TESTING OF CHEMILUMINESCENCE ANALYSERS AGAINST EN 14211:2005

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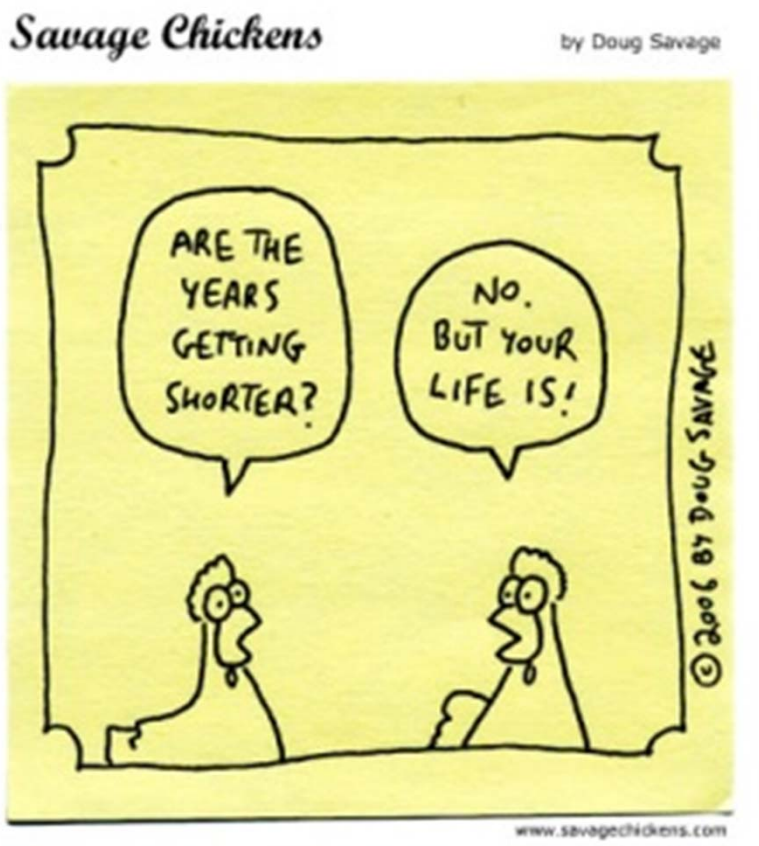
When?

- Tests performed in 2008-2009
- According to EN 14211:2005



Where?

- University of Murcia

UNIVERSIDAD DE MURCIA

Why?

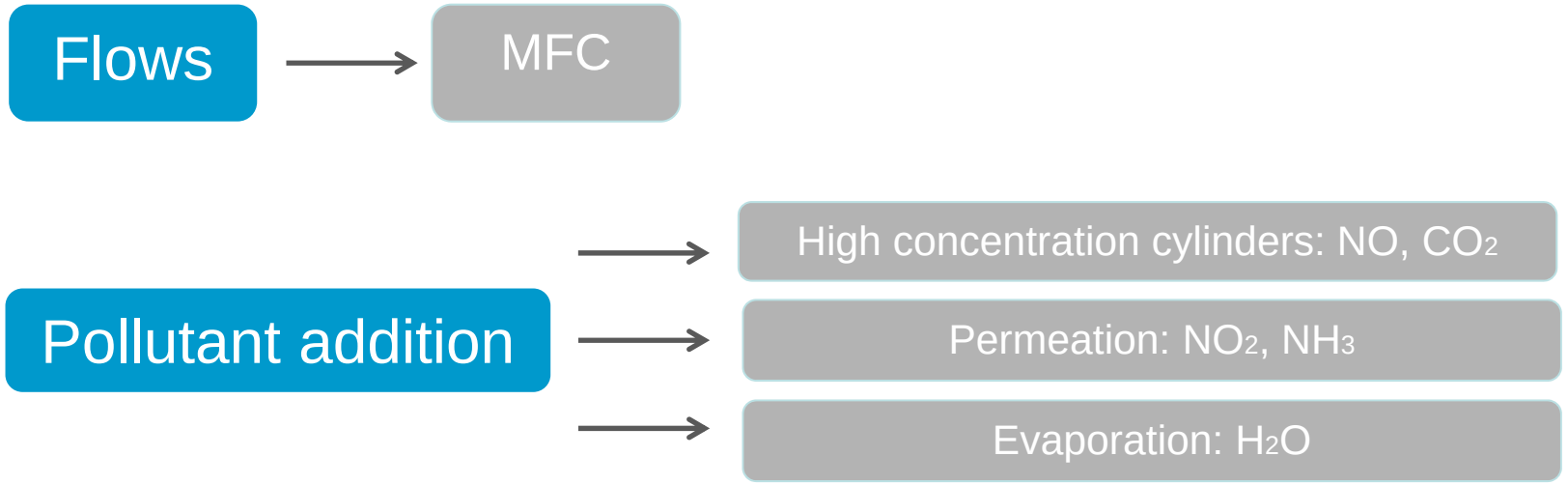
- To assess the local authority of Murcia on the performance of air pollution analysers
- No competences for certification of the analysers

How?

- Reproducing the type approval tests described in EN 14211:2005
- 2 commercially available analysers were used:
  - Thermo Scientific 42i
  - SIR S5012
- We also performed some extra tests that are now stated in EN 14211:2012

How?

- Controlled atmosphere chamber at the University of Murcia used to generate dynamic standards



How?

	Group	Test
Laboratory	I—Intrinsic characteristics of the analyser	Response time
		Standard deviation of repeatability at zero
		Standard deviation of repeatability at the hourly limit value
		Lack of fit
		Difference between sample and calibration ports
		Short term drift at zero
		Short term drift at span concentration
		Averaging time
		Efficiency converter
	II—Ambient conditions	Sensitivity coefficient to sample pressure (and IV)
		Sensitivity coefficient to sample temperature
	III—Interferent substances	Water vapour (and II)
		Carbon dioxide
		~~Ozone~~
		Ammonia
	IV—External characteristics	Sensitivity coefficient to electrical voltage
		Uncertainty of calibration gas
		Sensitivity coefficient to surrounding temperature
		Increase of NO_2 concentration due to $NO–O_3$ reaction in the sampling lines
Field		Long term drift at zero
		Long term drift at span concentration
		Standard deviation of reproducibility

to be checked in the NO_2 channel

Maximum increase in concentration changed to maximum residence time

Results (the most remarkable ones)

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Lack of fit

Maximum deviation from the linear regression line of the average of a series of measurement results at the same concentration

TS: $y = 1.001x + 2.90$, $R^2=1$ → 0.49%

SIR: $y = 1.008x + 1.26$, $R^2=0.9998$ → 0.89%

$y = x$

2.1% 2.3%

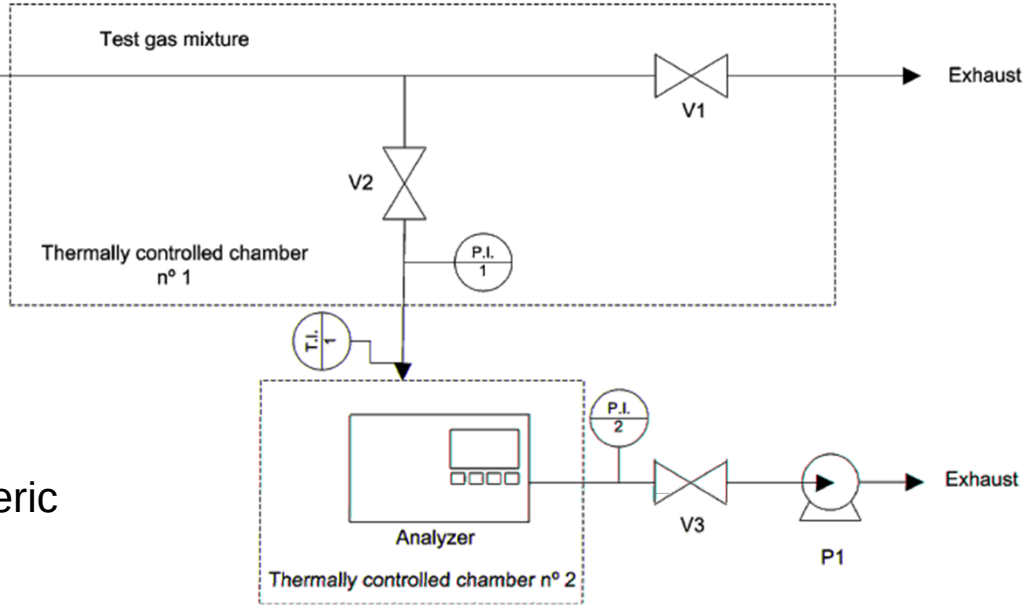
- The highest residuals were obtained at the lowest concentrations tested (193 nmol/mol).
- The calibration concentration was 770 nmol/mol.
- Calibration at lower concentrations to match better ambient levels?

Results (the most remarkable ones)

Sensitivity coefficient	Performance criterion	Tested range	TS results	SIR results
To sample pressure	≤8 nmol mol^{-1} kPa^{-1}	80–110 kPa	4.8 nmol mol^{-1} kPa^{-1}	7.9 nmol mol^{-1} kPa^{-1}
To sample temperature	≤3 nmol mol^{-1} per °C	0–30 °C	−0.9 nmol mol^{-1} per °C	−1.1 nmol mol^{-1} per °C
To surrounding temperature	≤3 nmol mol^{-1} per °C	15–30 °C	1.3 nmol mol^{-1} per °C	1.9 nmol mol^{-1} per °C
To electrical voltage	≤0.3 nmol mol^{-1} V^{-1}	220–240 V	0.2 nmol mol^{-1} V^{-1}	0.0 nmol mol^{-1} V^{-1}

Influence of sample pressure

Additional tests were performed to study this variable in detail



Simulation of changes in atmospheric pressure and in the inlet pressure

Results (the most remarkable ones)

TS

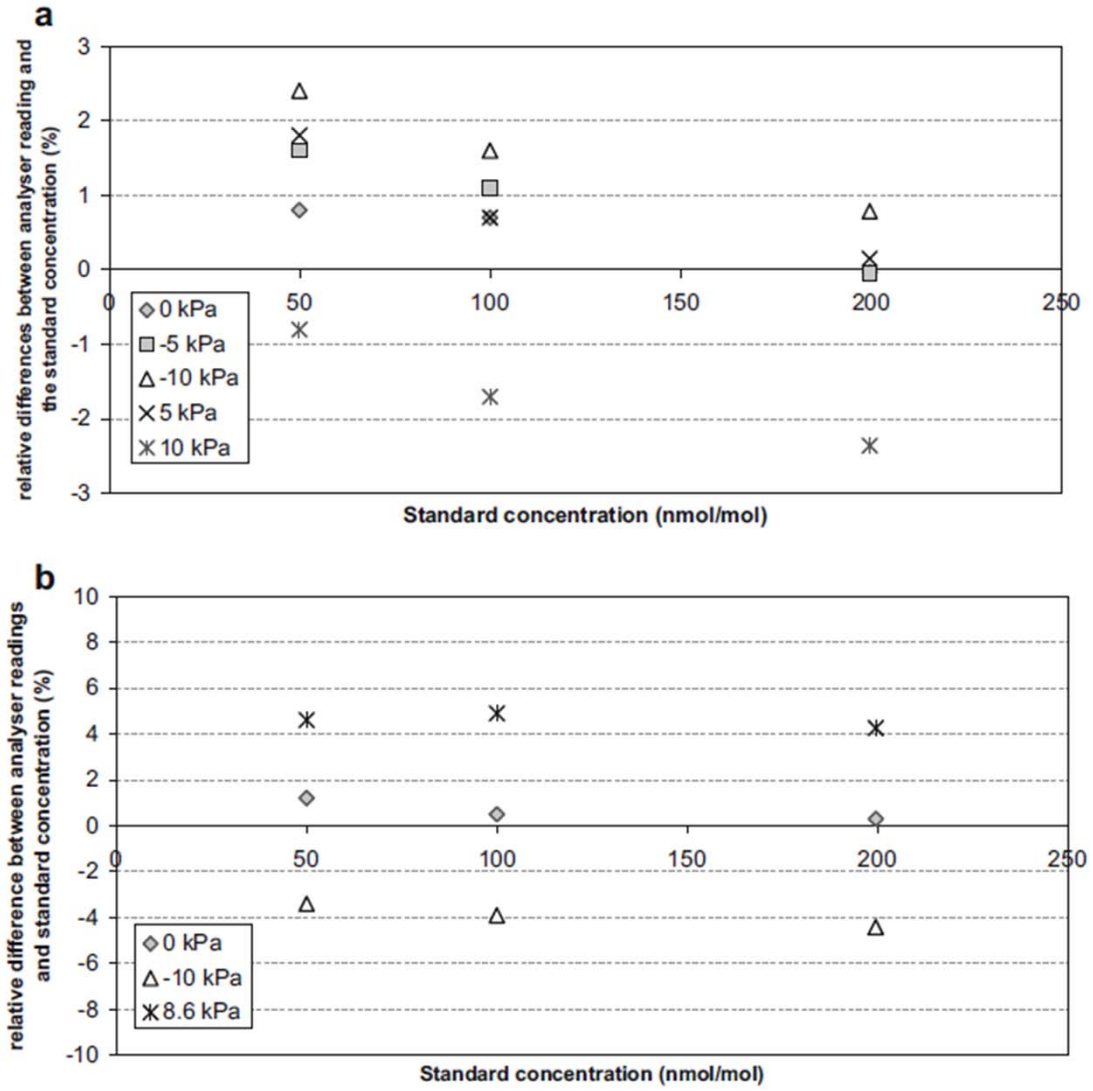


Fig. 3. Relative differences between analyser readings and the standard concentration generated vs the standard concentration, as a function of PI1, when PI1 = PI2. a) Pressure compensator on; b) pressure compensator off.

Results (the most remarkable ones)

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Influence of sample pressure

TS

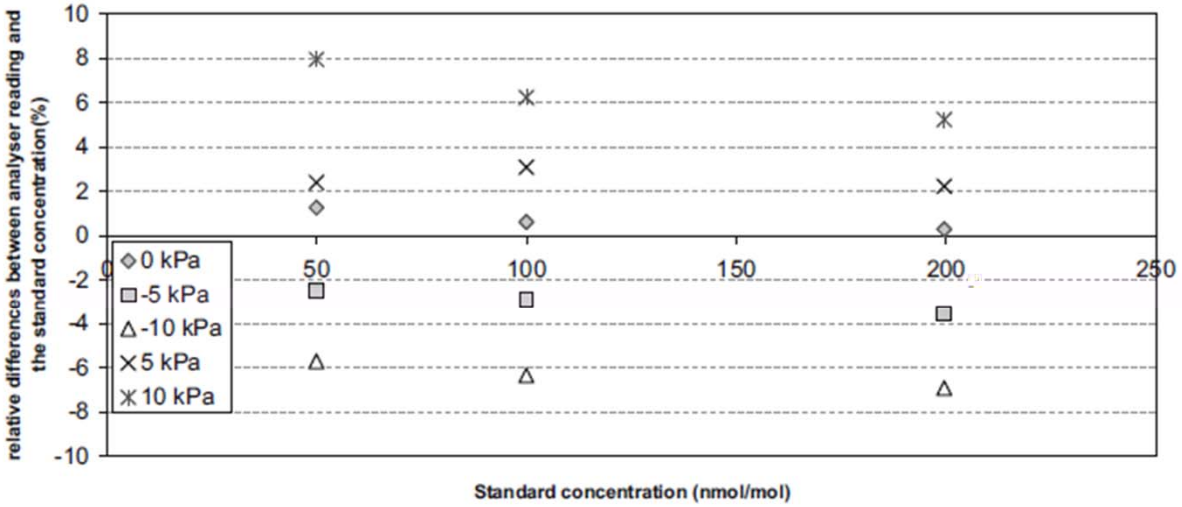

Fig. 4. Relative differences between analyser readings and the standard concentration generated vs the standard concentration, as a function of PI1, when PI2 = 101.3 kPa. Pressure compensator on.

Ref.: Doval Miñarro M et al. (2011), Atm. Environ. 45, 5366-5375

Results (the most remarkable ones)

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Influence of sample temperature

TS

3% diff. for 15 ºC

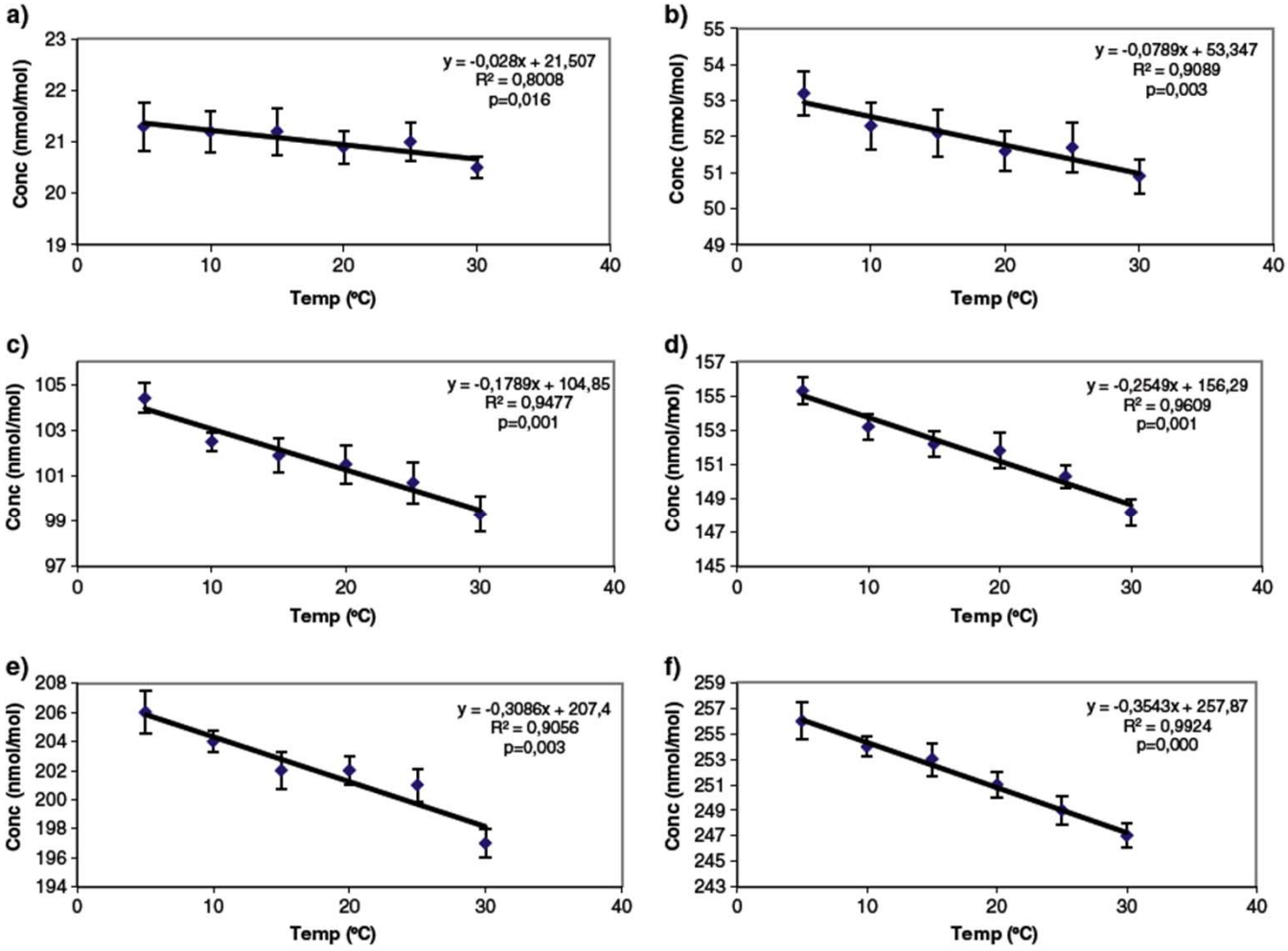

Fig. 3 Analyzer readings vs. sample temperature at different concentration levels. a 20.0 nmol/mol, b 50.0 nmol/mol, c 100.0 nmol/mol, d 150.2 nmol/mol, e 200.0 nmol/mol and f 250.2 nmol/mol

Ref.: Doval Miñarro M et al. (2012), Environ. Monit. Assess. 184, 5669-5678

Results (the most remarkable ones)

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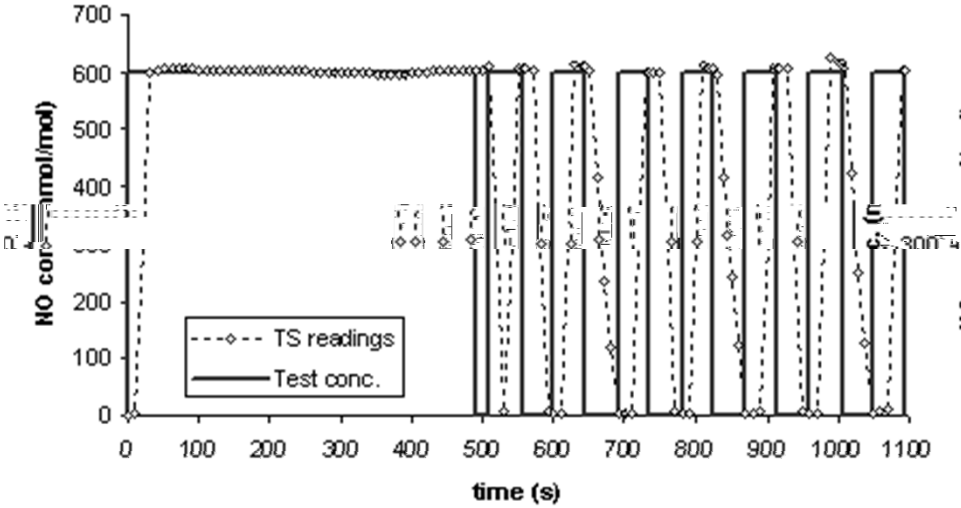
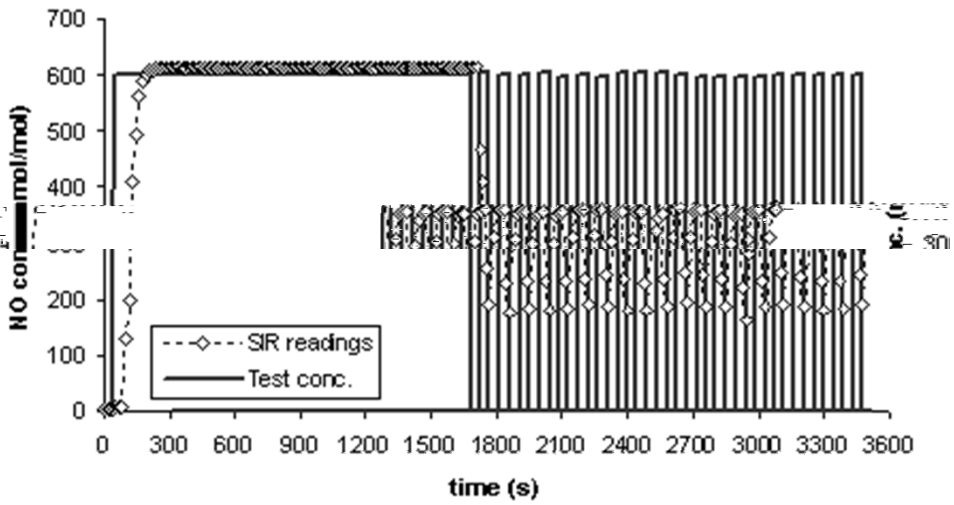
Averaging effect

The averaging test gives a measure of the uncertainty in the averaged values caused by short-term concentration variations shorter than the time scale of the measurement process in the analyser.

NO channel





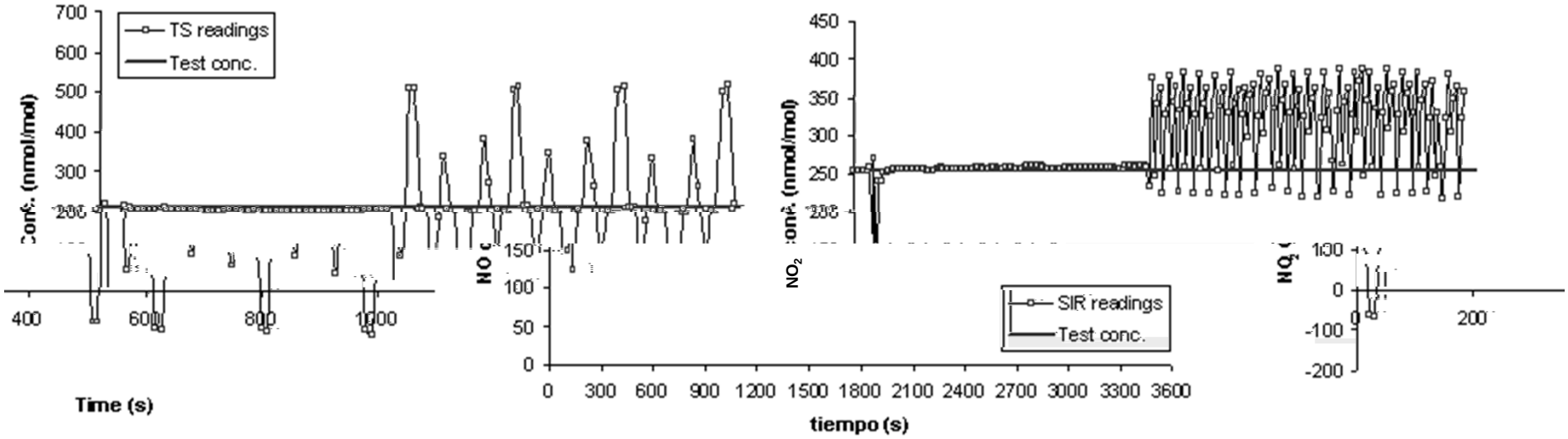
X_{av}= -3.1%

X_{av}= 2.4%

Results (the most remarkable ones)

Averaging effect

NO_2 channel



X_{av}= 1.9%

X_{av}= 24 %

Results (the most remarkable ones)

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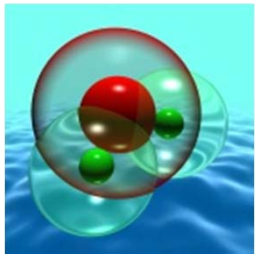
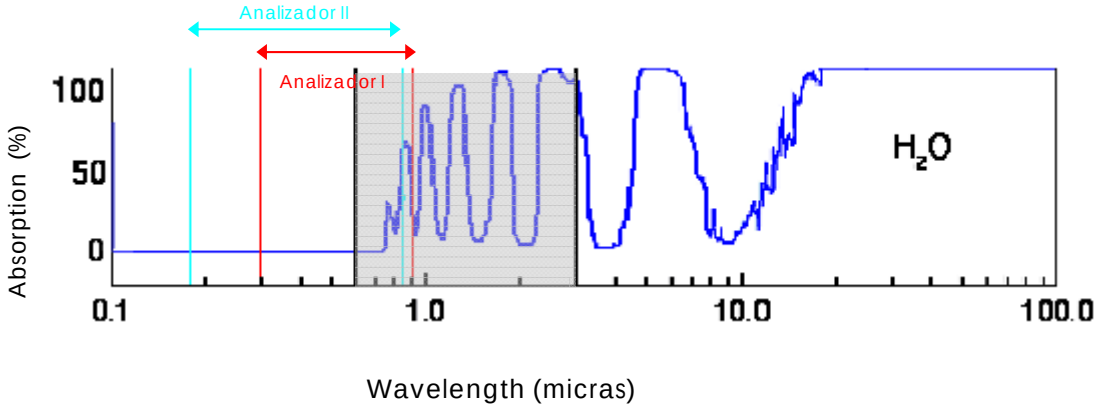
Water vapour interference



- Acceptability criterion: 5 ppb (<0.99%)
- Results:
  - TS: X_{H_2O}= -25 ppb ☒
  - SIR: X_{H_2O}= -22 ppb (-5% deviation) ☒

- Possible solutions:
  - Calibrating with humidity
  - Application of corrections.



Results (the most remarkable ones)

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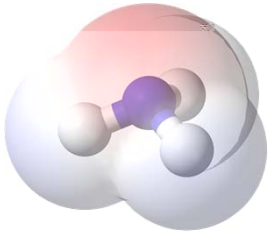
Ammonia interference

- Acceptability criterion: 5 ppb (<0.99%)



	Analizador I				Analizador II			
Concentración de NO patrón (ppb)	0		494		0		508.4	
Concentración de amoniaco (ppb)	200		200		200		200	
Especie	[NO]	$[NO_2]$	[NO]	$[NO_2]$	[NO]	$[NO_2]$	[NO]	$[NO_2]$
Lecturas medias (ppb)	0.2	22.6	495	15.6	-1.45	0.0	508.7	0.0

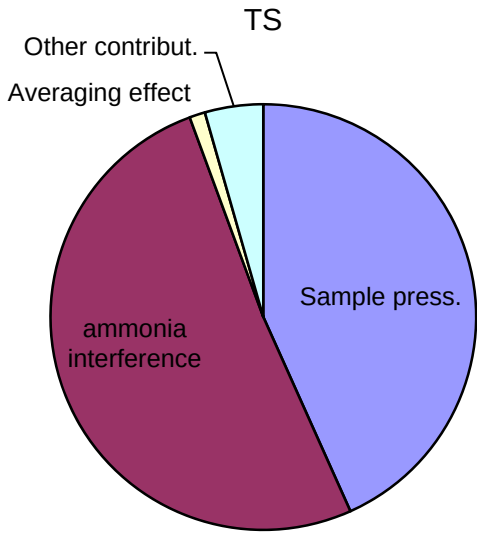
Results

Summary of conformity

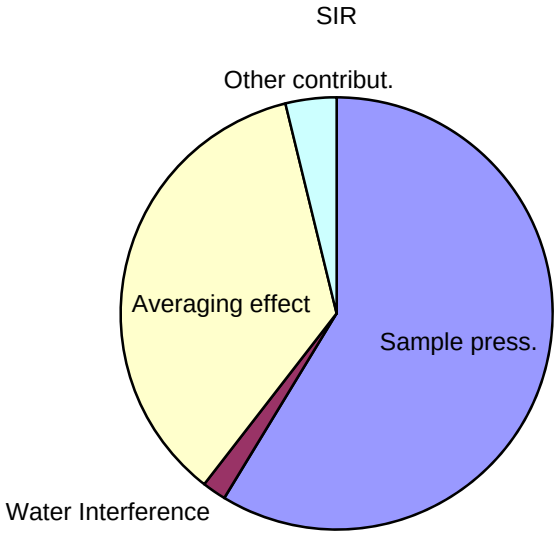
Group		Test	TS	SIR
	I- Intrinsic characteristics of the analyzer	▪ Response time	Yes	**No**
		▪ Standard deviation of repeatability at zero	Yes	Yes
		▪ Standard deviation of repeatability at the hourly limit value	Yes	Yes
		▪ Lack of fit	Yes	Yes
		▪ Difference between sample and calibration ports	Yes	Yes
		▪ Short term drift at zero	Yes	Yes
		▪ Short term drift at span concentration	Yes	Yes
		▪ Averaging time (and II)	Yes	Yes
		▪ Efficiency converter	Yes	Yes
	II- Ambient conditions	▪ Sensitivity coefficient to sample pressure (and IV)	Yes	Yes
		▪ Sensitivity coefficient to sample temperature.	Yes	Yes

Results

Uncertainty budget



U= 32 %



U= 37 %

Too extreme conditions to estimate the uncertainty?:

- NH_3 levels too high (200 ppb)
- Pressure interval too wide (30 kPa)
- Concentration changes too big (0 – 600 nmol/mol)

Conclusions

- The two analysers tested failed to pass some of the tests of the TAT.
- Interestingly, both analysers passed the pressure sensitivity test but this is a major source in the final uncertainty budget.

$$u_{gp} = \frac{104}{770} \cdot 8 \sqrt{\frac{(30)^2}{3}} = 18.7\,ppb$$

- Main real contributions coming from water vapour and other N-species.
- Corrections?
- Current and future developments to substitute the current reference method.

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