New data products and processing chain

Development of measurement standardization and a data submission protocol for VOCs based on PTRMS and TOF-MS measurements

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Inlet (recommendation):
~4mm ID PFA tubing, max 15m, flow 2 L/min,
protected by PFA filter holder with 47mm PTFE filter 5 µm pore size
PTR-MS samples from this inlet line with a short, low volume (1/8“or 1/16“) line.
Recommended materials: PFA, PEEK

Background determination:
The 2L main sample flow is passed through a Pt catalyst at a temperature of 350 C.

Critical instrument settings (recommendation):
Drift tube pressure: 2.2 mbar
Drift tube voltage: 600V
Drift tube temperature: 50C
Voltage between last drift ring and exit lense: 30V (instrument dependent, maybe define a procedure to optimize this)
Ratio O2+/H3O+ below 0.03

PTR-TOF-MS:
SV valve setting (describe optimazation procedure)
Peak shape standards
MCP voltage

Q-PTR-MS
Tuning of mass scale and resolution
SEM voltage

Working standard (recommendation)
Methanol, m33; Acetonitrile, m42; Acetaldehyde, m45; Acetone, m59; MBO, m87, m69, m41;
MVK, m71; MEK, m73; Benzene, m79; Toluene, m93; Xylene, m107, m91, m121;
a-pinene, m137, m81, Trifluorobenzene, m133; Trichlorobenzene, m181, m183, m185

Intercalibration standard (recommendation):
same compounds Prepared and distributed by EMPA twice per year. (I think it is not necessary)
to ship pressurized cylinders ~1-2 liters of gas standard should be sufficient)

In field operation:
When and how often:
background measurements
working standard
Full mass scan

Calculation of VMR
recommended rate constants
tranmission
recommended procedure

ACTRIS WP4, Deliverable 4.1:

“Drafts for standardized operating procedures (SOPs) for VOC measurements”

Outline

→ Operating the PTR –MS instruments in the field.

→ Data Processing

→ Data products

→ Quality control

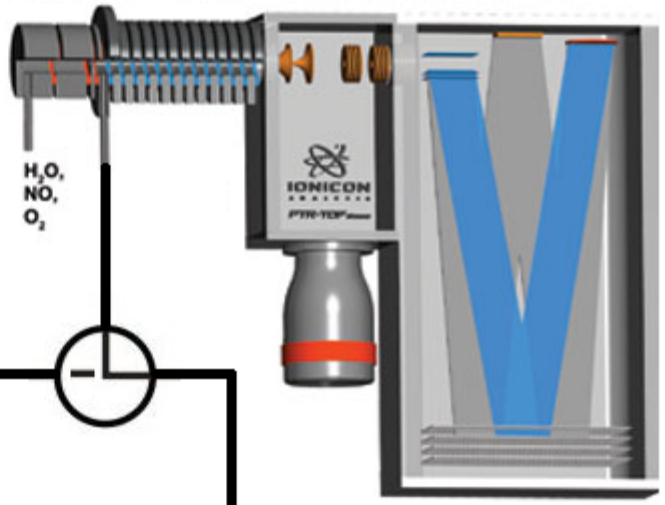
→ Data Submission

→ Post submission quality control

Recommended PTR-MS field setup

ACTRIS II:

Standard addition every 6 hours



Gas Standard

FC flow contr.

ACTRIS II:

Pt catalyst
Max Flow 0.5 L/min
Temp 400C

Pt Catalyst ~400C

short, low volume (1/8“or 1/16“)

PFA, PEEK

Min. EVERY 6 hours!

PFA filter holder with 47mm PTFE filter 5 µm pore size

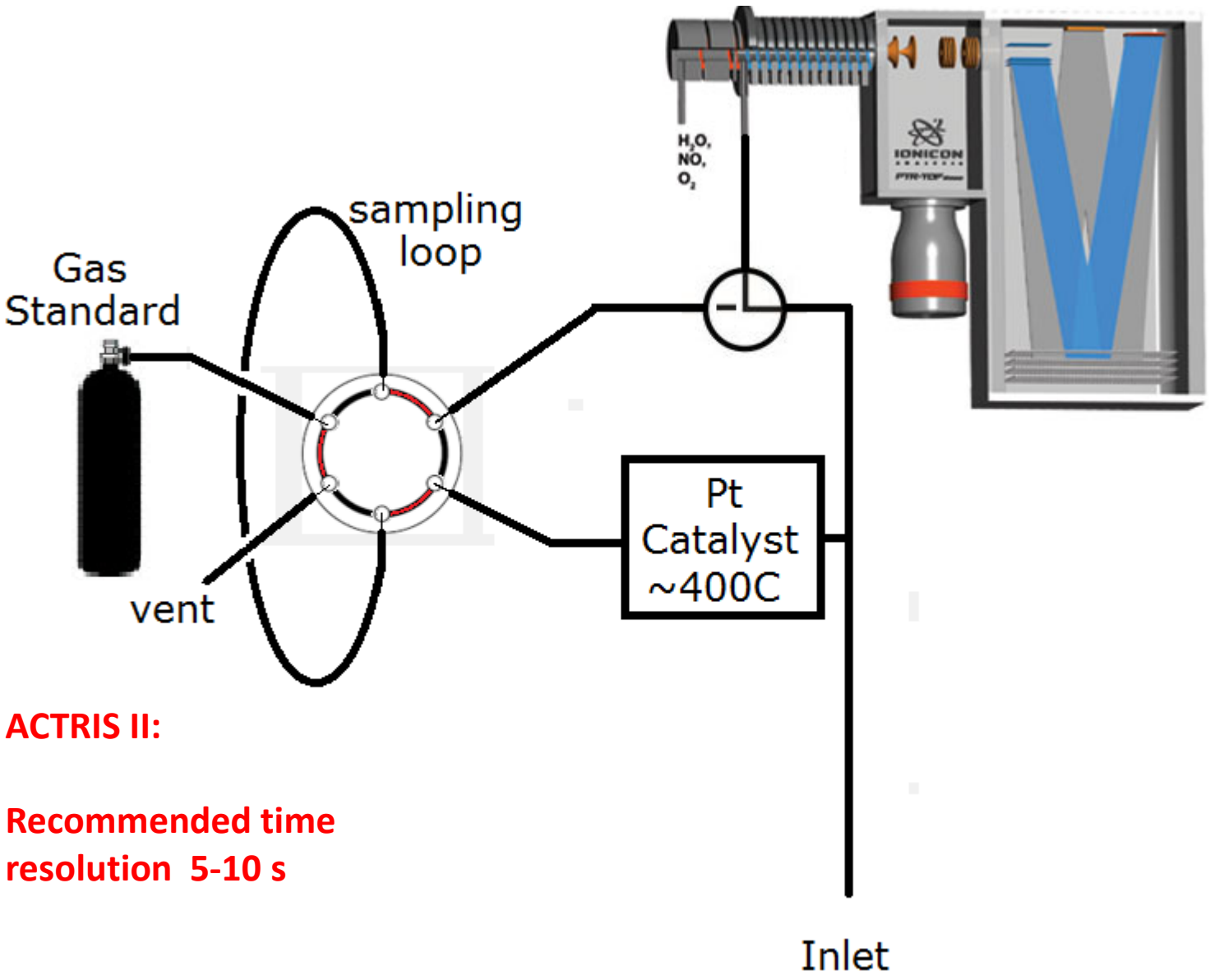
Inlet

~4mm ID PFA tubing, max 15m, flow 2 L/min

Pump

PM filter
rain/ice protection

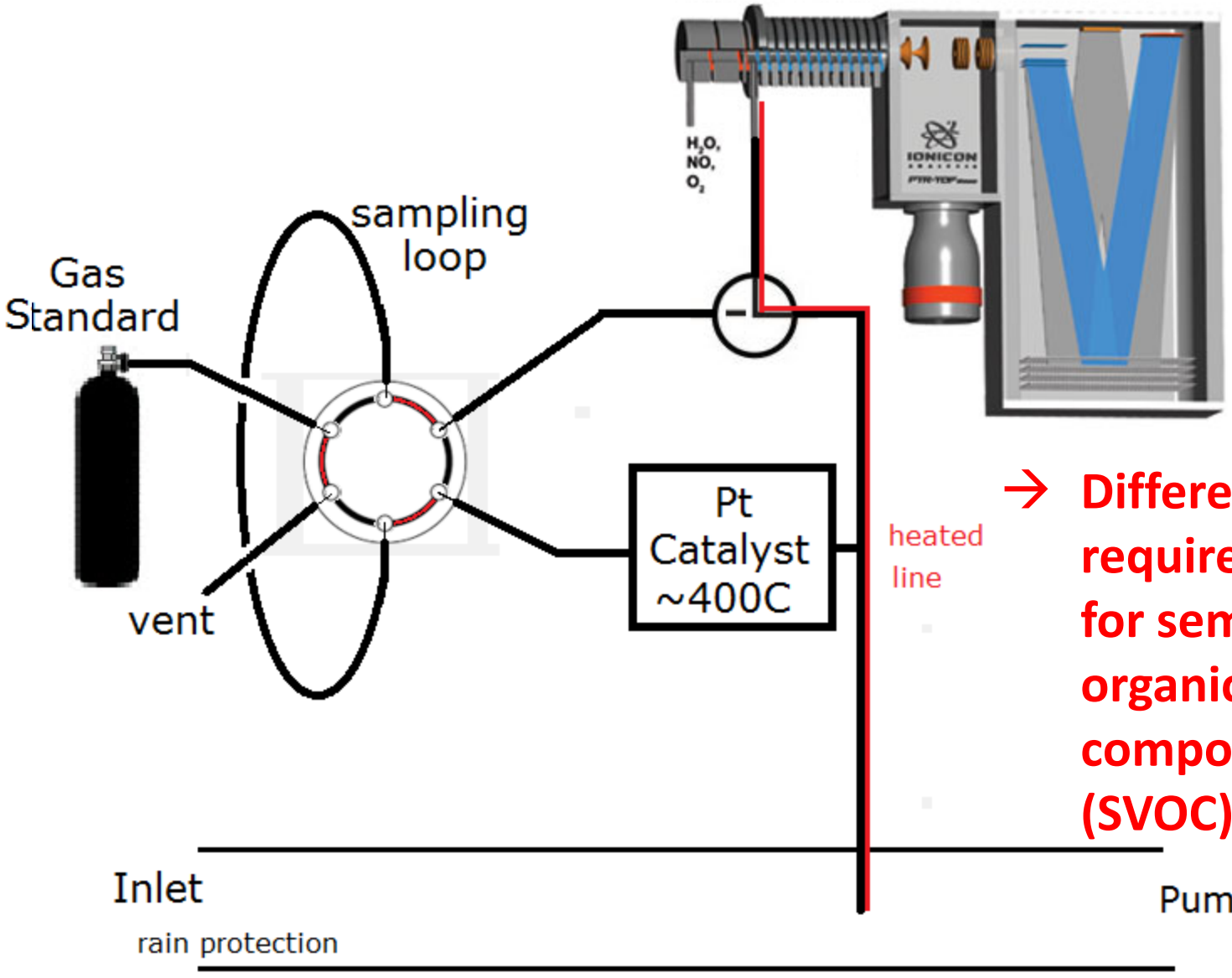
Alternative standard hook-up



ACTRIS II:

Recommended time resolution 5-10 s

Best setup is science driven!



→ **Different requirements for semivolatile organic compounds (SVOC)**

The gas standard contains:

→Compounds to be directly calibrated.

→Compounds with known reaction rate constants.

→Compounds with known fragmentation pattern.

Other requirements:

→Cover full mass scale (~30-200 Da).

→No overlapping signals

Requirements for NO+ and O2+ mode?

→To be discussed…

Example gas standard:

Methanol, m33;
Acetonitrile, m42;
Acetaldehyde, m45;
Acetone, m59;
MBO, m87, m69, m41;
MVK, m71;
MEK, m73;
Benzene, m79;
Toluene, m93;
Xylene, m107,
TMB, m121;
a-pinene, m137, m81,
Trifluorobenzene, m133;
Trichlorobenzene, m181, m183, m185

Intercalibration standard (recommendation): same compounds Prepared and distributed by EMPA twice per year. (I think it is not necessary to ship pressurized cylinders ~1-2 liters of gas standard should be sufficient)

Data processing:

Critical instrument settings (recommendation):

Drift tube pressure: 2.2 mbar
Drift tube voltage: 600V **ACTRIS II: rather specify E/N**
Drift tube temperature: 50C

Voltage between last drift ring and exit lense: 30V (instrument dependent, maybe define a procedureto optimize this) ACTRIS II action: provide procedure!
Ratio O2+/H3O+ below 0.03 ACTRIS II action: provide procedure!

From standard/background measurements:

→ Transmission **ACTRIS II action: provide procedure and/or tool**
→ Calibration factors **ACTRIS II action: spec. compound(class) ‚instructions sheets'**
→ Background levels

Calculating VMRs: **NO** **recommended procedure**

Data products:

Calibrated compounds:

Methanol, acetonitrile, acetaldehyde, acetone, isoprene, MVK+MACR, benzene, toluene, C8-benzenes, C9-benzenes, monoterpenes, OTHERS

ACTRIS II: accuracy target 10%

Uncalibrrated compounds:

Report all enhanced m/z, provide possible formula (e.g. 113.070, C6H8O2H+)

ACTRIS II: provide recommendations for reaction rate constant and/or calibration factors

Bulk products?

total gas phase (oxygenated) organic carbon, O/C, H/C, N/C, carbon oxydation state , OH reactivity etc.

ACTRIS II: provide 'instruction sheets'

Data quality prerequisites:

TOF parameter:

Peak shape
MCP voltage
baseline
resolution

QMS parameter:

Tuning of mass scale and resolution
SEM voltage

PTR parameter:

SV valve setting (describe optimization procedure)
pdrift, voltages, Tdrift, etc.
Primary ion signal
Production signal

Data quality control:

Limit of detection (LOD):

Background + 3 * (sigma of background)

ACTRIS II action : Calculate & measure LOD (w.r.t. reported time resolution) Instruction sheet.

Signal to Noise (S/N):

(raw signal- background)/ (sigma of background)

ACTRIS II action : Calculate and measure S/N (w.r.t. reported time resolution) Instruction sheet.

Precision:

(sigma of signal)/signal

ACTRIS II action : Calculate & measure Precision (w.r.t. reported time resolution) Instruction sheet.

Data submission:

2 types of data:
VMR, QC/QA data

ACTRIS II action: prepare instructions SHORT and USEFUL

Post submission QC:

Much possible but no resources…