Electrochemical Gas Cells in Air Quality Networks - Solving the Problems

Dr John Saffell
Technical Director
Alphasense Ltd.
Great Notley, Essex UK
jrs@alphasense.com

Alphasense air
Sensors for Air Quality Networks

COST Action TD1105 **EuNetAir**

Second Scientific Meeting
Queens' College Cambridge
18-20 December 2013

cost
EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

Who is Alphasense ?

- Private UK limited company, 10 minutes from Stansted airport.
- Started January 1997.
- 65 people: 15 Technical, 40 manufacturing.
- Significant R&D investment, mostly with UK Universities.
- Markets: Industrial Safety and Air Quality gas sensors.

Sensor technologies: electrochemical, metal oxides, Optical particle counting, NDIR, PID, MEMS, spectroscopy.

We make Gas Sensors and PM2.5/10 OPCs. That's all.

Air Quality standards differ in USA and Europe, but we want to resolve 10-20 ppb with an error less than 20-50 ppb

	USA		Europe		
Pollutant	**ppb**	**Period**	**ppb**	**Limit**	**EN standard**
Ozone	75	8 hour average	120	Alert threshold	EN 14625
NO_x /NO_2	50	Annual mean	210	Alert threshold	EN 1421 1
NO_x /NO_2	100	1 hour mean	105	1 hr limit value	EN 1421 1
SO_2	500	3 hour mean	200	Alert threshold	EN 1421 2
SO_2	140	24 hour mean	140	1 hr limit value	EN 1421 2
CO	35 ppm	1 hour average	8 ppm	8 hr limit value	EN 14626
	$\mu g/m^3$		**$\mu g/m^3$**		
PM 10	150	24 hour average	40	Annual mean	EN 12341
PM 2.5	15	Annual	25	Annual mean	EN 14907

Most difficult targets to measure accurately: NO_2 and PM 2.5

Electrochemical amperometric gas sensors

Used in the AQMesh pods, **MESSAGE and Heathrow projects**

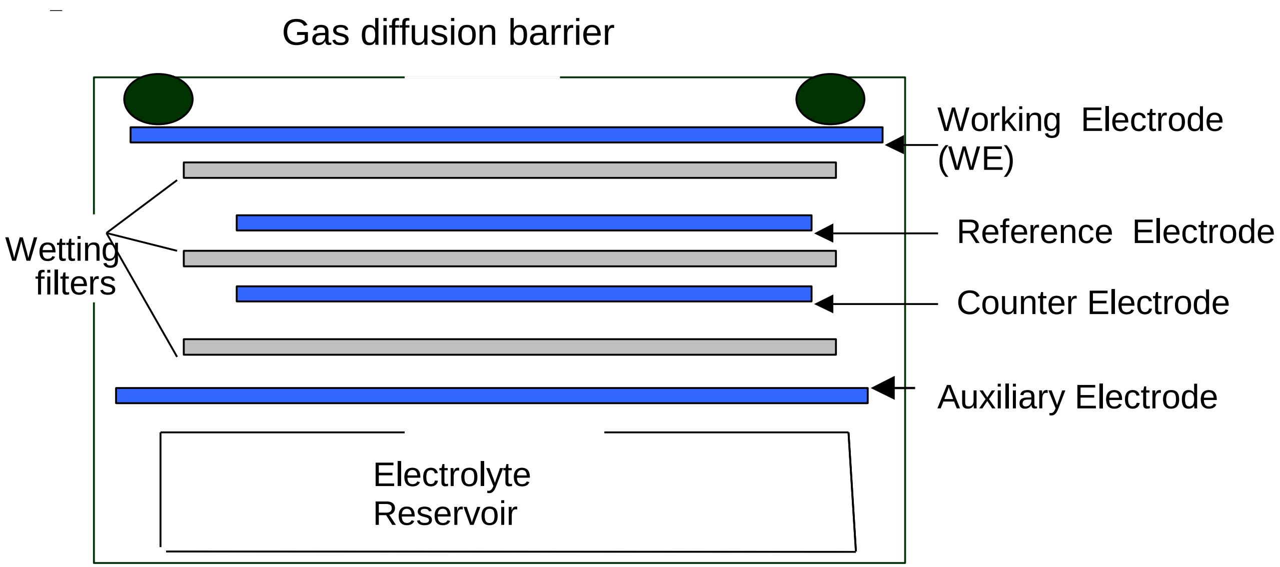
B series sensors for fixed site networks

32 mm diameter

A series sensors for mobile networks

Inside a 4- electrode amperometric electrochemical gas sensor

Working electrode	analyte reaction: oxidation or reduction
Counter electrode	balances the Working electrode reaction
Reference electrode	sets the WE potential for selectivity
Auxiliary electrode	corrects the zero current of the WE



Required sensor performance for Air Quality networks

Three requirements:

- ppb **Sensitivity** / Limit of Detection
- Long term zero and sensitivity **Stability**
- **Selectivity**, removing interfering gases

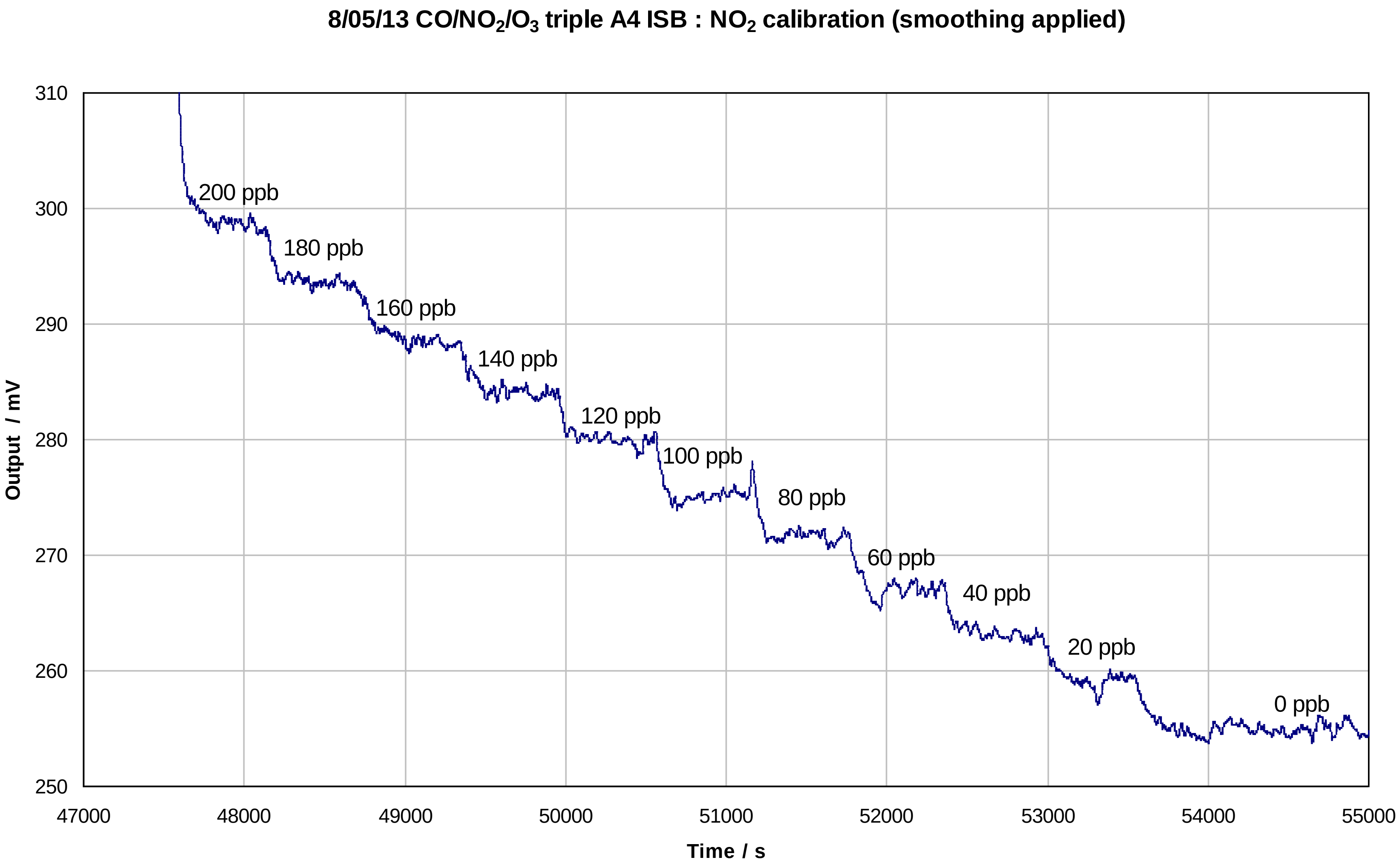
Gas Sensor Limit of Detection

(2 sd as the concentration approaches 0 ppb)

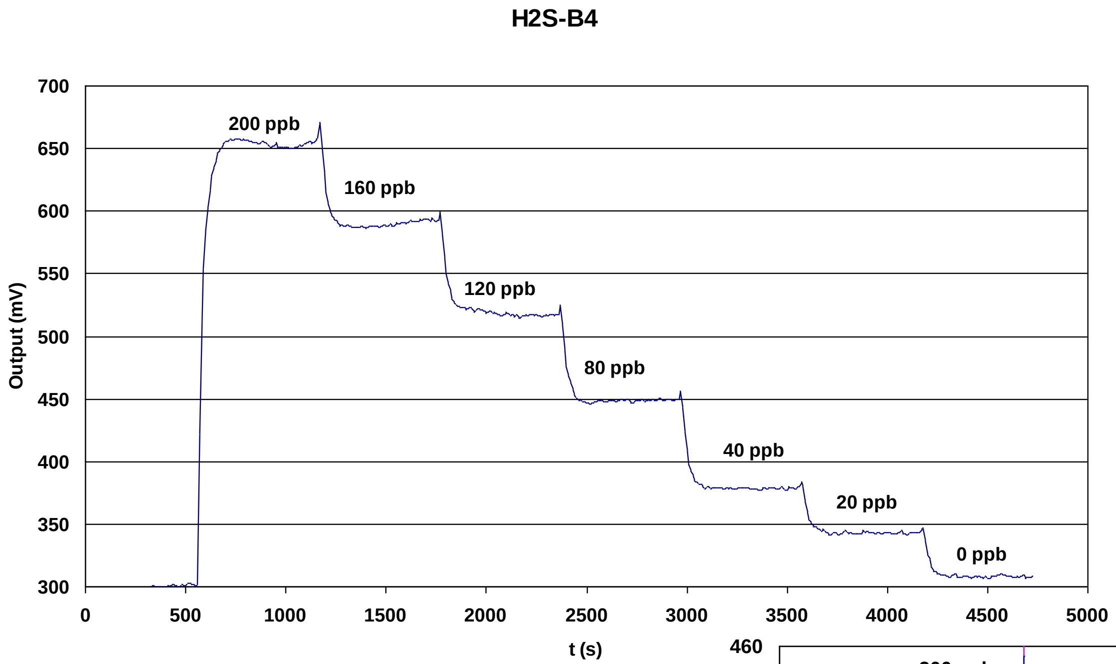
LoD (ppb)	CO	H_2S	NO	NO_2	O_3	SO_2
A series	20	5	80	15	5	15
B series	4	1	15	12	4	5

Mobile A series sensors have **higher limit of detection**, but this is being improved with quieter electronics (esp. NO)

NO2-A4
0-200 ppb linearity test (raw data)

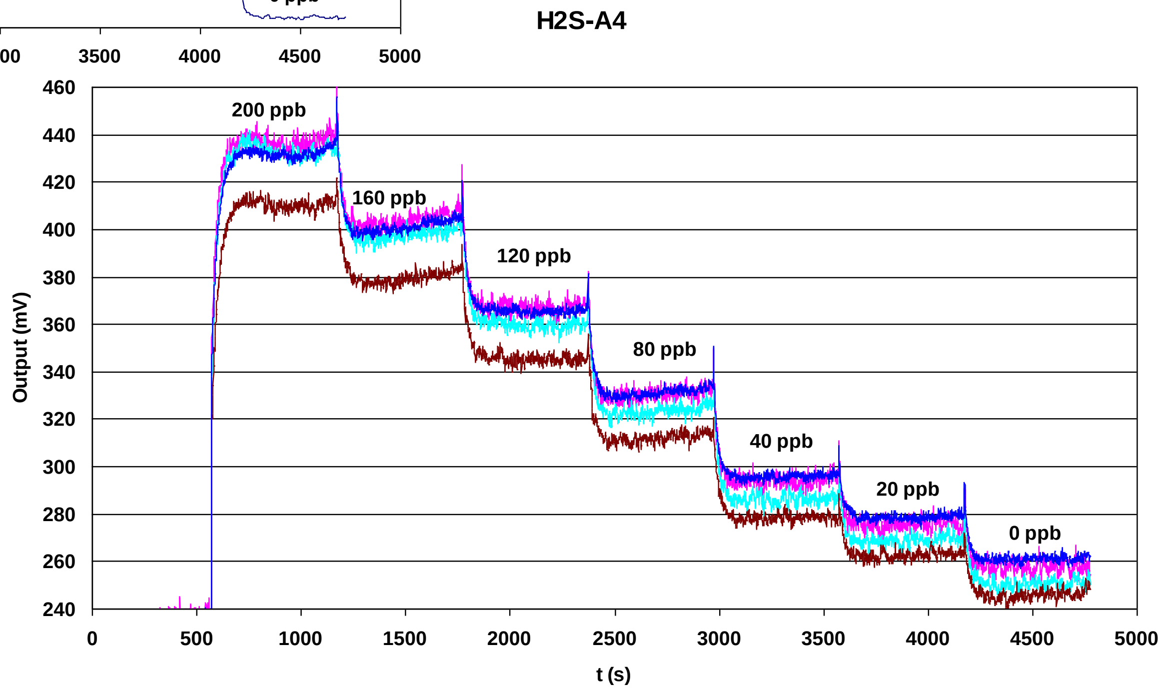


Some examples of low level sensitivity



H2S-B4
(for odour detection)
shows 1 ppb noise!

Data before smoothing

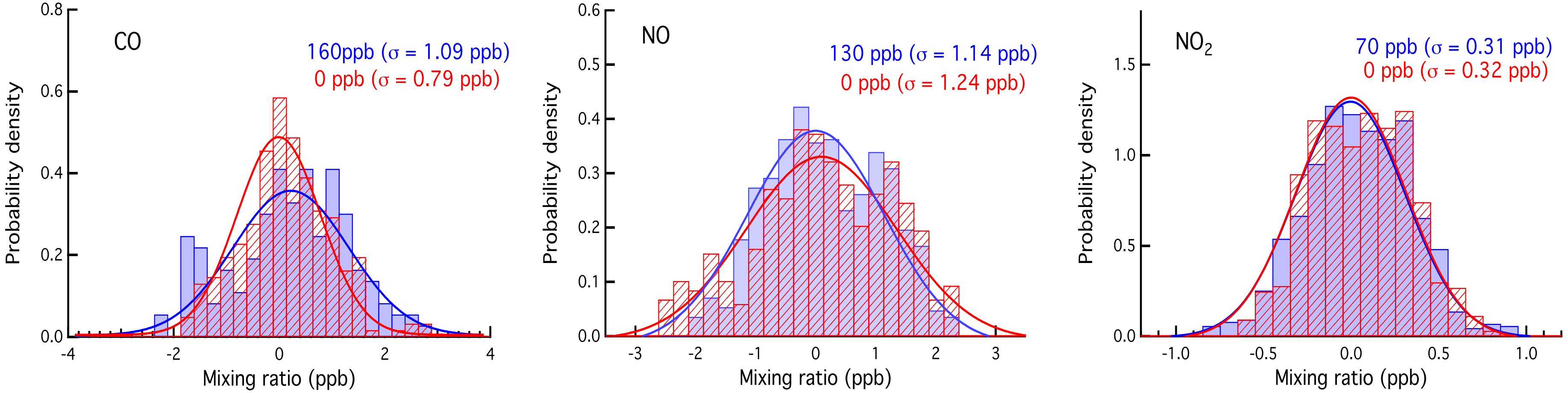


H2S-A4 has higher
noise- but still
5 ppb resolution

Data before smoothing

Cambridge laboratory measurements define noise at 1-2 ppb after smoothing.

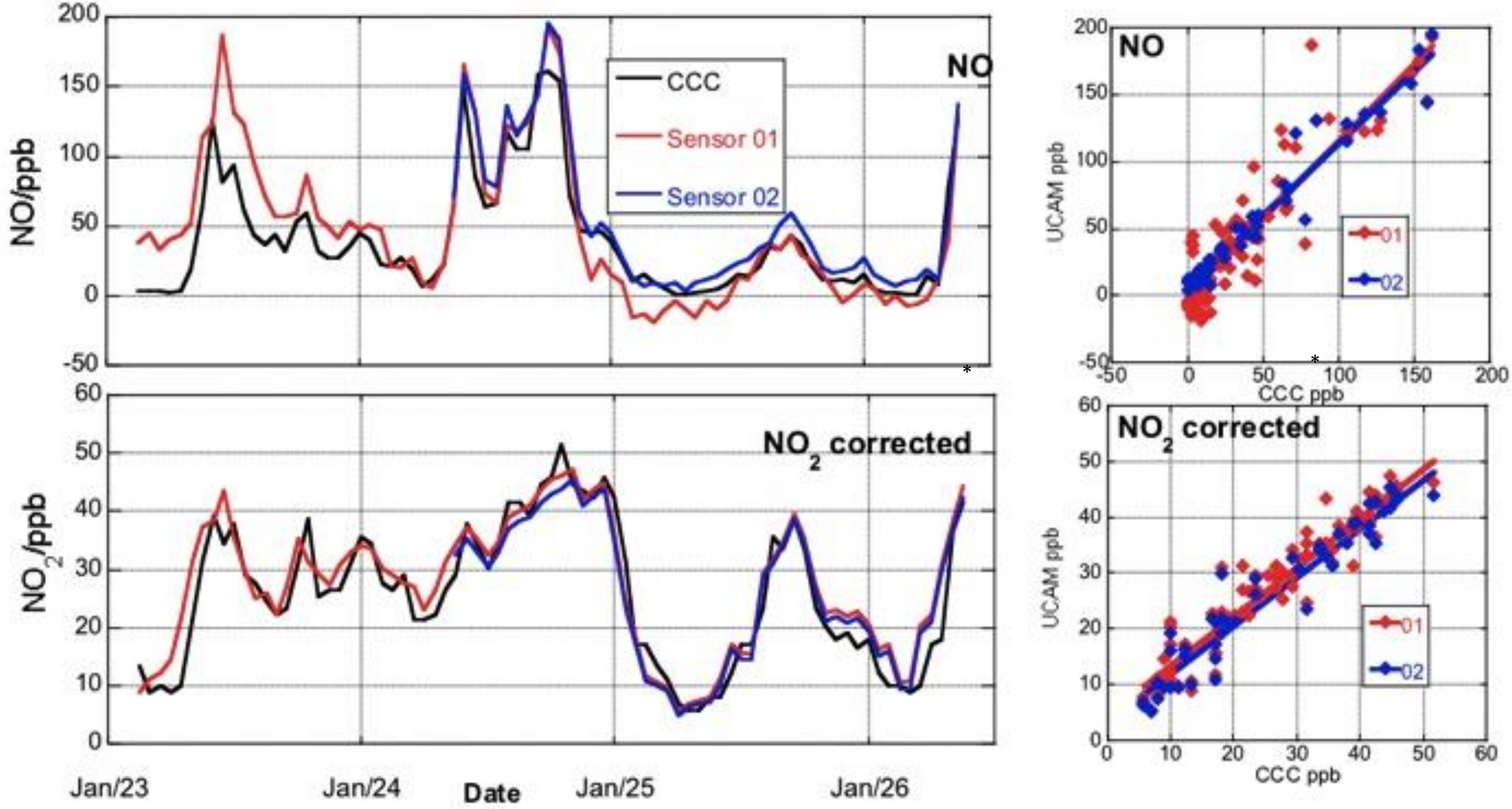
Noise characteristics:



- Typical sensor sensitivities/LoD are < 5ppb (< 7μg/m^3) for CO, 1-2 ppb (~2-4 μg/m^3) for NO and NO_2.
- SO_2, O_3 have comparable performance to NO_x.
- Typical sensor t_{90} ~ 10-20s (determined by diffusion)

UNIVERSITY OF CAMBRIDGE

‘Real world’ comparison of NO_2 and NO with ratified AURN/ AQM site shows good correlation at low ppb levels



* Corrected for O_3 interference

Performance is replicated in the field

Zero baseline stability and correction

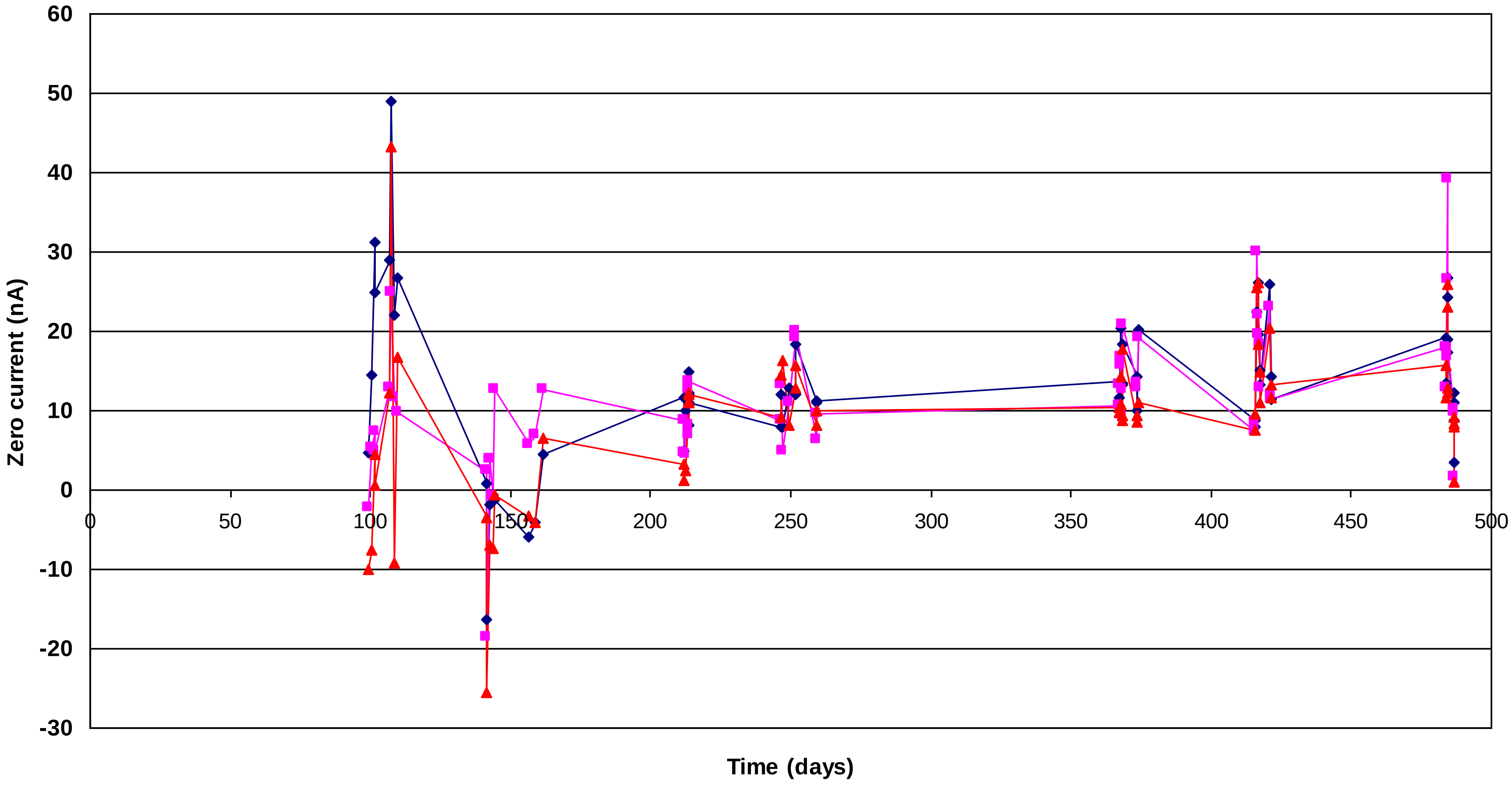
Is the zero baseline stable over time? If not, then the calculated absolute concentration using baseline correction will drift.

The zero baseline also changes with temperature. At low temperatures we are fine, but above 25°C then the correction algorithm must be good.

How to correct?

- Using **knowledge of atmospheric chemistry**
- Using **statistics and oversampling**: used by some users
- **Electrochemistry**: the underpinning process of the sensors- our method

NO2-B4 zero current shows reasonable stability over 500 days ±12 nA (equivalent to ±20 ppb)

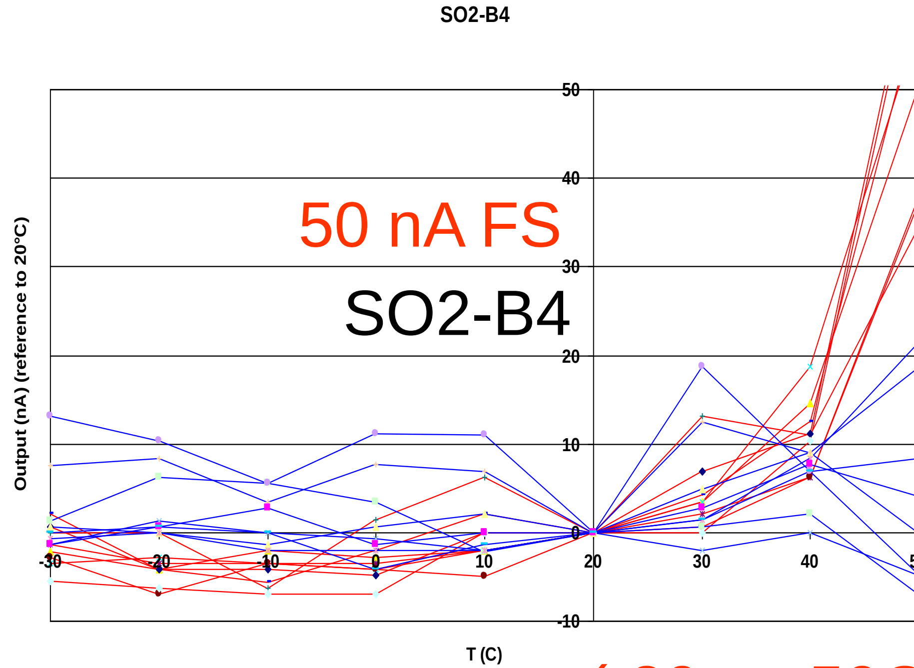


Electrochemical correction of Zero current:

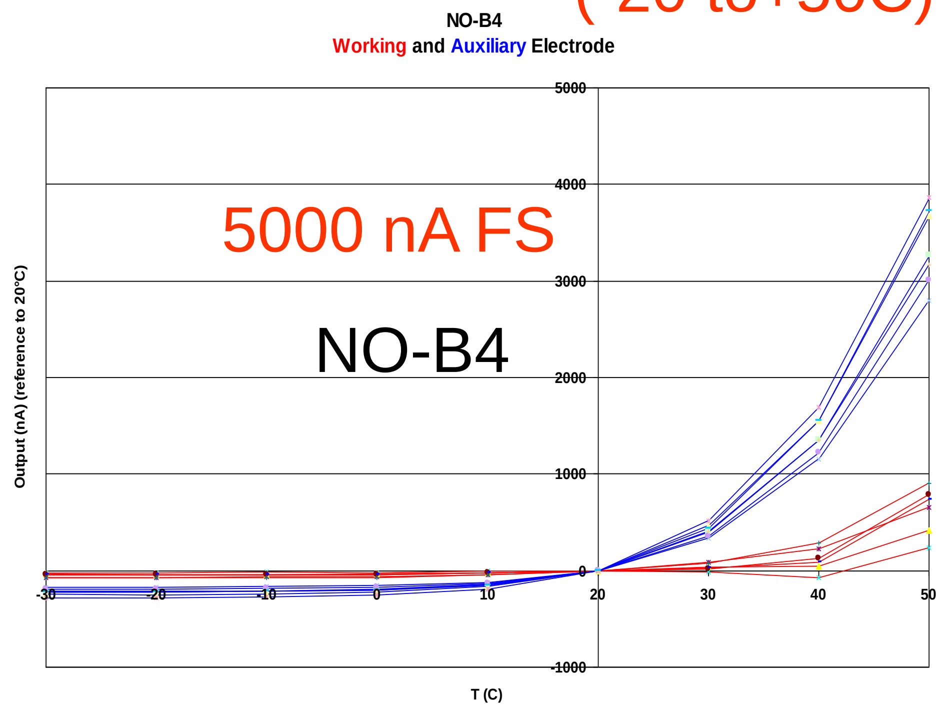
use the 4th electrode

zero current temperature dependence is very different (x10, x100) for each sensor.

Follows Arrhenius behaviour, so we can model and predict.

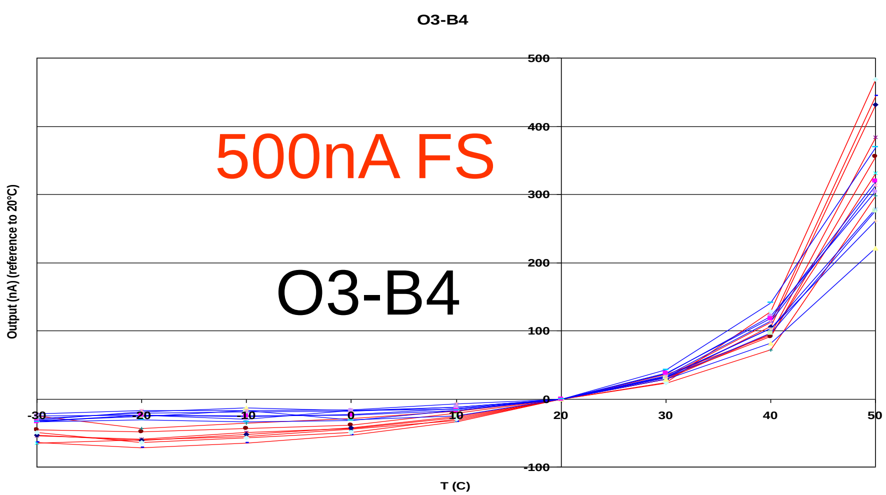


(-20 to+50C)

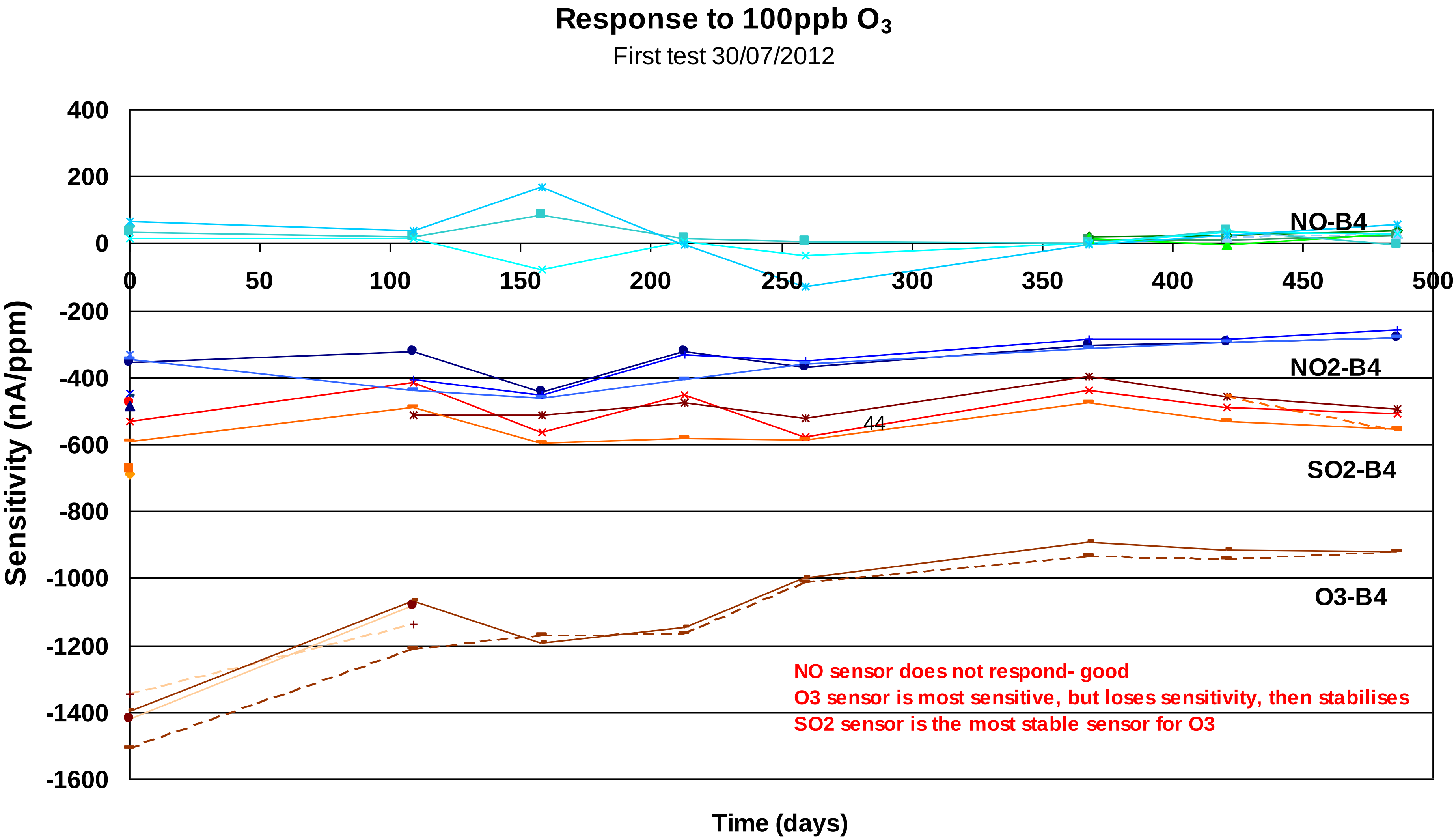


Red: working electrode

Blue: auxiliary electrode

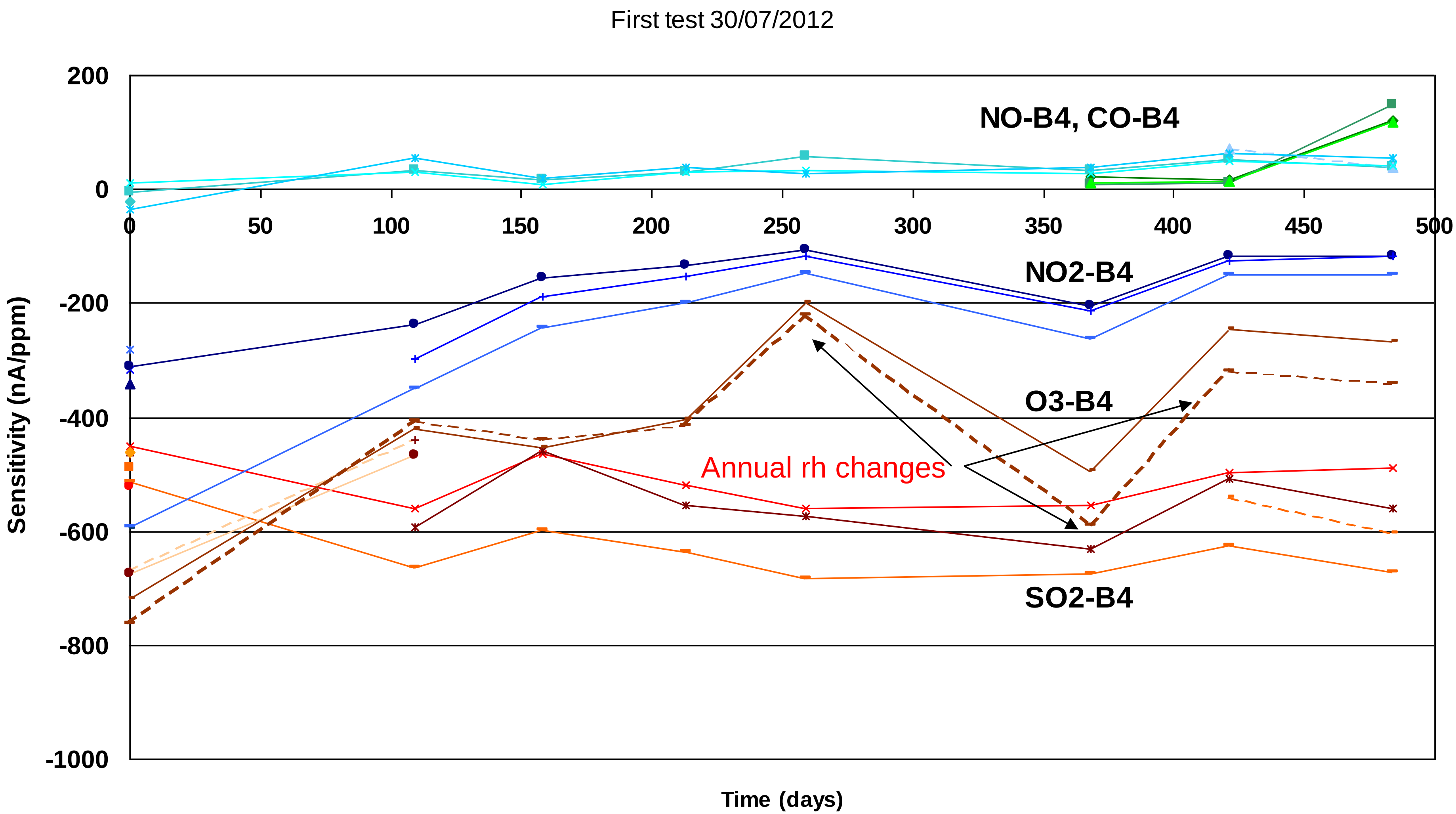


Stability to 100 ppb ozone

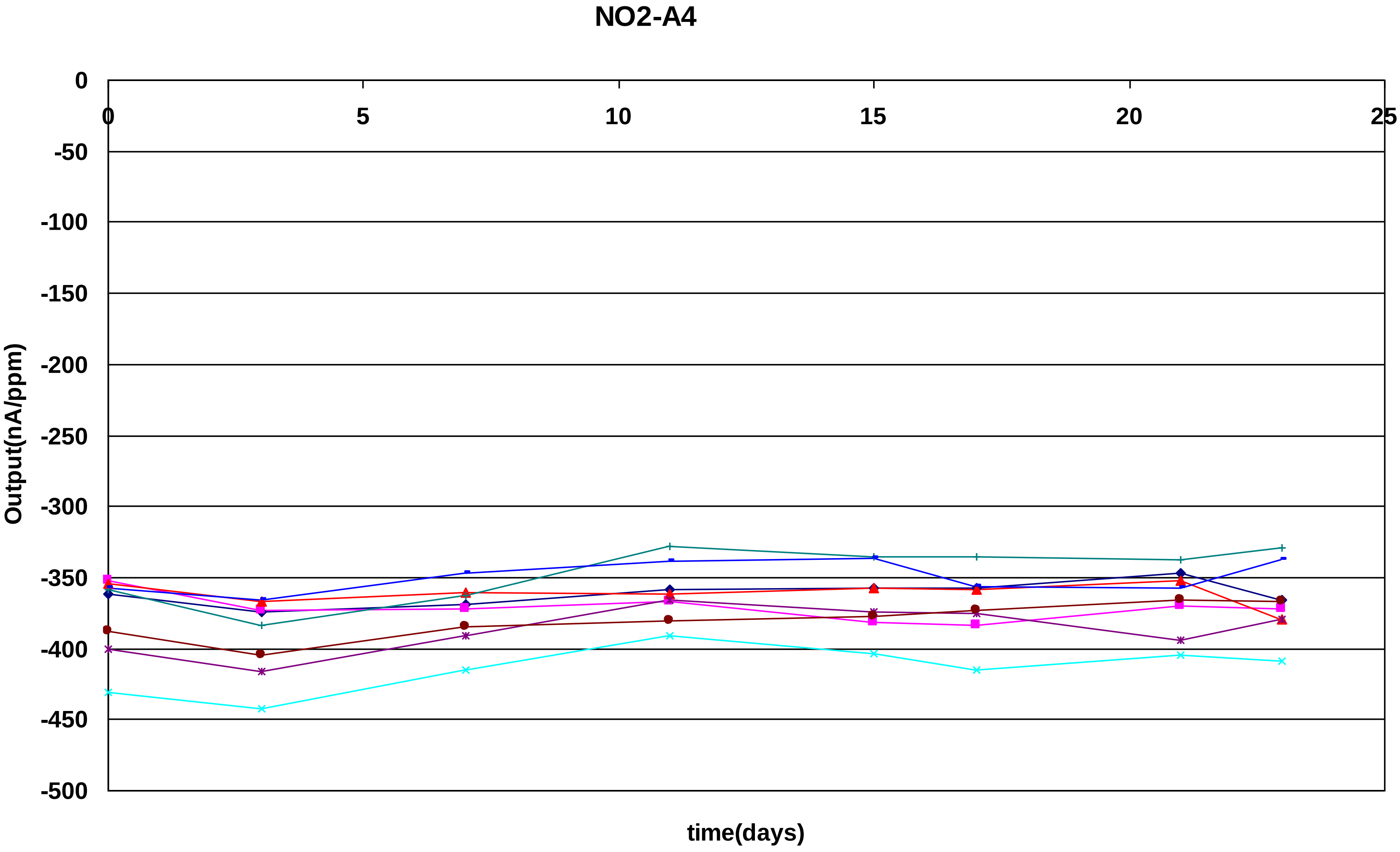


Stability to 350 ppb NO_2

Better stability after first 100 days



Initial 100 day stabilisation in the lab is minimal: it needs to stabilise in the actual environment



NO_2 and ozone

Difficult to separate: both are powerful oxidants

Separation Methods:

1 use multiple sensors: you cannot measure two parameters with one sensor. We recommend 3 sensors.

2 Ensure the x-sensitivites are stable and use the small ratio differences to deconvolve.

3 Use chemical filters to remove, for example the ozone from NO2 sensor- so one summed sensor, one speciated sensor.

Conclusions

- Low power, low cost electrochemical sensors can measure low ppb concentrations of inorganic gases.
- Wireless air quality networks are not replacing AURNs, but are adding the extra data for research, filling in fine detail, locating emission sources and enticing the citizen to get involved.
- Our work is not done: better speciation, improving stability and modelling sensors (both transport and chemistry/ electrochemistry) are our continuing work.
- VOCs and PM are necessary partners in any complete air quality network.

Acknowledging our Air Quality network of friends and colleagues

- Wah On Ho, Mark Giles, Ronan Baron — Alphasense Ltd.
- Rod Jones, Iq Mead, Vivien Bright — Cambridge University Chemistry
- Michael Hitchman — Innovative Coatings Ltd.
- Joe Stetter — SPEC Sensors and KWJ Engineering Inc.
- Jeff Neasham — Envirowatch Ltd. and Newcastle University
- Roger Riley, Stephen Earp, Dean Kavanaugh — Geotech Instruments Ltd.
- Frank Dean, Mark Stockdale — Ion Science Ltd.
- Nicolae Barsan — Universitat Tubingen
- Paul Kaye — University of Hertfordshire
- Paul Williams — University of Manchester
- Mike Jerrett — School of Public Health UC Berkeley
- Rex Britter, Rich Fletcher — MIT Media Lab
- Jane Hodgkinson, Ralph Tatam — Engineering, University of Cranfield
- Michele Penza — ENEA
- CITISense FP7 — NILU
- Julian Gardner, James Covington — Dept Engineering, Warwick University
- Florin Udrea, Bill Milne — Cambridge CMOS Sensors