Sensors for Monitoring Regulated Compounds

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Current & Future Air Quality Monitoring
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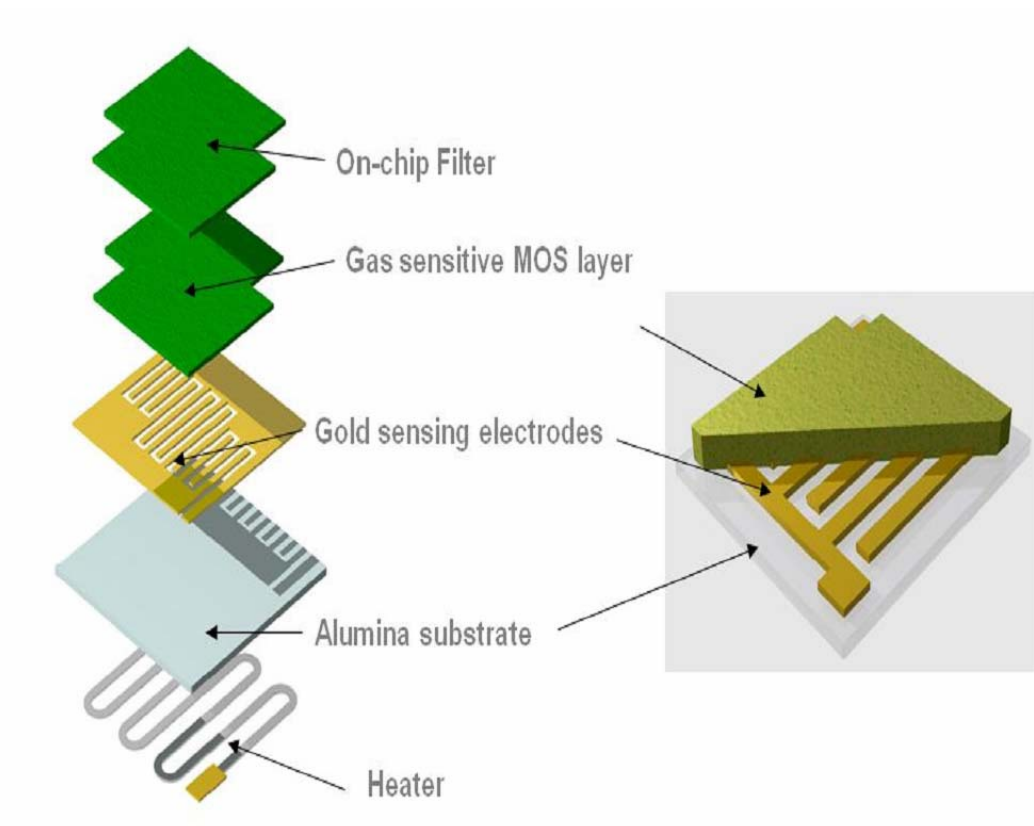
Micro-sensors could be used for :

- Monitoring of ambient air, forest monitoring at forest, rural or remote sites, traffic on road network;
- Near-to-real-time mapping of air pollution by connecting several sensors through wireless networks or GSM;
- Validation of dispersion models;
- Evaluation of exposure of population.

Metal oxide sensors



- **Modification of electrical conductivity due to adsorbed gas species**
- **Thick of thin films, grain sizes, surface to volume ratio affect sensitivity**
- **Selectivity can be fine tuned by varying crystal structure and morphology, dopants, contact geometries, operation temperature or mode of operation.**

Actors in the field of development of sensors

1. Developers: improve sensor technologies by optimizing the preparation of sensors materials
2. Scientists: identification of atomistic processes involved in gas sensing with development of simplified models for controlled gas mixtures and conditions
3. Users: field comparison of sensor responses against measurements of reference methods

Just a few studies combining the three approaches

Validation of sensors: where do we stand?

Manufacturing of new gas sensors showing high sensitivity to air pollutants (a lot of papers)

↓

Manufacturing of a commercial gas sensor (a few)

↓

Field test showing "correlation" between gas sensors and reference methods (a few studies)

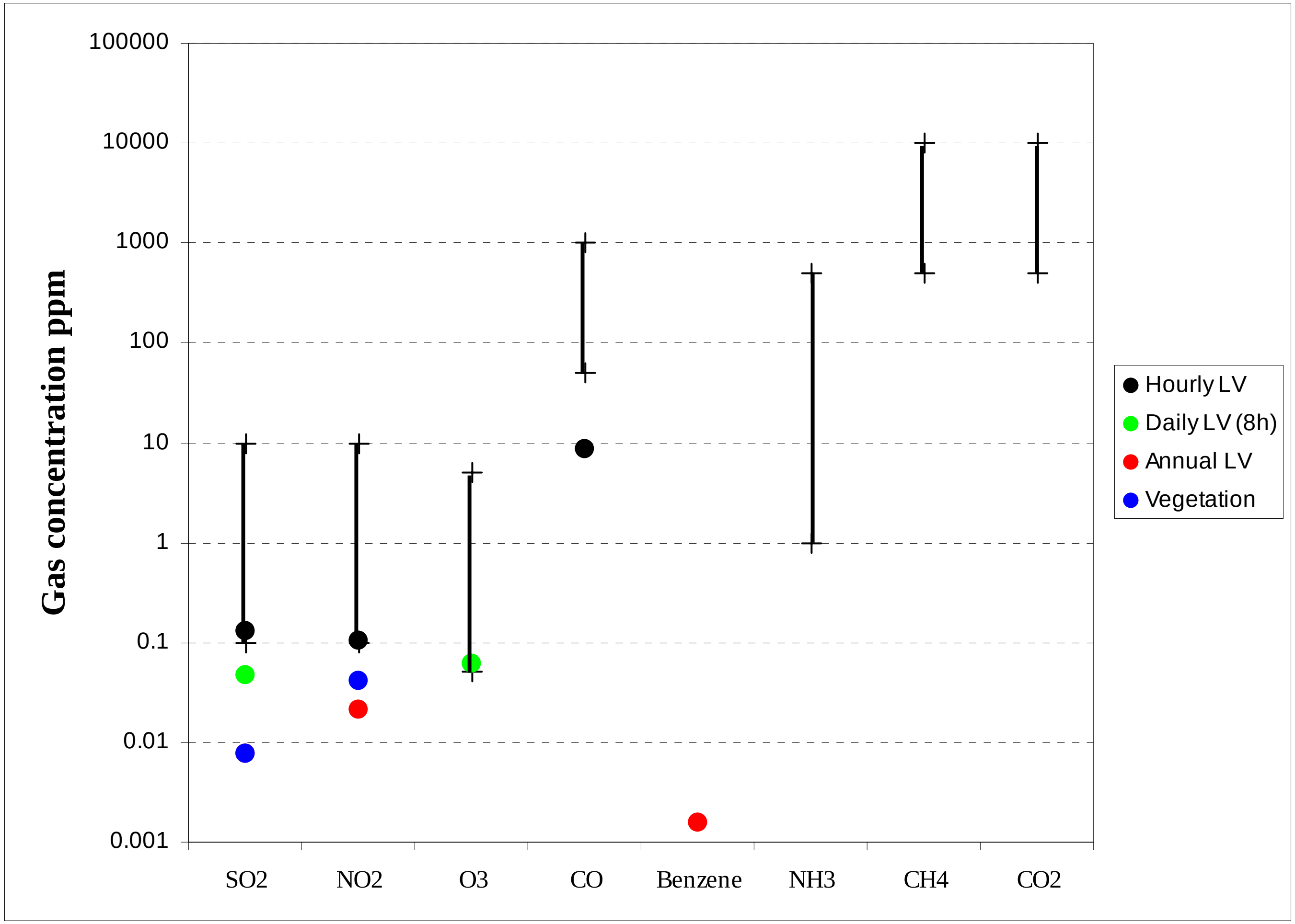
↓

Development of calibration procedures to use sensors independently to the reference methods (starting)

↓

Validation of sensor according to protocol to be defined (future work)

Sensitivity of sensors in 2005 (in lab)



Adapted from Noboru Yamazoe, Review Towards innovations of gas sensor technology Sensors and Actuators B 108 (2005) 2–14

NO_2 selected literature

Sensor type	Range (ppb)	Test in	Commerc	Reference
In_2O_3-SnO_2 better than SnO_2 , In_2O_3	2000-20000	Lab	No	NO_2-gas sensing properties of mixed In_2O_3-SnO_2 thin films, A.Forleo et al., Thin Solid 490 (**2005**) 68-73.
WO_3-based sensor	500-2000	Lab	No	Micro-machined WO_3-based sensor selective to oxidizing gases', S. Vallejos et al., Sensors and Actuators B 132 (**2008**) 209-215.
SnO_2 nanowire	500-5000	Lab	No	Novel fabrication of an SnO_2 nanowire gas sensor with high sensivity, Y.Coi et al., Nanotechnology 19 (**2008**).
SnO_2 nanofiber mats	150-50000	Lab	No	Electron spun SnO_2 nanofiber mats with thermo-compresion step for gas sensing applcations, I. Kim et al., J. Electrocream (**2010**) 25:159-167.
WO_3+SnO_2	50-1000	Lab	No	Microstructure control of WO_3 film by adding nano-particles of SnO_2 for NO_2 detection in ppb level, K.Shimanoe et al., Procedia Chemistry 1 (**2009**) 212-215.
WO_3+Na_2WO_4	50-1000	Lab	No	Highly sensitive NO_2 sensors using lamellar-structured WO_3 particles prepared by an acidification method, Tetsuya Kida et al., Sensors and Actuators B 135 (**2009**) 568-574.
In_2O_3 nanowire	20-1000	Lab	No	Detection of NO_2 down to ppb levels Using individual and Multiple In_2O_3 nanowire Devices, Daihua Zhang et al., Nano Letters (**2004)** Vol.4 No.10 1919-1924.
phthalocyanine gas sensor+filter	20-100ppb	Lab/ Field	No	Improvement in real time detection and selectivity of phthalocyanine gas sensor dedicated to oxidizing pollutants evaluation, J.Brunet et al., Thin solid films 490 (**2005**) 28-35.
WO_3	1-40	Field	Aeroqual?	Development of low-cost ozone and nitrogen dioxide measurement instruments, based on semiconducting oxides, suitable for use in an air quality monitoring network, David E Williams et al., Proceedings of IEEE sensors Conference (**2009)**.
Graphene sensor	< 1 - ?	Lab	No	Detection of individual gas molecules adsorbed on graphene, .Schedin et al., Nature Materials Vol.6 September (**2007)**.

O_3 selected literature

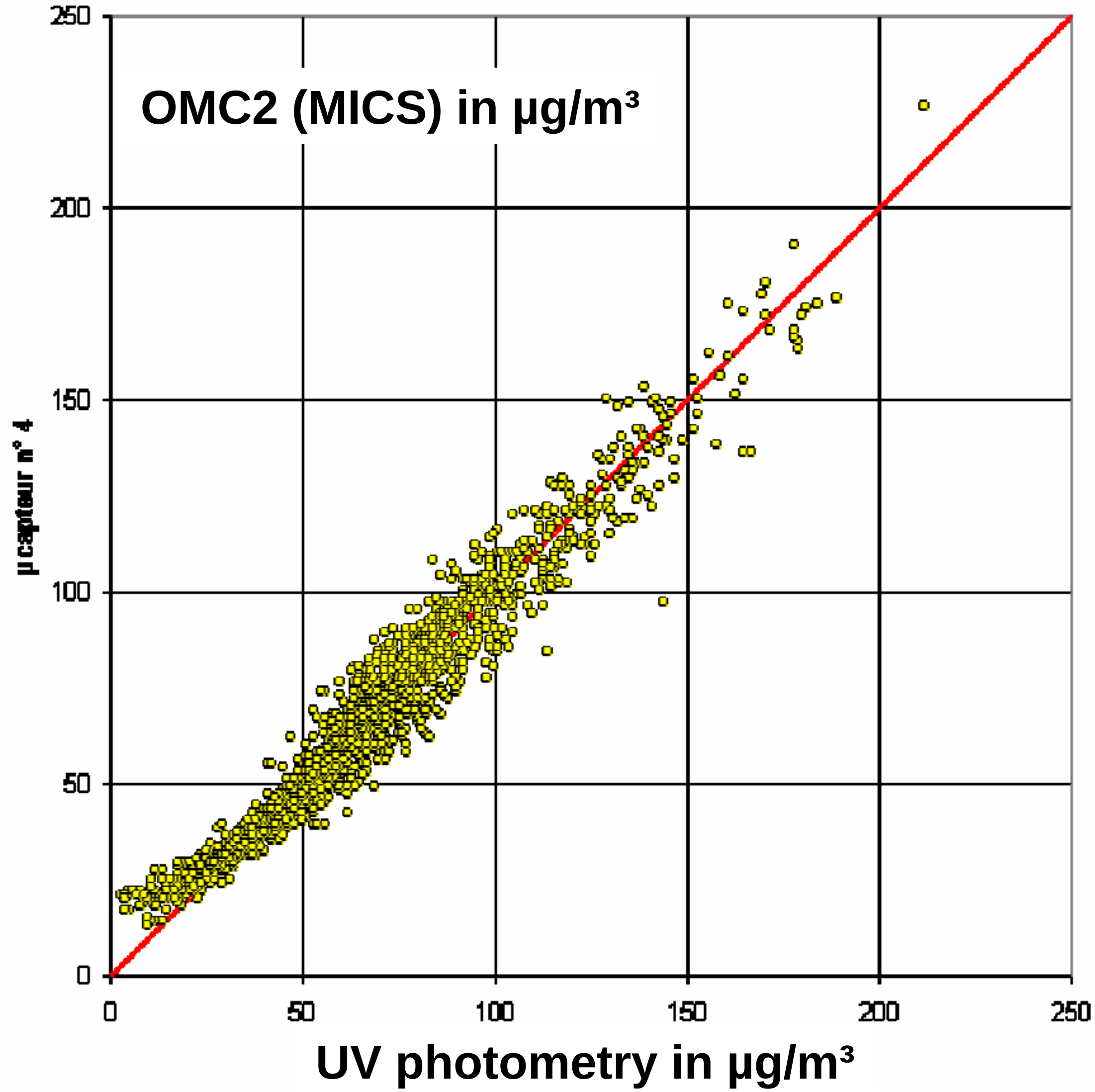
Sensor type	Range (ppb)	Test in	Commerc	Reference
WO_3	1400-20000	Field	CAP 21 City Technology	A low cost instrument based on a solid state sensor for balloon-borne atmospheric O_3 profile sounding, M. Hansford et al., The Royal Society of Chemistry (**2005**).
WO_3-based sensor	200-800	Lab	No	Micro-machined WO_3-based sensor selective to oxidizing gases, S. Vallejos et al., Sensors and Actuators B 132 (**2008**) 209-215.
In_2O_3 thick film	200 – 500	Field	Unitec?	Array of thick film sensors for atmospheric pollutant monitoring, M.C. Carotta et al., Sensors and Actuators B 68 (**2000**) 1-8.
In_2O_3 Thick sensor	Ambient ?	Lab/ Field	No	Environmental monitoring field tests using screen-printed thick-film sensors based on semiconductor oxides E. Traversa et al., Sensors and Actuators B 65 (**2000**) 181-185.
?	20-100	Lab	MiCS 2611	Ozone detection in the ppb-rang with improved stability and reduced cross sensitivity, M.Losch et al., Sensors and Actuators B 130 (**2008**) 367-373.
WO_3+Co	12-100	Lab + field	City Technology	An ozone monitoring instrument based on the tungsten trioxide (WO_3) semiconductor, S.R. Utembe et al., Sensors and actuators B 114 (**2006**) 507-512.
Phthalocyanine gas sensor	10-100	Lab/ Field	No	Improvement in real time detection and selectivity of phthalocyanine gas sensor dedicated to oxidizing pollutants evaluation, J.Brunet et al., Thin solid films 490 (**2005**) 28-35.
WO_3	1-10	Field	Aeroqual?	Development of low-cost ozone and nitrogen dioxide measurement instruments, based on semiconducting oxides, suitable for use in an air quality monitoring network, David E Williams et al., Proceedings of IEEE sensors Conference (**2009**)

NO, CO and NH_3 Recent literature

Gas	Sensor type	Range (ppb)	Test in	Commerc	Reference
NH_3	Micro-machined WO_3-based sensor	1000-3000	Lab	No	Micro-machined WO_3-based sensor selective to oxidizing gases, S. Vallejos et al., Sensors and Actuators B 132 (**2008**) 209-215.
NH_3	Graphene sensor	< 1 - ?	Lab	No	Detection of individual gas molecules adsorbed on graphene, F.Schedin et al., Nature Materials vol.6 September **2007**.
CO	SnO_2	50000-1000000	Lab	No	Application of semiconductor sol-gel sensor array to the discrimination of pollutants in air, S. Capone et al., Thin Solid films 391 (**2001**) 314-319.
CO	Micro-machined WO_3-based sensor	10000-30000	Lab	No	Micro-machined WO_3-based sensor selective to oxidizing gases, S. Vallejos et al., Sensors and Actuators B 132 (**2008**) 209-215.
CO	SnO_2 nanofiber mats	5000-5000000	Lab	No	Electron spun SnO_2 nanofiber mats with thermo-compresion step for gas sensing applcations, I. Kim et al., J. Electrocream (**2010**) 25:159-167.
CO	SnO_2 Thick sensor	Ambient ?	Lab/ Field	No	Environmental monitoring field tests using screen-printed thick-film sensors based on semiconductor oxides E. Traversa et al., Sensors and Actuators B 65 (**2000**) 181-185.
CO	$TaTiO_2$ and SnO_2	400 – 1700	Field	(Unitec?)	Array of thick film sensors for atmospheric pollutant monitoring, M.C. Carotta et al., Sensors and Actuators B 68 (**2000**) 1-8.
NO	$LaFeO_3$ Thick	Ambient concentration	Lab/ Field	No	Environmental monitoring field tests using screen-printed thick-film sensors based on semiconductor oxides E. Traversa et al., Sensors and Actuators B 65 (**2000**) 181-185.
NO	$LaFeO_3$	50-450	Field	(Unitec?)	Array of thick film sensors for atmospheric pollutant monitoring, M.C. Carotta et al., Sensors and Actuators B 68 (**2000**) 1-8.
NOx	WO3-based sensor	1000-3000	Lab	No	Micro-machined WO3-based sensor selective to oxidizing gases, S. Vallejos et al., Sensors and Actuators B 132 (**2008**) 209-215.

Limited number of papers for SO_2 in general electrochemical sensors in the ppm range

O_3 sensors, OMC2, MICS (e2v)



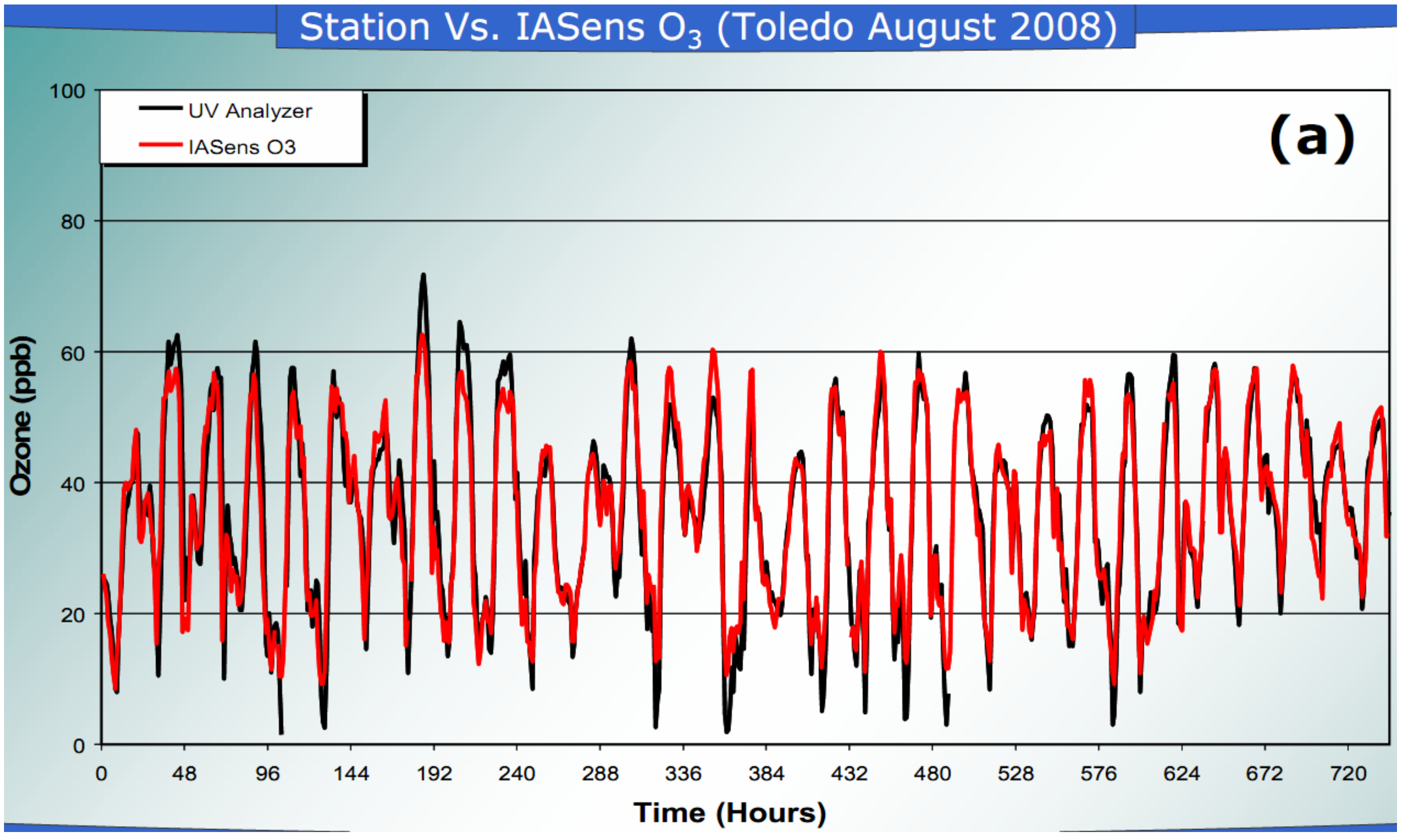
$$O_3 = x_0 + x_1 Rs + x_2 Rs^2 + x_3 Rs^3$$

$$Rs = R \exp K(T - 25)$$

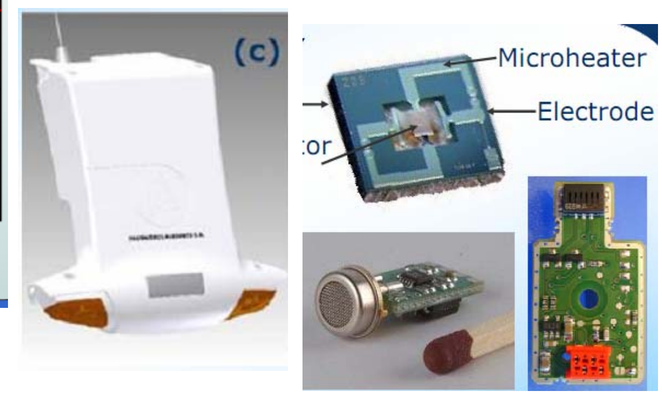
- 6 periods of 2 to 3 weeks
- 4 sensors, SnO2 thin film
- wrong values when heavy rain
- hourly values: relative diff. 8.6 %
- K changes from period to period

Air Normand, 2004, Report of measuring campaign in Honfleur, http://www.airnormand.asso.fr/

O_3, IASens O3, Ingeniores Assessores (S)

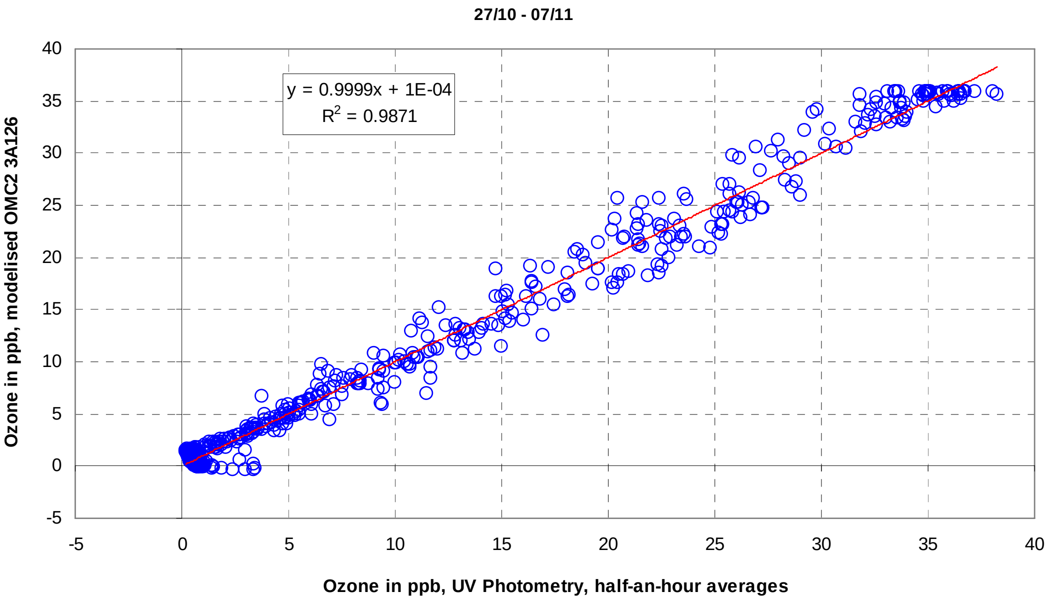


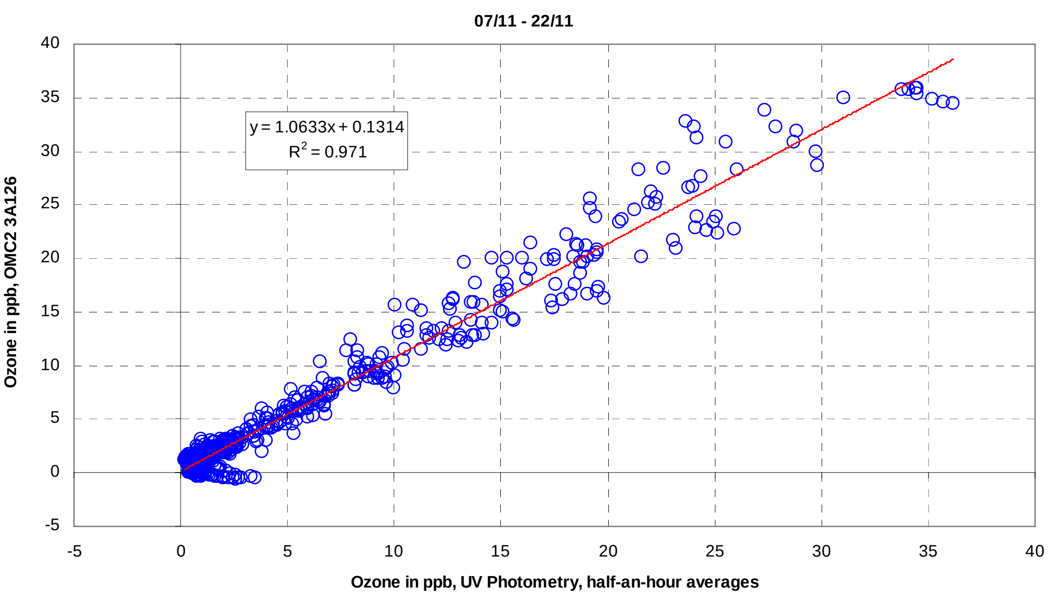
- two sites, 30 days
- hourly values: differences a few ppb (min. and max.)
- Good fit with UV photometry O3 values.



A. Pérez-Junquera et al. , Ozone analyzer for Air quality monitoring based Ozone analyzer for Air quality monitoring based on Semiconductor Oxide Sensors on Semiconductor Oxide Sensors, Measuring Air Pollutants by Diffusive Sampling and Other Low Cost Monitoring Techniques, 2009, Krakow, Poland

O_3 sensors, OMC2, MICS (e2v)

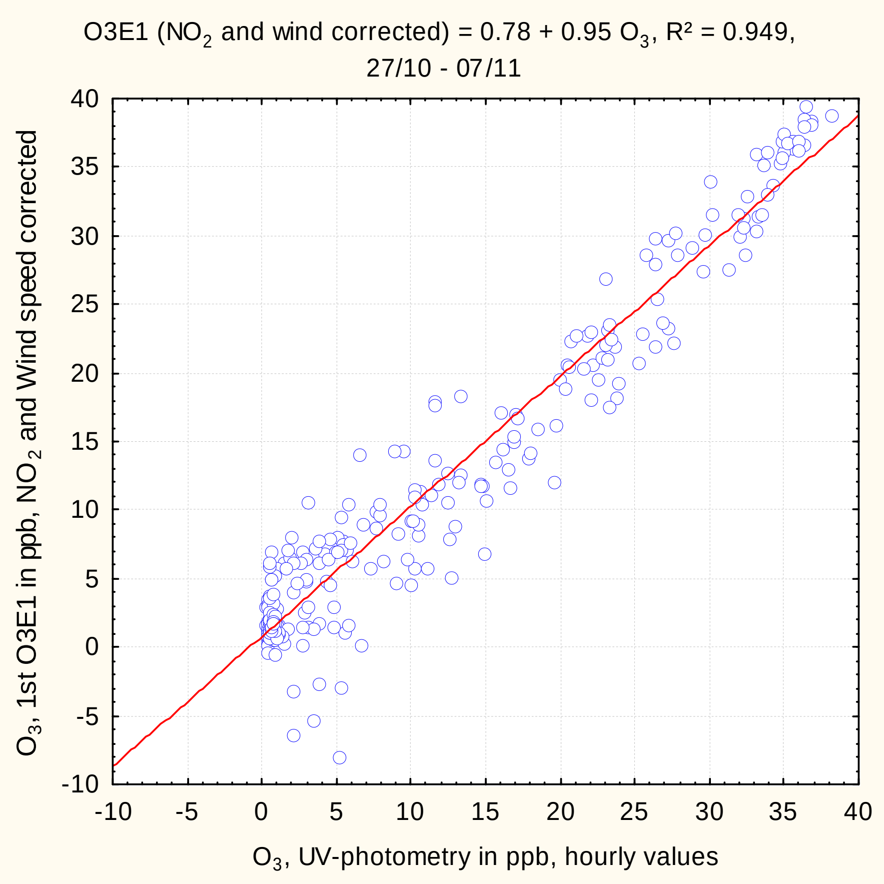


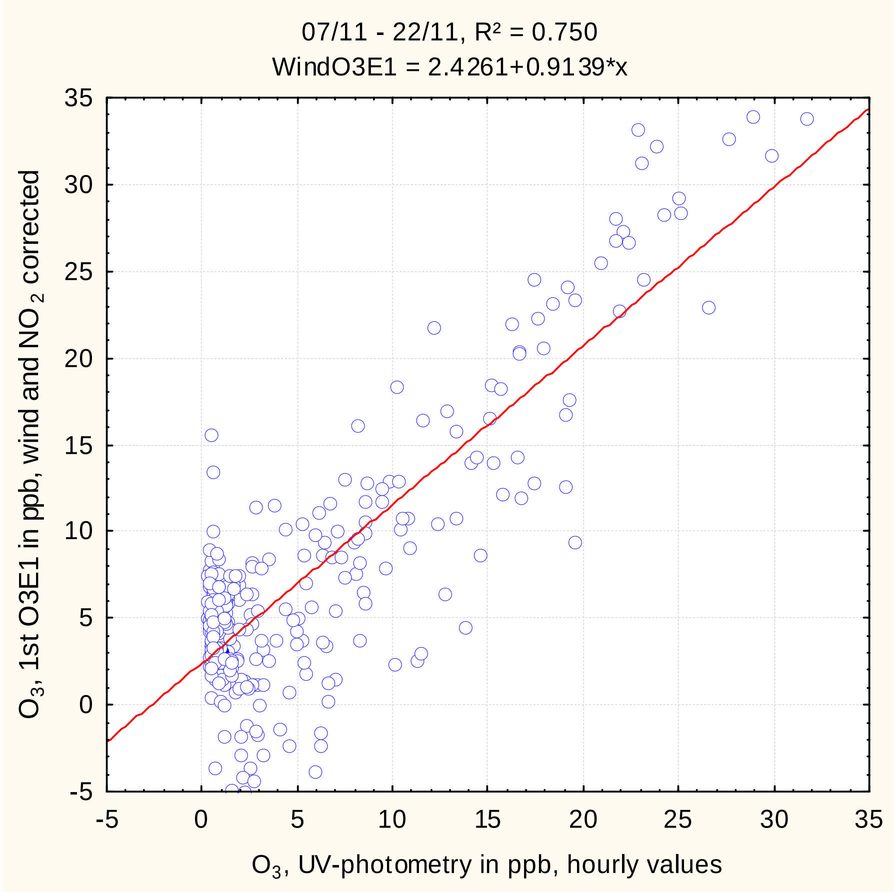


- **2 periods of 2 weeks at a rural site**
- **1st period calibration**
- **2nd period for checking drift**
- **hourly differences of 2nd period < 8 ppb**
- **U calculated using: lack of fit, repeatability and bias ~ 15 %**

M. Gerboles et al., Evaluation of Micro-Sensors to monitor Ozone in Ambient Air, EUR 23676 EN, ISBN 978-92-79-11104-4, DOI 10.2788/5978, 2009.

Gel electrolyte O_3 sensors, O3 3E1 , Sensoric (City Technology)

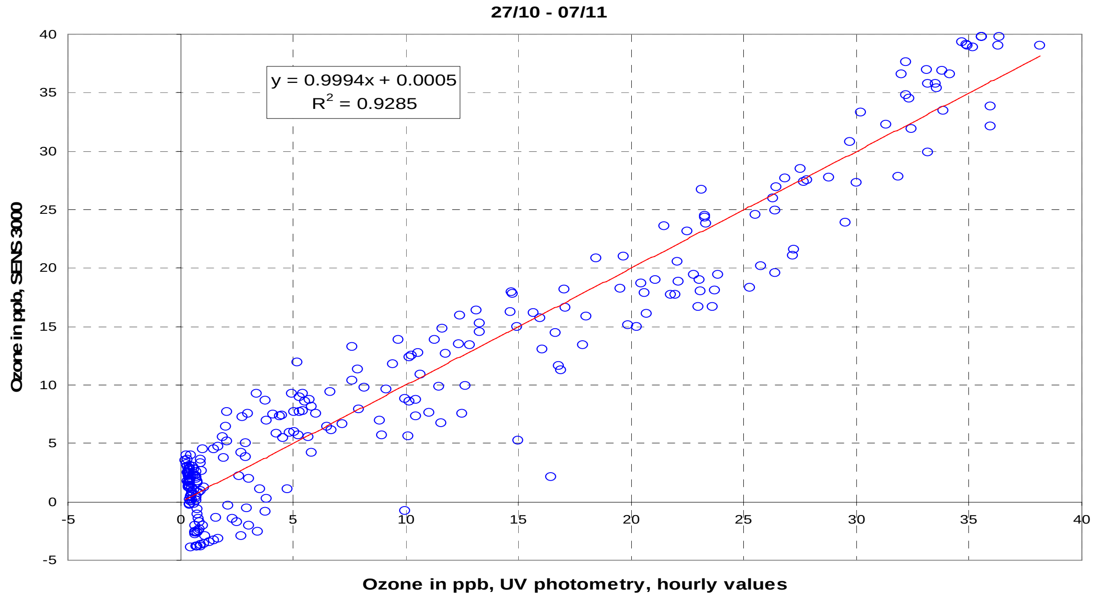


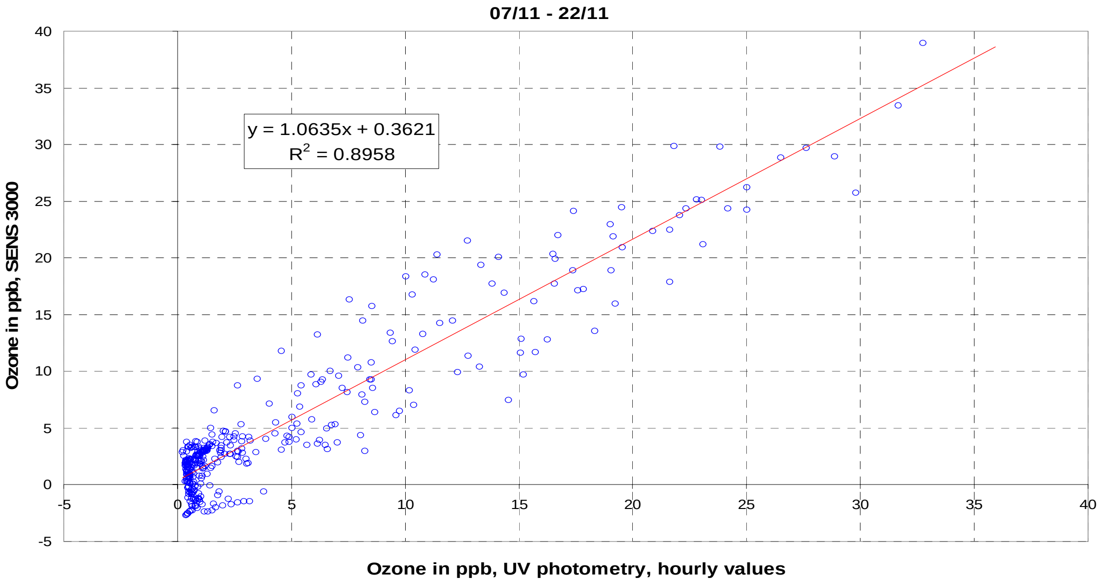


- **2 periods of 2 weeks at a rural site: 1st period calibration with NO_2 and wind speed correction, 2nd period for checking drift**
- **2nd period: hourly differences up to 20 ppb**
- **U of hourly values calculated using: lack of fit, repeatability and bias ~ 25 %**

M. Gerboles et al., Evaluation of Micro-Sensors to monitor Ozone in Ambient Air, EUR 23676 EN, ISBN 978-92-79-11104-4, DOI 10.2788/5978, 2009.

O_3 sensors, SENS3000, Unitec



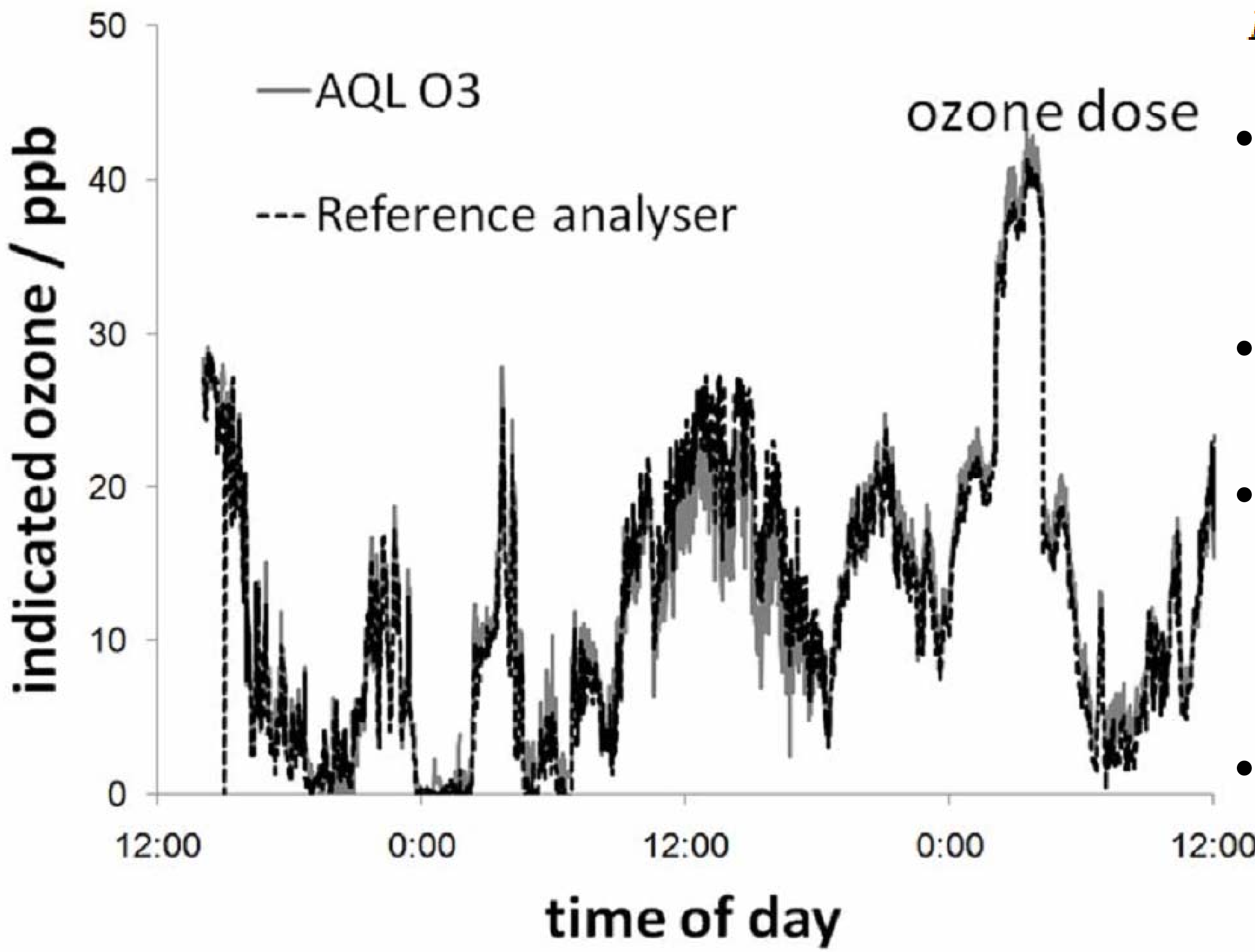


$$O3\ [\mu g/m^3] = a + b\ V^c$$

- **2 periods of 2 weeks at a rural site**
- **1st periods calibration**
- **2nd period for checking drift**
- **2nd period hourly differences up to 10 ppb**
- **U calculated using: lack of fit, repeatability and bias ~ 21 %**

M. Gerboles et al., Evaluation of Micro-Sensors to monitor Ozone in Ambient Air, EUR 23676 EN, ISBN 978-92-79-11104-4, DOI 10.2788/5978, 2009.

O_3 sensors, WO_3, Aeroqual

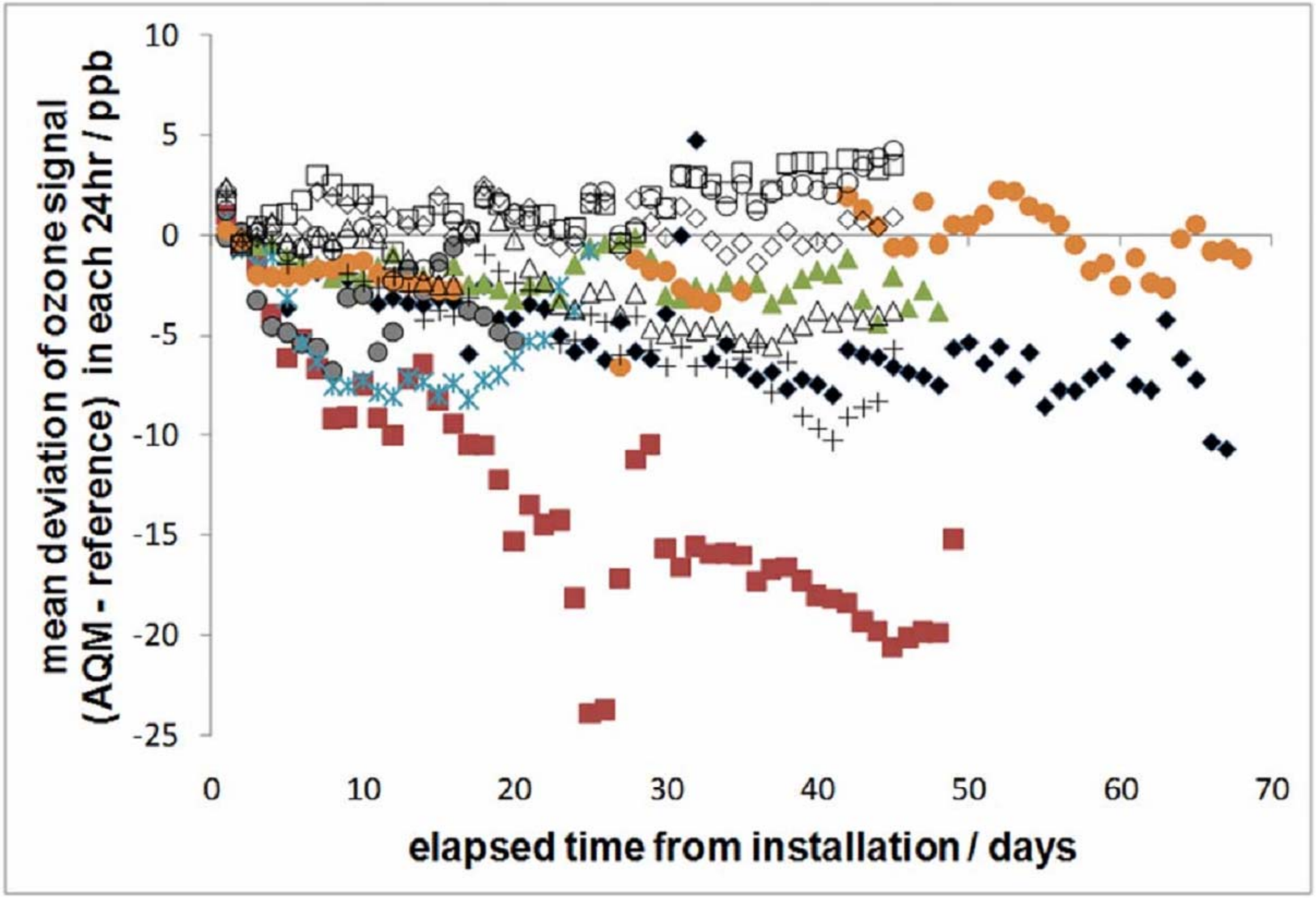


2009, David E Williams et al., Sensors, 10.1109/ICSENS.2009.5398568

$$P(O_3) = \frac{1}{a}\Delta G + \frac{b}{a^2}\Delta G^2 + 0(\Delta G)^3$$

- Continuous zero monitoring (stop flow + warming)
- WO_3 sensitive to O_3 >> NO_2 > Cl_2 + H_2S
- Small effect of hydrocarbons, solvents, SO_2, NO and water vapor.
- Claim that WO_3 is not affected like SnO_2 sensors to zero and calibration drifts or cross sensitivities

O_3 sensors, WO_3, Aeroqual



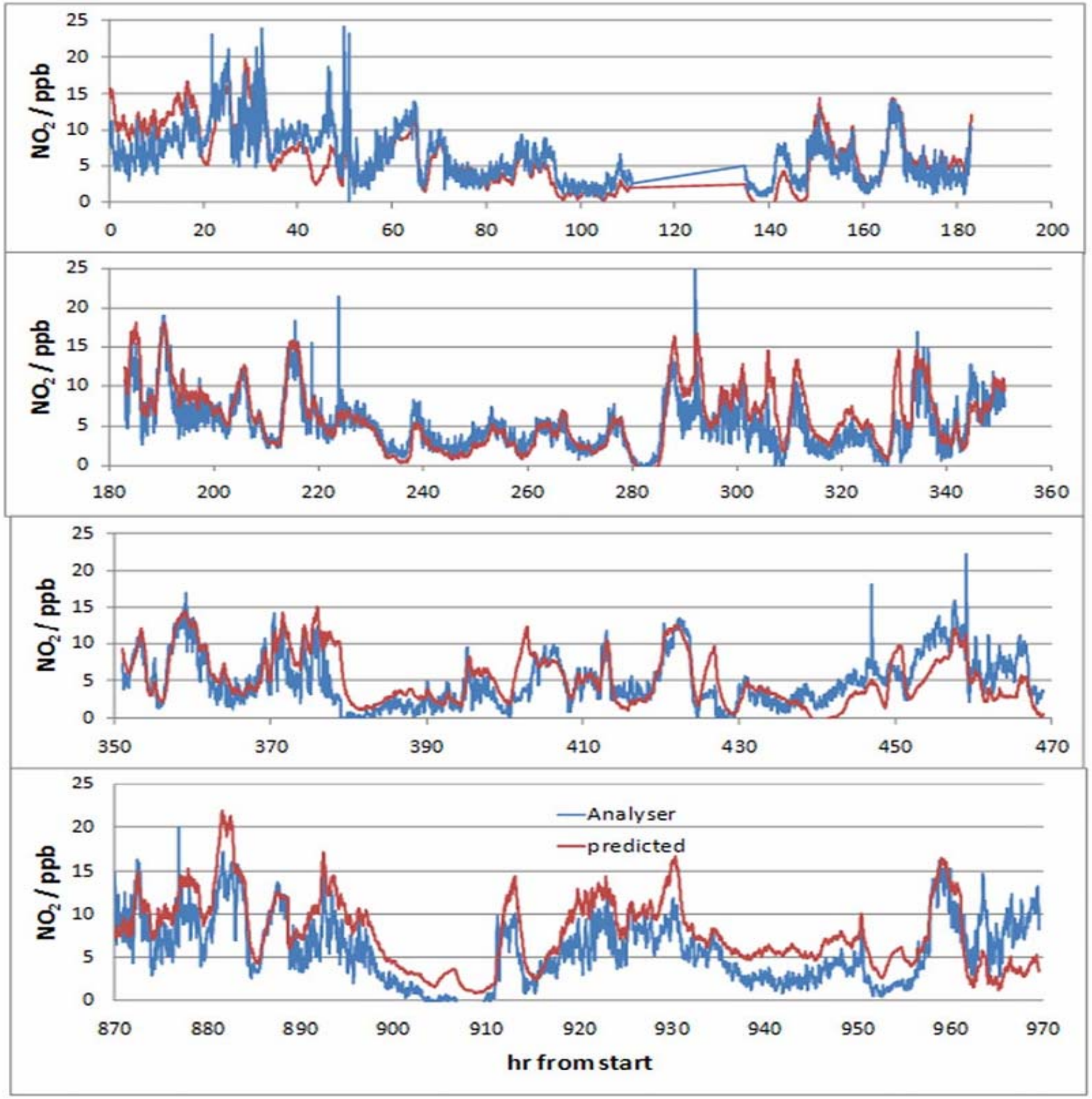
2009, David E Williams et al., Sensors, 10.1109/ICSENS.2009.5398568

- One field site, 10 sensors, about 2 months of measurements against UV photometry
- Initial calibration, no recalibration
- Daily differences mainly between 10 ppb showing independence to water vapor and temperature
- Higher drift associated with pump failure, filter dirt or WO_3 destruction

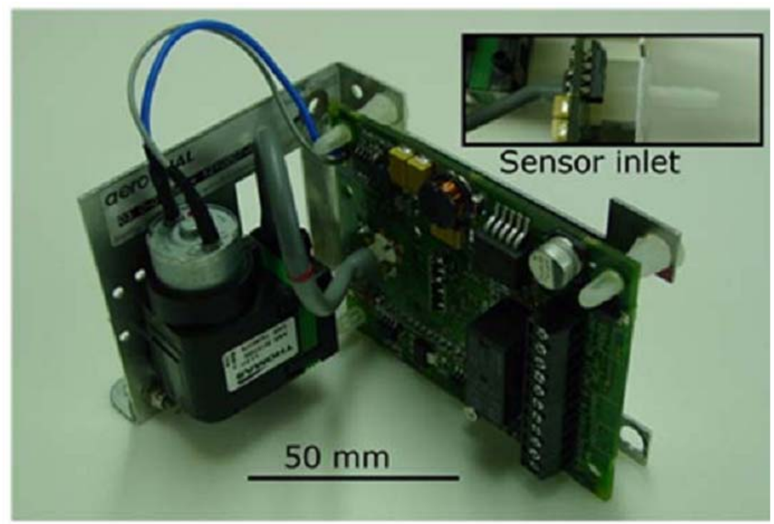
EUROPEAN COMMISSION

NO_2 sensors, WO_3, Aeroqual

Institute for Environment and Sustainability

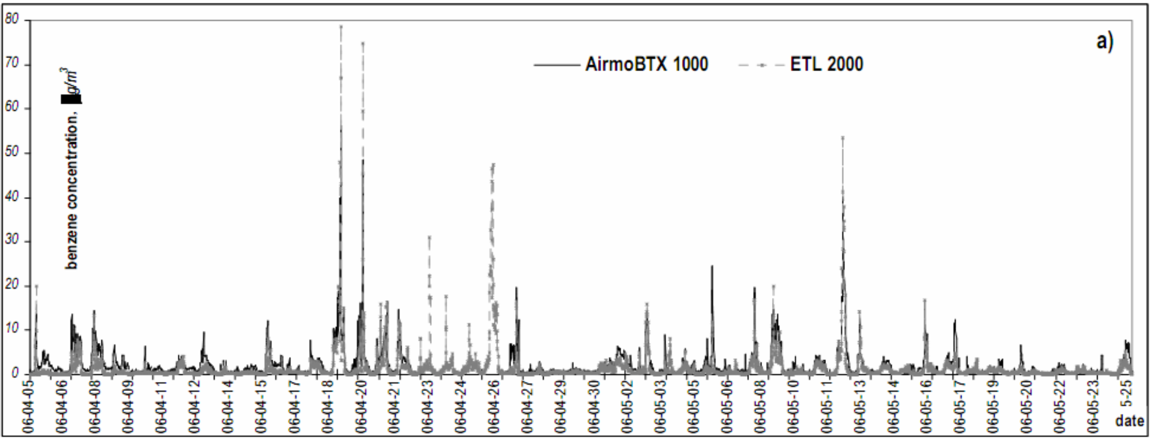


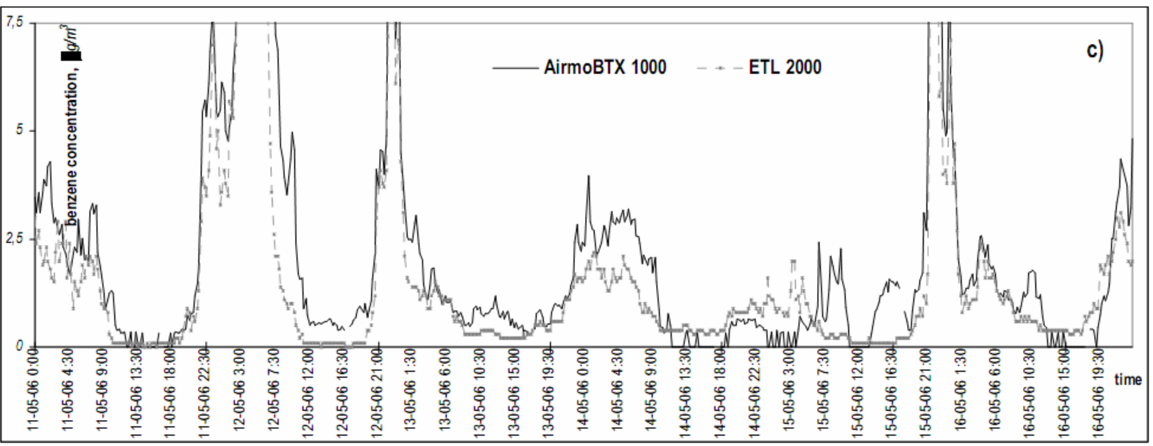
- **Different grain size and heater temperature for NO_2 compared to O_3**
- **Ozone scrubber for NO_2 (might modify the NO/ NO_2 /O_3 equilibrium) . No NO and O_3 interference (?)**
- **Slow response time (at least hourly values**
- **One site, 40 days. Daily differences < 2 ppb, low NO_2 (rural site? low NO)**



2009, David E Williams et al., Sensors, 10.1109/ICSENS.2009.5398568

Benzene sensors, ETL2000, Unitec (I)

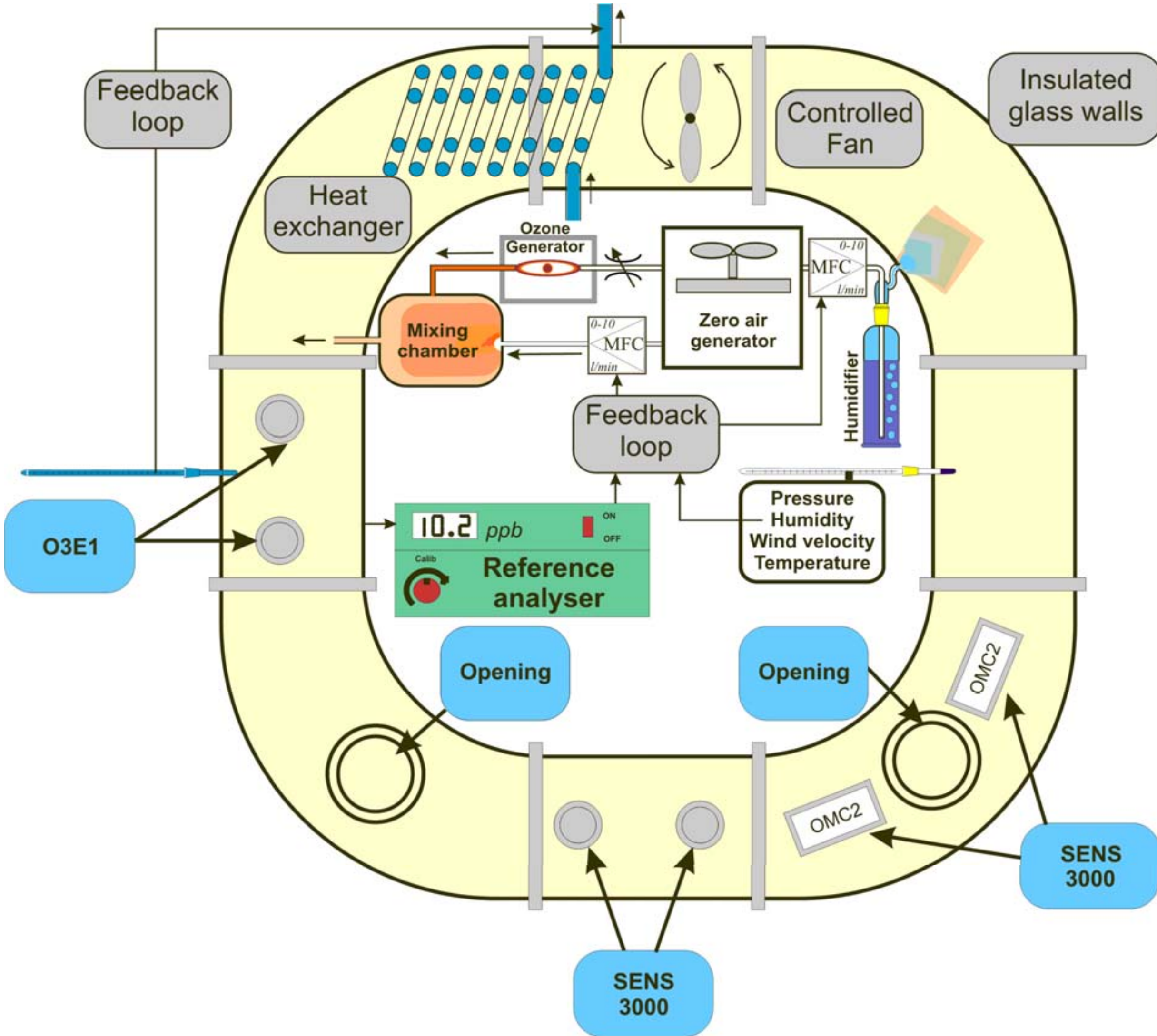


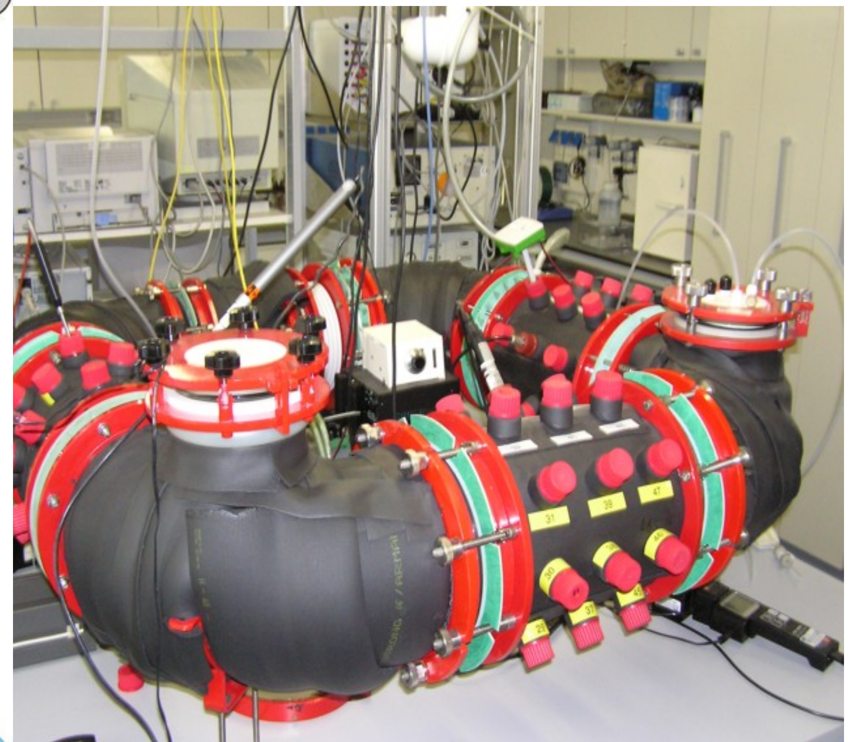


- 7 weeks of sampling at Zabrze-P (urban background sation)
- 15’ values of ETL2000 compared to AIRMOBTX1000
- Correct sensor values for high concentrations
- Decrease of sensitivity and selectivity for concentrations up to 3 µg/m³

Halina Pyta, Marek Pawłowski, Application of semiconductive chemical sensors to control the concentration of benzene in the air, www.ecomonitoring.com/

Gas mixtures prepared with an ambient air matrix
Temperature and humidity control may be necessary



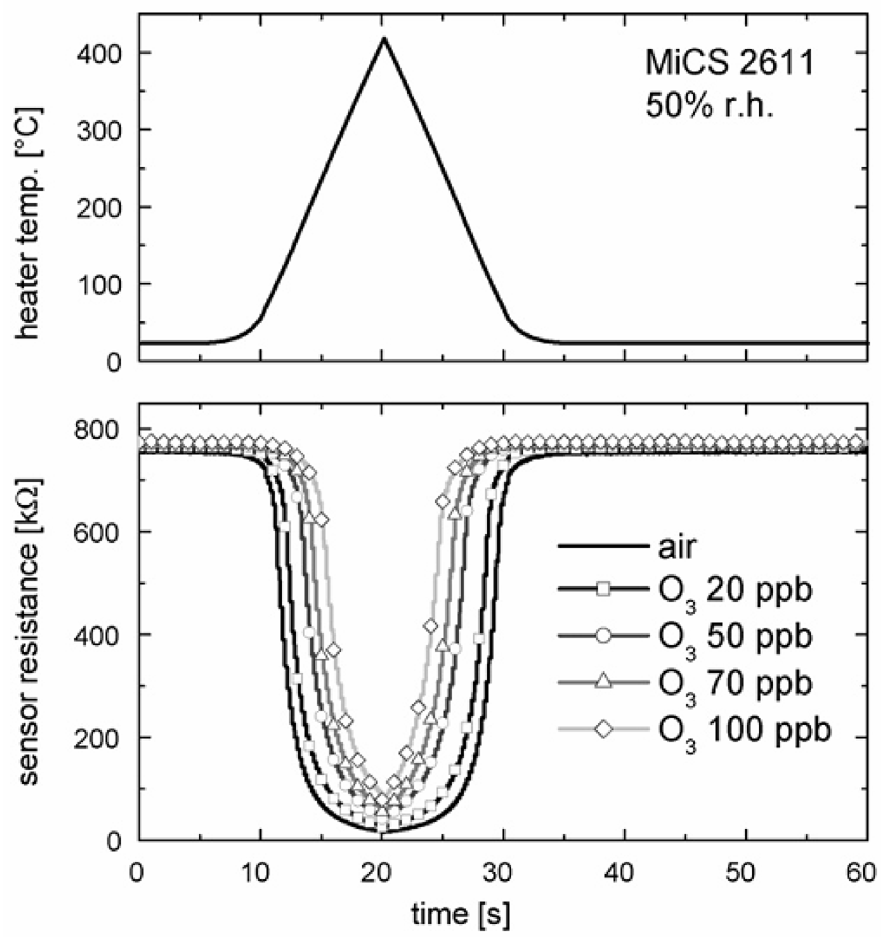


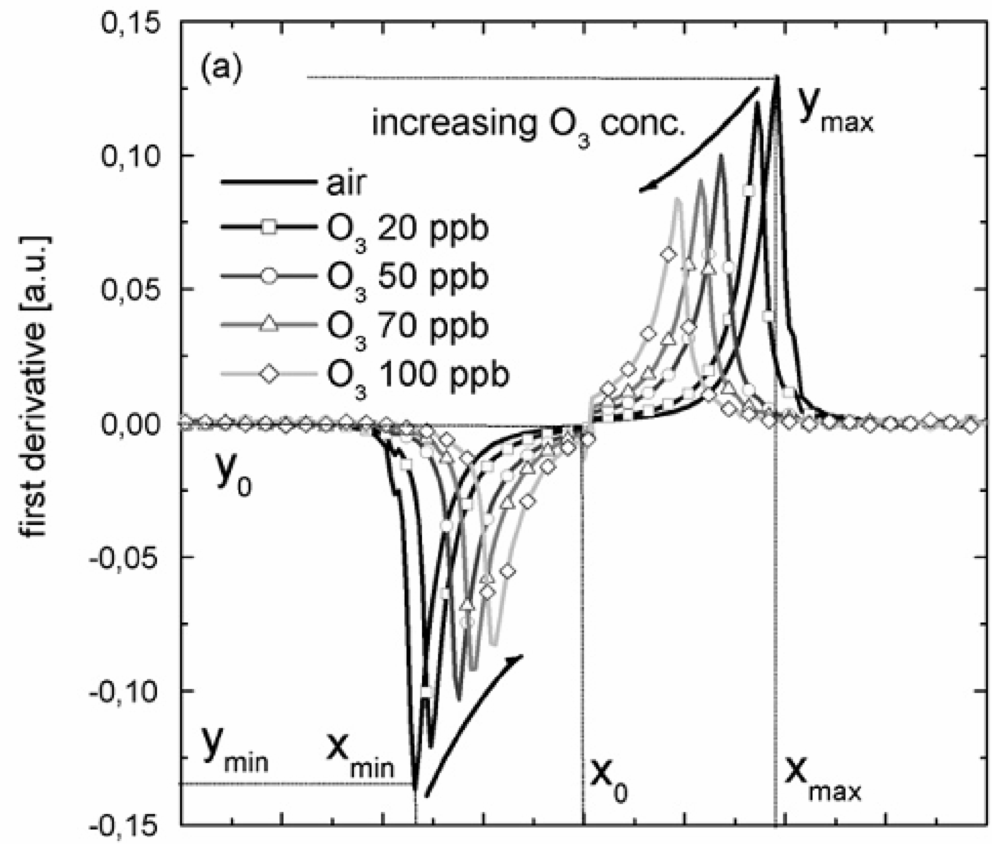
Field Calibration

- **Calibration using the direct comparison method against a reference method analyser co-located at the field site generally gives better results.**
- **The questions to be tackled are:**

1. *Interpolation or extraplation of levels of concentration of pollutant, temperature, humidity and interference*
2. *Duration of the calibration phase*
3. *Periodicity of re-calibration*

Pulsed heating, discriminant analysis





Markus Losch et al., Ozone detection in the ppb-range with improved stability and reduced cross sensitivity, Sensors and Actuators B 130 (2008) 367–373

Zero drift corrections are possible by :

- overheating of the sensors
- pausing sample flow rate
- filtering and/or absorption of compounds through filtering
- detection of time windows with level of air pollutant near zero…

For sensors with a constant change of conductivity versus the level of air pollutant concentration and baseline drift.

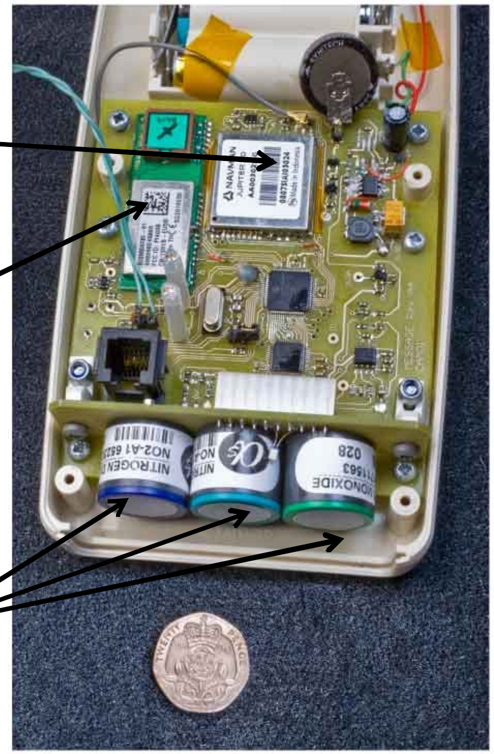
Mobile sensors equipped with GPS may also be corrected using the measurements of automatic station when moving in its neighbourhood

Sensor units components

Satellite navigation

Mobile phone

Gas sensors



Simple operation!

400 gm (incl. batteries)

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UNIVERSITY OF CAMBRIDGE

Lisbon
13-14 November 2009

message

Statistical evaluation CO

CO	MEAN	MAX
CAR	0.674	6.745
BIKE	0.630	5.013
WALK	0.481	7.860

Membrapor SO_2 electrochemical sensor

PERFORMANCE CHARACTERISTICS

Nominal Range	0 – 20 ppm
Maximum Overload	100 ppm
Expected Operation Life	2 years in air
Output Signal	1000 ± 300 nA/ppm
Resolution	0,1 ppm
Temperature Range	- 20 °C to 45 °C
Pressure Range	Atmospheric ± 10%
Pressure Coefficient	No data
T_{90} Response Time	< 20 sec
Relative Humidity Range	15 % to 90 % R.H. non-condensing
Typical Baseline Range (pure air, 20°C)	< 0,1 ppm
Maximum Zero Shift (+20°C to +40°C)	N.D.
Long Term Output Drift	< 2% signal loss/month
Recommended Load Resistor	10 Ohm
Bias Voltage	Not required
Repeatability	< 2 % of signal
Output Linearity	Linear

CROSS-SENSITIVITY DATA

Interfering Gas	Concentration	Reading
CO	100 ppm	< 1 ppm
H_2S	34 ppm	~ 30 ppm
NO	100 ppm	0 ppm
NO_2	100 ppm	~ -125 ppm
H_2	100 ppm	< 1 ppm
Ethylene	100 ppm	0 ppm

Performance data conditions:
20 °C, 50% RH and 1013 mbar

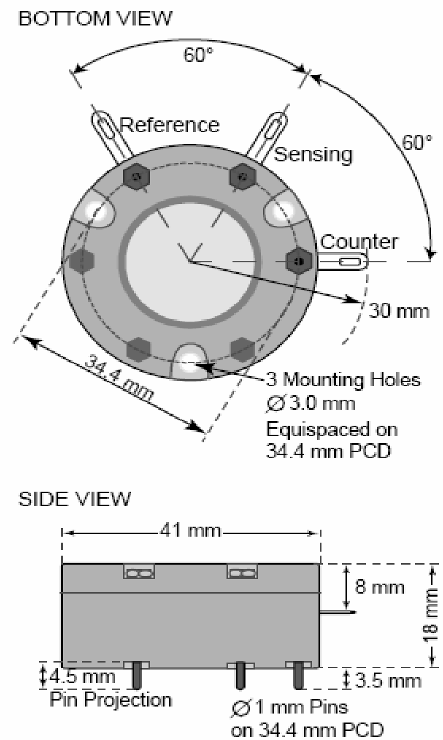
APPLICATIONS

Safety and Environmental Control

PHYSICAL CHARACTERISTICS

Weight	~ 27 g
Position Sensitivity	None
Storage Life	Six months in container
Recommended Storage Temperature	5 °C – 20 °C
Warranty Period	12 months from date of dispatch

Slim-Size Outline Dimensions



Membrapor NO_2 electrochemical sensor

PERFORMANCE CHARACTERISTICS

Nominal Range	0 – 20 ppm
Maximum Overload	200 ppm
Expected Operation Life	2 years in air
Output Signal	- 1200 ± 200 nA/ppm
Resolution	0,1 ppm
Temperature Range	- 20 °C to 45 °C
Pressure Range	Atmospheric ± 10%
Pressure Coefficient	No data
T_{90} Response Time	< 60 sec
Relative Humidity Range	15 % to 90 % R.H. non-condensing
Typical Baseline Range (pure air, 20°C)	< 0.1 ppm
Maximum Zero Shift (+20°C to +40°C)	- 0,2 ppm
Long Term Output Drift	< 2% signal loss/month
Recommended Load Resistor	10 – 33 Ohm
Bias Voltage	Not required
Repeatability	< 2 % of signal
Output Linearity	Linear

CROSS-SENSITIVITY DATA

Interfering Gas	Concentration	Reading
CO	300 ppm	0 ppm
SO_2	5 ppm	0 ppm
NO	35 ppm	0 ppm
H_2	300 ppm	0 ppm
Ethylene	100 ppm	0 ppm

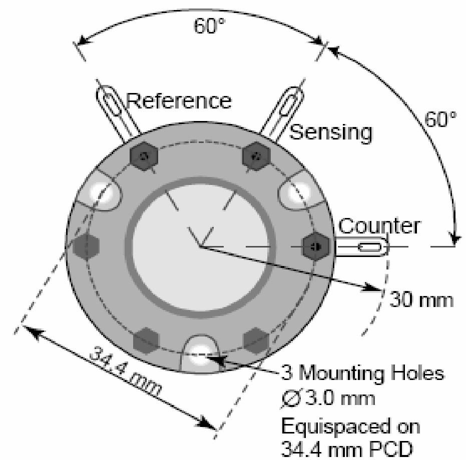
Performance data conditions:
20 °C, 50% RH and 1013 mbar

PHYSICAL CHARACTERISTICS

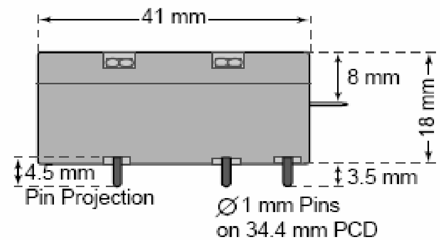
Weight	~ 27 g
Position Sensitivity	None
Storage Life	Six months in container
Recommended Storage Temperature	5 °C – 20 °C
Warranty Period	12 months from date of dispatch

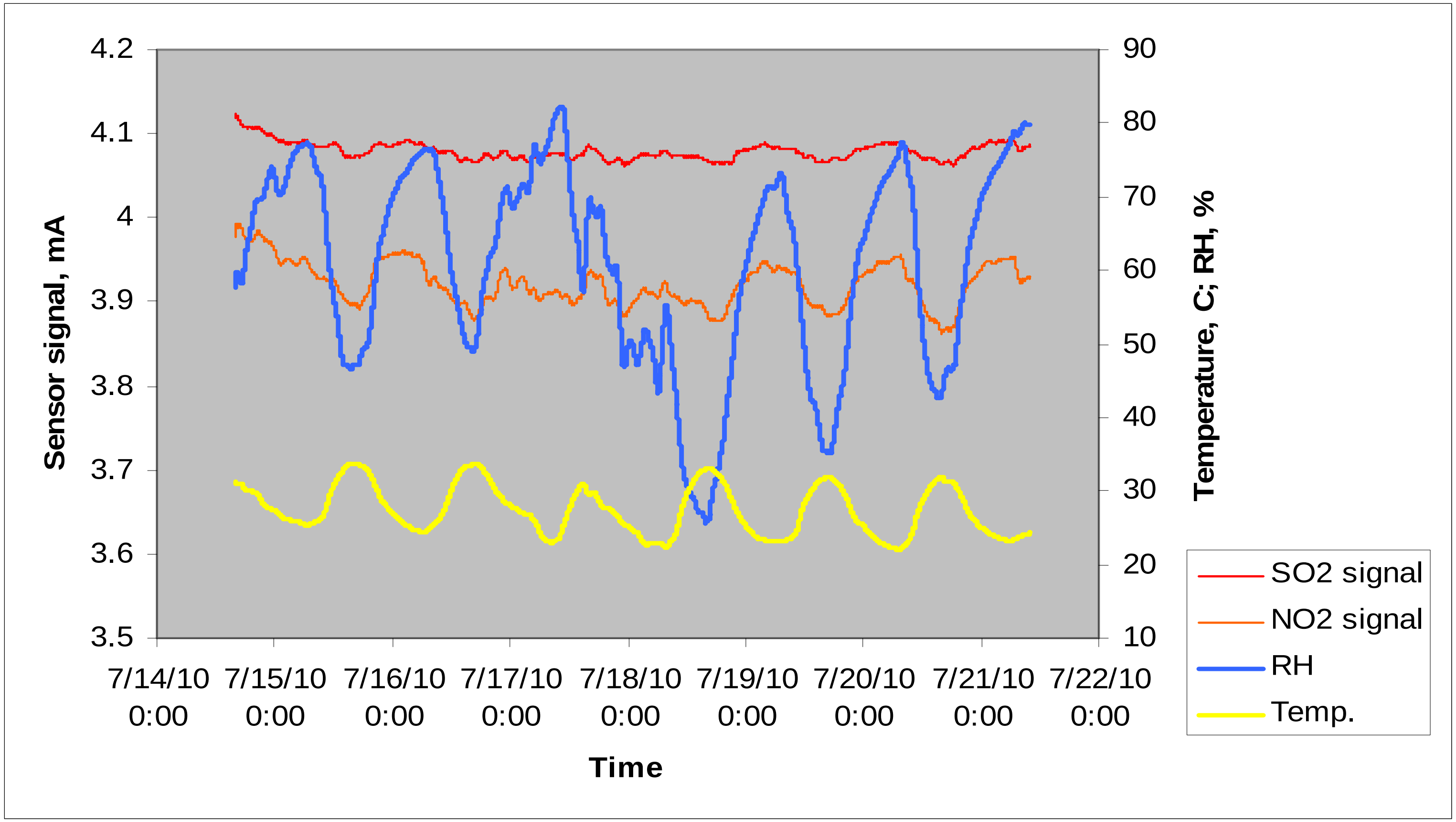
Slim-Size Outline Dimensions

BOTTOM VIEW



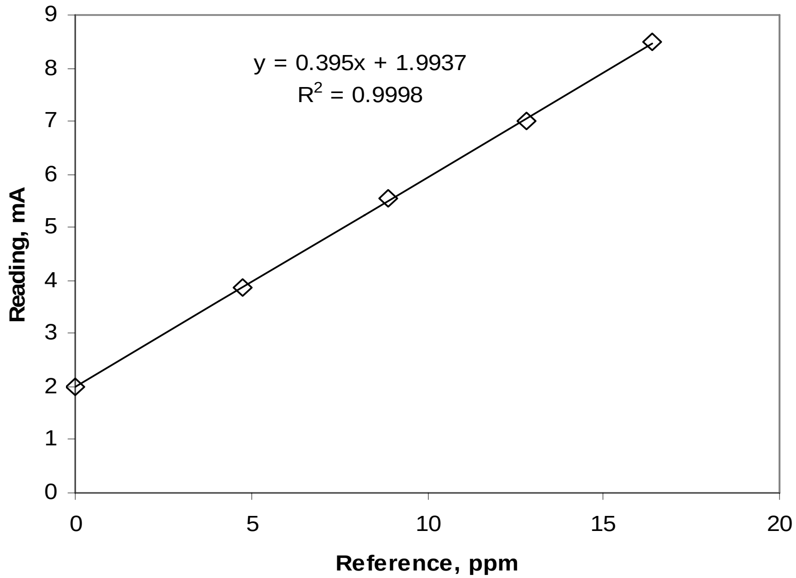
SIDE VIEW



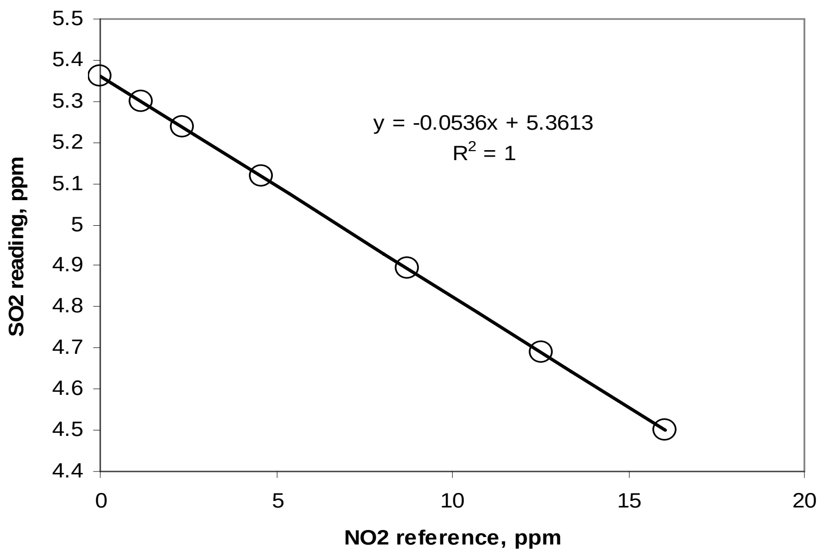


Outdoor test of temperature and humidity dependence of SO_2 and NO_2 baseline

Calibration

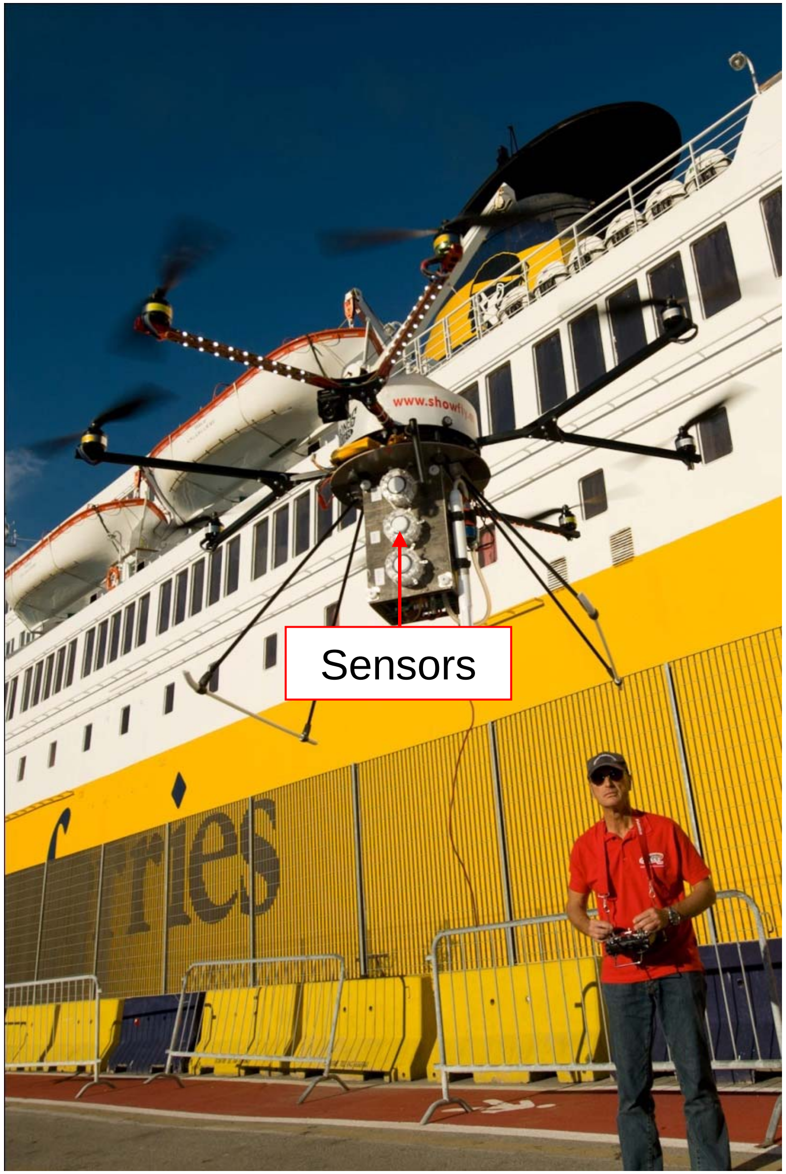


SO_2 response function in the 0-20 ppm concentration range



NO_2-SO_2 cross sensitivity plot

An extraordinary application



Exhaust plume measurement from unmanned flying platform (ppm concentration range):

<u>CONFIGURATION 1</u>:

- Real time measurements by electrochemical sensors:

  -NDIR CO_2 GASCARD (0-3000 ppm),

  -NO, NO_2, SO_2 electrochemical sensors (0-100,0-20,0-20 ppm),

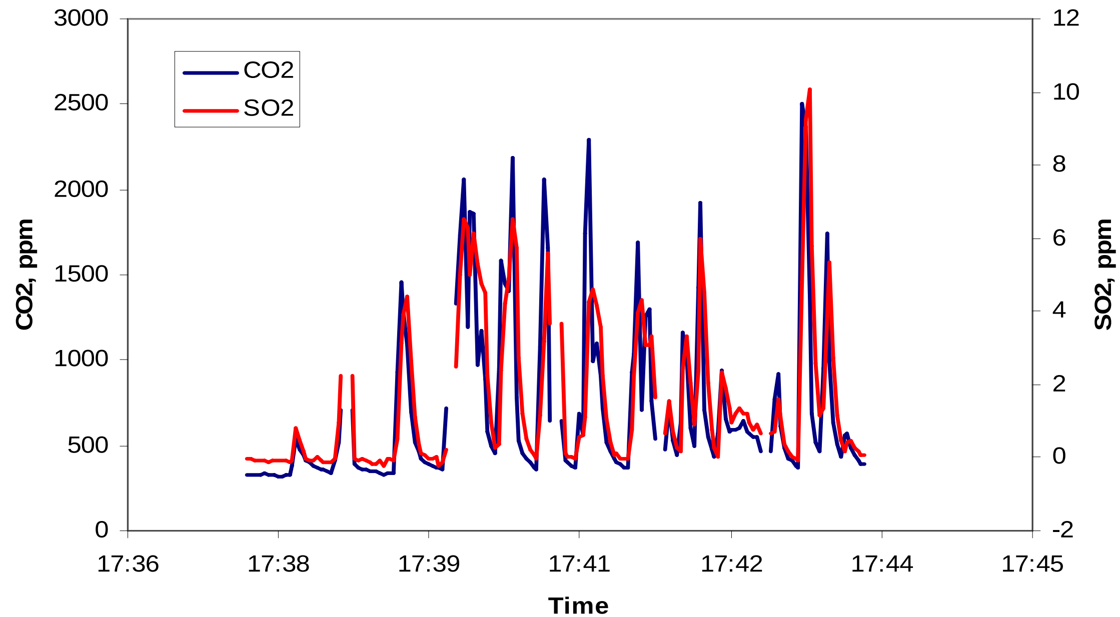
- Temperature.

<u>CONFIGURATION 2</u>

- Sampling by under-pressurized canister with a remotely controlled valve,
- Measurement in laboratory by traditional gas analyzers.

Sensor unit

Transmitter unit

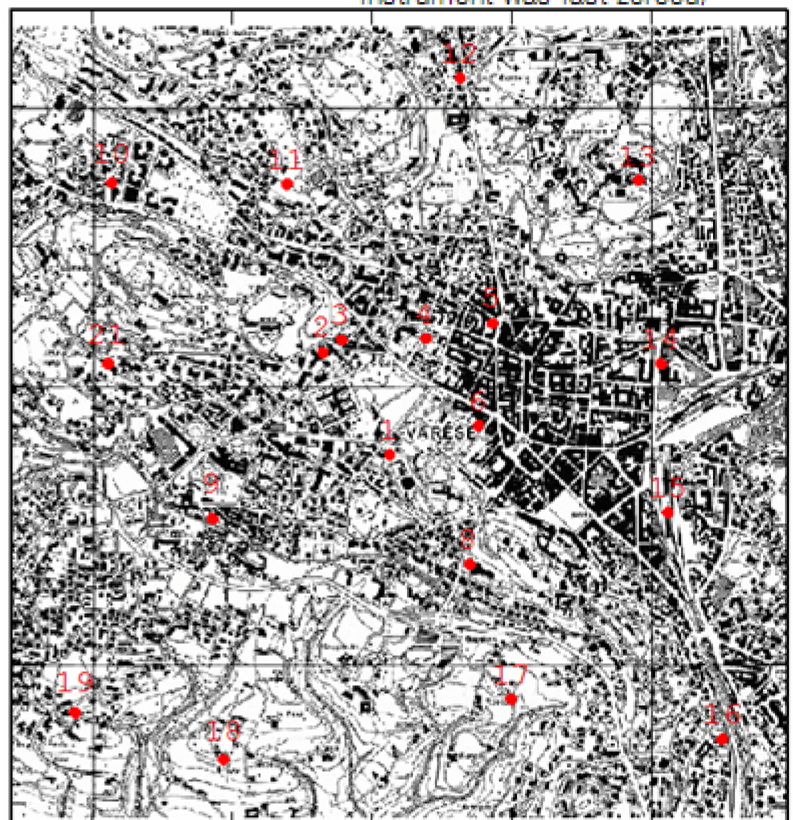


Simultaneous SO_2, CO_2 concentration plots

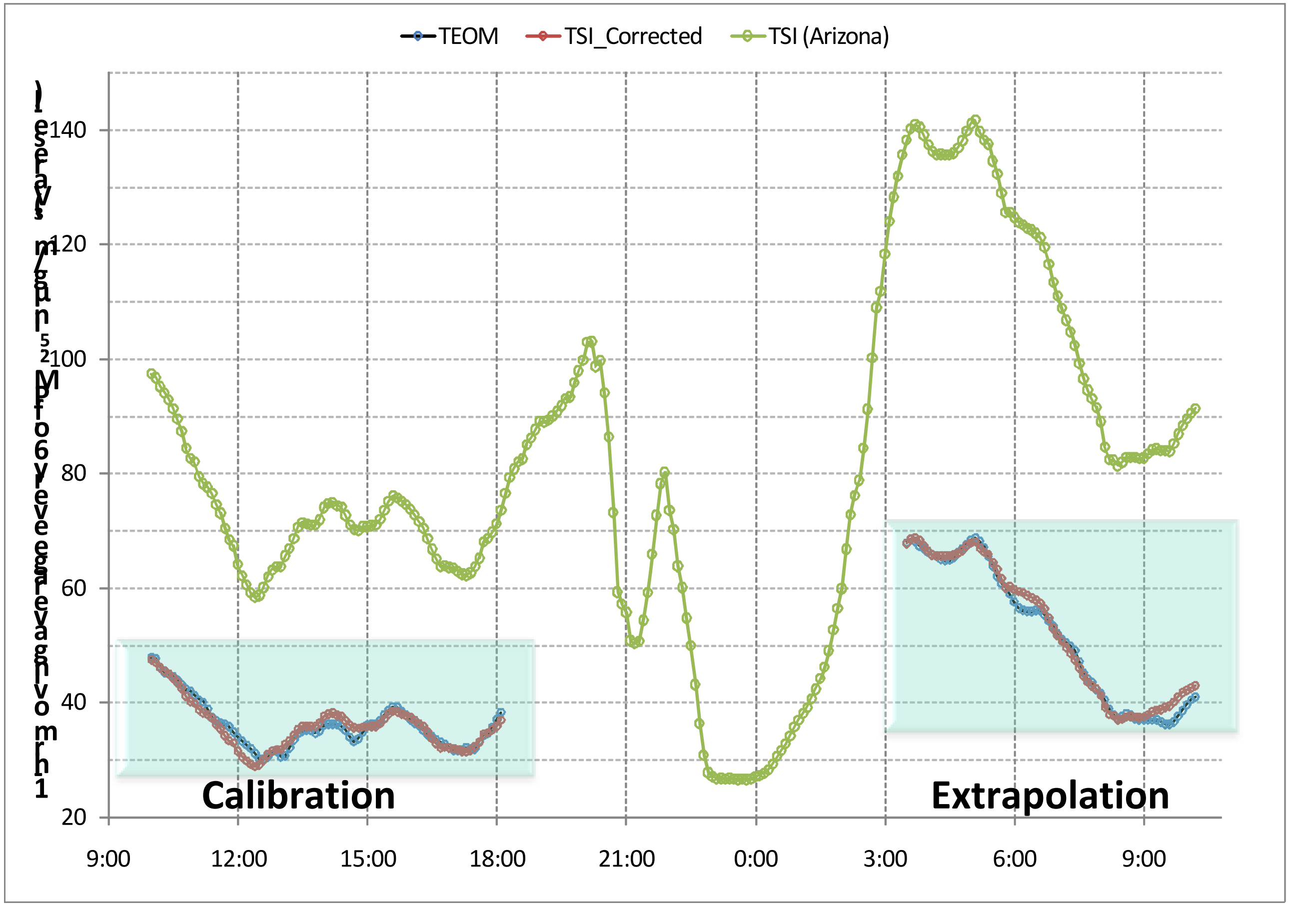
- SO_2/CO_2 ratio: 4.13 ppb/ppm,
- Measurement of canister sample by gas analyzers gives: 3.84 ppb/ppm,
- Difference < 8%.

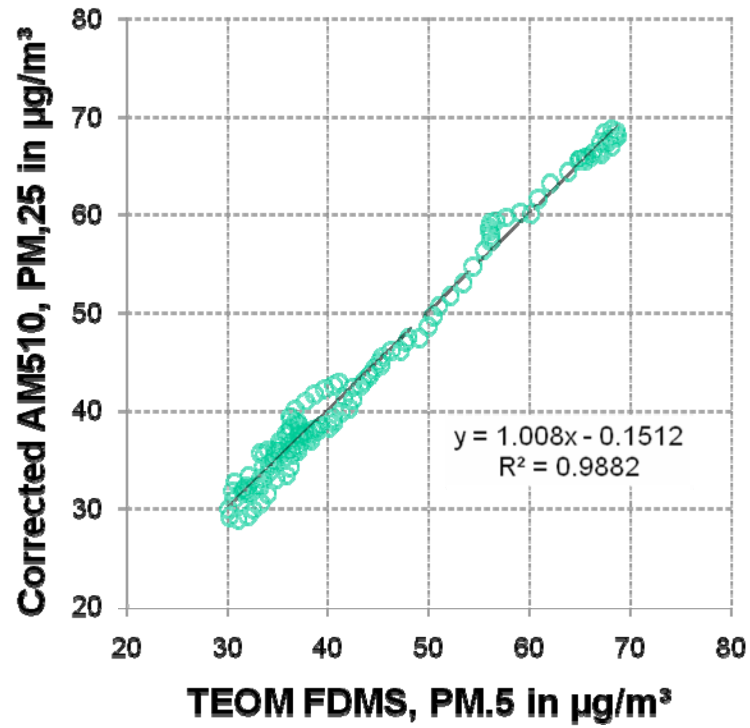
Portable Nefelometer, SidePak AM510, TSI (USA)

Sensor Type	90° light scattering, 670 nm laser diode
Aerosol Concentration Range	0.001 to 20 mg/m^3 (calibrated to respirable fraction of ISO 12103-1, A1 test dust)
Particle Size Range	0.1 to 10 micrometer (µm)
Minimum Resolution	0.001 mg/m^3
Zero stability	±0.001 mg/m^3 over 24 hours using 10-second time-constant
Temperature Coefficient	Approximately +0.0005 mg/m^3 per °C (for variations from temperature at which instrument was last zeroed)



Field calibration against a TEOM FDMS





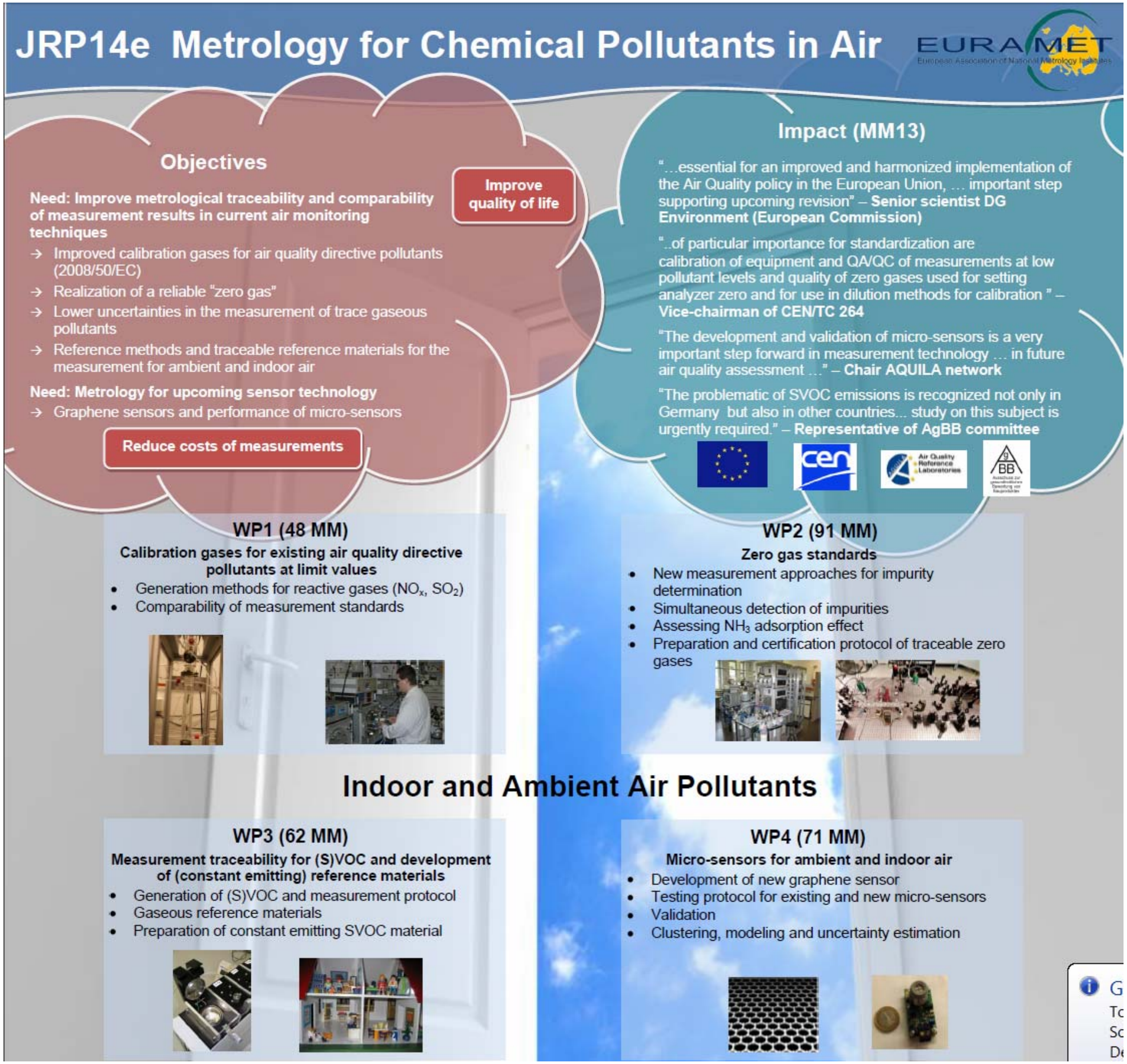
$$\mathrm{TSI_i} = \mathrm{a}_0\left(TEOM_{BM} + GF \times TEOM_{EV}\right) + a_1$$

$$GF = (1 - RH)^{-\gamma}$$

$$TSI_{corr} = \frac{TSI - a_1}{a_0 \times \left(1 - R_{EV} + R_{EV} GF\right)}$$

$$R_{EV} = \frac{TEOM_{EV}}{TEOM}$$

FUTURE PROJECT: JRP14 WP4 Sensors



- **NO_2 graphene sensor.**
- **Calibration procedure and a testing protocol**
- **Validation as 'indicative' methods of NO2 and O3 sensors**
- **Grouping of different sensors to monitor the pollutants regulated by the Air Quality Directive.**

Conclusions

- NO_2 and O_3, these are the gaseous compounds to focus on. The development of field calibration procedures, estimation of the periodicity of recalibration and its site dependency, field validations at several sites are needed
- DQO of indicative methods could be met for NO_2 and O_3
- CO: old validation studies, currently a lack of interest at ambient air level?
- SO_2: only ppm levels in field application

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Thank you!

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