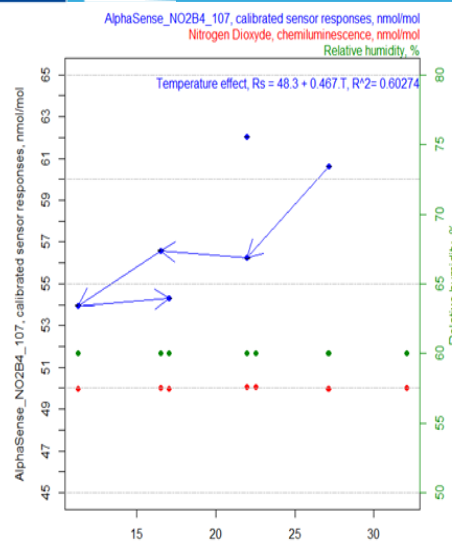
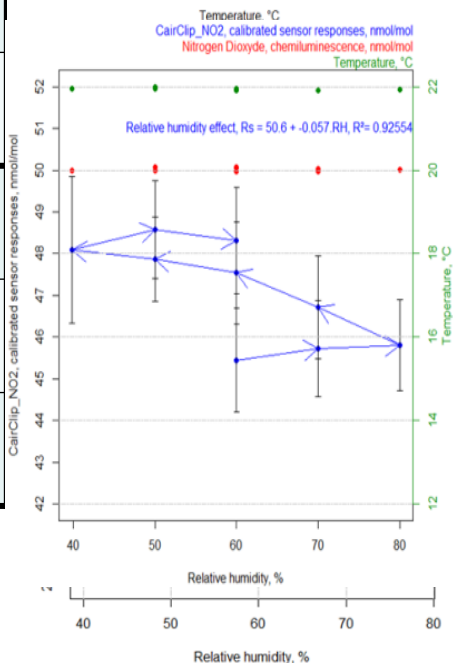
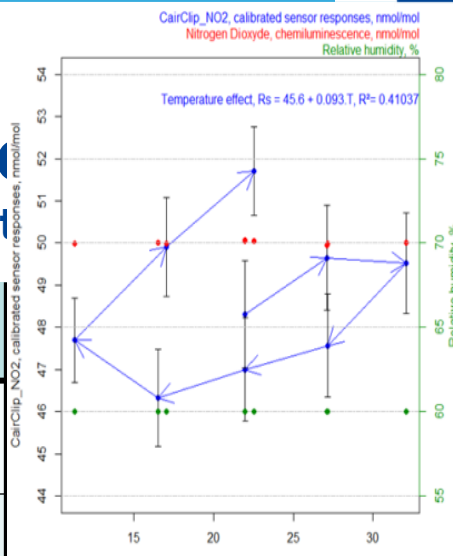
O₃ + 92 % NO₂, nmol/mol, UV-photometry and chemiluminescence





Temperature Sensitivity coefficient

Sensors	
NO ₂	CairClipNO ₂ (filt.)
	NO2-B4
O ₃ or O ₃ + NO ₂	NO2 3E50
	CairclipNO ₂ /O ₃
	O3-B4
	O3 3E1F



NO₂

u	CairClip (filt.)	NO2-B4	NO2 3E50	Cairclip	O3-B4	O3 3E1F
Cal. (lof)	1.7	1.8	2.4	2.6	1.5	2.2
Hysteresys	-	-	-	-	-	-
r, short term	1.7	2.9	0.8	3.3	0.4	0.6
Long term	4.0	45	7.9	1.7	3.0	5.8
Interference	1.4	39.1	37.1	5.9	5.6	5.0
Air matrix	3.0	14.2	5.0	1.1	1.0	
Temperature	1.7	8.3	2.2	1.9	1.5	7.4
Humidity	2.2	5.1	2.1	1.4	16.3	1.7
Combined uncertainty, uc	12.7	124	77	15.8	35.3	22.0



our date 2014-12-19

our reference Dr. Ne/pe

For action:

To the members of CEN/TC 264

CEN/TC 264 N **2275**

For information:

To the Chairman and Vice-Chairman of CEN/TC 264

To the CEN/CENELEC Management Centre

Dear Sir or Madam

New work item proposal "Gas sensors"

Please find enclosed a new work item proposal dealing with adoption of the following preliminary work item:

prCEN/TS xxxxx *Air quality – Performance evaluation of sensors for the determination of concentrations of gaseous pollutants and particulate matter in ambient air*
(Doc. N 2274)

All members of CEN/TC 264 are kindly asked to let us know whether they agree to the adoption of this preliminary work item by making use of the **CEN eBalloting portal (Committee Internal Balloting)**.

In case of adoption Mr. Michel Gerboles, JRC Ispra, has been kind enough to accept project leadership. **Any members who would be willing to take over the secretariat of the new WG are kindly invited to inform the TC secretariat accordingly (by e-mail to perschau@vdi.de).**

Deadline for voting is **2015-03-20**.

Thank you in advance for your kind co-operation!

Yours sincerely

Dr. Rudolf Neuroth

Thank You...

Reports of evaluation of sensors at:

ftp://ftp_erlap_ro:3rlapsyst3m@s-jrciprvm-ftp-ext.jrc.it/ERLAPDownload.htm

Or send a mail to michel.gerboles@jrc.ec.europa.eu