Measurements of Nitro-Phenols

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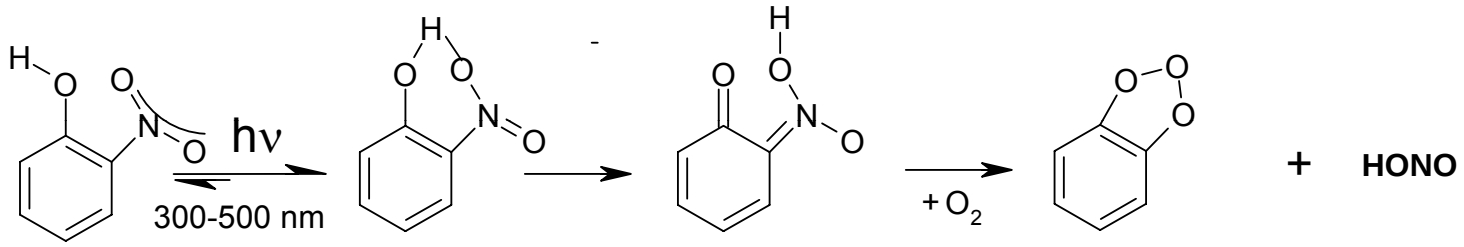
Importance of *ortho* nitrophenols (esp. 2-Nitrophenol in Atmospheric Chemistry

Generation of Hydroxyl Radical via HONO

Irradiation (λ = 300-500 nm) of 2-Nitrophenol to give ȮH, atm. vacuum cleaner



HONO + hν ⟶ NȮ + ȮH

Nitrophenols in general may have health or ecological consequences

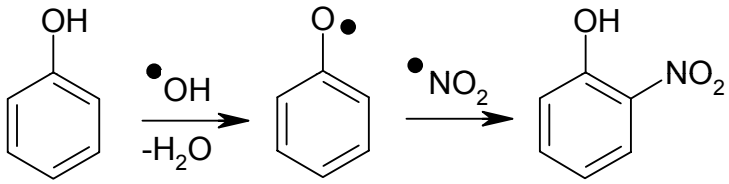
Potent vasodilator
Phytotoxic,
Female hormone mimic: Estrogenic & anti-androgenic

Sources & sink of atmospheric 2-Nitrophenol

SOURCES

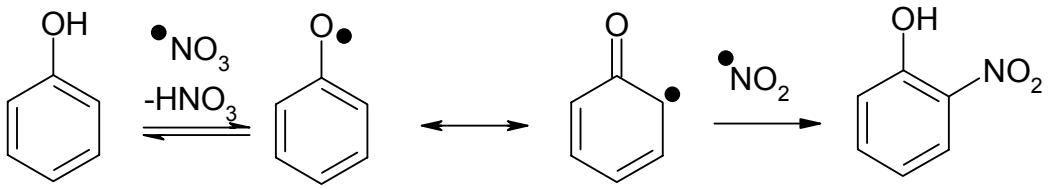
1. Emission from combustion process of motor vehicles
2. Degradation of pesticides & herbicides
3. Photo-oxidation (ȮH initiated) from aromatic hydrocarbons

Day time formation:



Phenol 2-NP

Night time formation:



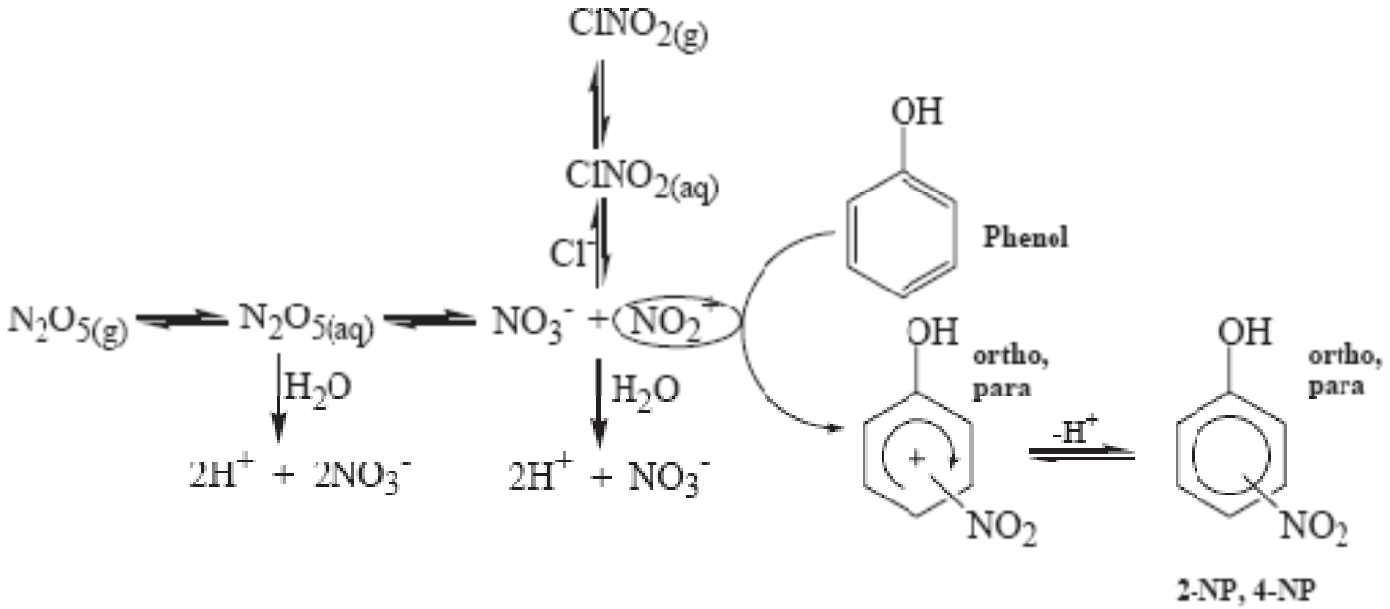
Phenol Phenoxy radical 2-NP

SINK

1. Gas phase reaction with hydroxyl radical – minor effect
2. Wet deposition, i.e., scavenging by rain & fog – major effect
   (i) Nitration of 2-Nitrophenol to 2,4-Dinitrophenol
   (ii) Reaction of 2-Nitrophenol with ȮH and $\dot{N}O_3$.

Potential relation to $ClNO_2$

suggested interconversion of N_2O_5 and $ClNO_2$ and subsequent reaction with phenols (nighttime):



Harrison et al., Atmos. Env., 2005

In numerous field experiments in US urban areas we have seen daytime gas phase HONO concentrations from sub- to 2 ppbv levels on wet denuder ion Chromatography measurements. Initially they were ignored as artifacts. Later direct spectroscopic measurements including both DOAS and TDLAS have confirmed this. Recent wet LOPAP measurements also reconfirm this.

In TEXAQS 2000 Houston, this daytime HONO ranged from 1-2 ppbv HONO. This is a substantial source of OH. Bejan (Phys. Chem. Chem. Phys., 2006, 8, 2028–2035) suggests that 100-500 pptv HONO/h will be formed from nitrophenols in semi-urban areas. This alone can account in Houston for the unexplained HONO source.

History of 2-Nitrophenol Measurement

5824 S.E. Lafa
April 1984 ([2-
(Leuenberger et al.,

Switzerland
)
988, 511–515)

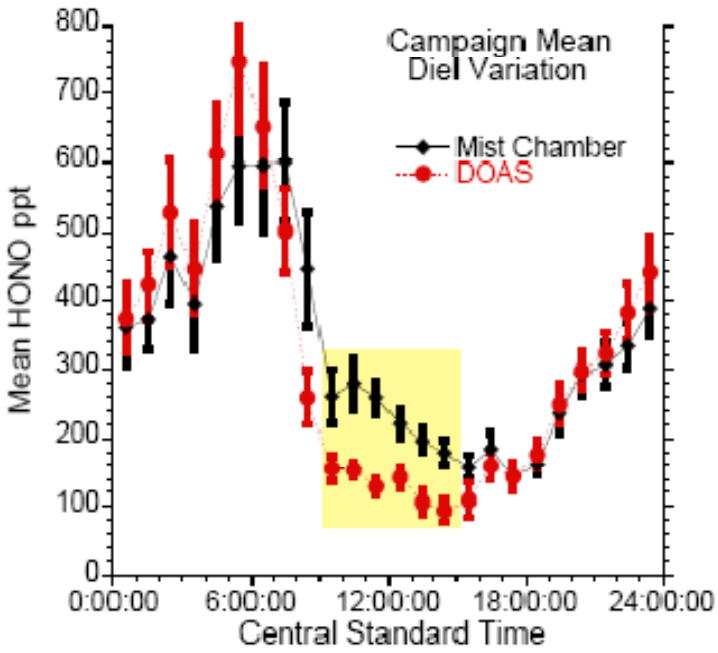
2-Nitrophenol in Houston (2009)?

Great Dun Fell summit (848 m), England
May 1993, ([2-NP]= 1-6 ng.m^{-3})
(Lüttke et al., Atmospheric Environment, 31, 1997, 2637–2648)

Villa Ada Park, Rome, Italy
April 2003 ([2-NP]=10.4 ng.m^{-3})
(Cecinato et al., Chemosphere, 59, 2005, 679–683)

NPs as potential interferents in HONO measurements

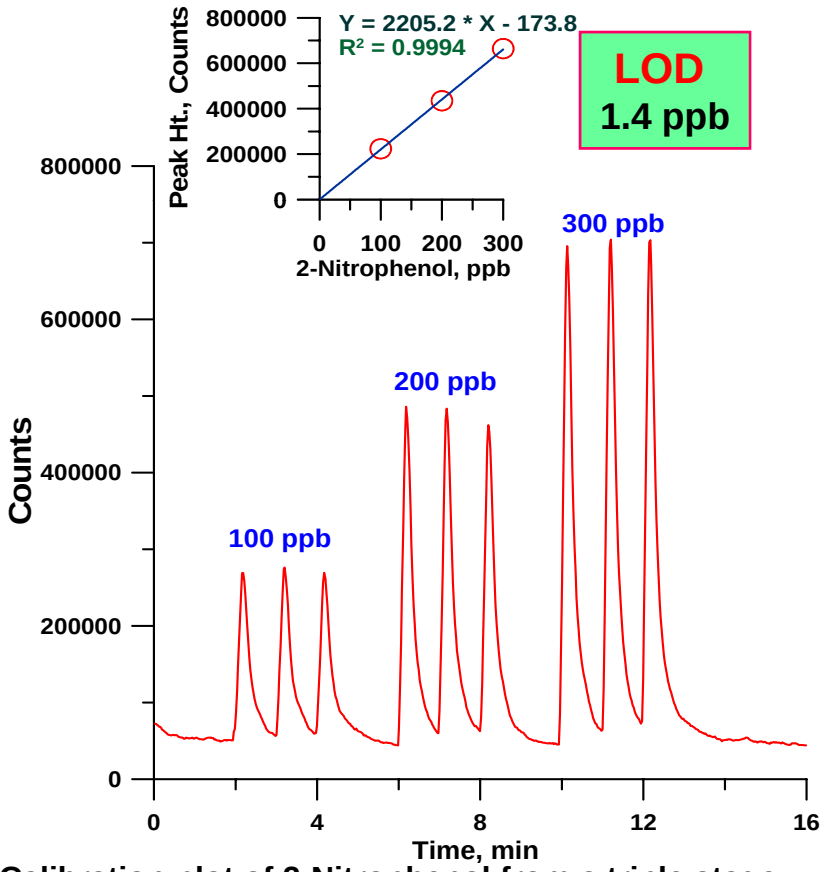
- **NPs are highly polar and generally show high solubility (Sander, 1999)**
- **NPs are potential candidates as interferents in wet-chemistry based instruments, including HONO measurement systems.**
- **Data so far is virtually unavailable, but HONO intercomparison performed in Houston suggest an interferent under specific polluted conditions which so far has not been able to identify (Stutz et al., 2008).**



Measurement of 2-Nitrophenol at UTA

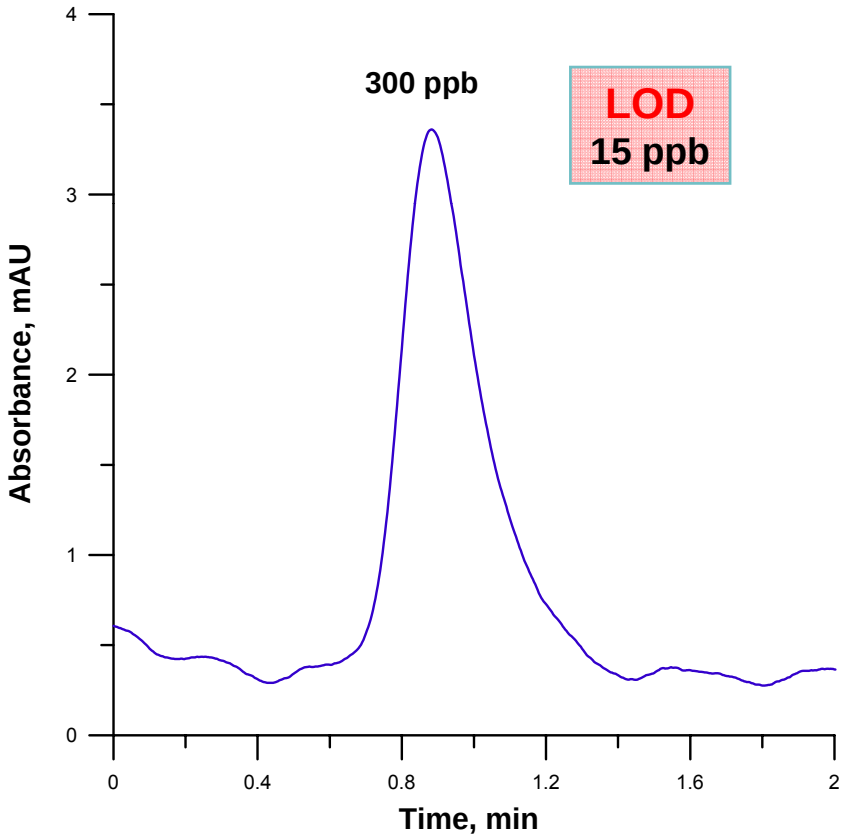
$[2\text{-Nitrophenol}]_{air}$ = 500 $ng.m^{-3}$ Ξ 500 ppb solution
(Air sampling Rate = 100 L/hr & Extraction with 100 µL ACN)

1. MS/MS detection, preliminary



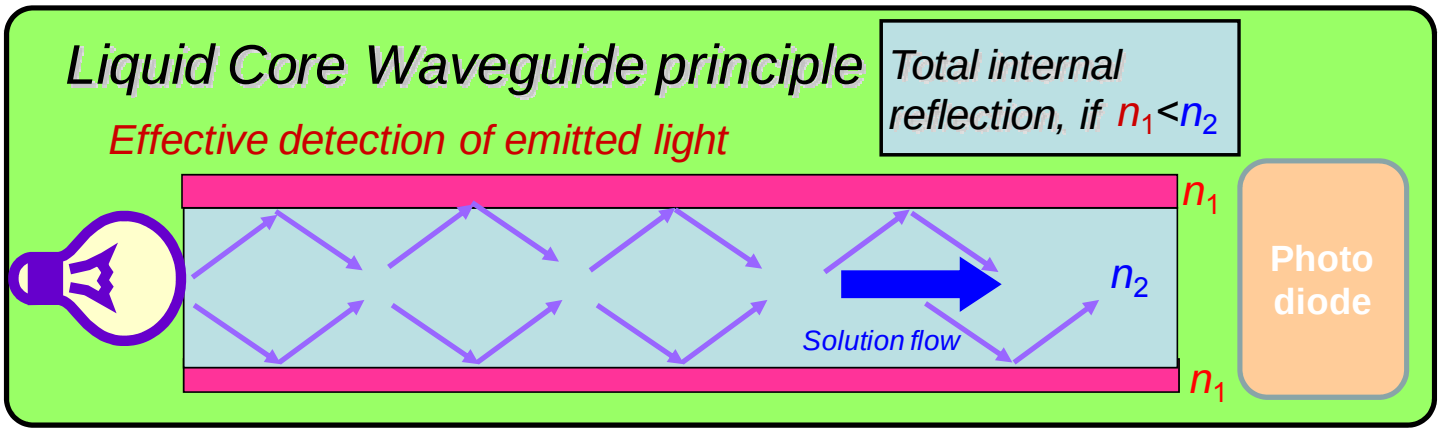
Calibration plot of 2-Nitrophenol from a triple stage quadrupole mass spectrometer (TSQ-MS) at m/z = 108. Carrier: 10 mM Ammonium carbamate; FR: 250 µL/min, Injection volume: 20 µL.

2. IC-PDA detection

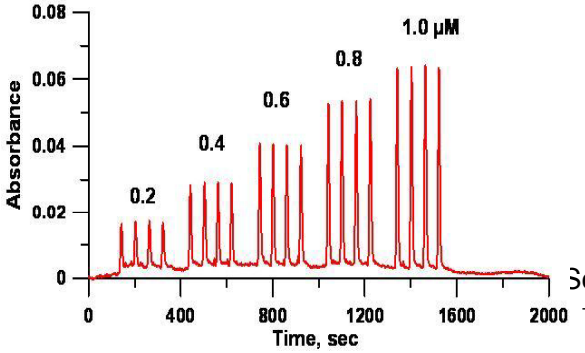


Chromatogram of 300 ppb 2-Nitrophenol obtained from Ion Chromatograph equipped with a PDA detector. Mobile phase: 20 mM Na_2CO_3/ 10% ACN; FR: 1 mL/min.; Injection volume: 50 µL, λ = 400nm.

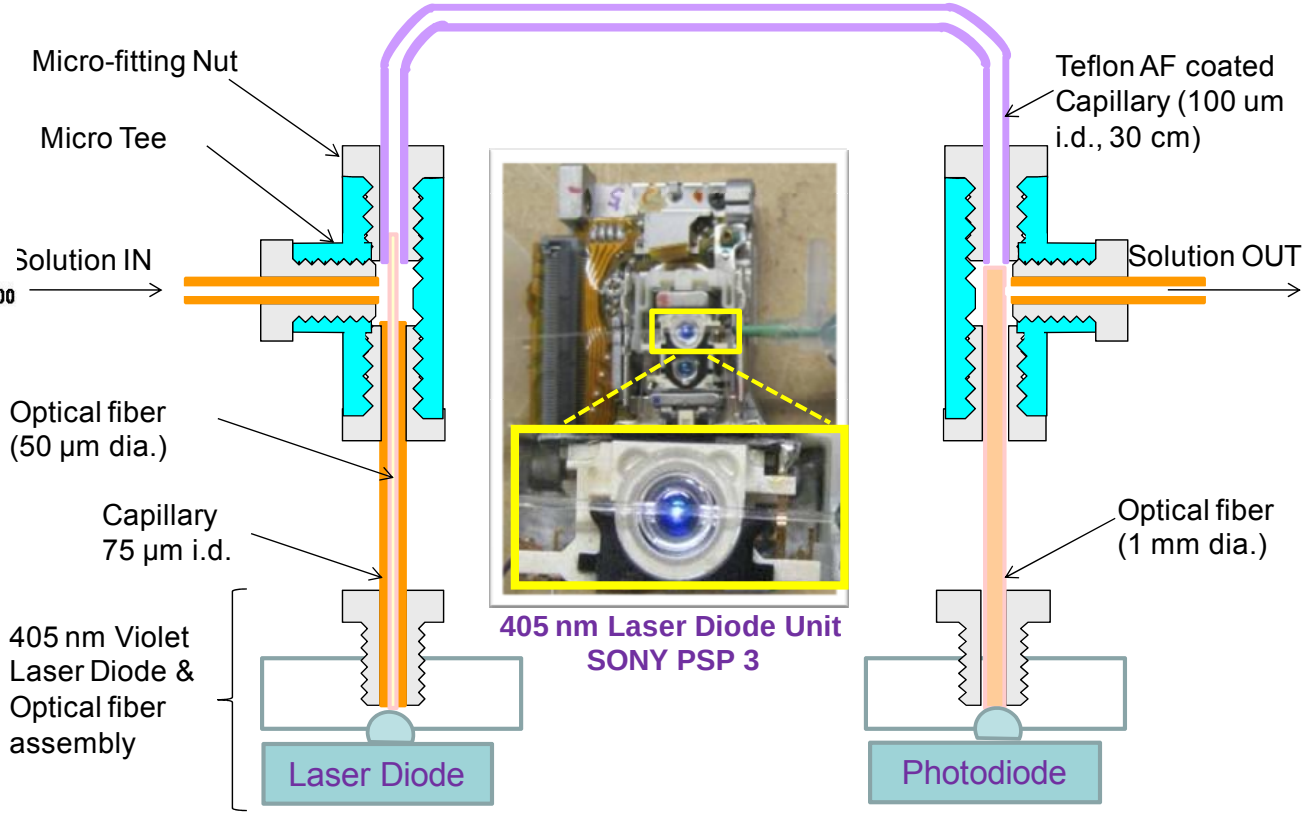
Liquid Core Waveguide Absorbance Detector



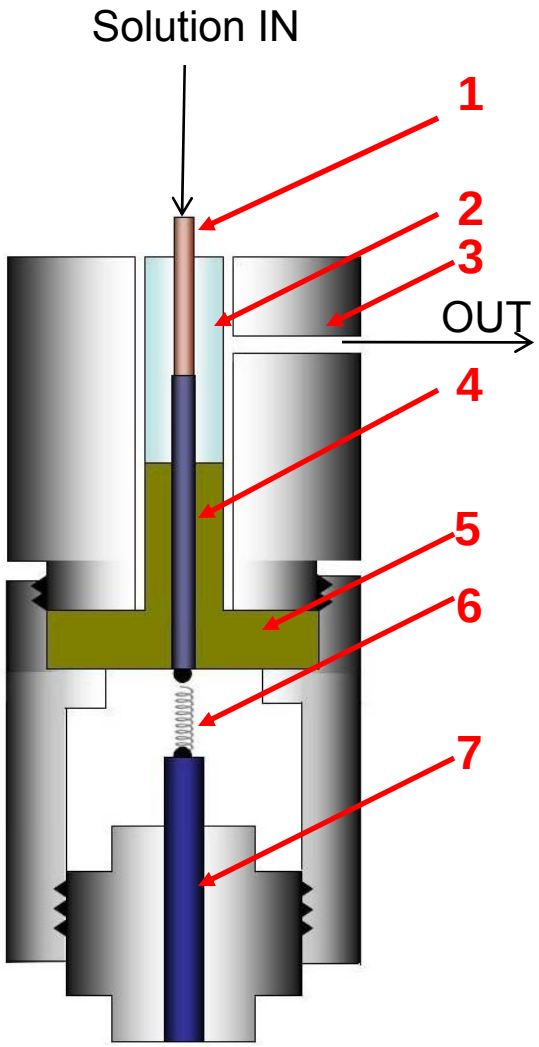
Our Preliminary Work



LOD 10 cm cell ca. 5 ppb, should be 10x better with a 1- m cell, still <8 µL in volume, very inexpensive fieldable nondestructive LC detector



Amperometric-type electrochemical detector



Claimed LOD (large volume injection)**: 4 -18 ppt for *o-*, *m-*, *p-* Nitrophenol**

Experimental condition

- **Column: 70 x 0.34 mm, 5 µm Lichrosorb RP-18**
- **Eluent: acetonitrile - 0.1 M sodium perchlorate in distilled water (1:9)**
- **Flow rate: 15 µL/min**
- **Sample volume: 20 µL**
- **Gold electrode potential: +1.5 V**

Design of electrochemical detector cell

1)100 x 0.34 mm packed fused silica capillary column
2)1.6 x 0.52 mm fluoroplastic capillary tubing;
3) cell body;
4) 2 x 0.48 mm measuring electrode;
5) fluoroplastic insert;
6) spring contact;
7) electrical conductor.

Reference: Ruban, V. F. J. HRC CC 16: 663-665 (1993)

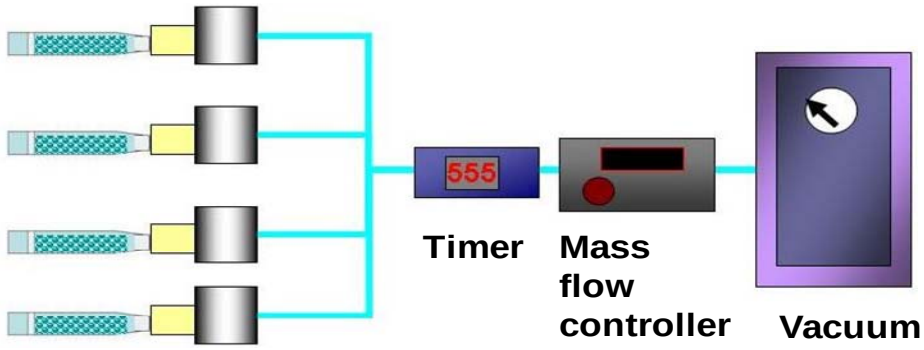
Trapping of 2-Nitrophenol & Auto sampling system

Tested cartridge materials

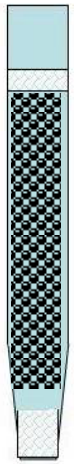
- **XAD-2**
- **XAD-4**
- **XAD-16**
- **Silica gel (>120 mesh)**
- **Silica gel (80-120 mesh)**
- **Silica gel (35-60 mesh)**

Best % Recovery for 35-60 mesh Silica gel

Auto-sampling unit



Cartridge



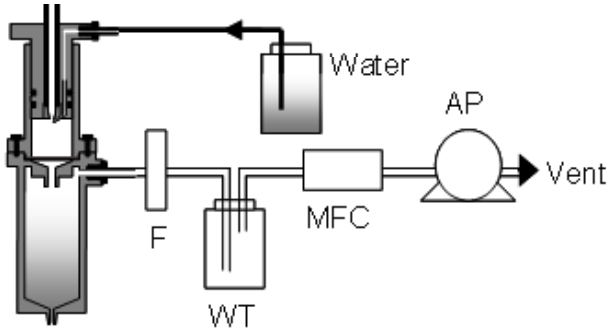
Glass wool

Packing material (35-60 mesh silica gel)

Glass wool

Will high flow rate gas particle concentrators that semicontinuously generate a liquid extract work?

Takeuchi, Dasgupta, et al. Anal. Chem. 2005, *77,* 8031



Relation to SHARP

- **Measurements of NPs will be performed during following SHARP experiments:**

- **Traffic Related Emissions of HONO and HCHO (TRENF)**
  - **planned for February- March 2009**

- **HONO Levels and their Impact on Radical Levels in Houston: Intercomparison of different analytical methods to measure ambient HONO (HINT)**
  - **planned for April- May 2009**

- **Study of HONO Surface Fluxes (HONO-FLUX)**
  - **planned for June- August 2009**

Timetable

(a) Create/synthesize a library of relevant NPs 0-2 mo
(b) Chromatographic Separation Method 0-4 mo
(c) Scouting Separations in rainwater 2-4 mo
(d) In the field sampling and measurement off and on during 4-10 mo
(e) Sorbent selection has already begun and settled on silica gel
(f) Prepare Sorbent cartridges for Rappenglueck group and automated sampler, 30 min-1-h resolution 0-4 mo
(g) Develop continuous sampler and analyzer 0-6 mo
(h) Deploy in HINT and HONO-Flux, Save some samples for later MS/MS analysis and confirmation 7-10 mo
(i) Analysis in the lab 11-12 mo
(j) Data analysis and preparation of Final Report 12-14 mo

Budget Breakdown
Approx k$

Salary and Fringe	
1 Graduate Student, 1 postdoctoral fellow	74.1
Graduate tuition	5.8
Equipment (Multiposition Sampler Engine)	17.0
Field Travel plus one meeting	16.5
Supplies	20.0
Overhead	16.6
Total	**150.0**