

Wet chemical Techniques for the Detection of Nitrous Acid (HONO) in the Atmosphere

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Additional information and slides provided by:

Jack Dipp (MC), *Xianliang Zhou* (HPLC), *Norimichi Takenaka*,
(DAN)

- The OH radical is a key species in atmospheric chemistry:
- Recent studies show a high contribution (up to 60 %) of nitrous acid (HONO) to the primary OH-production also during the day (*Ren et al., 2003, Kleffmann et al., 2005, Acker et al., 2006*)



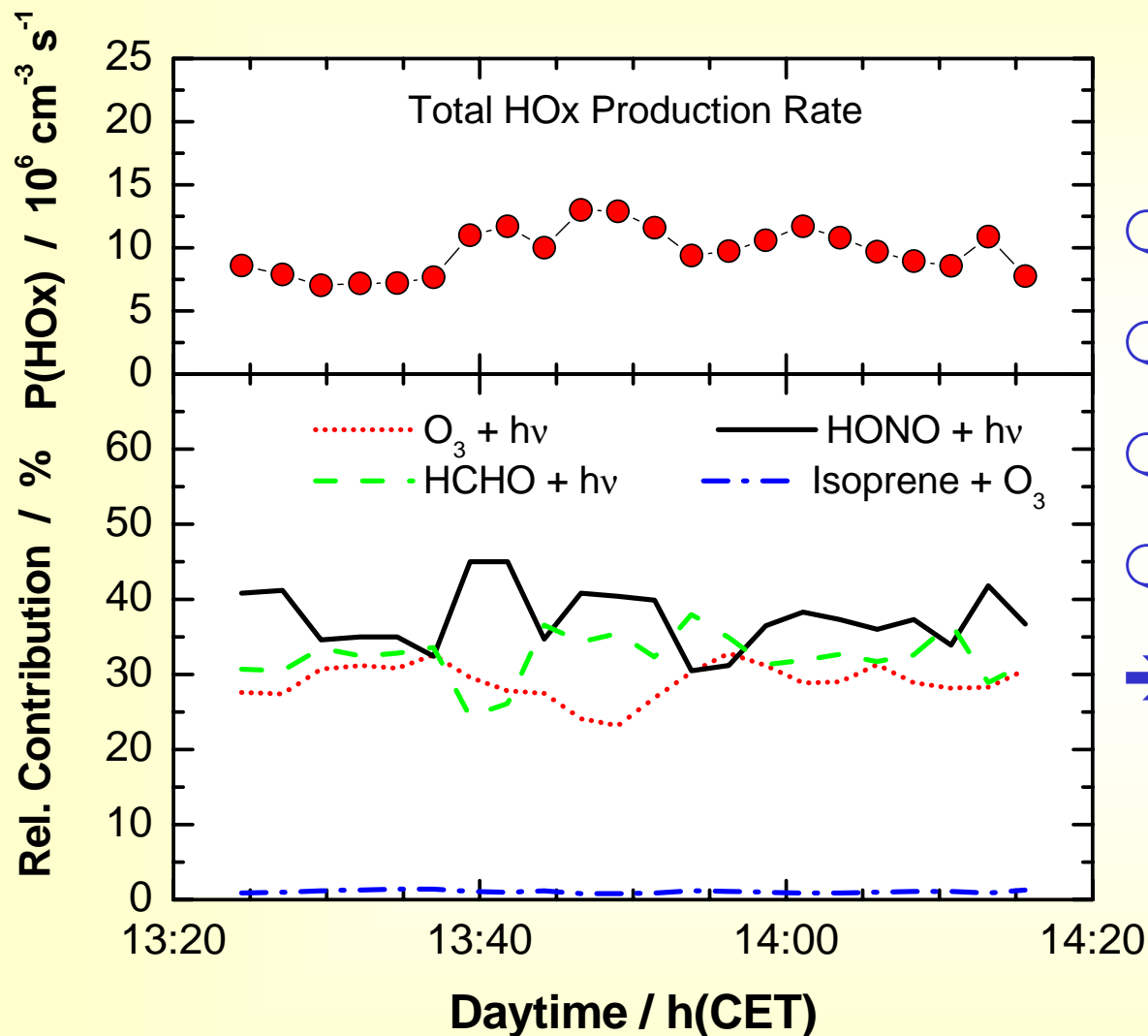
ECHO 2003:

Relative contribution:

- HONO: 35 %
- HCHO: 30 %
- O₃: 27 %
- VOC's+O₃: 8 %

➔ HONO most important OH source around noon!!

Kleffmann et al., 2005

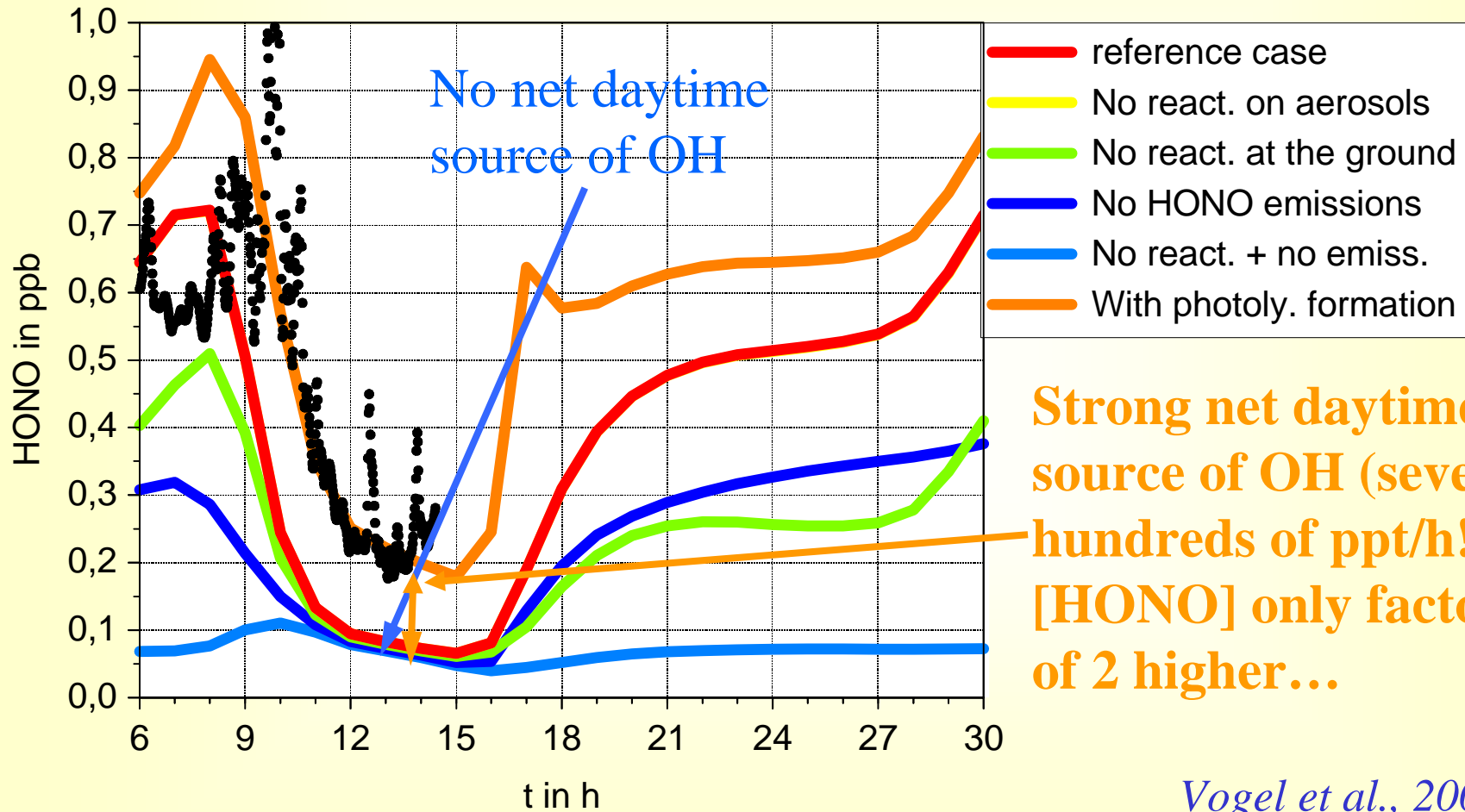


- The OH radical is a key species in atmospheric chemistry:
- Recent studies show a high contribution (up to 60 %) of nitrous acid (HONO) to the primary OH-production also during the day (*Ren et al.*, 2003, *Kleffmann et al.*, 2005)



- ➔ Mechanism still under discussion: photolytic sources of HONO were postulated (*Zhou et al.*, 2003, *George et al.*, 2005, *Stemmler et al.*, 2006+2007, *Bejan et al.*, 2006)
- ➔ HONO should be measured in field campaign besides other OH-sources (O_3 , HCHO, alkenes)

- Accurate determination of daytime HONO concentrations is of paramount importance!



Vogel et al., 2003

- HONO measured by many different types of instruments:
 - **Spectroscopic instruments:** HONO directly detected in the gas phase (DOAS, TDL, CRDS, *LIF*, *MS*...)
 - **Chemical instruments:** HONO detected after *chemical conversion* (for example, as nitrite, DAN, Saltzman, but also as OH (*LIF*)...)
 - **Wet chemical instruments:** HONO sampled on a humid/aqueous surface: *denuders (wet, dry)*, *stripping coil instruments*, *mist chambers*...
First HONO measurements by a wet chemical instrument (Nash, 1974)

○ **General features:**

- In-situ: comparison with other data/instruments: ☺
potential influenced by local sources, gradients...: ☹
 - Heterogeneous uptake of HONO on aqueous/humid surfaces
 - Detection in the aqueous phase by IC (nitrite), HPLC/UV (DNPH, azo dye), long path absorption (azo dye)
 - High sensitivity (<ppt) possible
 - Medium-low time response (1 min - 1 day)
 - Typically sensitive to any species, which form nitrite $(\text{NO}_2^-)_{\text{aq}}$
- ➔ Potential interferences 💣

○ Müller et al., 1999: RWAD ⇔ DOAS

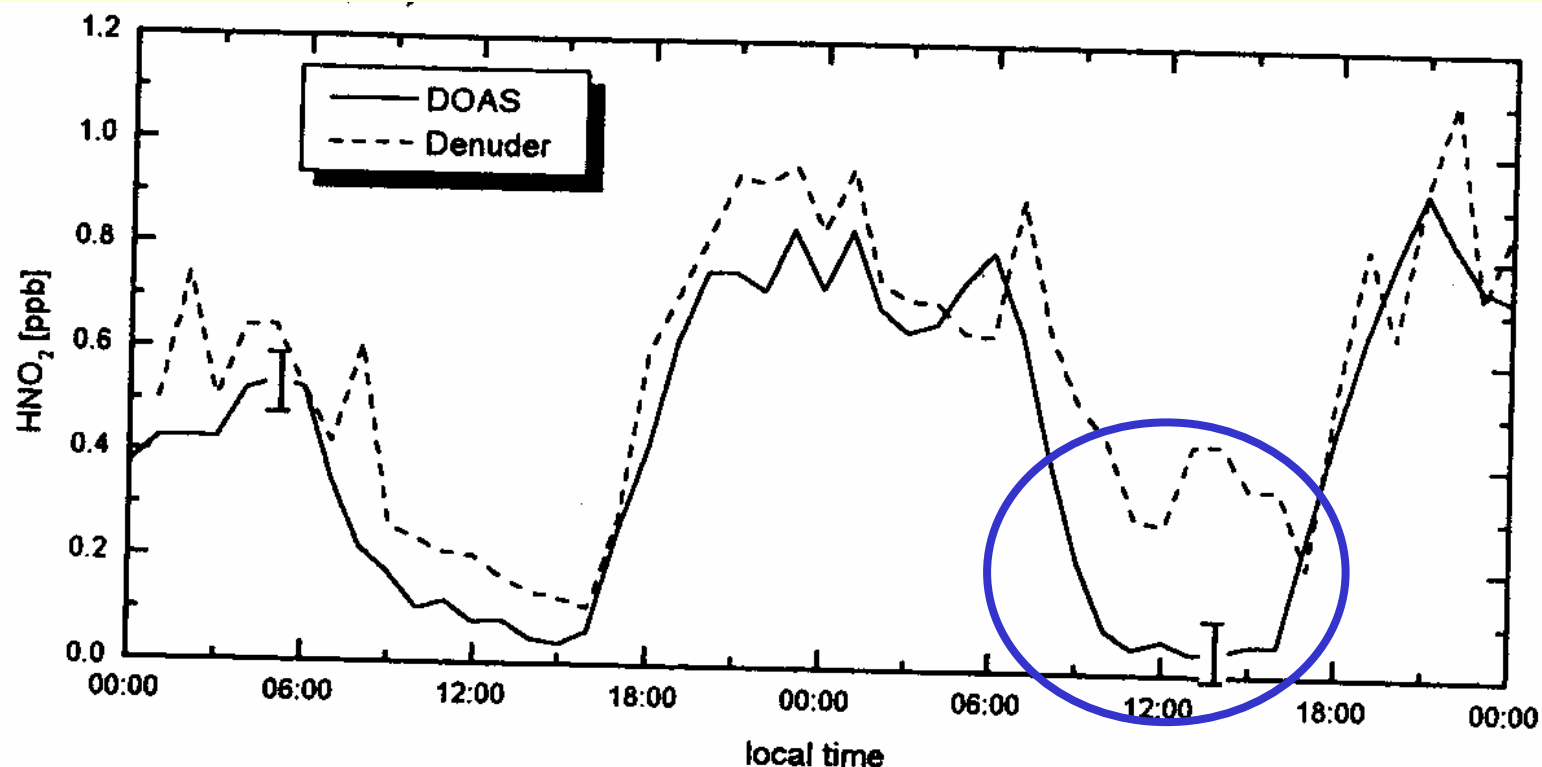
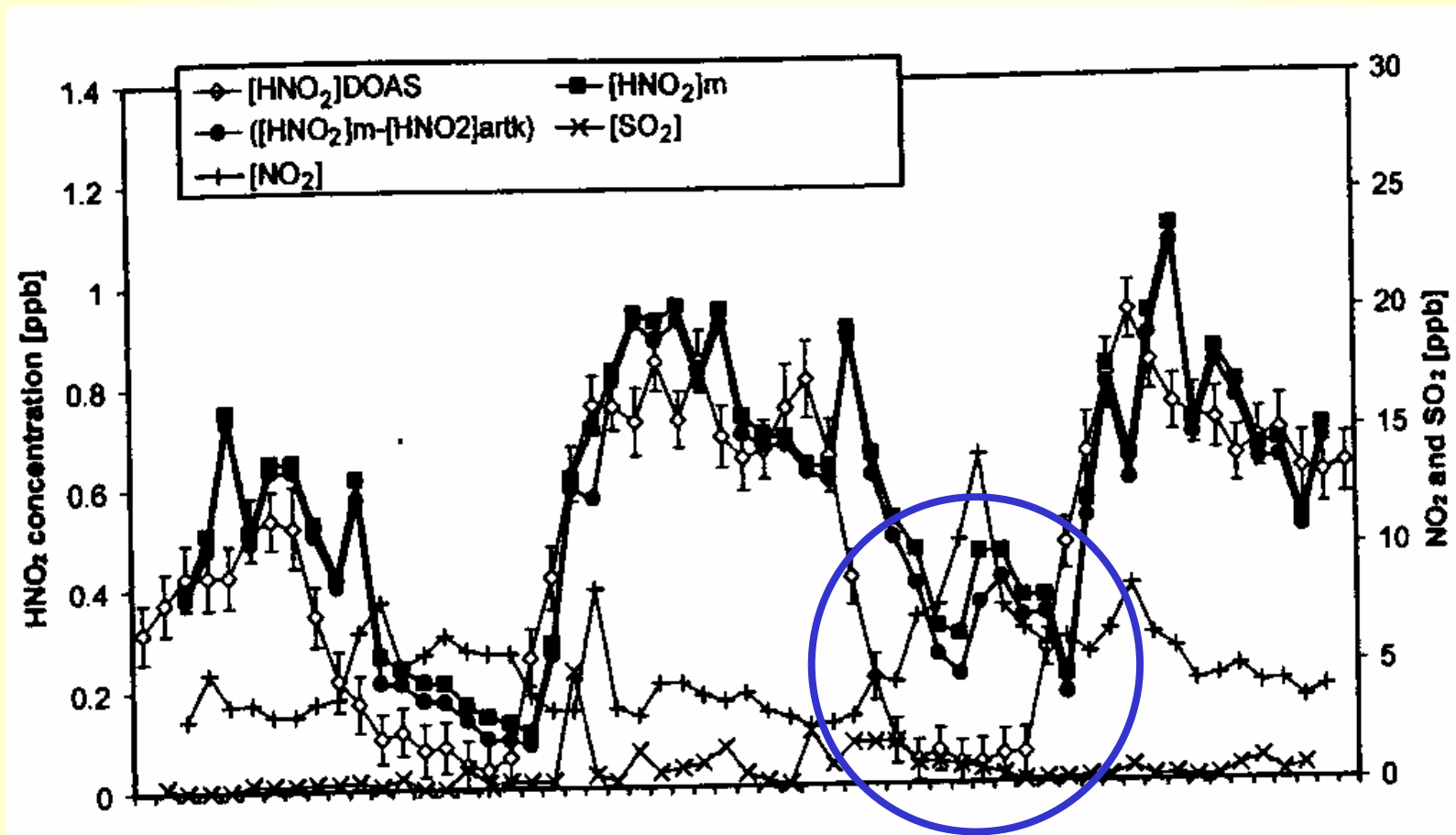
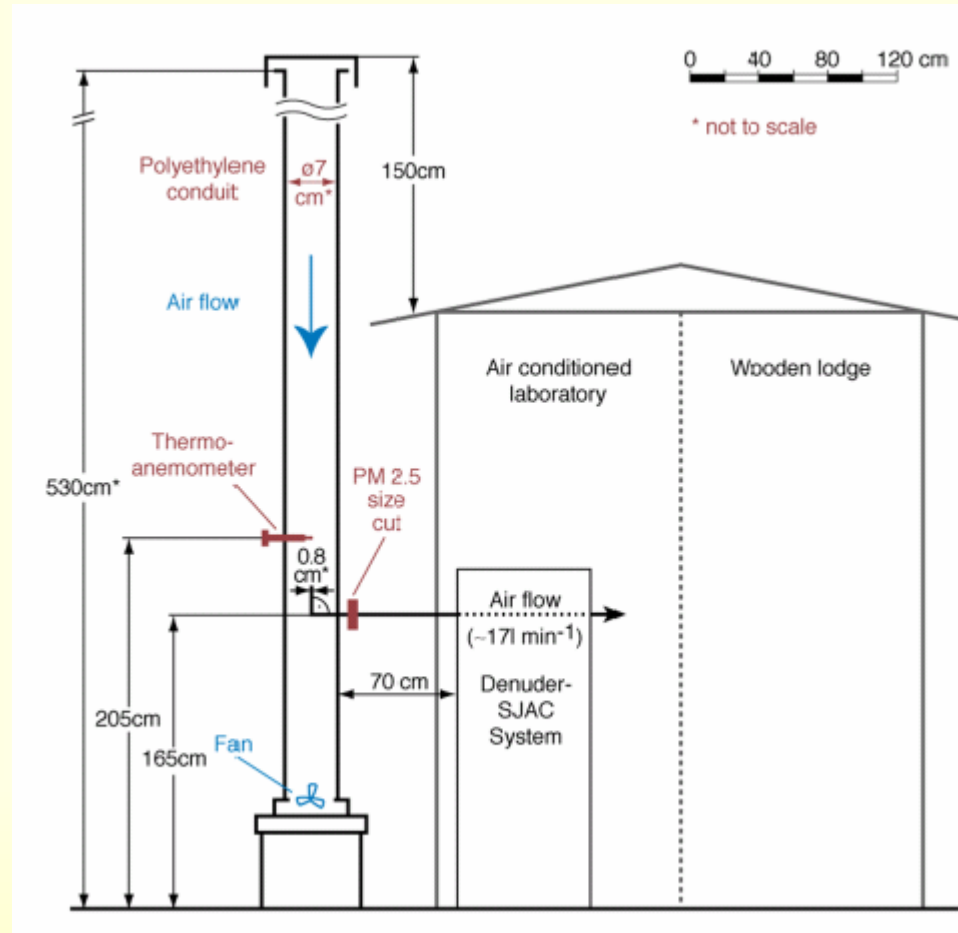


Fig. 1: Diurnal variation of hourly HNO₂ mixing ratio from DOAS and wet annular denuder measurements at the IfT-research station near Melpitz on September 24th and 25th, 1997. The error bars of the DOAS data correspond to the ± 60 ppt precision of the instrument.

- Spindler et al., 2003: same data, but corrected for known $\text{NO}_2 + \text{SO}_2$ interference, still not working...



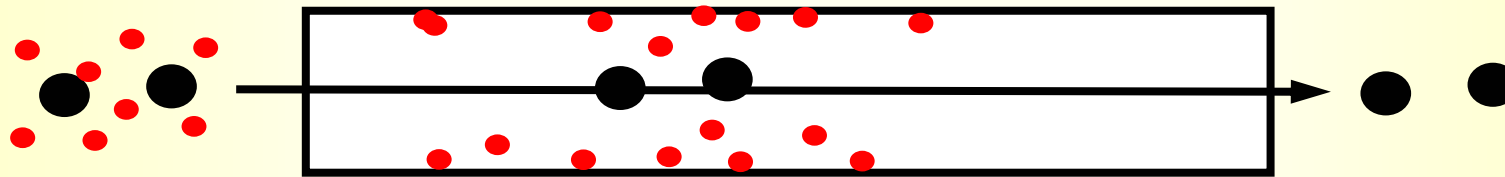
- Typically inlet lines (Teflon/glass) are used (up to 30 m length published...)



Trebs et al., 2004

- Typically inlet lines (Teflon/glass) are used (up to 30 m length published...)
- Artefacts are known
 - Photolytic formation (*Zhou et al.*, 2002)
 - Heterogeneous formation by $\text{NO}_2 + \text{H}_2\text{O}$ and $\text{NO}_2 + \text{organics}$ (see Christians presentation...).

- Denuder: Particles are efficiently separated from the gas phase analytes, which are sampled on the denuder surface



- HONO sampled on humid alkaline Na_2CO_3 surfaces as nitrite (NO_2^-), which is determined by ionchromatography (IC) after washing the denuder with pure water

Published for example in:

Ferm and Sjödin, *Atmos. Environ.* (1985) **19**, 979-983

Febo et al., *Atmos. Environ.* (1993) **27A**, 1721-1728

- High sensitivity possible (for long sampling time)
- Low time resolution (some h – 1 day)
- Time consuming off line analysis
- Interferences well known
- Pure NO₂ interference can be corrected by two denuder in series

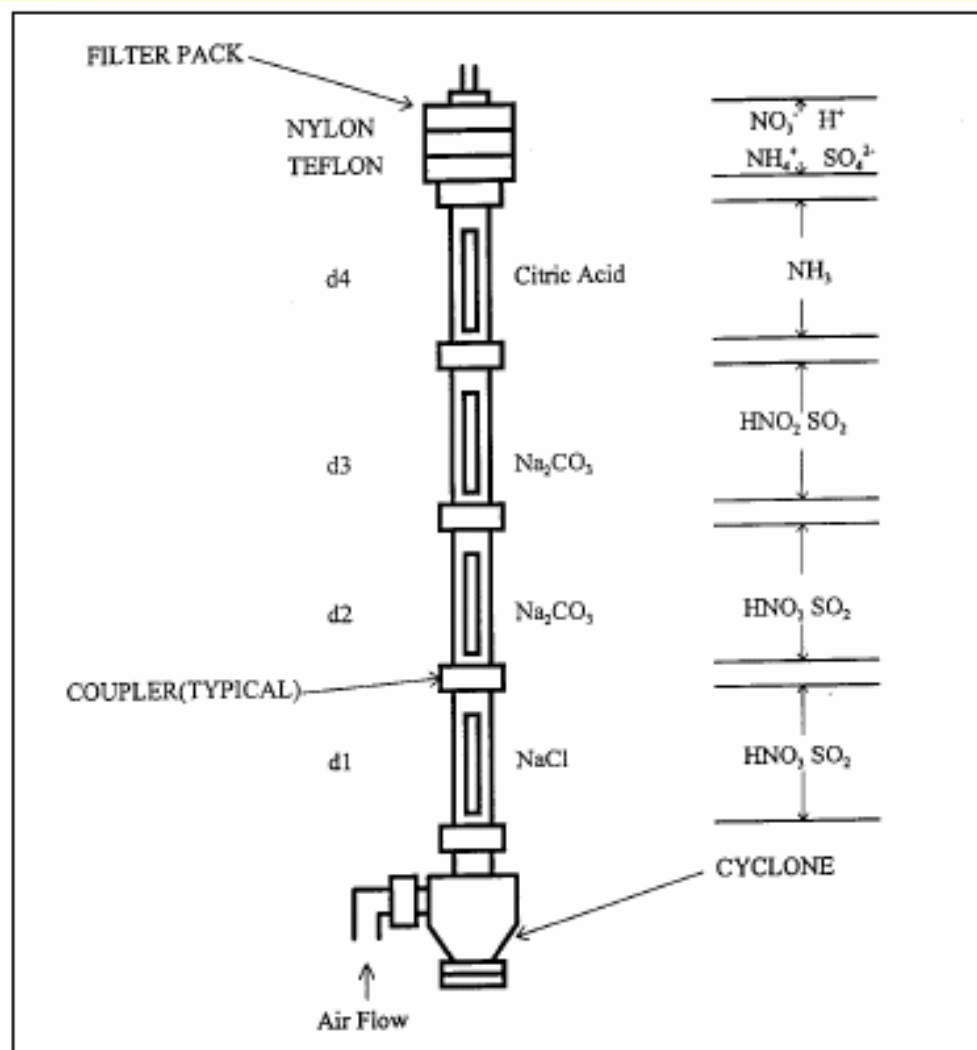


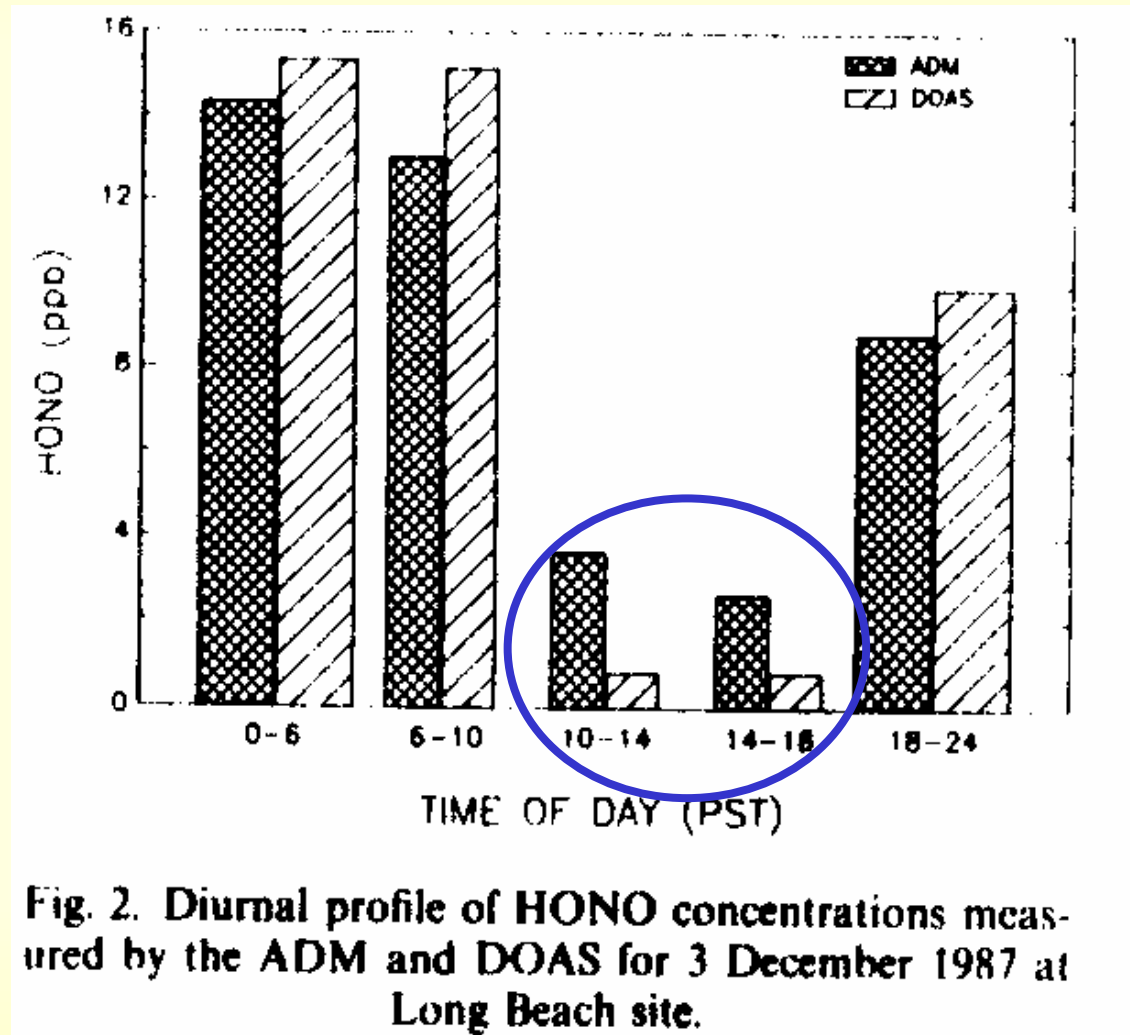
Figure 1. Schematic diagram of an ADS arrangement for evaluation basis (after EPA¹).

From:

Bay and Wen, *J. Air & Waste Manage. Assoc.* (2000) **50**, 123-130

However, other interferences (e.g. phenols+NO₂) cannot be corrected! (e.g. phenols are removed on alkaline surfaces...)

○ Appel et al., 1990: carbonate denuder \Leftrightarrow DOAS



- HONO sampled on aqueous denuder surfaces as nitrite (NO_2^-), which is typically determined by ionchromatography (IC)
- Different types of denuders possible:
 - **WEDD:** wet effluent diffusion denuder (cylindrical denuder)
 - **PPDN:** parallel plate diffusion denuder (often also referred as WEDD)
 - **RWAD:** rotated wet annular denuder
 - **ADAMD:** air dragged aqua-membrane denuder
- Higher time resolution (few min-1 h) compared to dry denuders
- High sensitivity possible (<1 ppt)

○ WEDD+mist chamber: here from *Neftel et al., 1996*

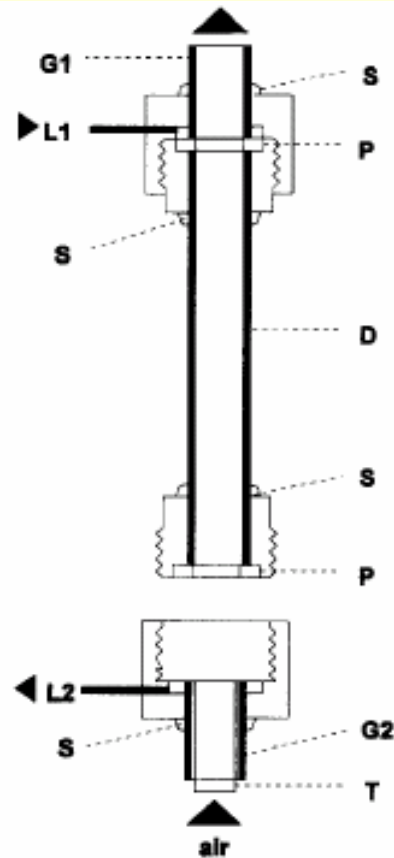


Fig. 1. Diagram showing the WEDD: (G1, G2) air inlet/outlet glass tubes ($l = 50$ mm, i.d. = 8 mm); (T) inlet PTFE tube; (L1, L2) liquid inlet/outlet; (D) denuder tube ($l = 500$ mm, i.d. = 8 mm) with inner layer of porous wetttable glass; (P) porous PVDF ring; (S) silicone rubber.

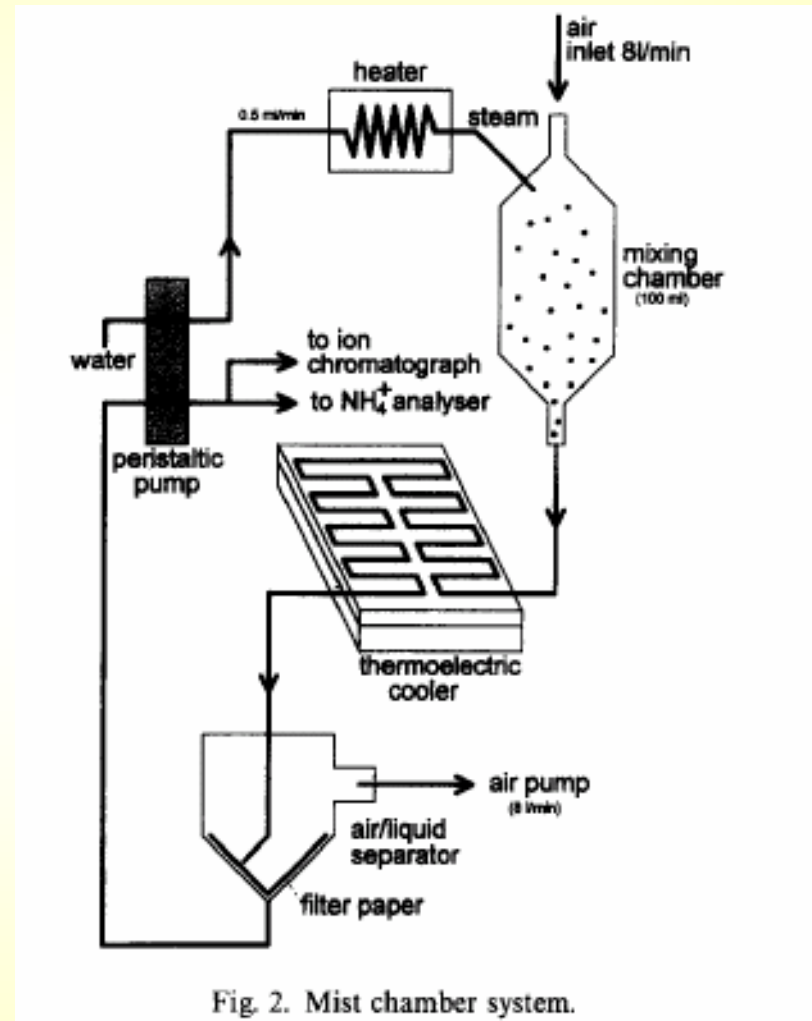
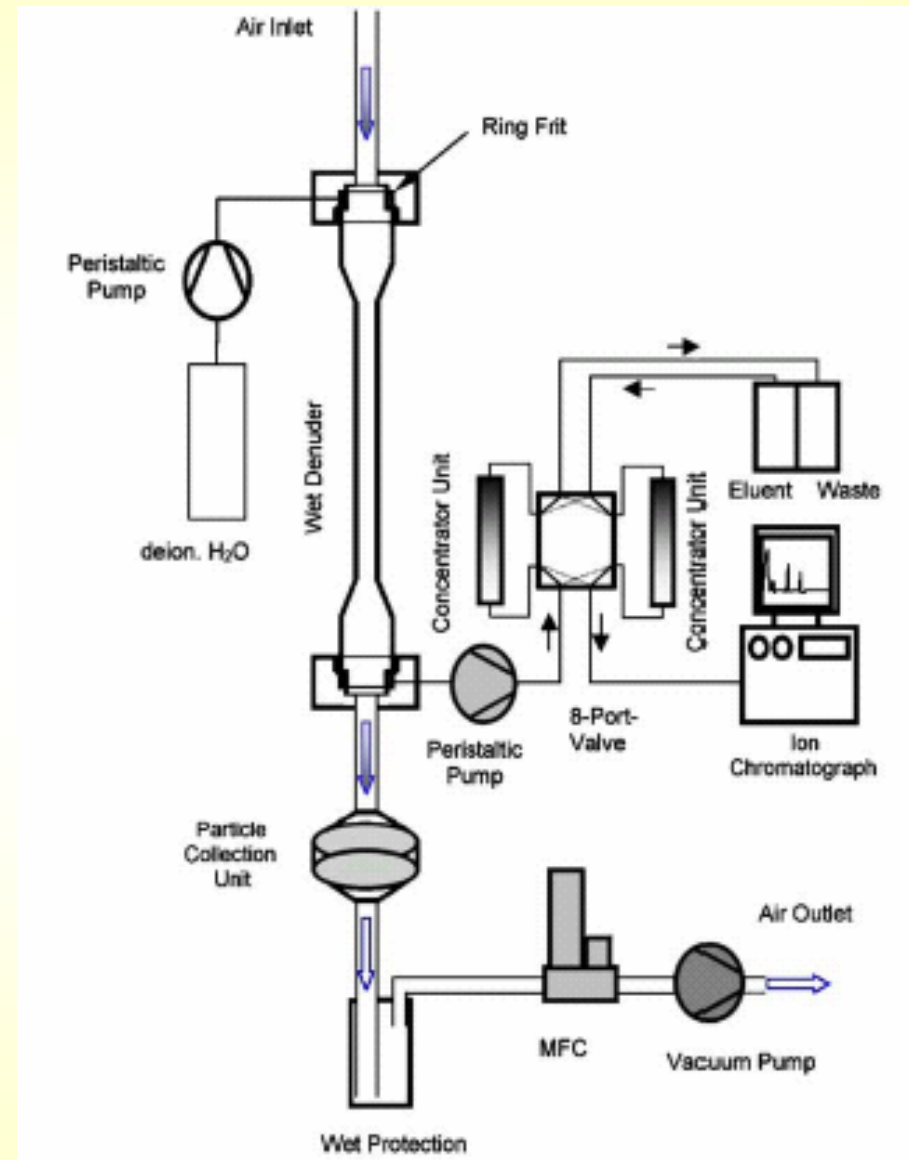


Fig. 2. Mist chamber system.

○ PPDN :

Here from *Acker et al., 2004*;
referred as WEDD



○ PPDD+mist chamber: here from *Simon+Dasgupta, 1995*

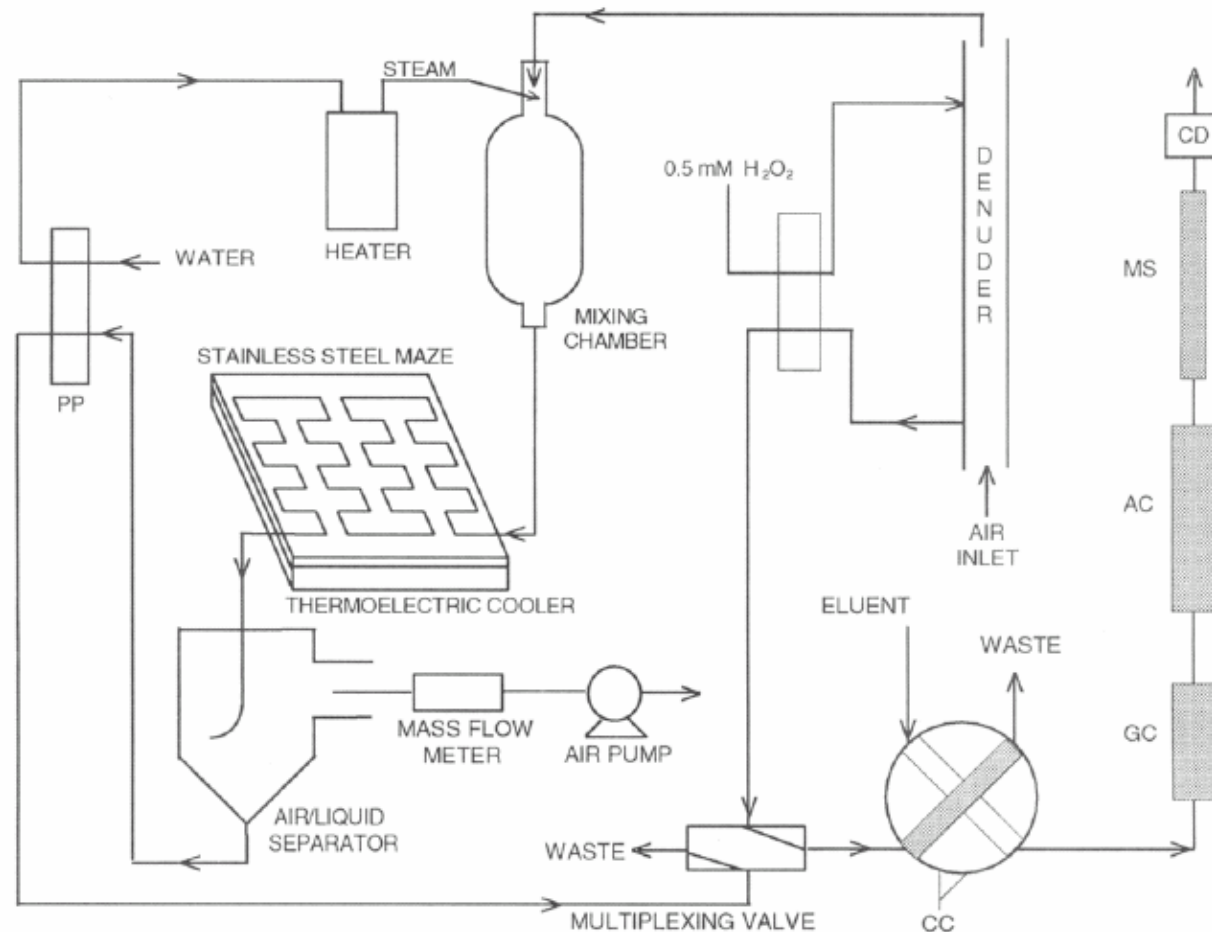


FIGURE 1. PPDD-PCS-IC system. PP, peristaltic pump; CC, concentrator column; GC, guard column; AC, analytical column; MS, membrane suppressor; CD, conductivity detector.

- PPDD+mist chamber: here from Zellweger et al., 1999 (WEDD)

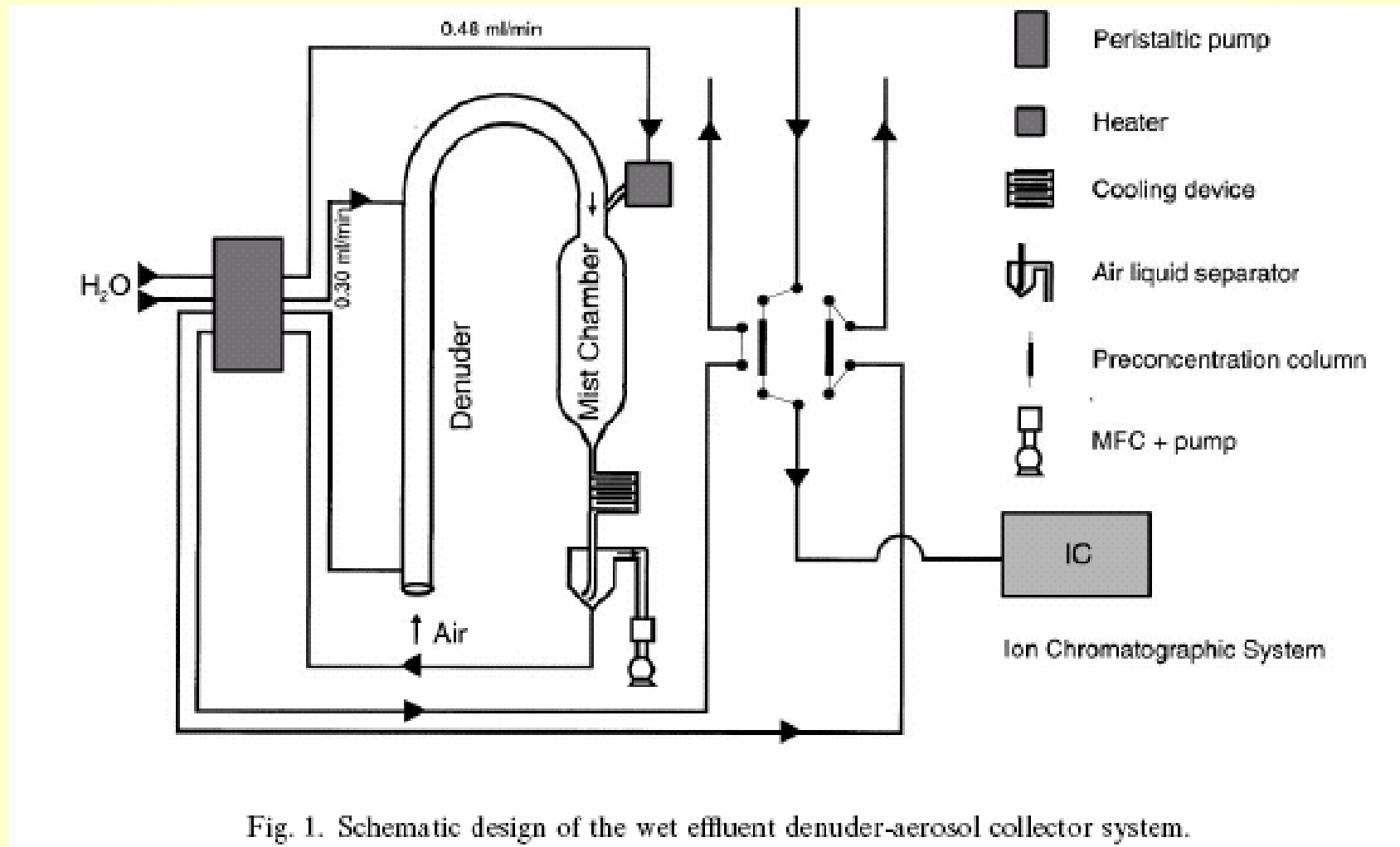
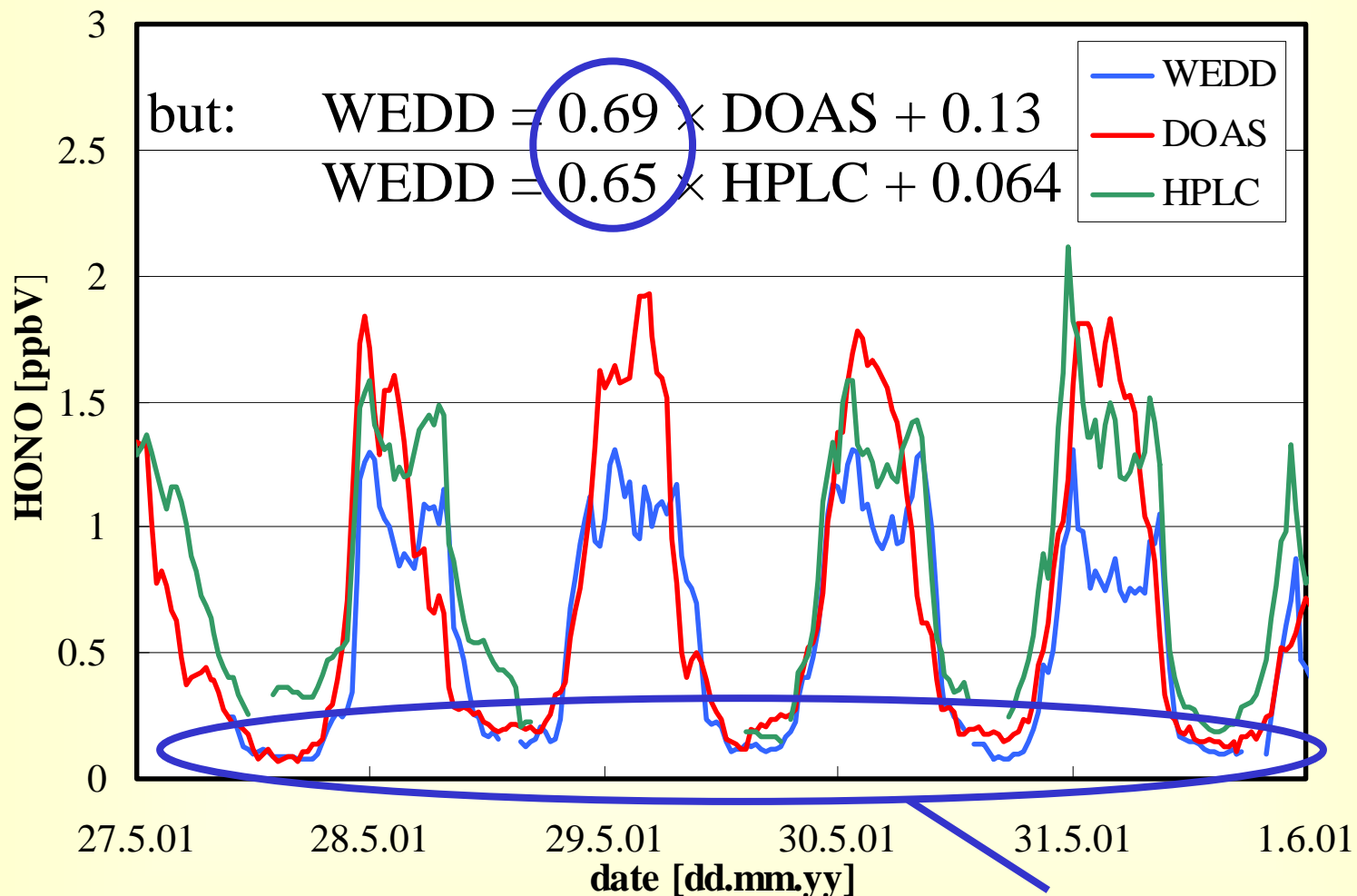


Fig. 1. Schematic design of the wet effluent denuder-aerosol collector system.

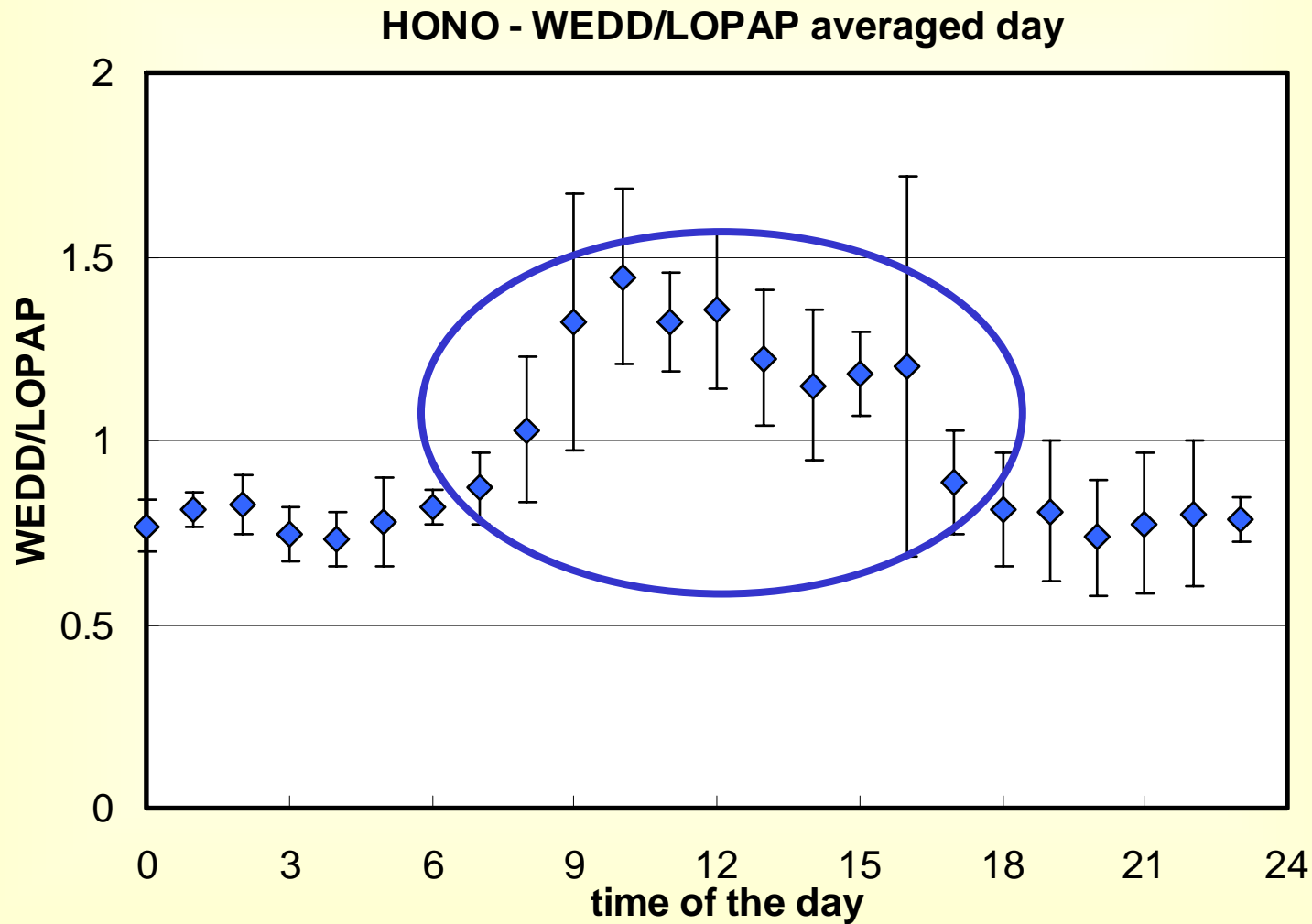
- Typically pure water is used for the wet denuders
- Losses of HONO possible for high acidity (for example in smog chambers); Henrys law constant of HONO decreasing with decreasing pH...
- In *Zellweger et al.* (1999) NaHCO₃ effluent used to avoid this problem
- However, not working for nitrite, which is replaced by HCO₃⁻ on the pre-concentration columns used... Now, PSI again use water...

○ NITROCAT: Two chemical in-situ instruments + DOAS....



daytime $[HONO]_{(WEDD)} = [HONO]_{(DOAS)}$

- Recent intercomparison from mountain Hohenpeissenberg



- RWAD (rotated wet annular denuder): here from *Acker et al.*, 2004

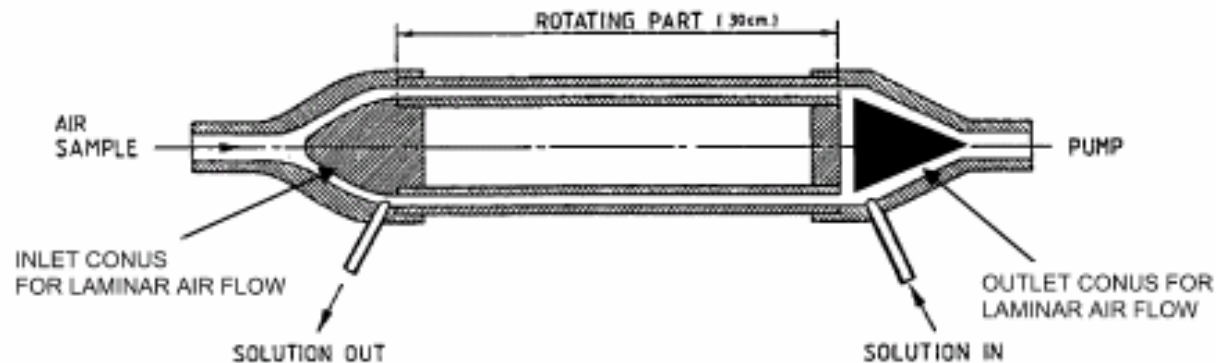


Fig. 2. Construction of the denuder in the rotating wet annular denuder system of the IFT and the steam jet aerosol collector (following Keuken et al. 1988). The black triangle marks the outlet cone in the original drawn (Slanina et al., 1992) that is available only in the used steam jet aerosol collector.

- RWAD: here from Trebs et al., 2004

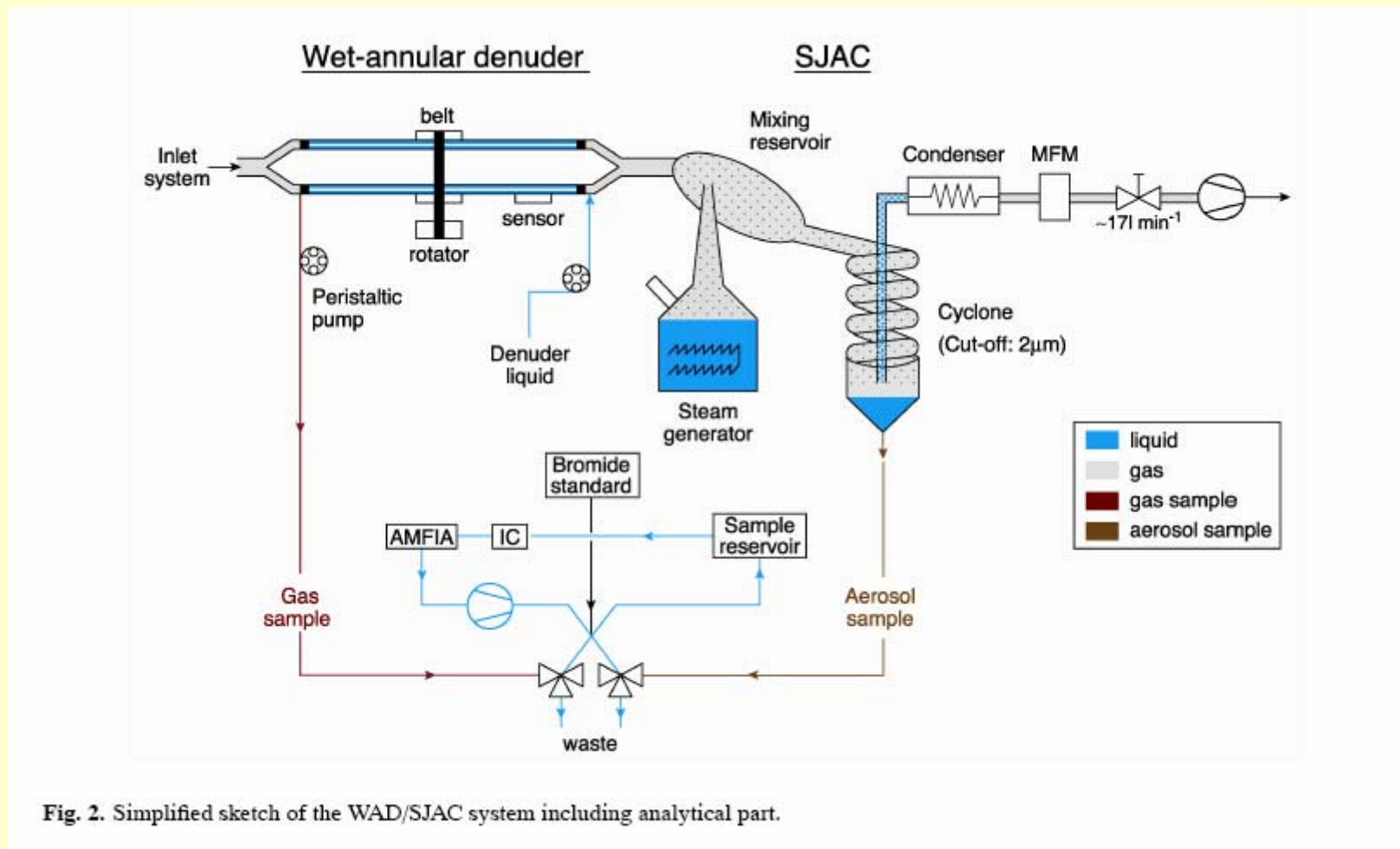


Fig. 2. Simplified sketch of the WAD/SJAC system including analytical part.

○ Müller et al., 1999: RWAD ⇔ DOAS

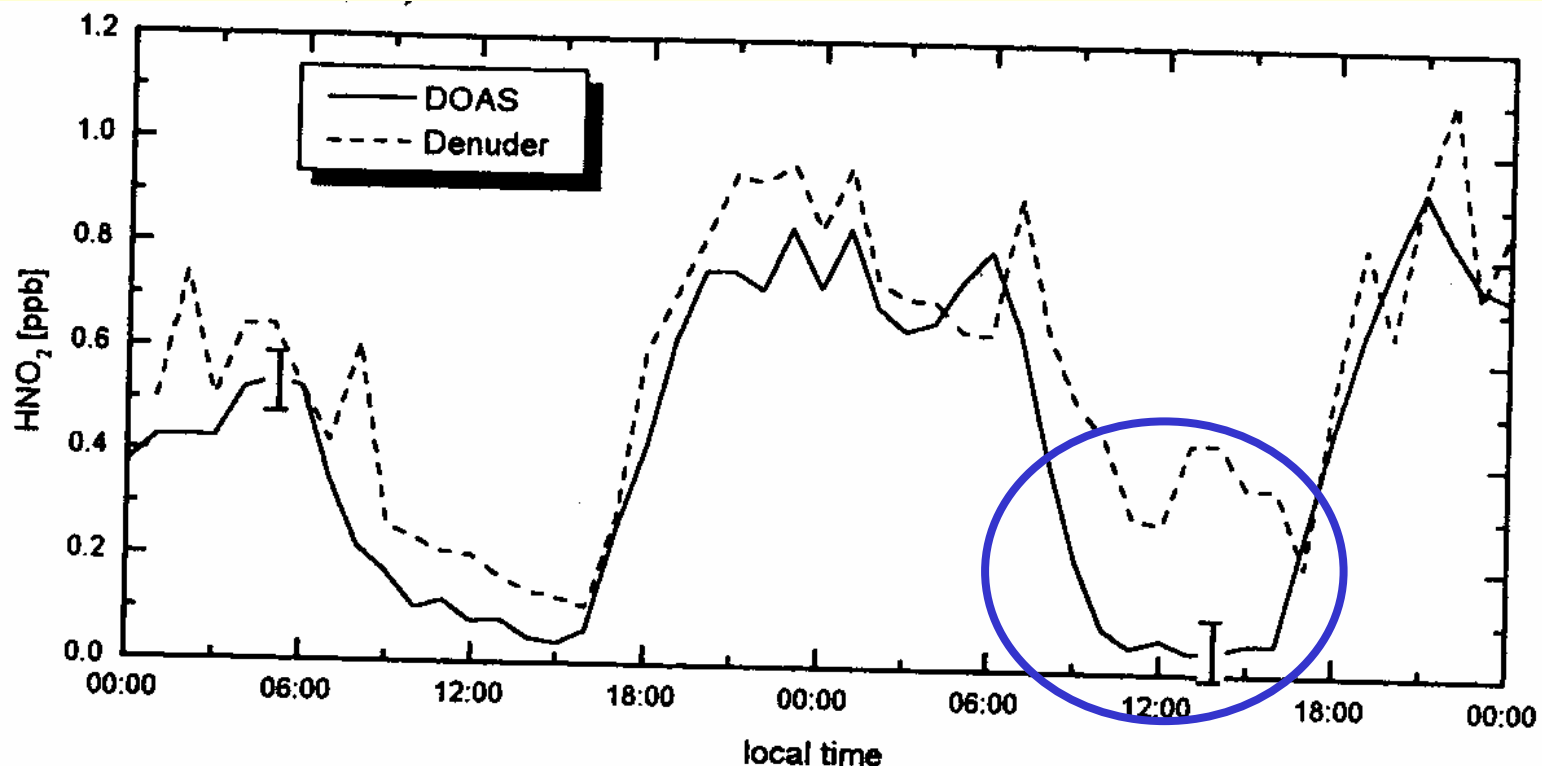
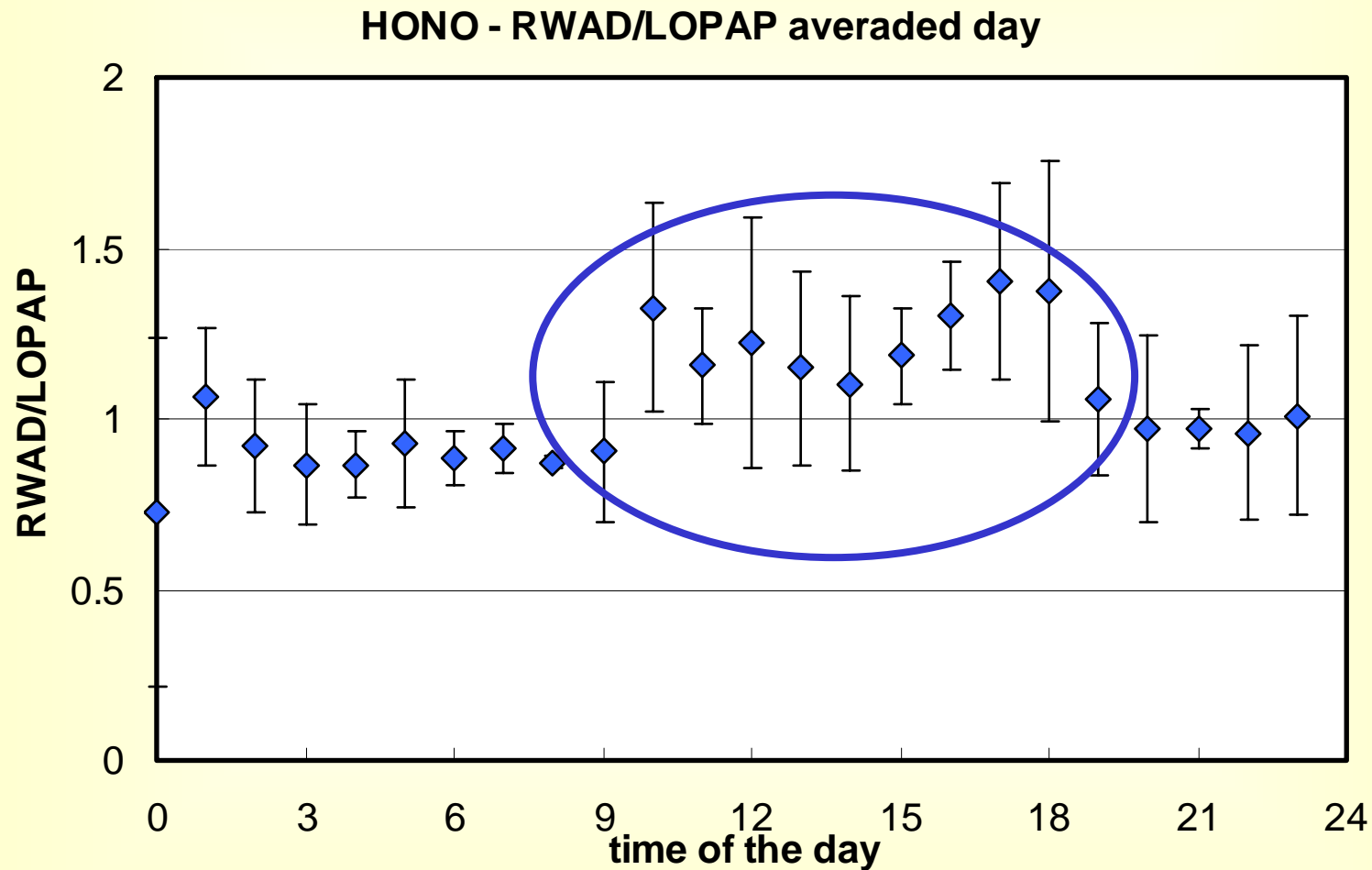


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- Recent intercomparison from mountain Hohenpeissenberg



Particle nitrite: mist chambers

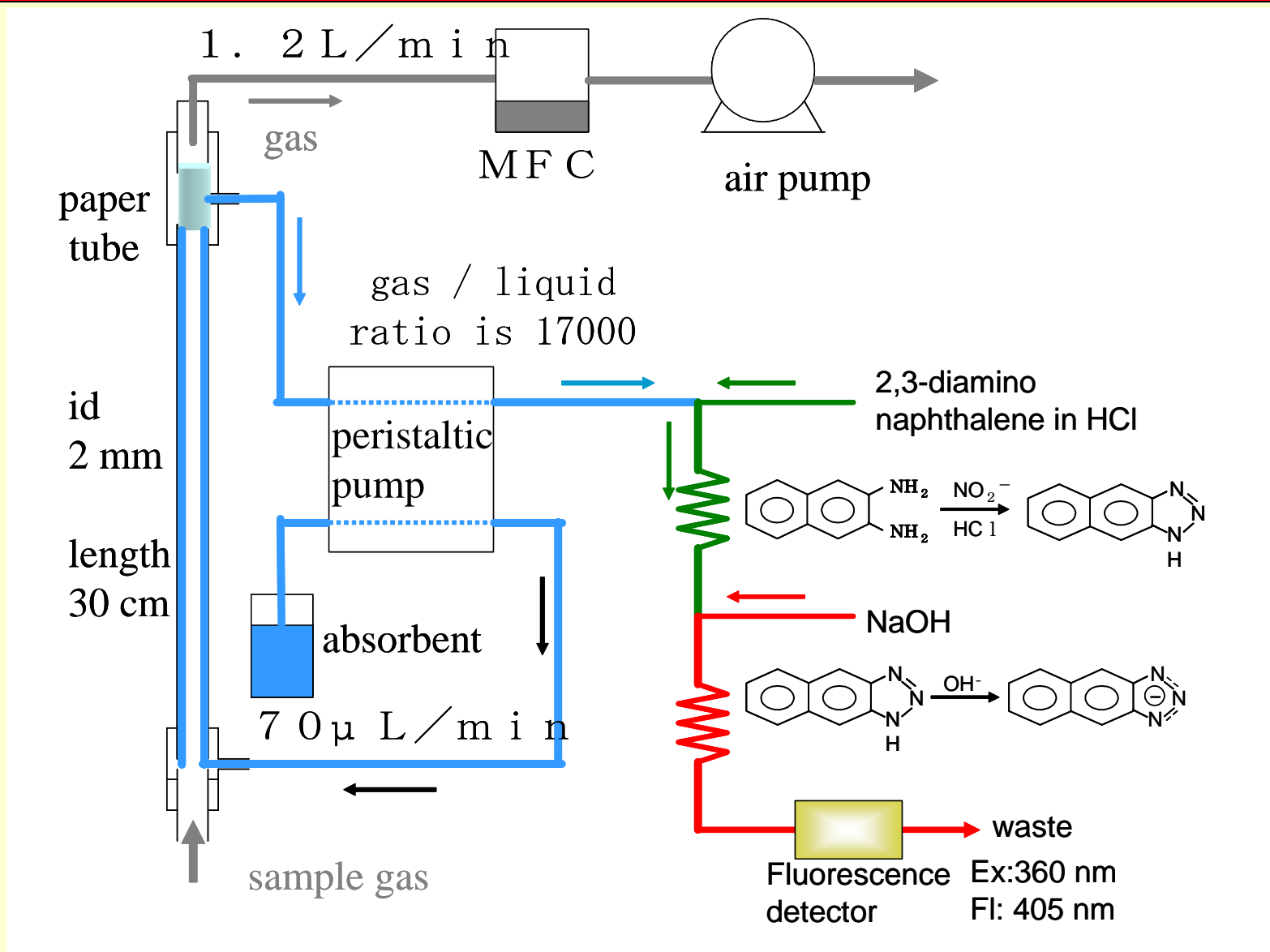
- Wet denuders are often combined with mist chambers to measure also particle nitrite
- However, even the pure NO_2 interference is an order of magnitude higher caused by the high temperatures and high S/V (see DIFUSO measurement with PSI WEDD)
- Published deviation from Henry's law (excess of nitrite in the particle) may be affected by this problem...

Fluorescence Technique: ADAMD/DAN (*Norimichi Takenaka*)

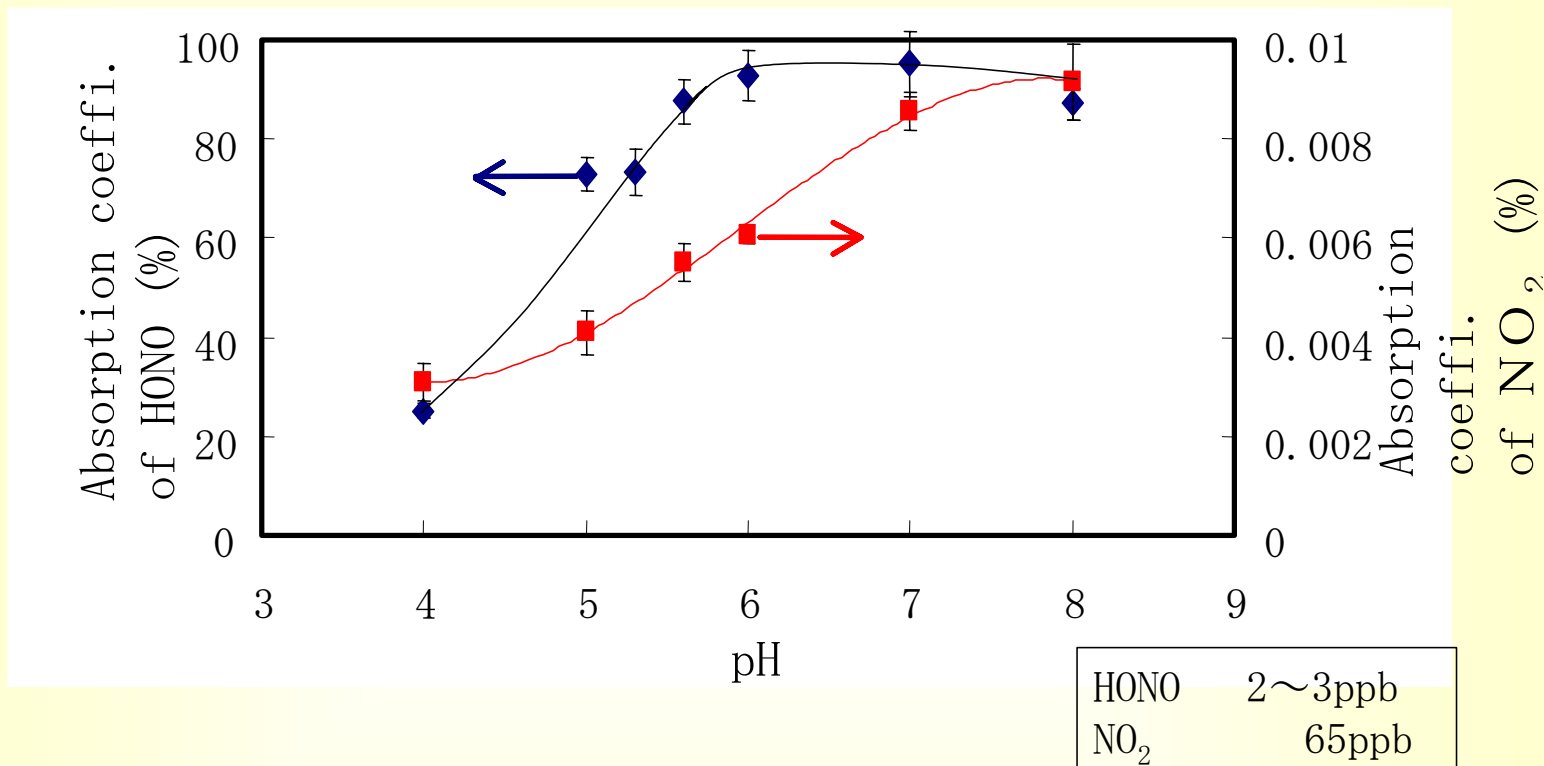
- HONO sampled in water in a “mini-denuder”, “air dragged aqua-membrane denuder”(ADAMD), converted into DAN and detected by fluorescence

Published in:

Takenaka et al., *Analyst* (2004) **139**, 1130-1136

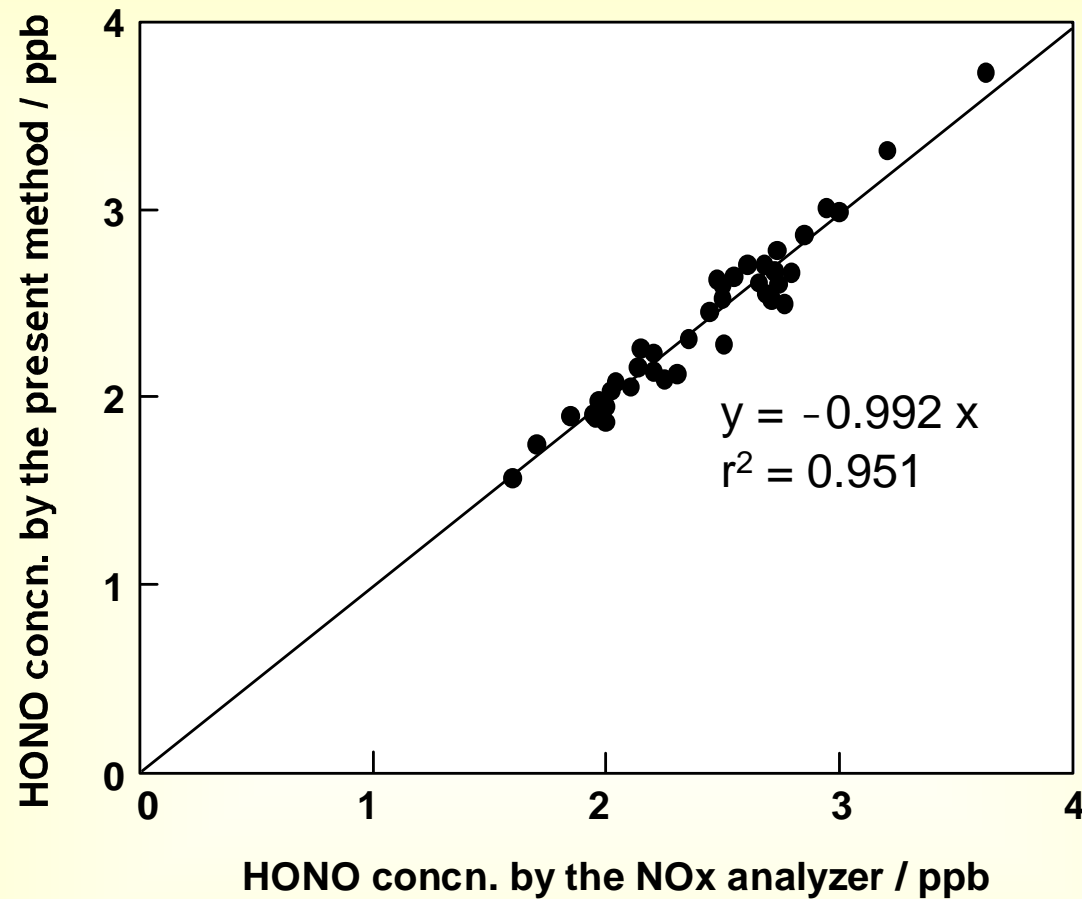


Absorption coefficients of HONO and NO₂ by the ADAMD



HONO : completely absorbed at > pH 6

Absorption of NO₂ can be ignored.



$[HONO] = ([NO_x] - [NO]) - ([NO_x - HONO] - [NO])$
HONO in NO_x is removed by Na₂CO₃-coated denuder

Table 1 Interference from the other gaseous species with HONO signal

Gaseous species ^{a)} (concentration / ppb)	Rel. sign. intens.
HONO	100
HONO + NO (120) + NO ₂ (100)	100.6 ± 2.1
HONO + NO (55) + NO ₂ (80) + O ₃ (53)	100.4 ± 4.3
HONO + NO (60) + NO ₂ (60) + NH ₃ (60)	101.6 ± 3.4
HONO + NO (75) + NO ₂ (60) + SO ₂ (80)	101.6 ± 3.4
HONO + NO (40) + NO ₂ (60) + O ₃ (40) + SO ₂ (50)	102.4 ± 5.7
HONO + NO (80) + NO ₂ (20) + SO ₂ (50) + NH ₃ (50)	101.7 ± 0.7
HONO + NO (50) + NO ₂ (50) + O ₃ (30) + SO ₂ (50) + NH ₃ (50)	101.5 ± 4.3
CH ₃ CH ₂ ONO (60)	Not detected
CH ₃ C(O)OONO ₂ (92 - 289)	1.3 ± 0.3 ^{b)}
Aliphatic carboxylic acids, C ₁ - C ₅	0.11 - 0.13 ^{b)}
Benzoic acid	0.10 ^{b)}
Aldehydes, C ₁ -C ₄	0.02 - 0.04 ^{b)}
Phenol	0.08 ^{b)}
Methanol	0.01 ^{b)}
Ethanol	0.05 ^{b)}
Acetone	0.03 ^{b)}

a) : HONO concentration could not be controlled for several days. Average concentrations in each measurement are defined as 100. They were about 1.5 ± 1 ppb HONO.

b) Percentages of (values measured as HONO) / (concentrations of the species).

Response time

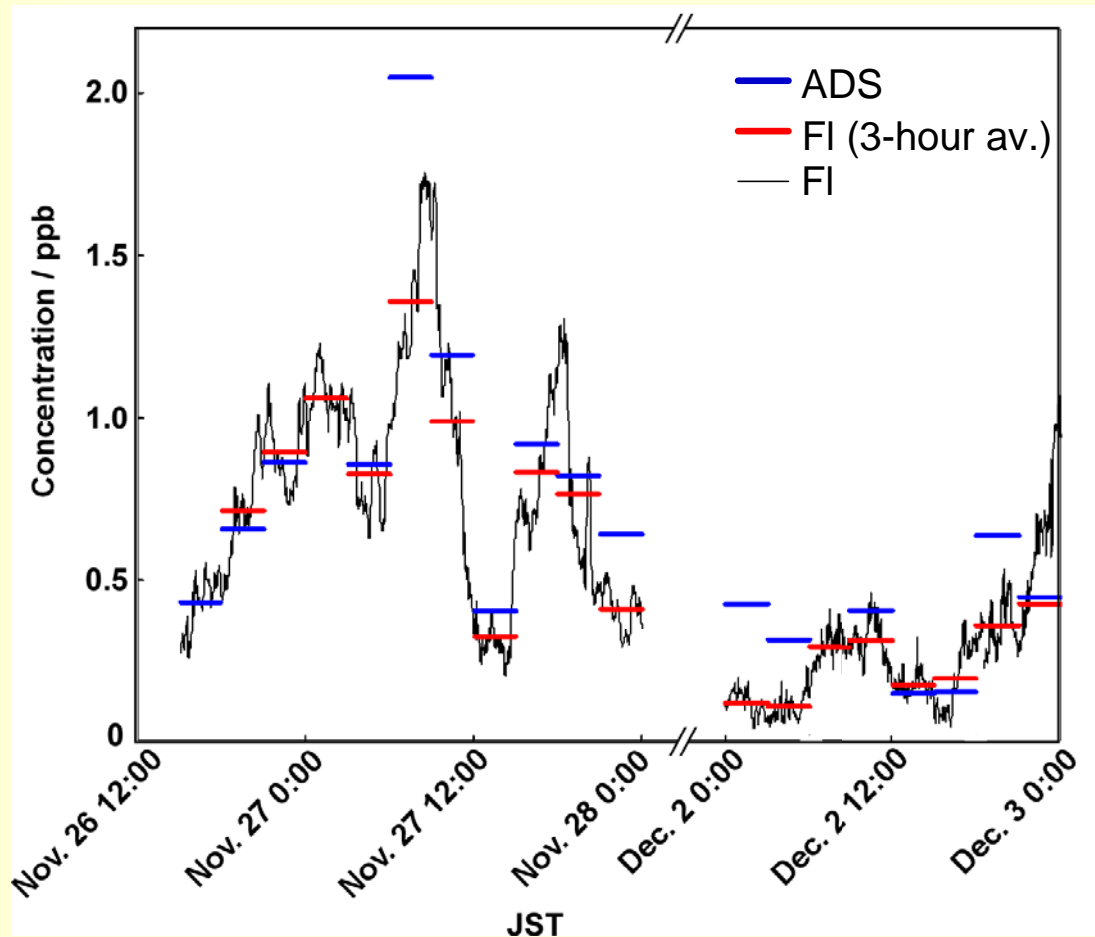
(time which needs to be stable by changing HONO concentration)

0 to ca. 1 ppb : about 2 minutes

0 to ca. 5 ppb : about 5 minutes

Detection limit : 8 ppt (3 SD of the zero air signal noise)

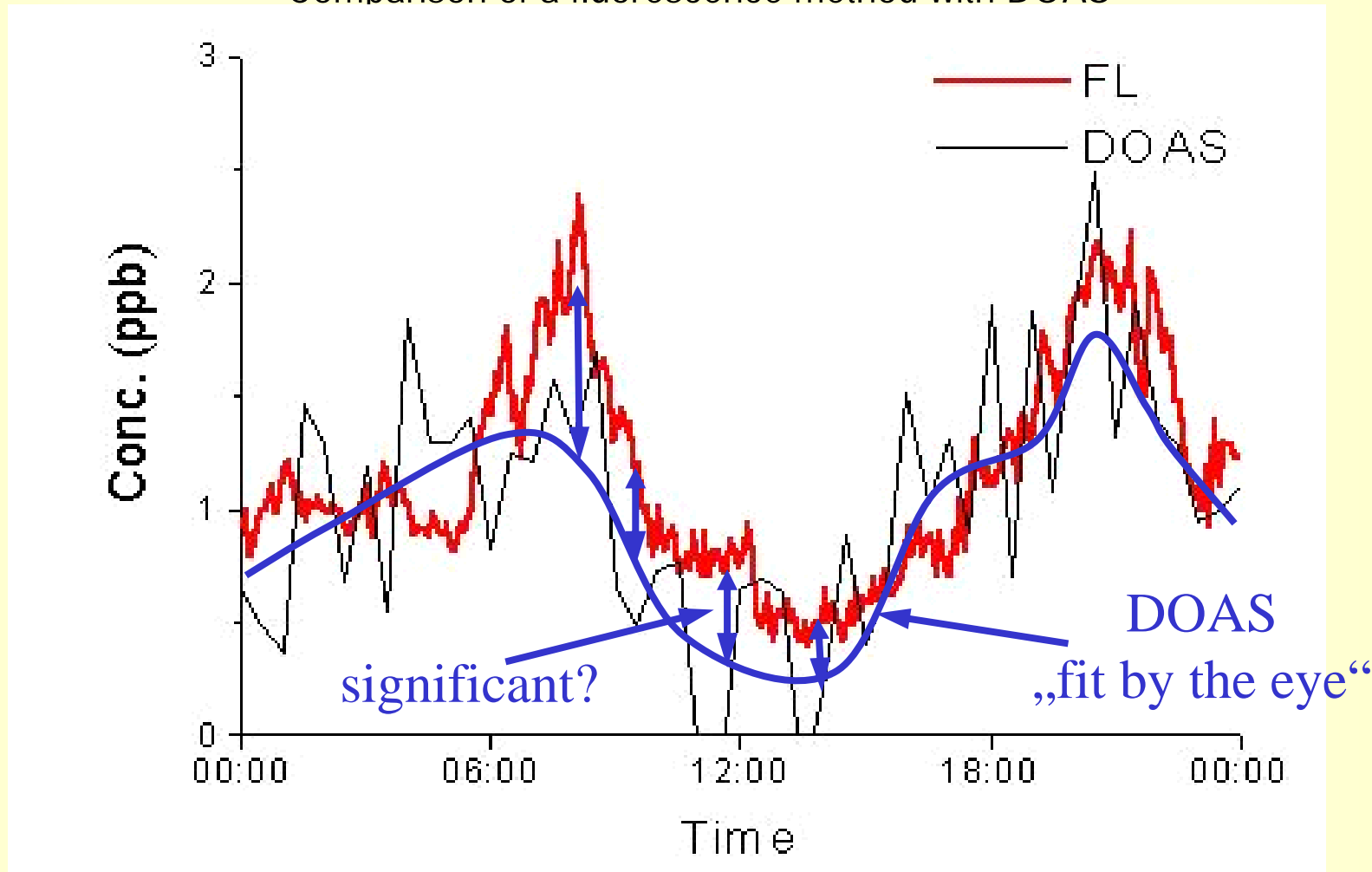
Comparison of a fluorescence method with ADS(Nov.-Dec,2003)



ADS : Annular denuder system, 3 hours sampling

Annular Denuder > DAN

Comparison of a fluorescence method with DOAS*



*DOAS: Optical path 1 km. UV-Absorption region 340~370 nm

Mist-Chamber/Ionchromatography (*Jack Dibb*)

- HONO sampled in ultra-pure water droplets in a mist chamber and nitrite is detected by IC

Published in:

Scheuer et al., *Journal of Geophysical Research*, **108** (D4), 8370, 2003.



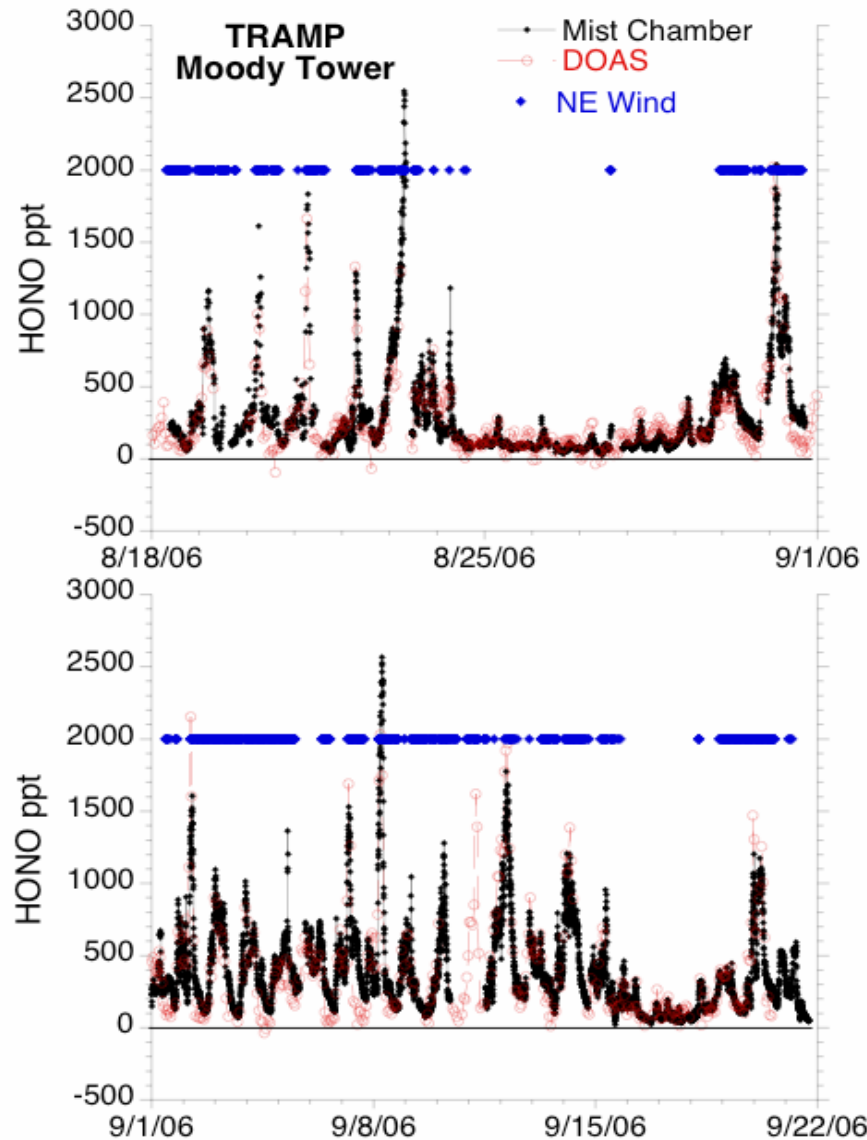
UNH automated dual-channel Mist Chamber Ion Chromatograph (MC/IC).

Can sample alternately or simultaneously.

Sample interval adjustable from 85 seconds (airborne) to 15 minutes (at Summit) or longer if needed.

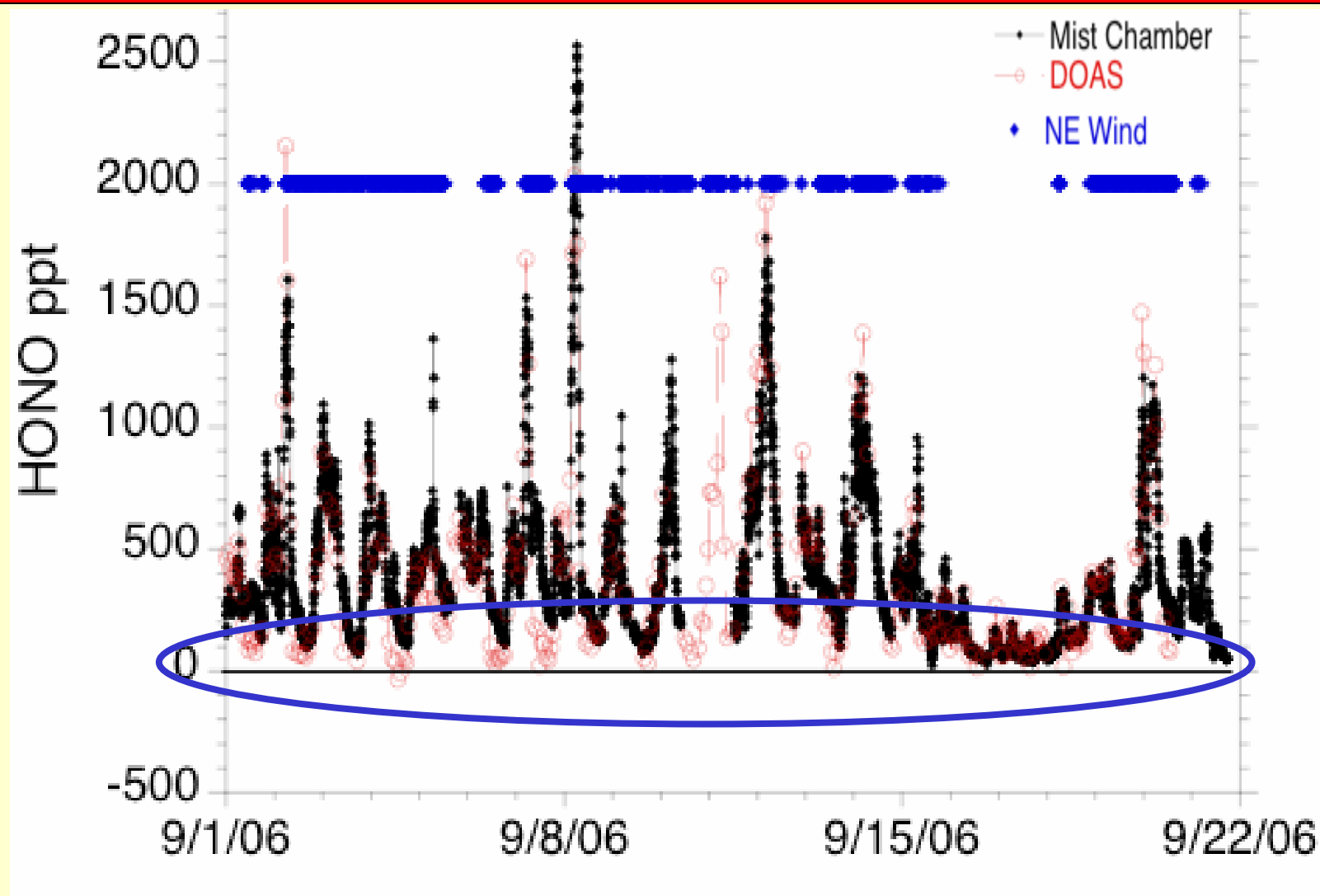
Detection limit better than 0.5 ppt for 15 minute samples.

Quantify soluble nitrite (and other ions). *HONO is a significant fraction of the nitrite signal (...).*



Six week campaign in Houston, MC/IC compared very well to long-path DOAS.





○ JK: Again higher daytime values by the chemical instrument...

- Good agreement with DOAS for high HONO concentration
- However, higher MC/IC values during daytime...
- In addition, at South Pole a *factor of seven* higher concentrations were measured compared to a LIF, see *Liao et al.*, 2006
- What is the interferant in polar regions and at low HONO concentrations?

- Many instruments known
 - HPLC (*Zhou*)
 - LOPAP (*Wuppertal*)
 - Chemiluminescence (*Kanda + Taira*)
 -
- Potential artefacts by uptake of particle nitrite
- However, small uptake for particles $<1 \mu\text{m}$ (*Bröske et al.*)
- In addition, small solubility of HONO for typical low pH of the aerosol → small interference to be expected

HPLC-technique (*Xianliang Zhou*)

- HONO sampled in a buffer at pH 7 in a stripping coil converted into DNPH or an azo-dye and measured by HPLC (UV/VIS) detection.

Published in:

Zhou et al., *Environ. Sci. Technol.*, 1999, **33**, 3672-3679;

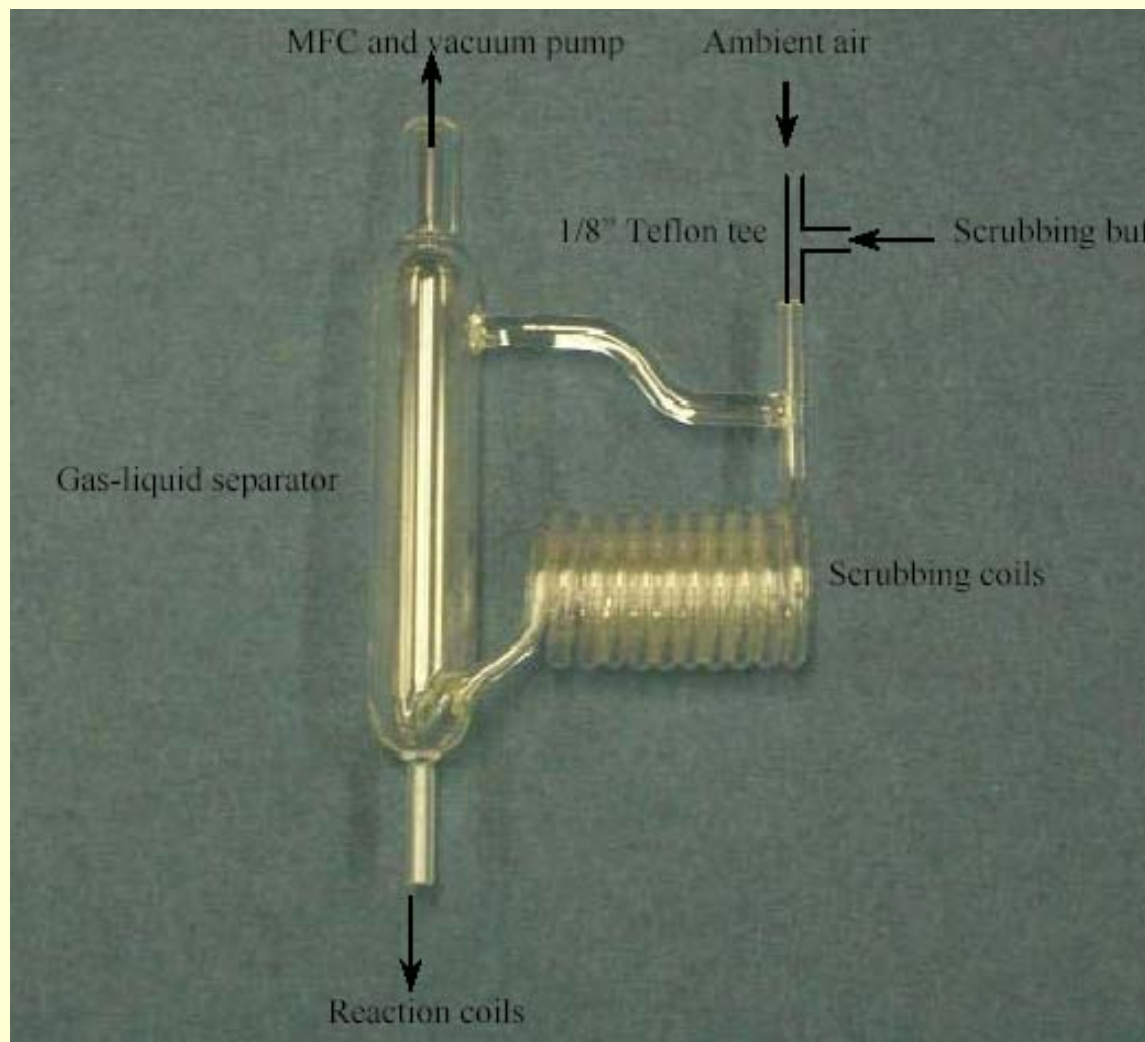
Huang et al., *Atmos. Environ.*, 2002, **36**, 2225-2235.

Summary of the method:

- Sampling: aqueous scrubbing of HONO using a 10-turn glass coil with a pH 7 phosphate buffer as scrubbing solution.

Collection efficiency >99% at an air sampling flow rate of 2.0 L min⁻¹ and liquid flow rate of 0.25 mL min⁻¹.

Glass coil sampler

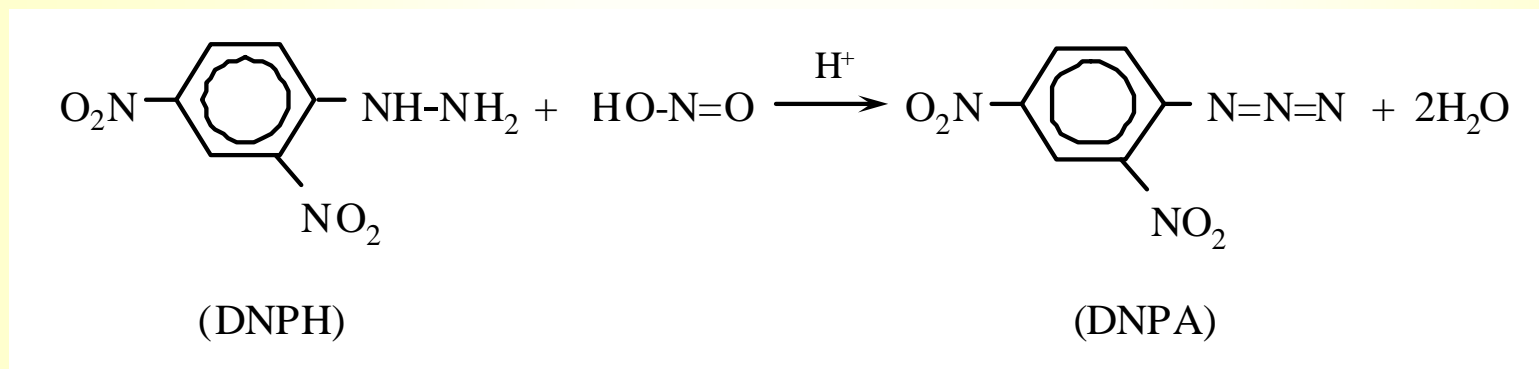


Summary of the method:

- Derivatization:
 - (1) DNPH derivatization (*Zhou et al.*, 1999)
 - (2) Griess reaction (*Huang et al.*, 2002)

Zhou et al., 1999

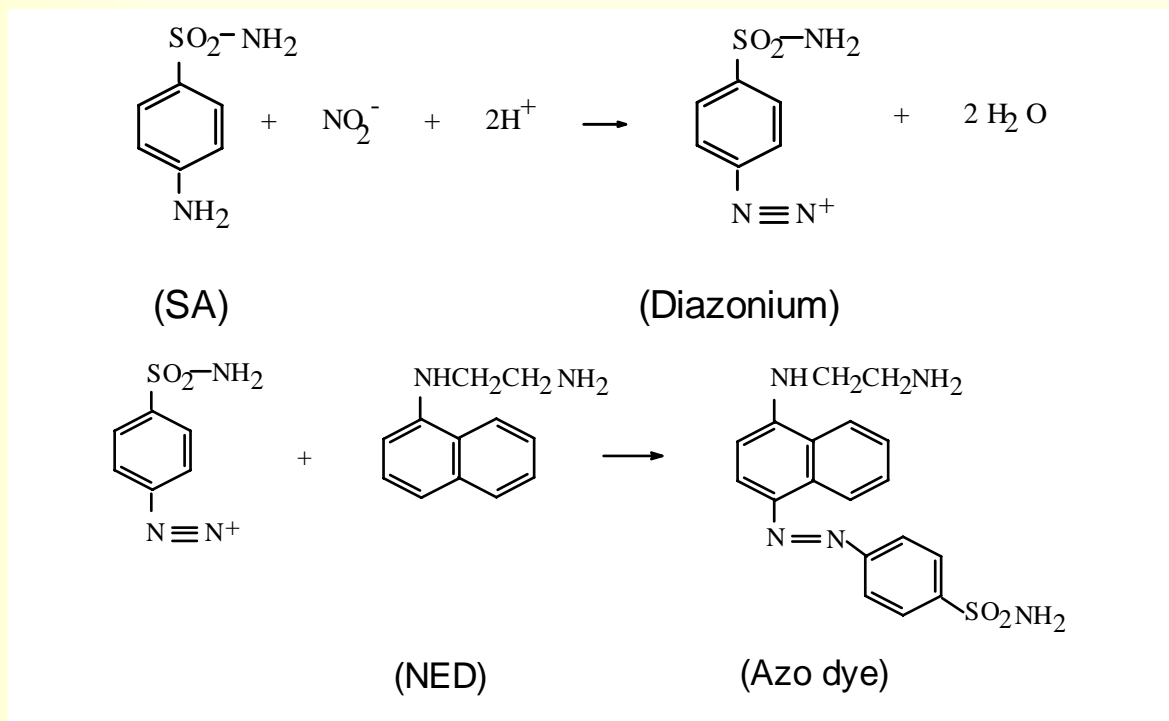
- Derivatization nitrite with 2,4-dinitrophenylhydrazine (DNPH) to form 2,4-dinitrophenyl azide (DNPA) :



- DNPA is separated from DNPH on C-18 HPLC column and detected by a UV detector at 290 nm.

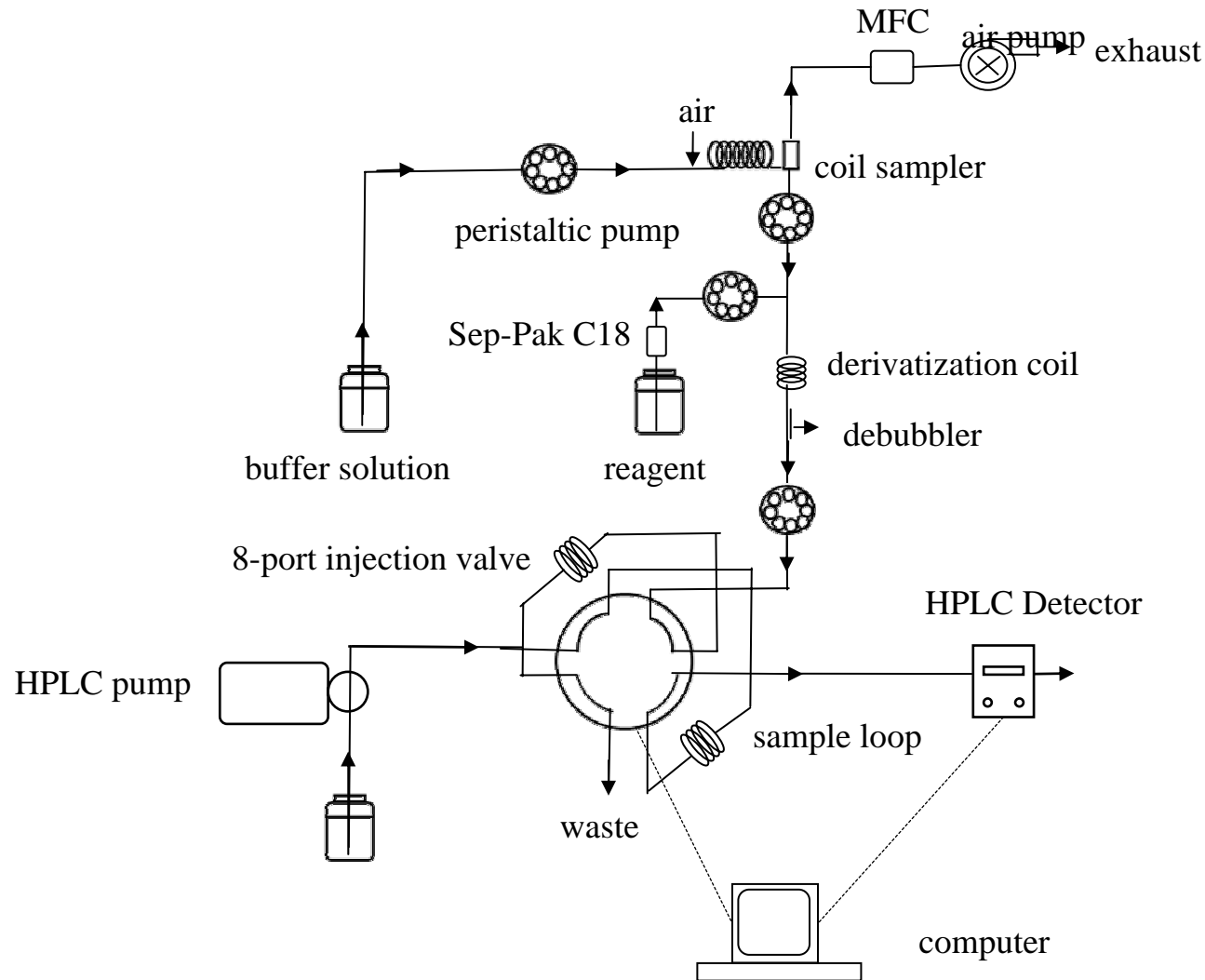
Huang et al., 2002; He et al., 2006

- Derivatization nitrite with 2 aromatic amines to form an azo dye:

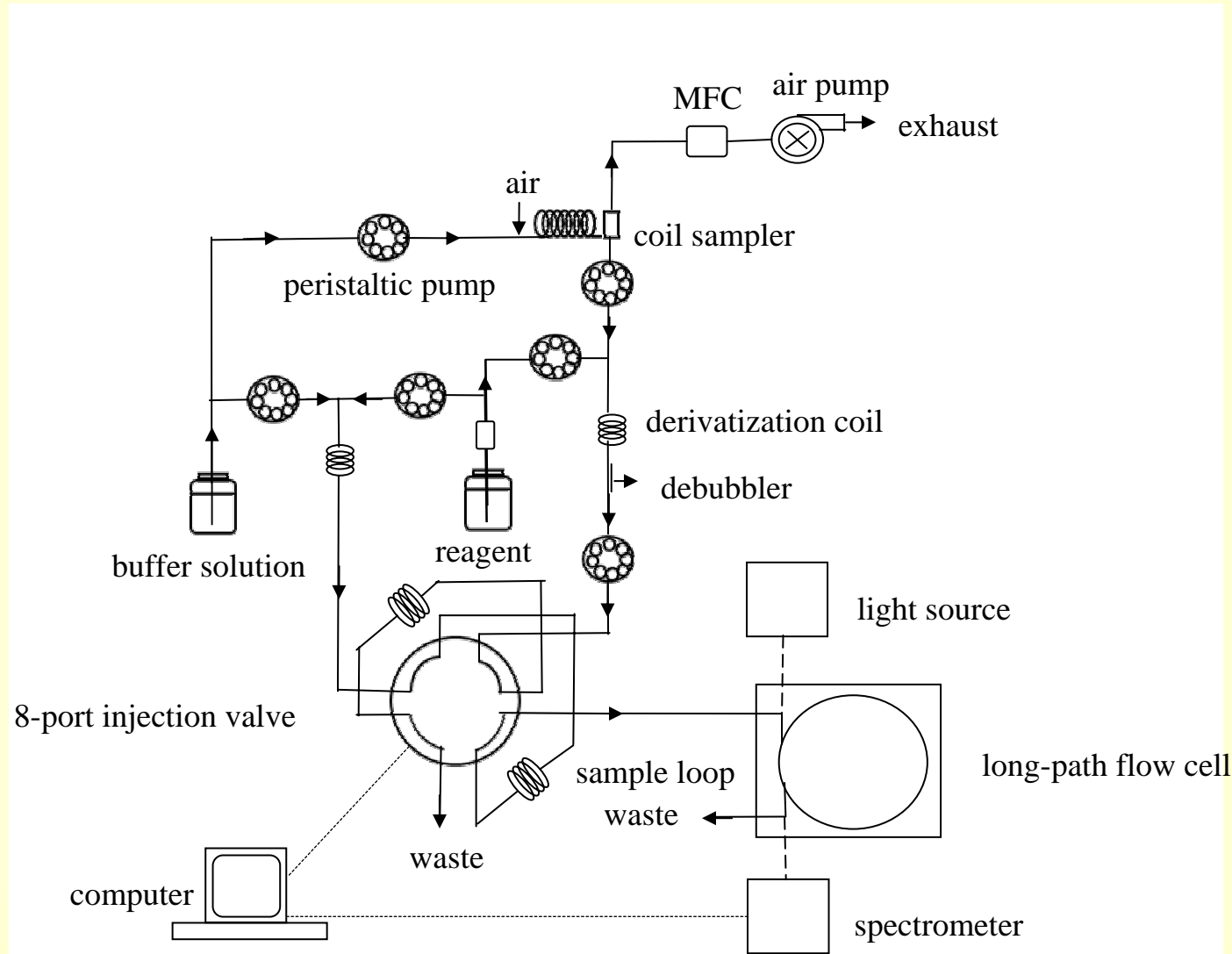


- Azo dye is separated from other impurities on C-18 HPLC column and detected by a UV detector at 540 nm;
OR detected by long path flow cell/fiber optic mini-spectrometer at 540nm.

A HONO measurement system with an HPLC/UV-visible detector



A HONO measurement system with LPFC/spectrometer



Summary of the method:

- Detection limit: 1 ppt by HPLC detection OR 3 ppt by LPFC detection.
- Time resolution: 1 min possible

Interference from gaseous and aerosol species (NO_x , PAN, particulates, HCs, O_3):

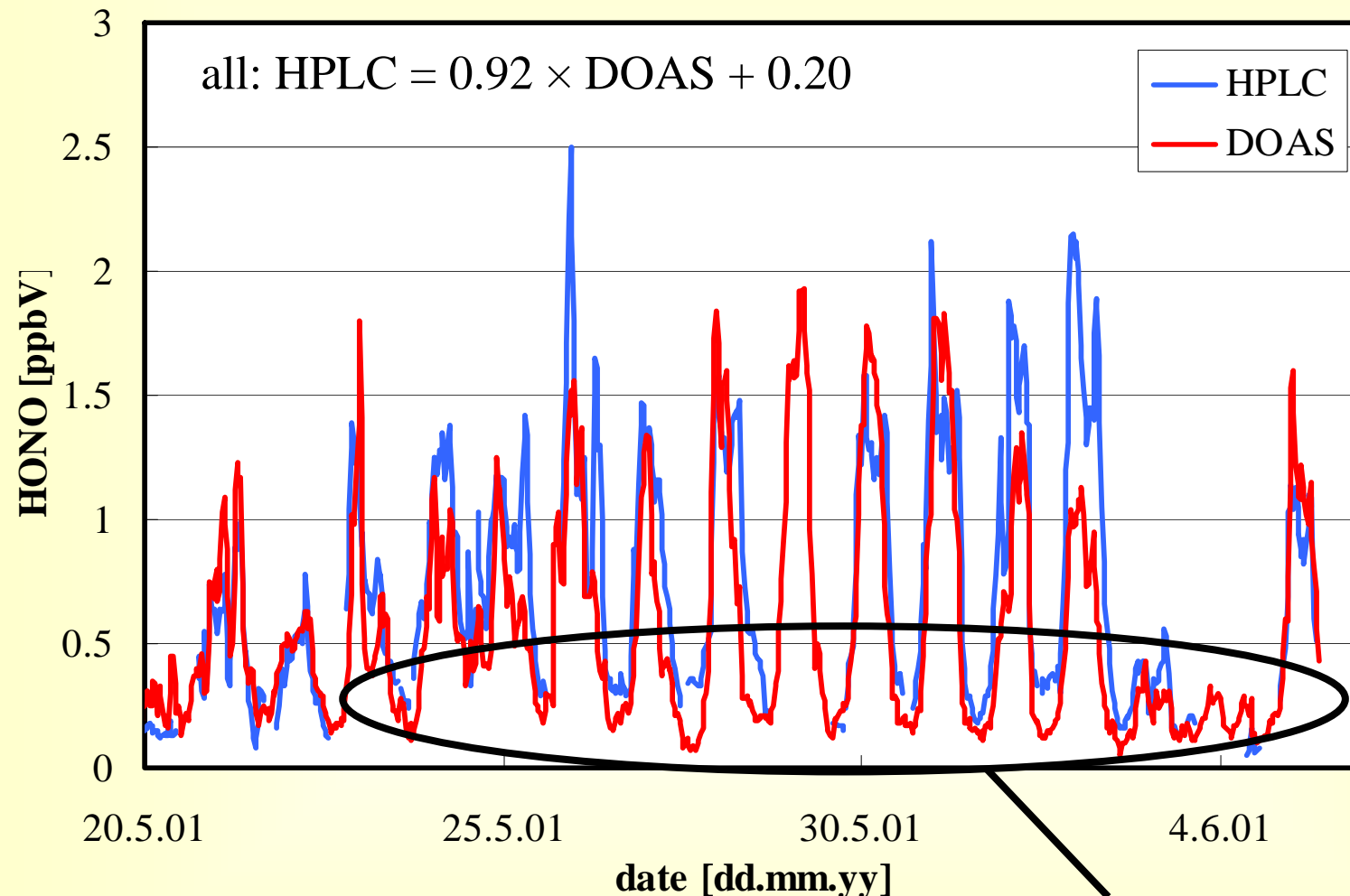
In 2-channel system, one channel sampled ambient air directly, while in another channel had a Na_2CO_3 -coated annular denuder (URG) to remove gaseous HONO before coil sampler.

- Urban (Albany, 3 days): the interference signal in channel 2 contributed <8% of the overall HONO signal in channel 1 (0.2-1.3 ppbv), with the highest during a high daytime high NO_x (~150 ppbv) pollution episode.
- Rural (Whiteface Mountain, 10 30-min periods over 30 days): the interference signal in Channel 2 was consistently below the detection limit of 3 pptv (ambient HONO concentration 10-300 pptv, ambient NO_x ~1 ppbv).

Comment JK:

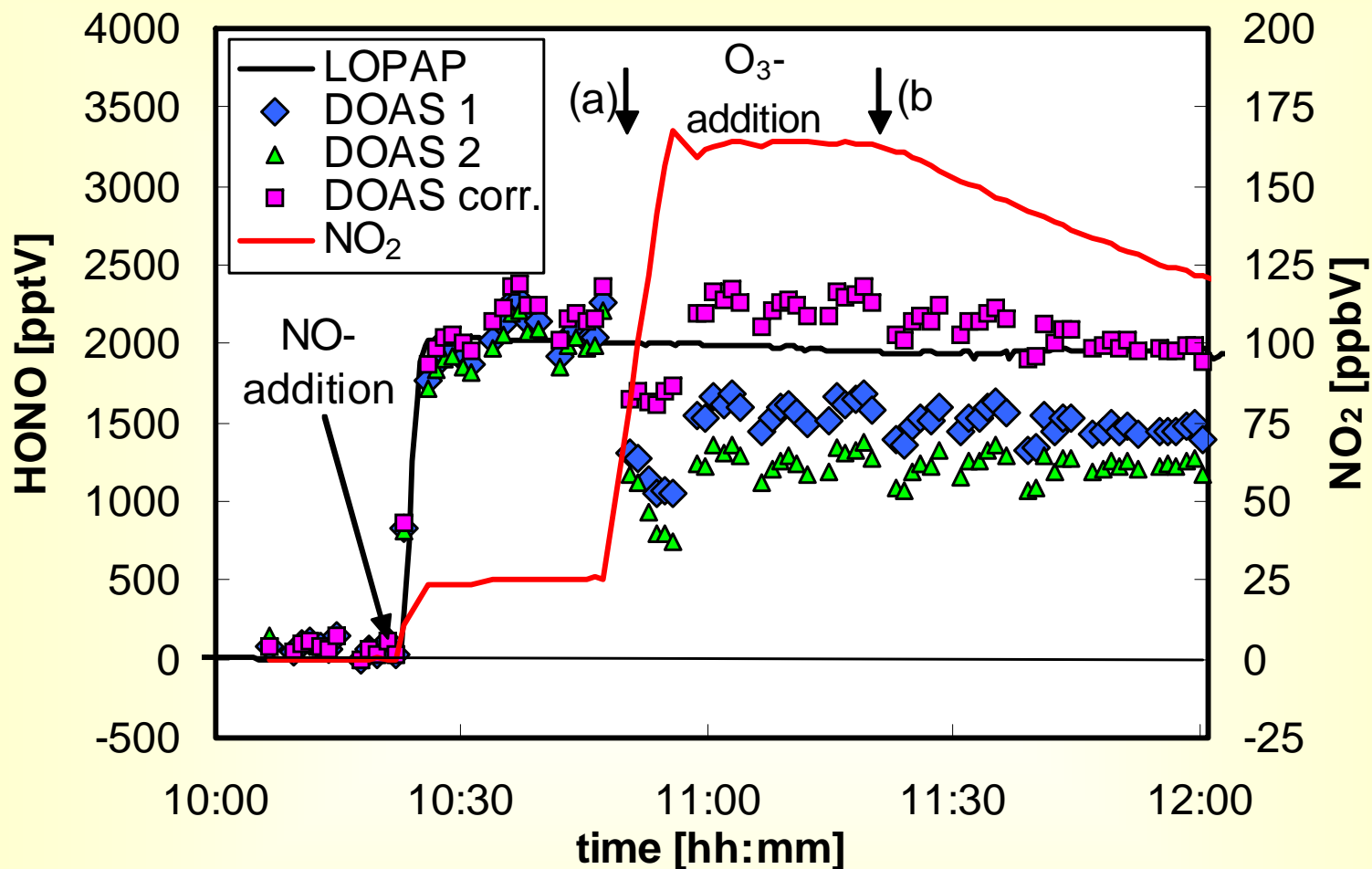
A Na_2CO_3 -coated annular denuder will removed interfering compounds, like phenols... (see *Gutzwiller et al.*, 2002)

○ NITROCAT: HPLC ↔ DOAS



Daytime $[\text{HONO}]_{(\text{chem})} > [\text{HONO}]_{(\text{DOAS})}$

- ☹ During the first campaign $[\text{HONO}]_{\text{LOPAP}} > [\text{HONO}]_{\text{DOAS}}$
during a photosmog experiment for high $[\text{NO}_2]$ in EUPHORE



○ DOAS problem: negative NO_2 -interference of 0.4-0.6 % HONO caused by the used NO_2 -reference spectra → must be corrected!

- Was this negative interference corrected in all former DOAS intercomparison studies? (*Febo et al.*, 1996; *Coe et al.*, 1997; *Müller et al.*, 1999; *Spindler et al.*, 2003)
- This could be another problem besides chemical interferences... (HONO_{DOAS} lower during the day caused by low HONO/NO₂...)
- But: was corrected for the intercomparison studies with the LOPAP instrument

LOPAP-Technique (*long path absorption photometer*)



LOPAP-Technique (*long path absorption photometer*)

○ Chemical instrument:

HONO sampled by a fast, selective chemical reaction in a stripping coil, converted into an azo dye, which is photometrically detected in long path absorption

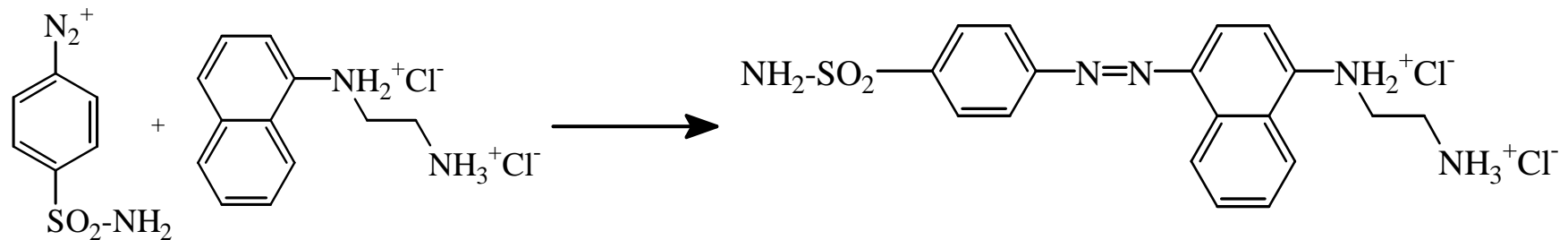
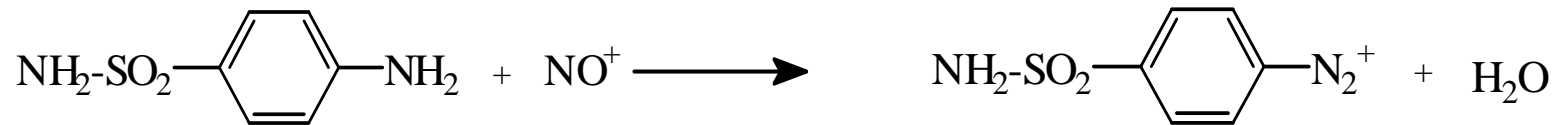
published in:

Heland, et al., *Environ. Sci. Technol.*, 2001, **35**, 3207-3212;

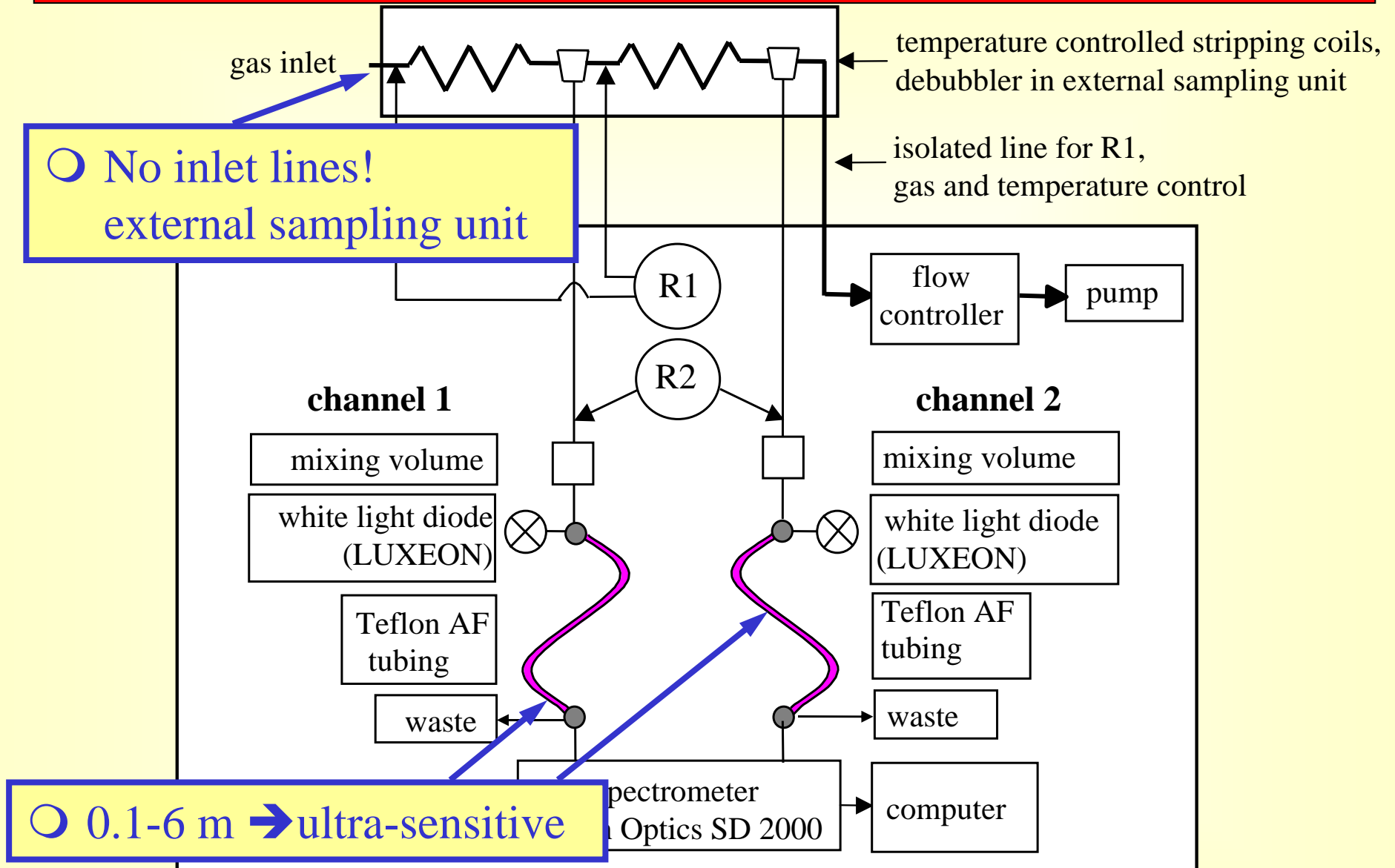
Kleffmann et al., *Environ. Sci. Pollut. Res.*, 2002, **9**, 48-54;

Kleffmann et al., *Atmos. Environ.*, 2006, **40**, 3640-3652

○ Reactions:

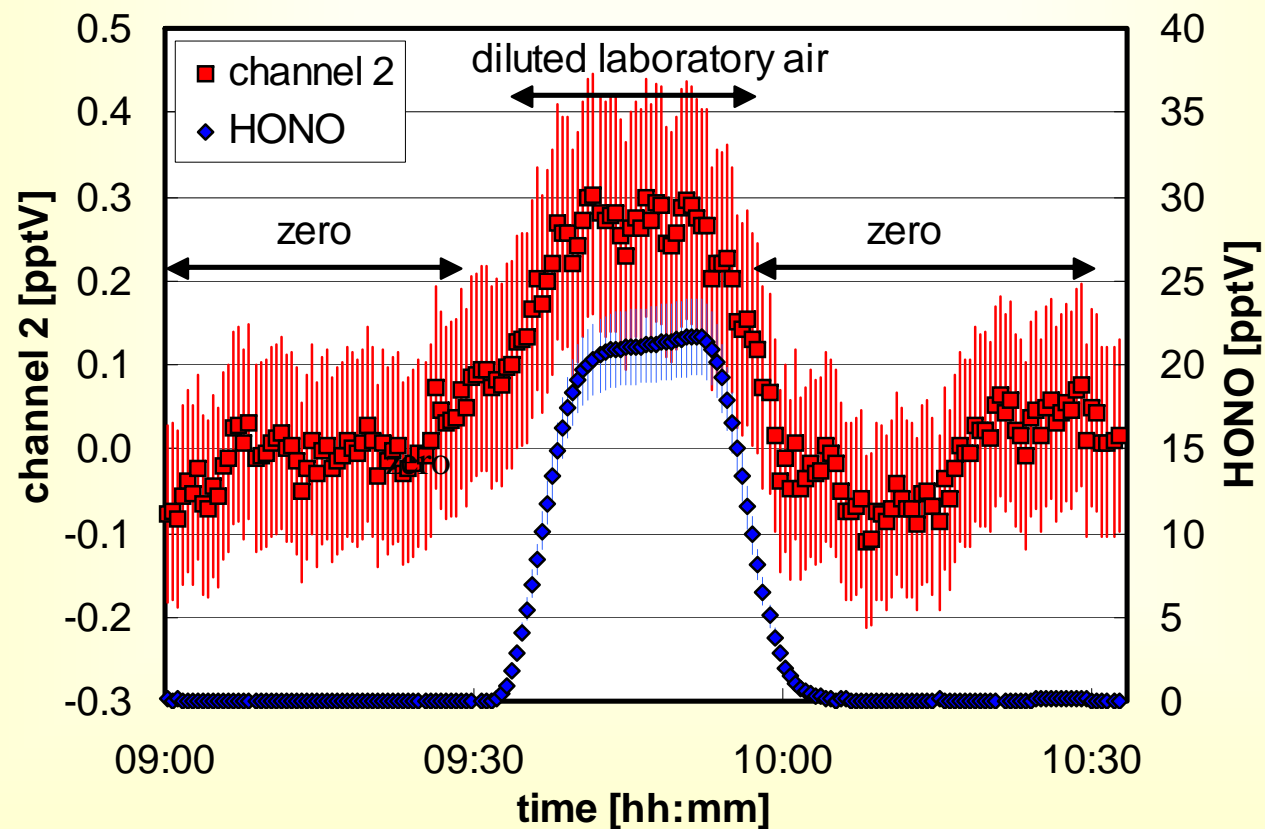


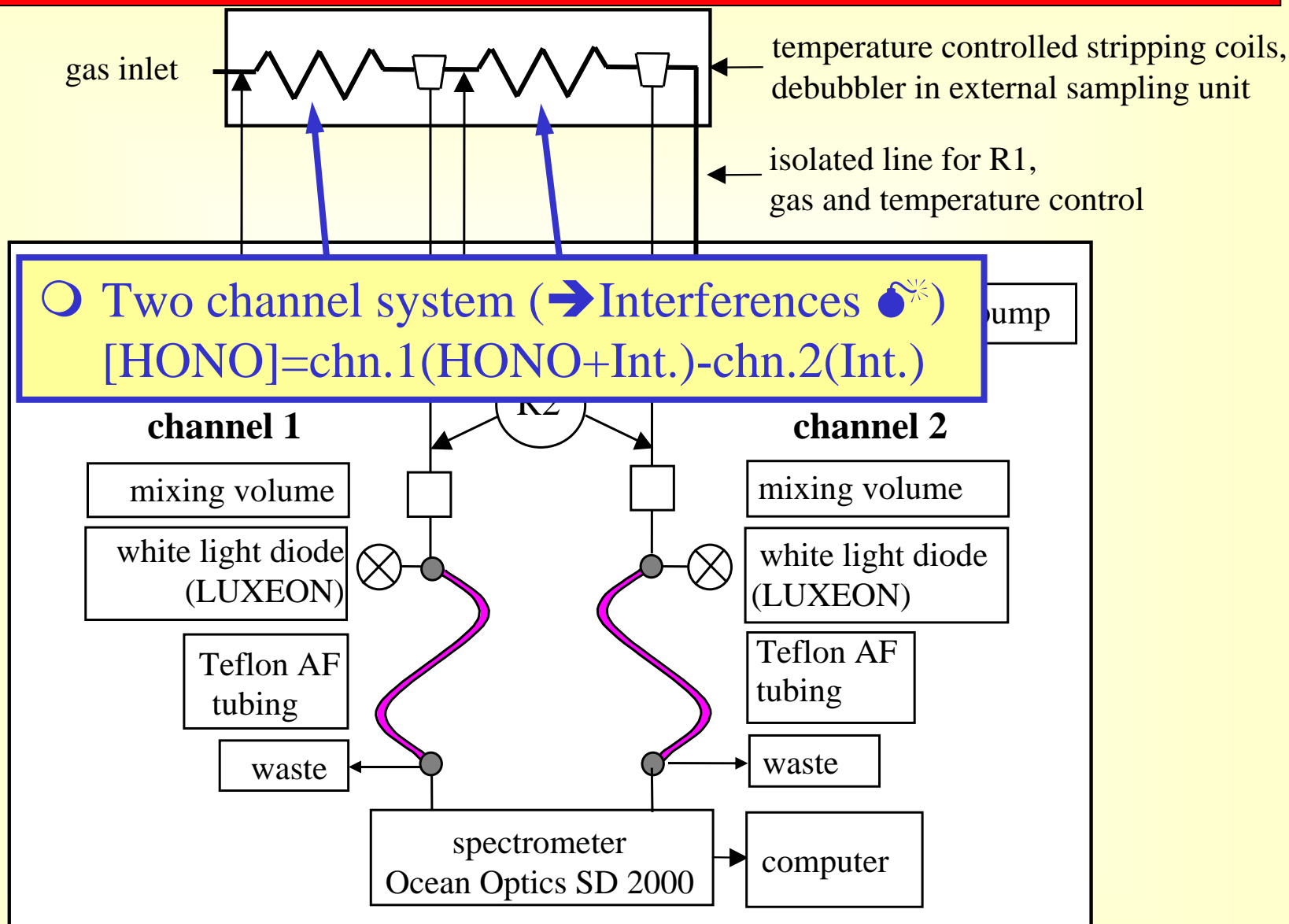
Formed azo-dye strong absorber: $\epsilon=50.000 \text{ M}^{-1} \text{ cm}^{-1}$, 540 nm)

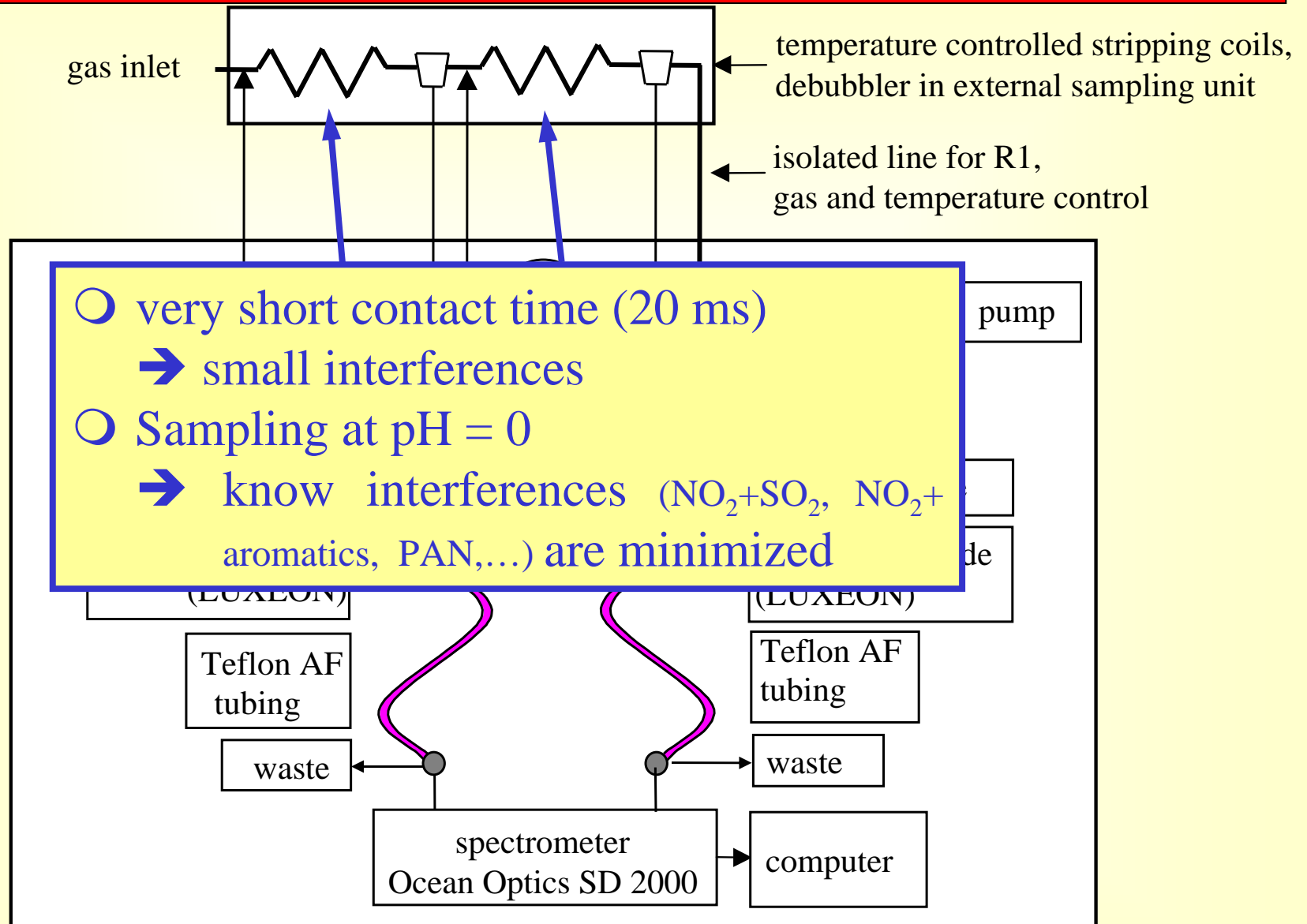


LOPAP-Technique (*long path absorption photometer*)

- DL: 0.2-2 pptV
- Time resolution: 7-2 min (10-90 % signal)





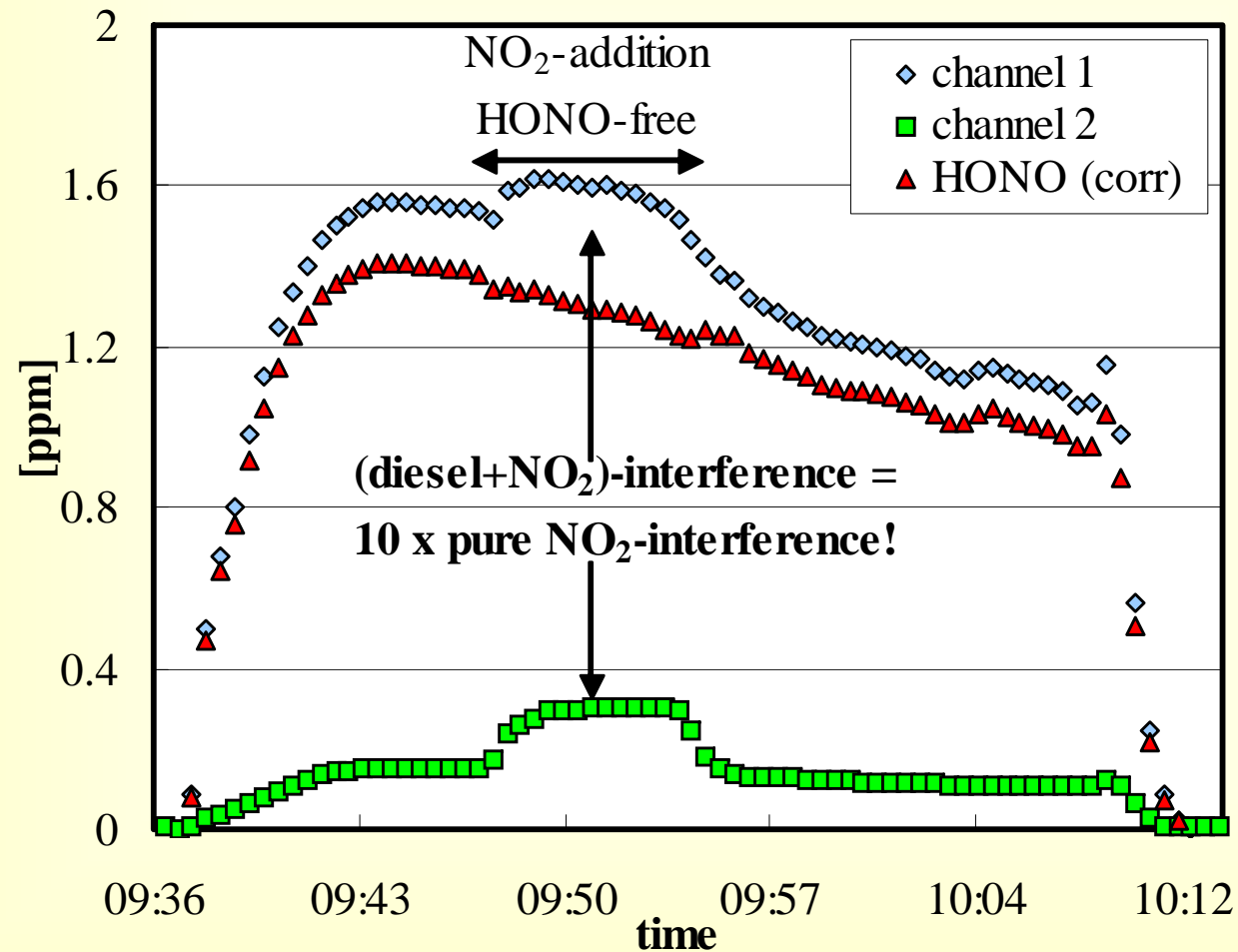


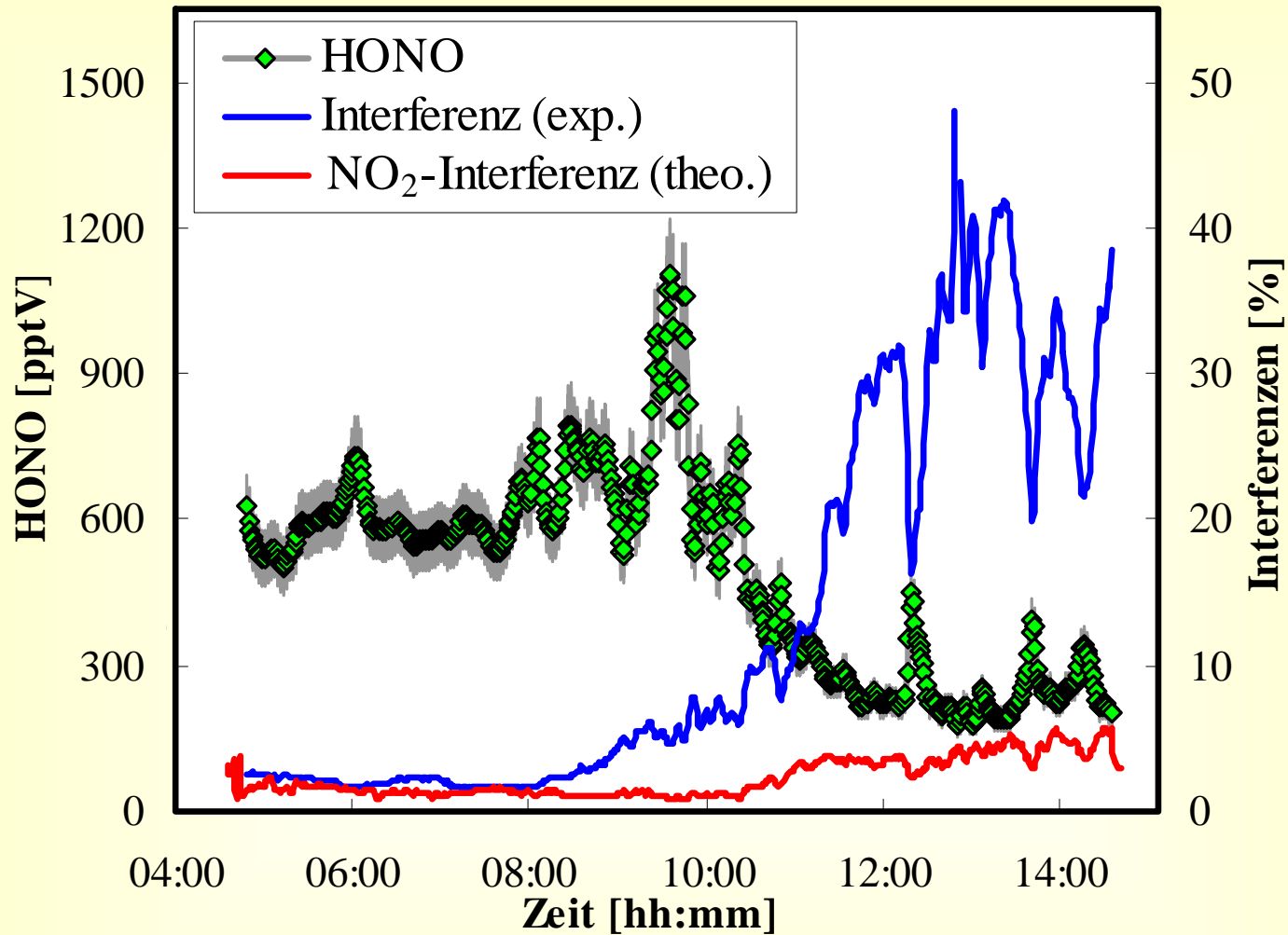
- Several interferences were quantified in the laboratory:

NO, NO₂, N₂O₅, O₃, O₃+HONO, H₂O₂, H₂O₂+HONO, NO₂+SO₂, HNO₃, HNO₃+HCHO, PAN, organic nitrates, NO_x+ethene, NO_x+toluene, NO_x+n-butane, NO₂+o-cresol, NO₂+diesel exhaust, particle nitrite...

- ➔ *Not measurable* or can be *corrected* for by the two-channel design of the instrument

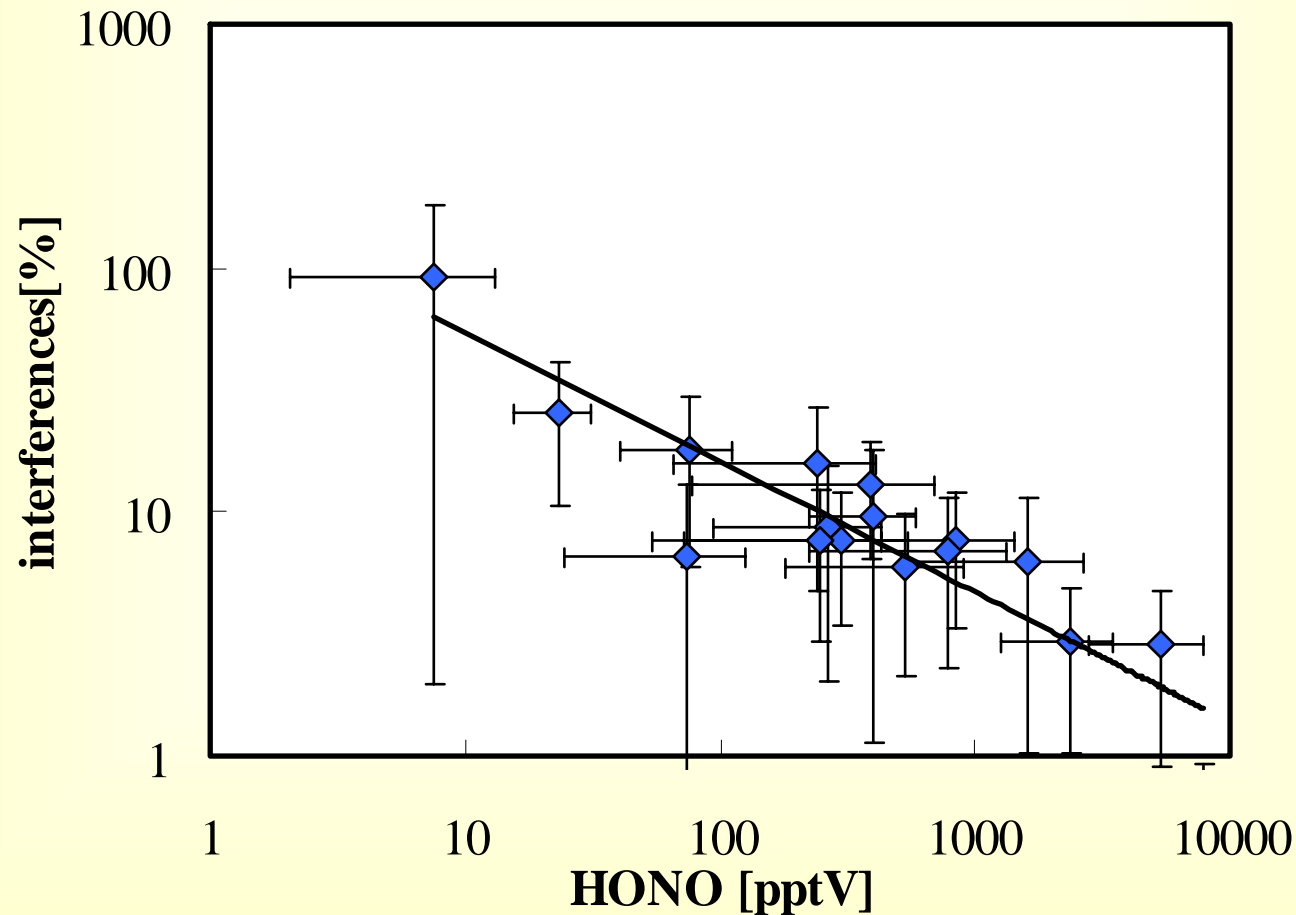
- 💣 NO₂+diesel exhaust interference significant! 😊 Is well corrected!
In contrast to a WEDD (see *Gutzwiller et al., 2002*)



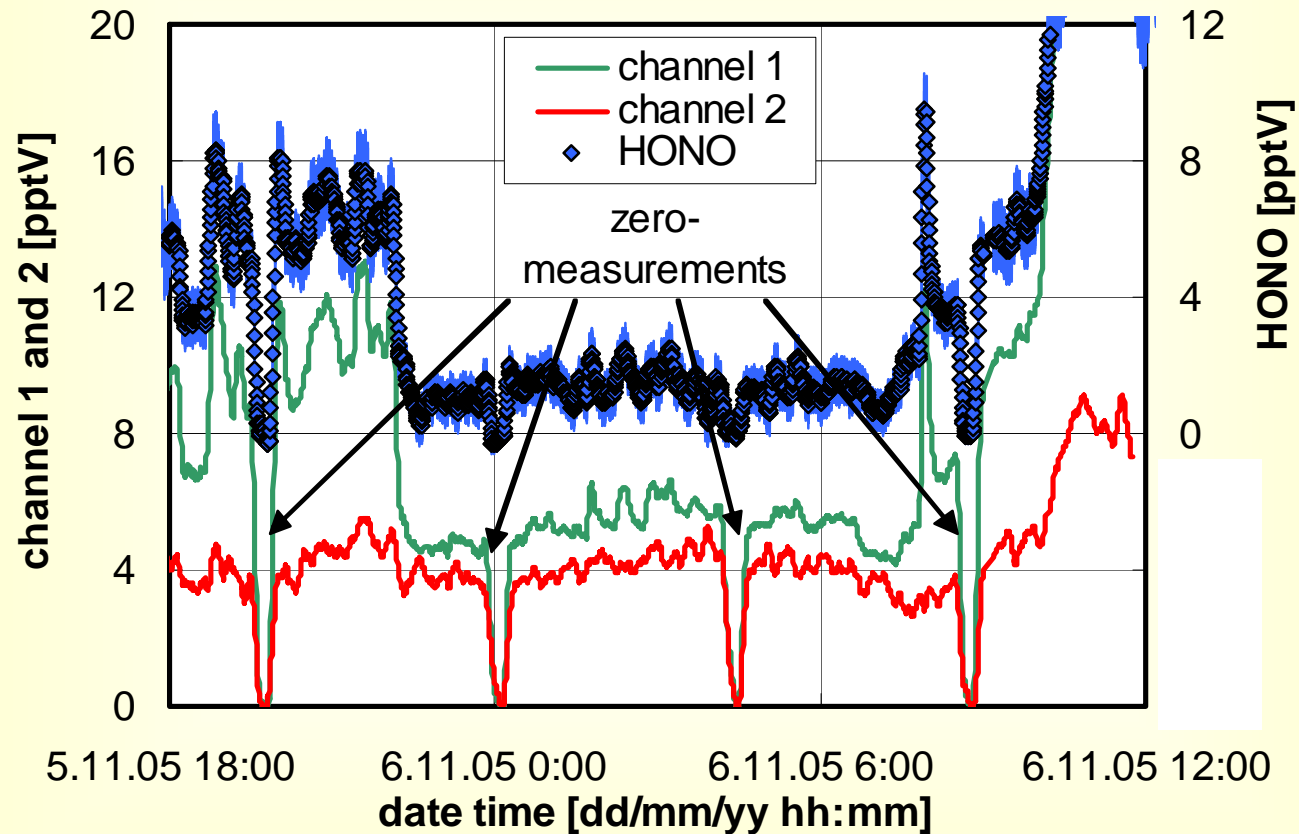


○ Measured interferences cannot be explained by known (pure) interferences

- Measured interferences increase with decreasing HONO-concentration, can explain deviations from intercomparison studies...



- Interferences are of special importance for remote conditions (here up to a factor of 4 correction...)



○ Interferences are of special importance for remote conditions
(here up to a factor of 4 correction...)

○ $\text{HONO/NO}_x \text{ (LOPAP)} = 2.5 \text{ and } 4.6 \%$ *Zugspitze and
Jungfraujoch*

⇔ Compared to other remote measurements using instruments
which do not correct interferences:

○ $\text{HONO/NO}_x = \sim 20\text{-}30 \%$ *Huang et al., 2002,
Zhou et al., 2007*

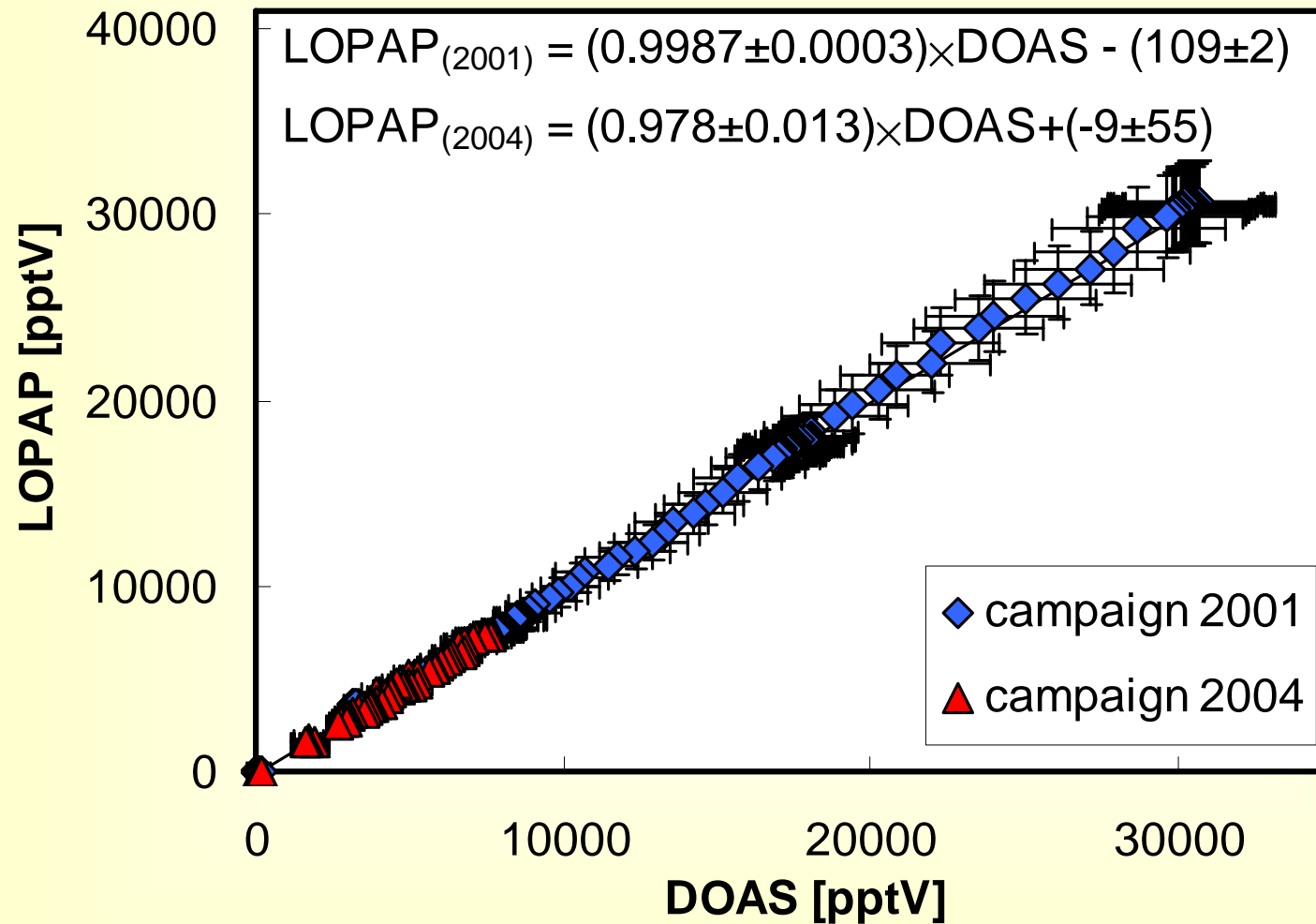
○ $\text{HONO/NO}_x = \sim 25\text{-}100 \%$ (polar..) *Beine et al., 2001
Jones et al., 2007*

- Several interferences were quantified in the laboratory:

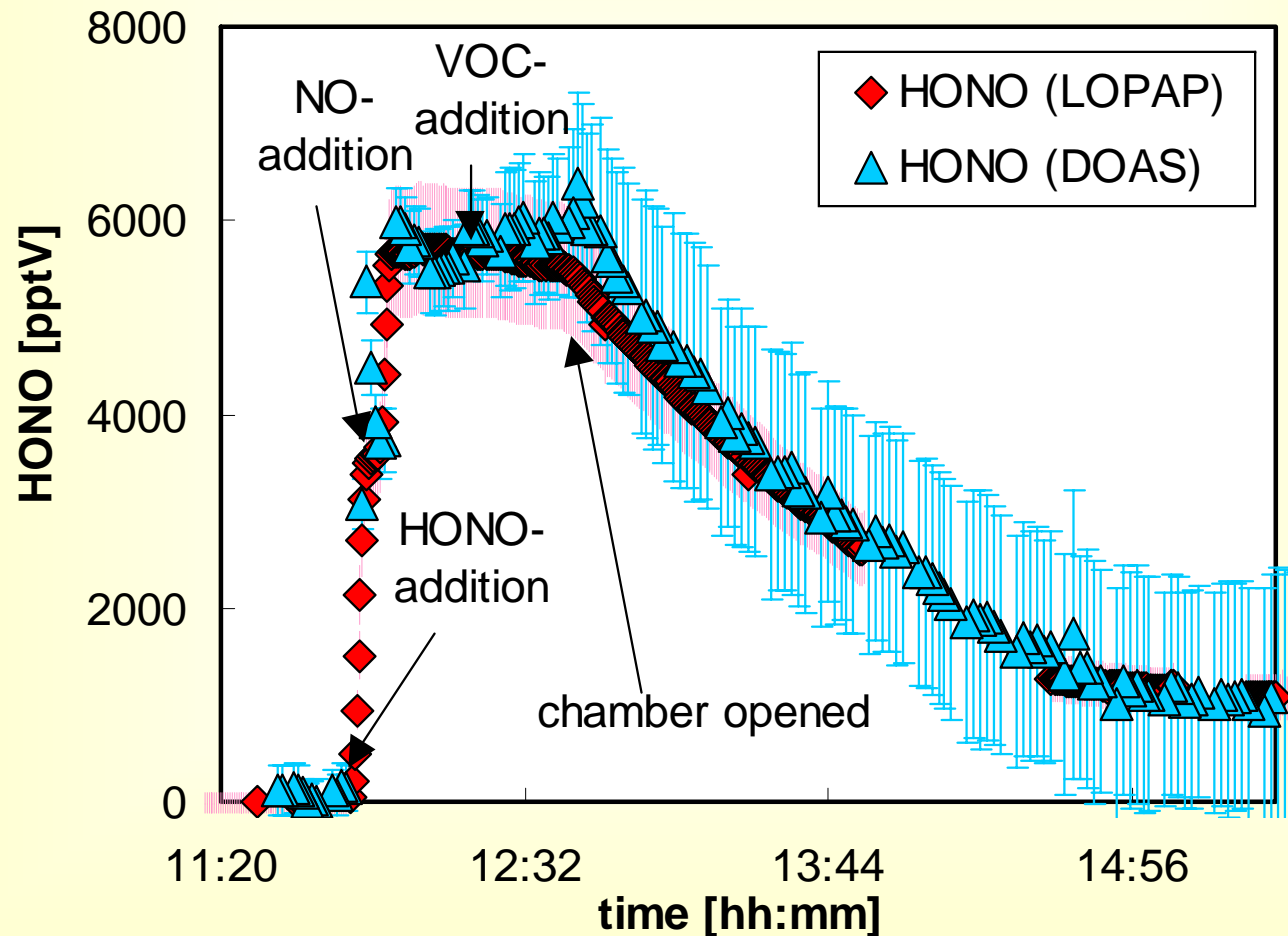
*NO, NO₂, N₂O₅, O₃, O₃+HONO, H₂O₂, H₂O₂+HONO,
NO₂+SO₂, HNO₃, HNO₃+HCHO, PAN, organic nitrates,
NO_x+ethene, NO_x+toluene, NO_x+n-butane, NO₂+o-cresol,
NO₂+diesel exhaust,...*

- ➔ *Not measurable or can be corrected for by the two-channel design of the instrument*
- 💣 unknown interferences might be still significant...
- ➔ Intercomparison with an optical instrument under “real world” conditions

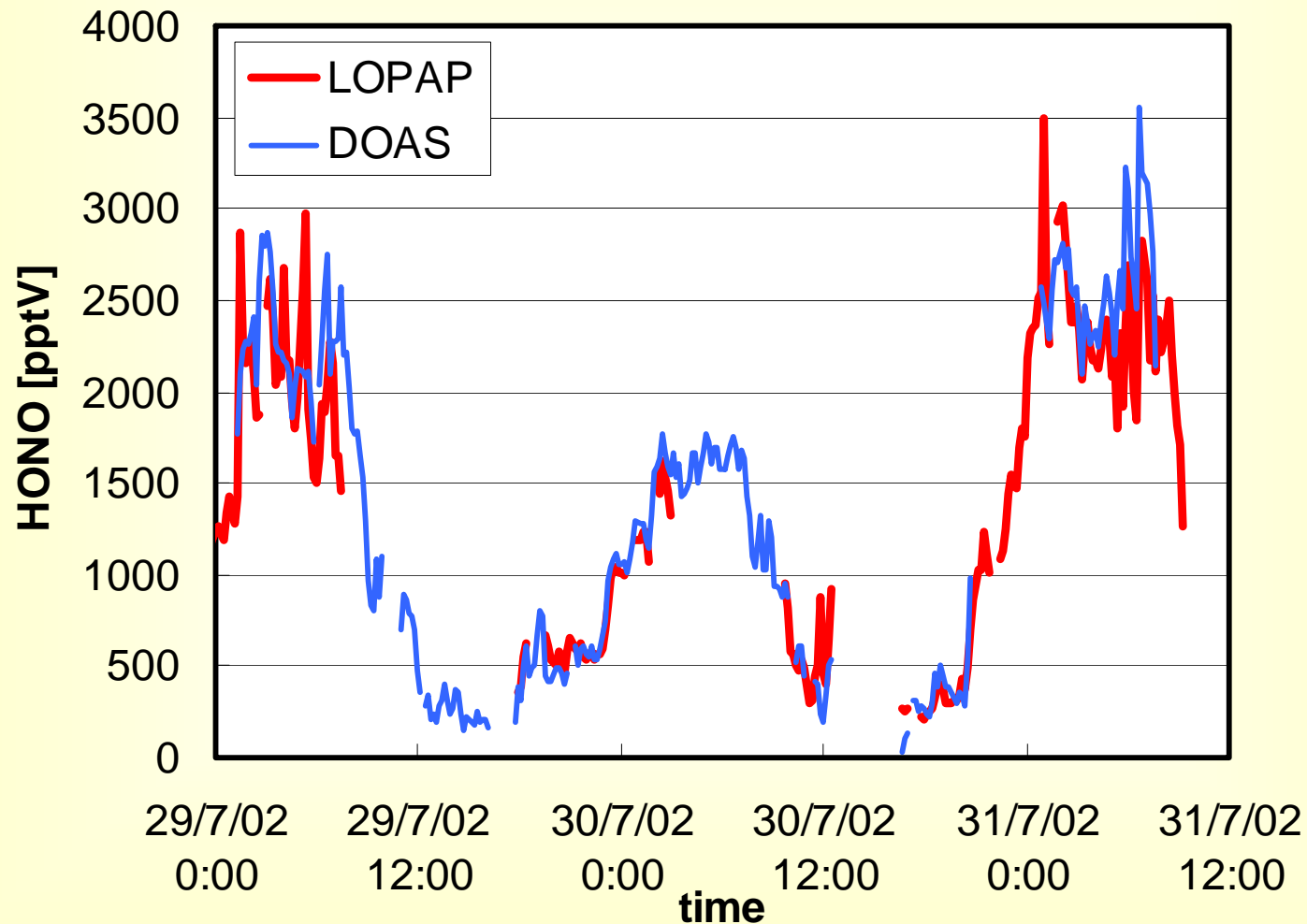
☺ Pure HONO/NO_x mixtures in the dark (EUPHORE)



- ☺ Photosmog experiment in a smog chamber (200 ppbv NO_x, 150 ppbv toluene, 450 ppbv ethene, 450 ppb n-butane + hv)

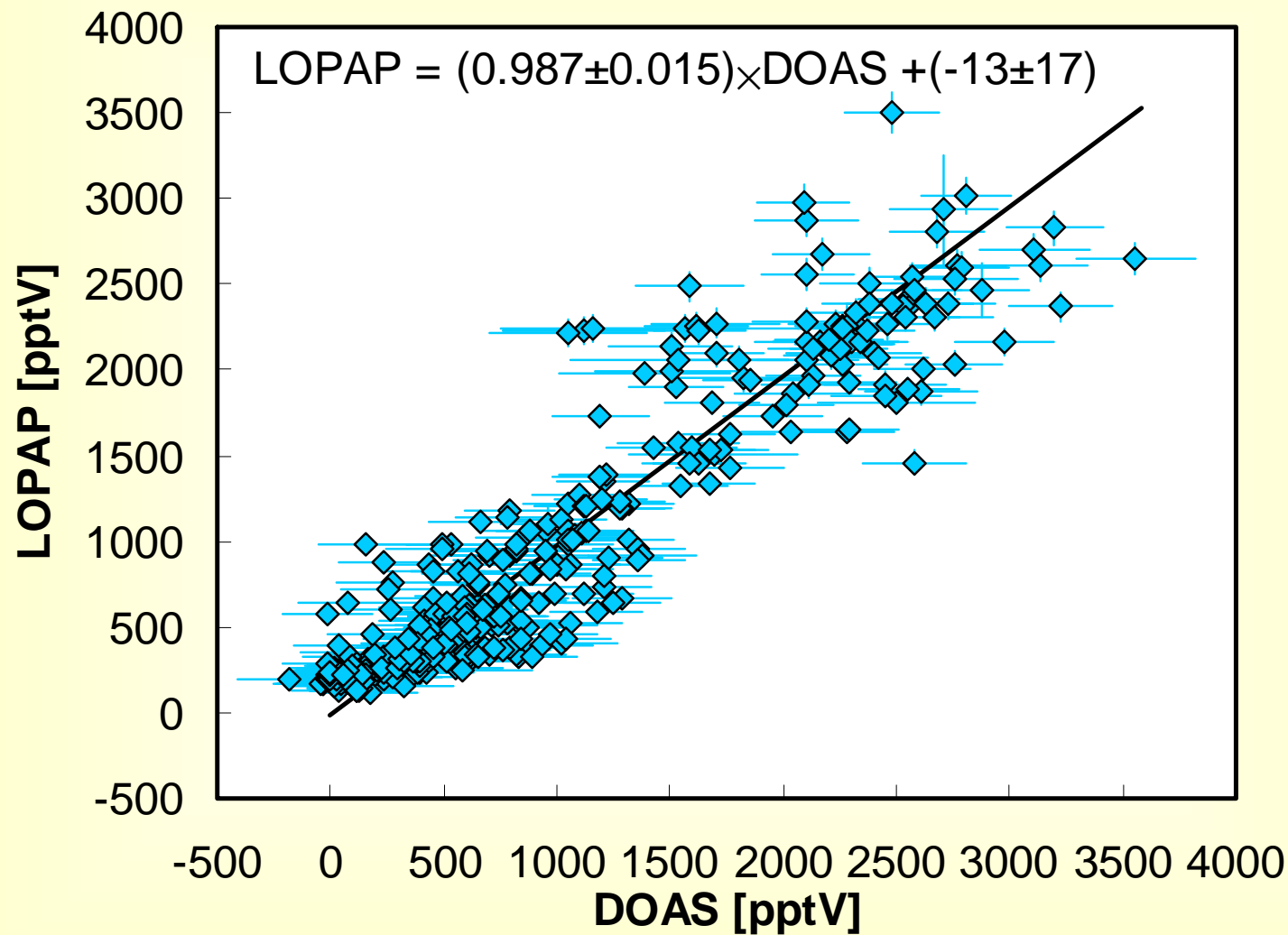


☺ Field measurement in Milan (FORMAT) using an open White mirror system for the DOAS (→ same air mass)

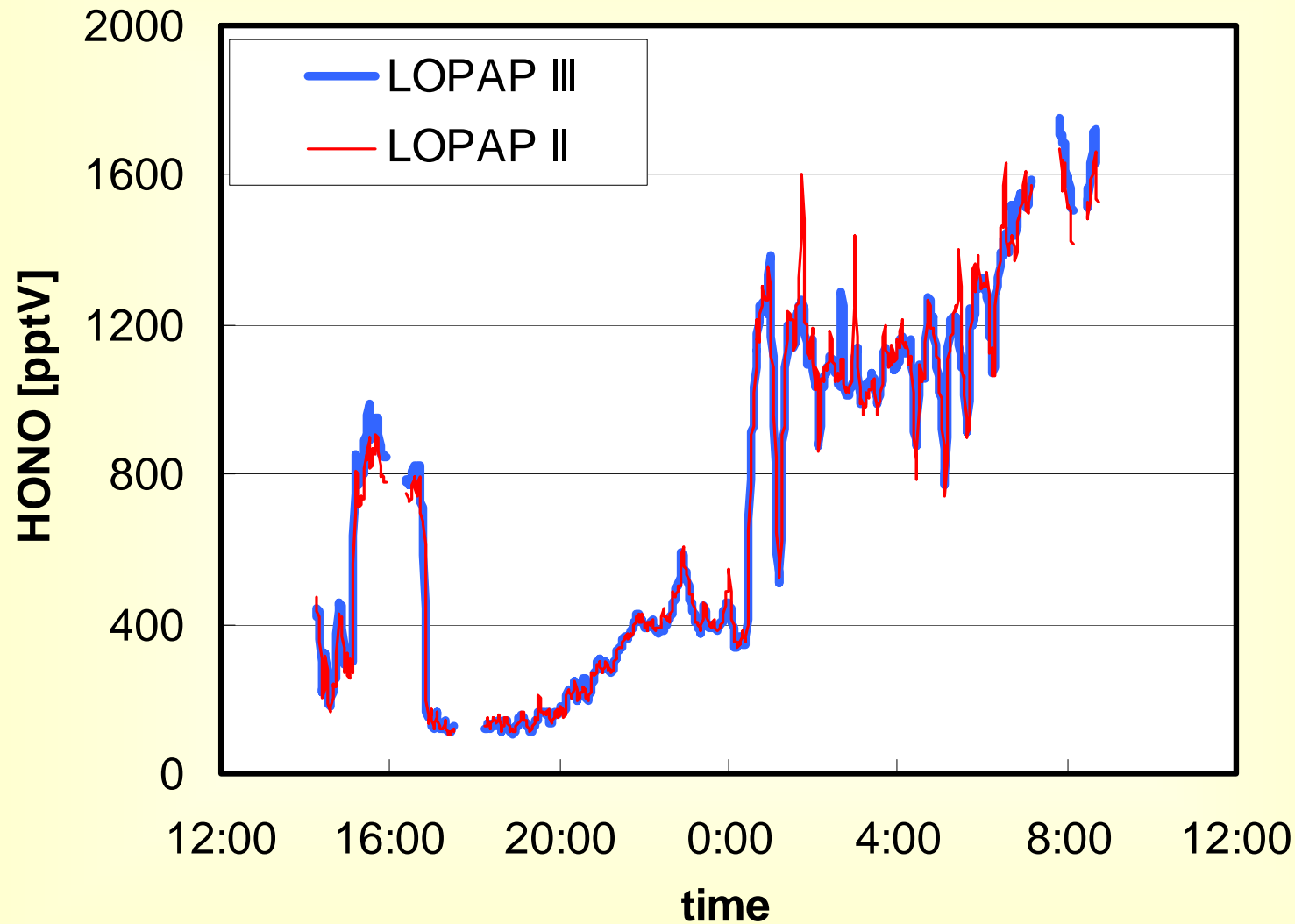


HONO workshop, Wuppertal, 04.03.08 **Intercomparison a) field campaign**

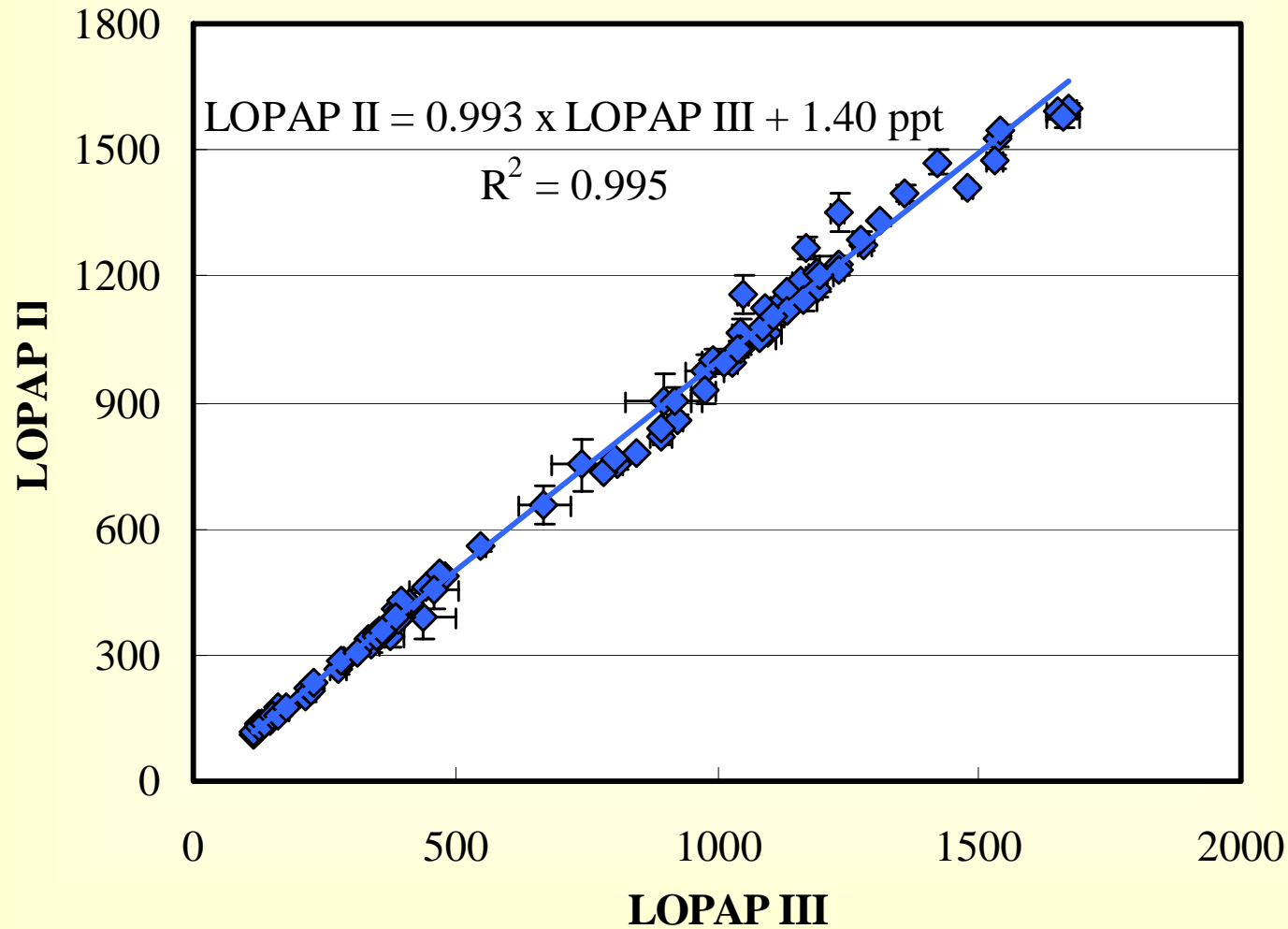
☺ All simultaneous 10 min data:



☺ Intercomparison between two LOPAP instruments: high precision



☺ Intercomparison between two LOPAP instruments: high precision



- ☺ Excellent agreement between the LOPAP and the DOAS instrument for all conditions including daytime measurements
- 💣 Interferences of LOPAP instrument are significant during the day
- ☺ Are corrected for by the two-channel design of the instrument
- ➔ Validation of chemical instruments against an optical instrument free of sampling artefacts is of paramount importance
- ☺ Recent results from the LOPAP instrument about high contribution of HONO to the primary OH sources were confirmed

- ☺ Wet chemical instruments have high sensitivity
- ☺ Reasonable time resolution
- ☺ Cheaper than spectroscopic instruments
- ☺ Easy to operate
- ☹ However, interferences and inlet artefacts are a severe problem
- ➔ Should be validated against spectroscopic instruments (LIF, DOAS...). *That's why we are here!*

- European Commission within the NITROCAT project (Contract no. EVK2-1999-00025),
- European Commission within the FORMAT project (EVK2-CT-2001-00120)
- Deutsche Bundesstiftung Umwelt (DBU) under contract No. 12634. R.
- QUMA Elektronik & Analytik GmbH, Wuppertal

Thank you for your attention!