NitroMAC : an instrument for the measurement of HONO and HNO3

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dépasser les frontières

Principe

NitroMAC : instrument for the parallel measurement of HONO and HNO3,
→ was developed relaying on the studies of
Heland *et al.* (2001) and Huang *et al.* (2002).

Technique :

- Based on aqueous scrubbing using two coil samplers,

HONO + H2O ⟶ NO2- + H3O+
HNO3 + H2O ⟶ NO3- + H3O +

-One followed by conversion of NO3- to NO2-,

-Both followed by **derivatization** of NO2- to a highly light-absorbing **azo dye** with sulfanilamide (SA) and N-(1-naphthyl)ethylenediamine (NED),

- Detection with an high performance liquid chromatography (HPLC) analysis (**detection with a UV-vis detector at 540 nm**).

-HNO3 concentration was obtained by the difference of the two channels.

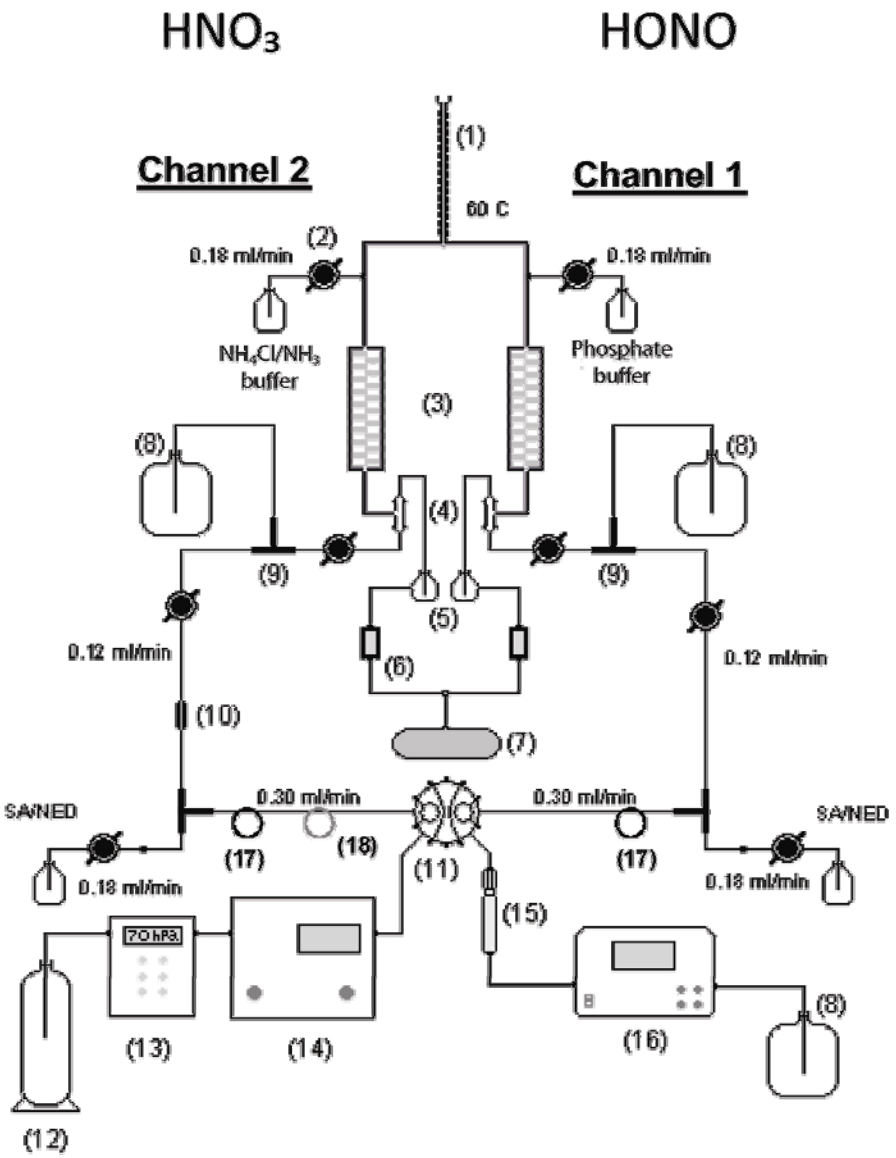
Schematic diagram of NitroMAC

Scrubbing solutions and scrubbing coils are kept at constant temperature.
The derivatization loop is maintained at 55°C to achieve quantitative derivatization.

Scrubbing solution flow rate = 0.18 ml.min-1

Gas sampling flow rate = 2 l.min-1.

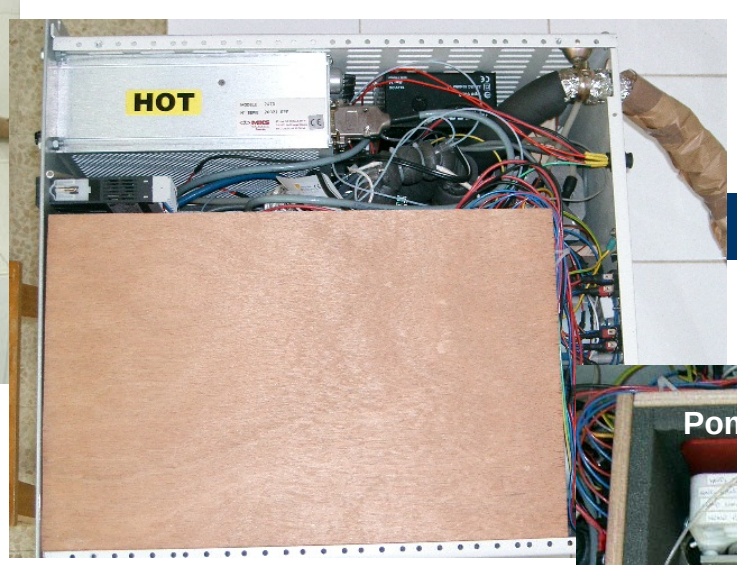
Detection limit is few pptv.
Sampling frequency : every 10 min.



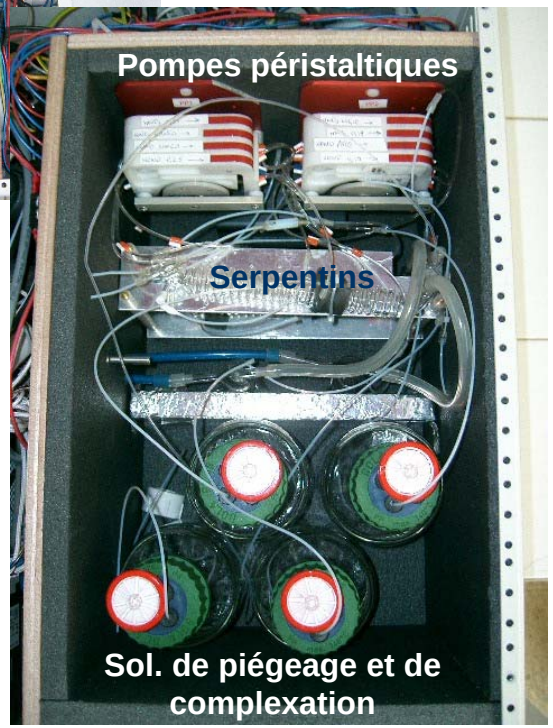
Legend:

(1) Sampling inlet
(2) Peristaltic pump
(3) Scrubbing coil
(4) Phase seperator
(5) Security flask
(6) Flow controller
(7) Air pump
(8) Trash
(9) Debubbler
(10) Reduction cartridge
(11) Injection Valve
(12) Eluent (acid/acetonitrile)
(13) Eluent Degazer
(14) HPLC Pump
(15) HPLC column
(16) UV-Vis Detector
(17) Derivatization loop
(18) Waiting loop

NitroMAC



Size : 26,5 x 80 x 50 cm^3
Weight : 40 Kg



Analytical system :

Sampling time : Every 10 minutes
HONO scrubbing efficiency : > 99,99 %
NO_2 scrubbing efficiency : < 0,02%
Detection limit (DL) : few pptv
Linearity : DL – 36 ppbv

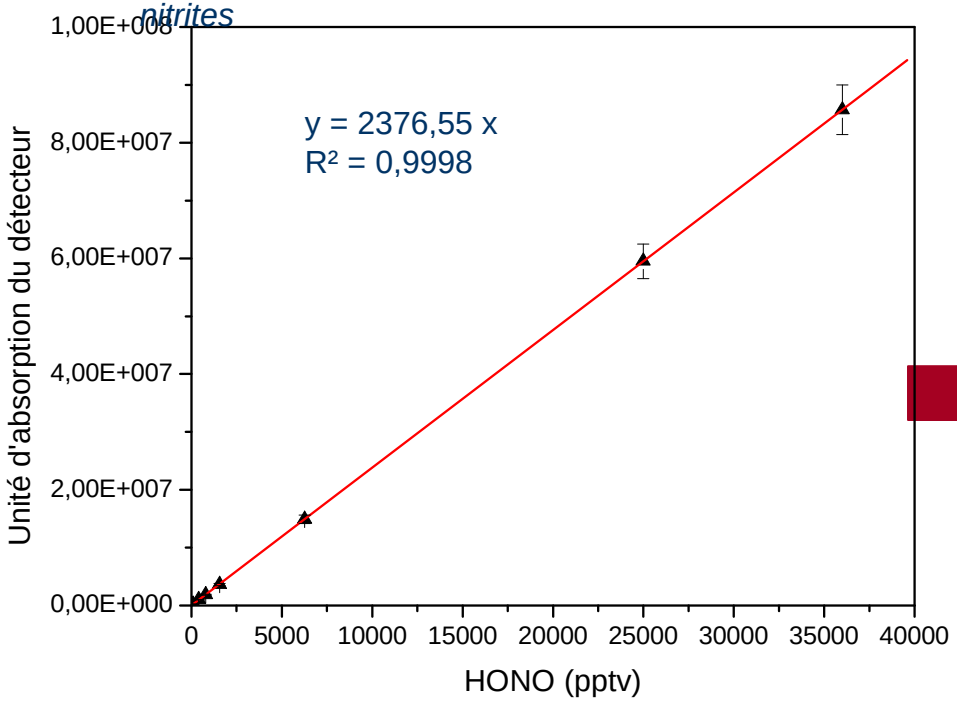
Calibrations

1/ ***C*****alibration with generation system** based on the work of Febo *et al.* (1995):): gas phase HCl at 40% relative humidity attacks a bed of solid phase NaNO2 to produce gas phase HONO.

2/ **Calibration using NaNO2 solutions**

→Difference of 4,5% between the two methods

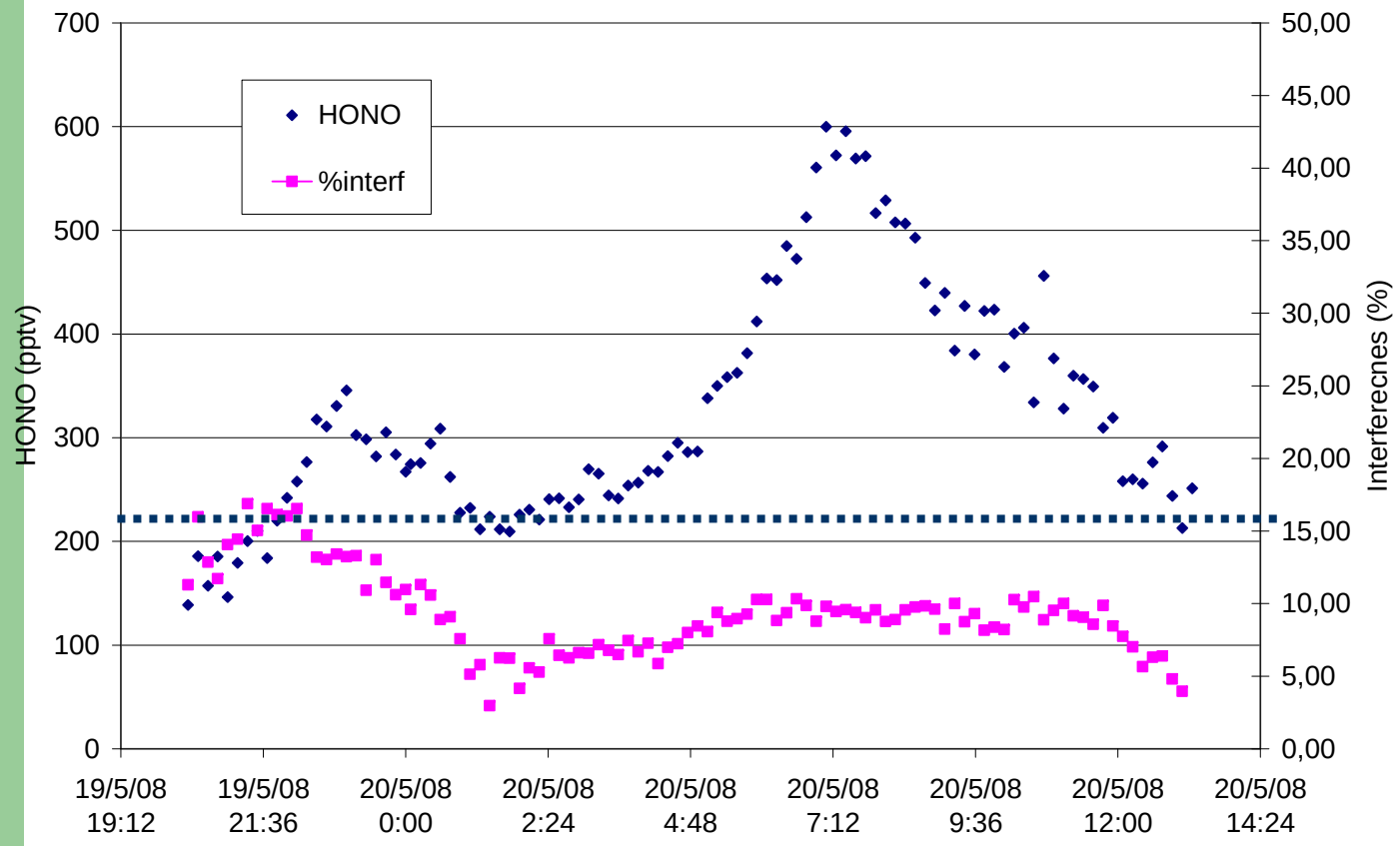
Droite d'étalonnage obtenue par les solutions de nitrites



On field campaign, calibration with NaNO2 solutions

Interferences

Test in ambient air : 2 scrubbing coil in series :
-First one (Serpentin 1) : HONO + interferences
-Second one (Serpentin 2): only interferences

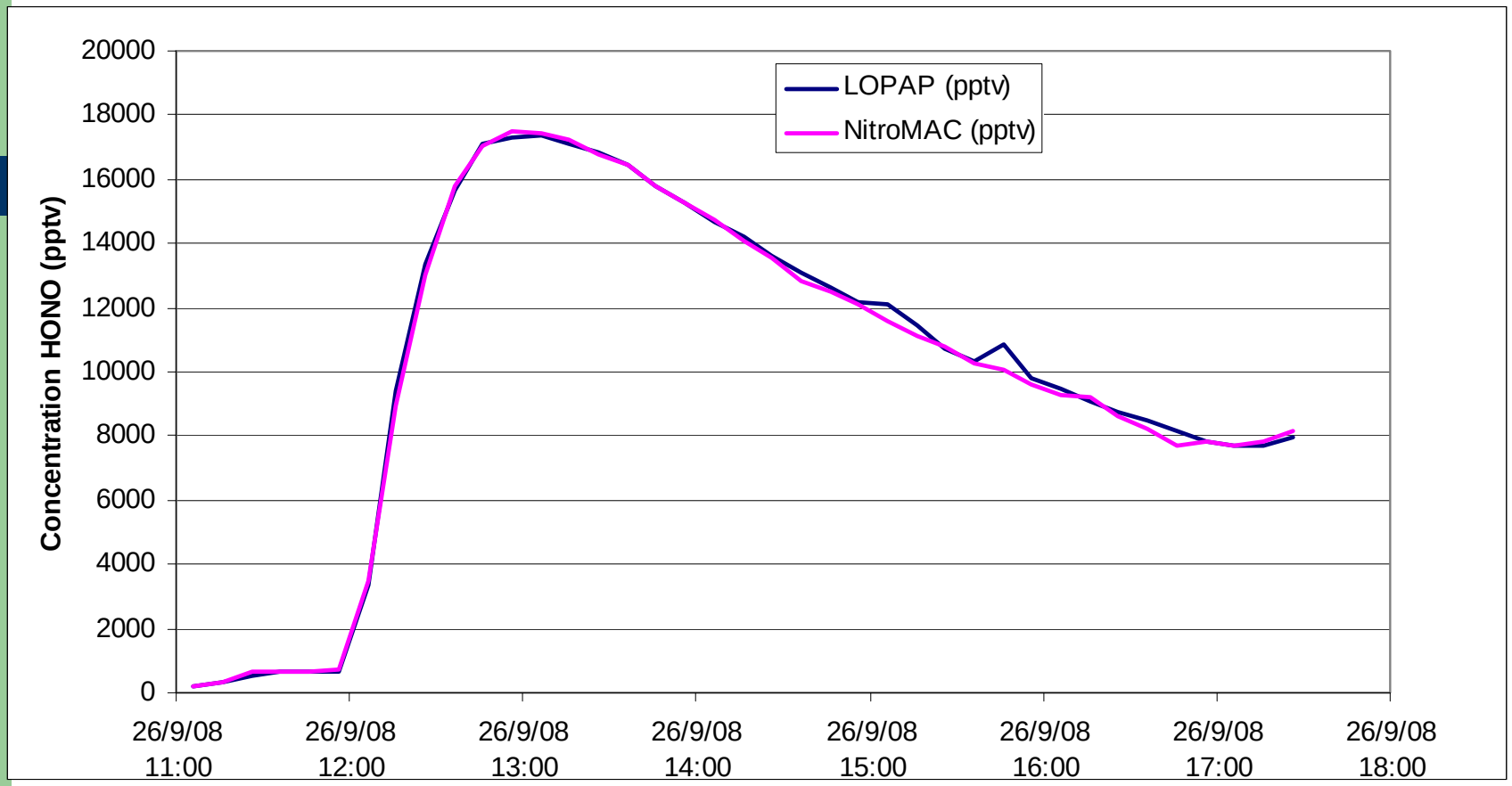


Total interferences < 16%

Intercomparison LOPAP-NitroMAC

Orléans---September 2008

In Simulation Chamber

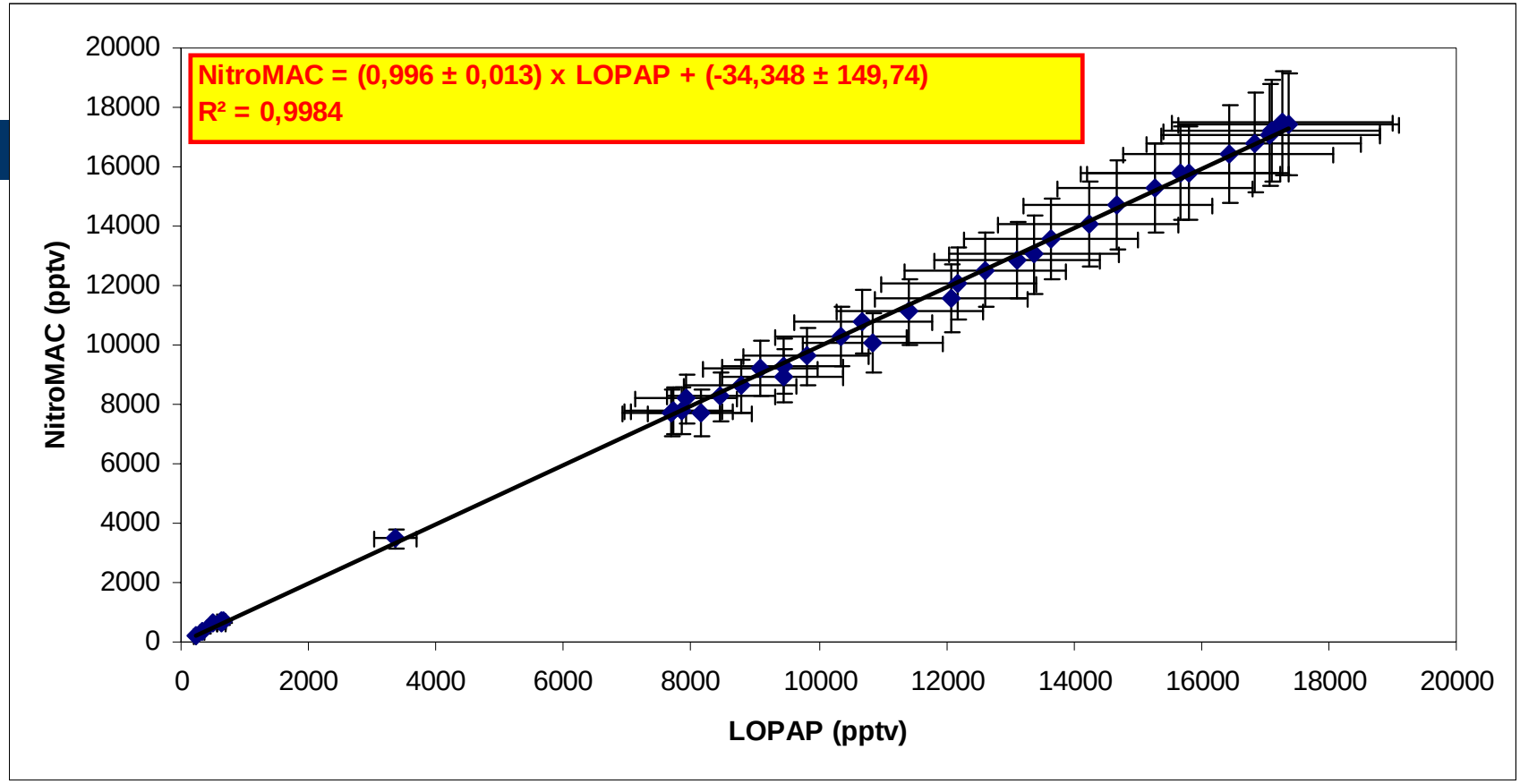


Uncertainty LOPAP : 10 %
Uncertainty NitroMAC : 10 %

→ [HONO]=[200 – 18000 pptv]

Very good correlation

Chamber



Uncertainty LOPAP : 10 %
Uncertainty NitroMAC : 10 %

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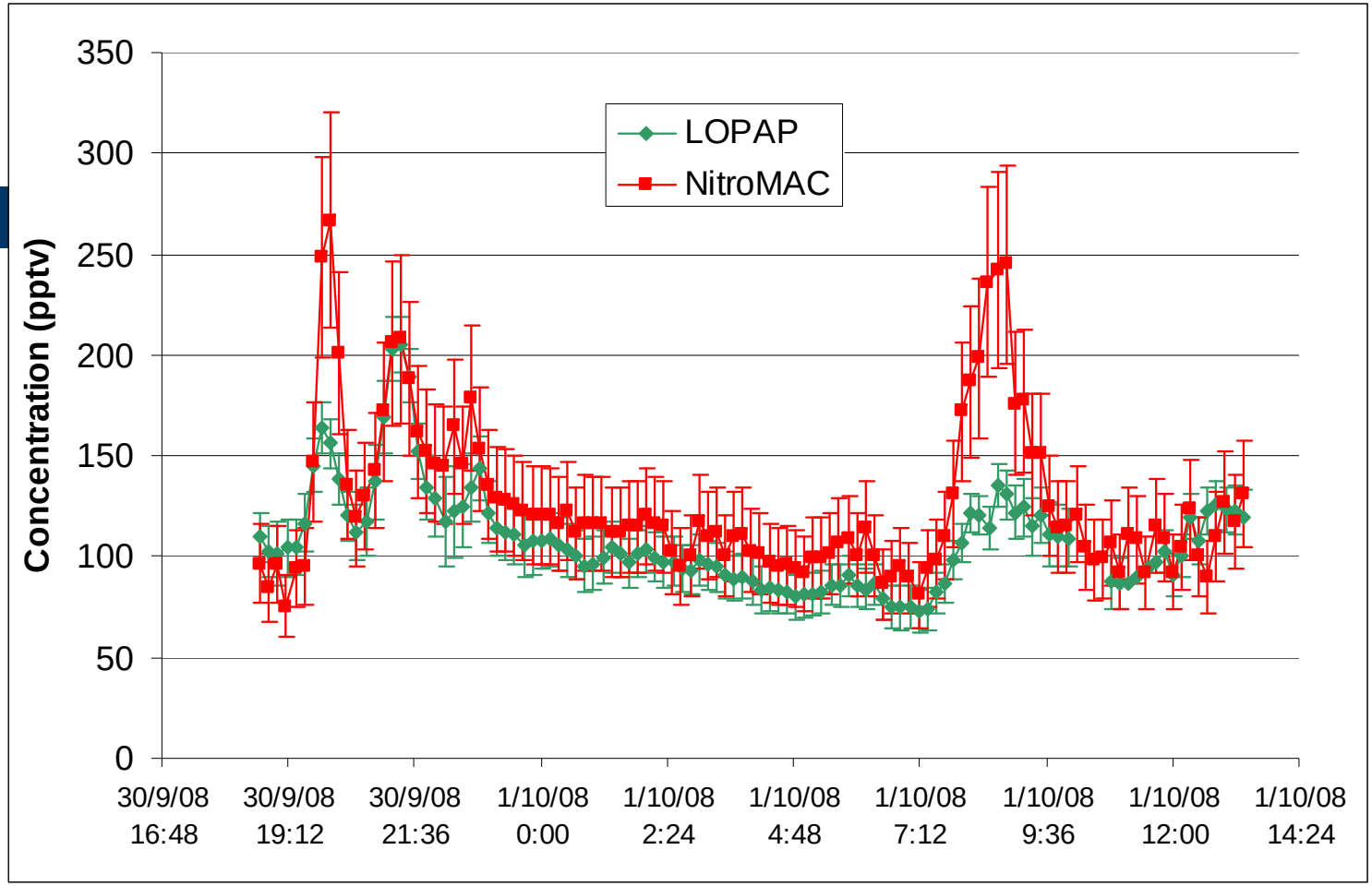
[HONO]=[200 – 18000 pptv]
Very good correlation
Slope : 0,996 ± 0,013 (2σ)

In Ambient Air

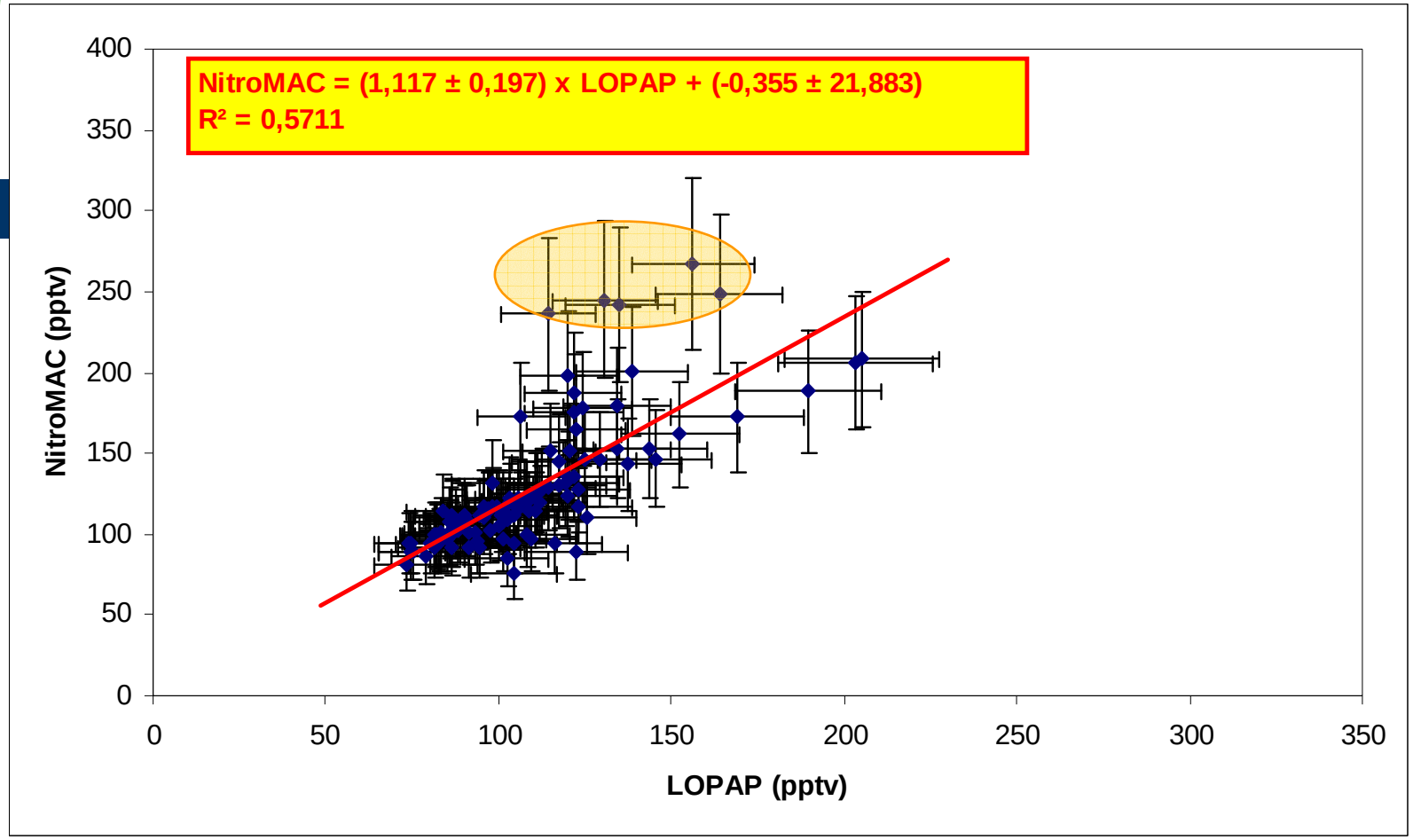


Uncertainty LOPAP : ~12 %
Uncertainty NitroMAC : 20 %

→

[HONO]=[50 – 300 pptv]
Good correlation : morning and evening peaks less sharp with LOPAP

In Ambient Air



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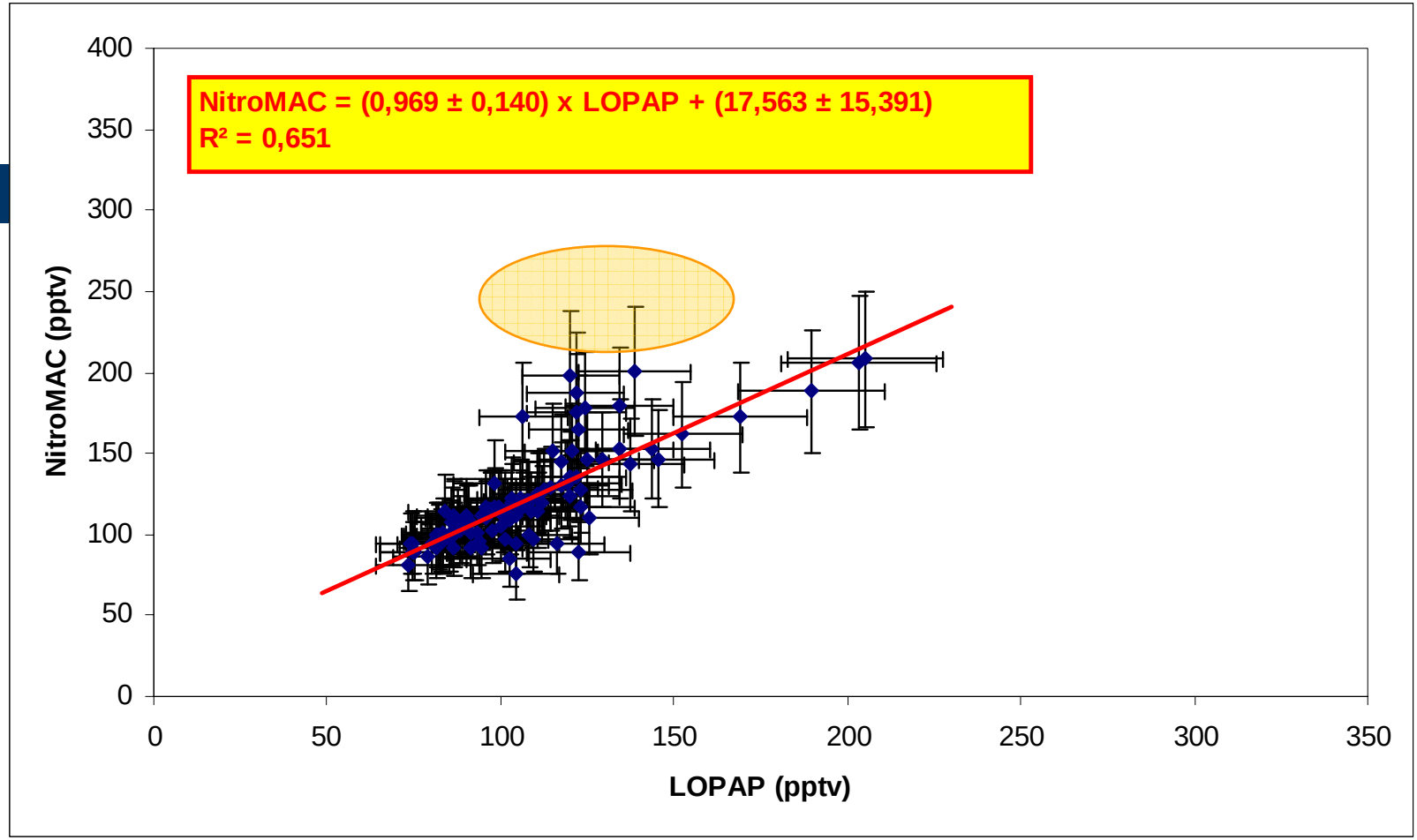

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Uncertainty NitroMAC : 20 %

→

[HONO]=[50 – 300 pptv]
Without 5 points…
Good correlation

Thank you …..

LOPAP Team at ICARE (Orleans): Gregory Eyglunent, Wahid Mellouki,..

NitroMAC Team at LISA: Charbel Afif, Pascal Perros, Corinne Jambert, Patricia Madec, Filipa Ribeiro, Vincent Michoud,…