Standard Operating Procedure

for trace gas measurements by Proton Transfer Reaction-Mass Spectrometry

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Published on April 2025

SOP / Outline of presentation

These guidelines contain the following topics:

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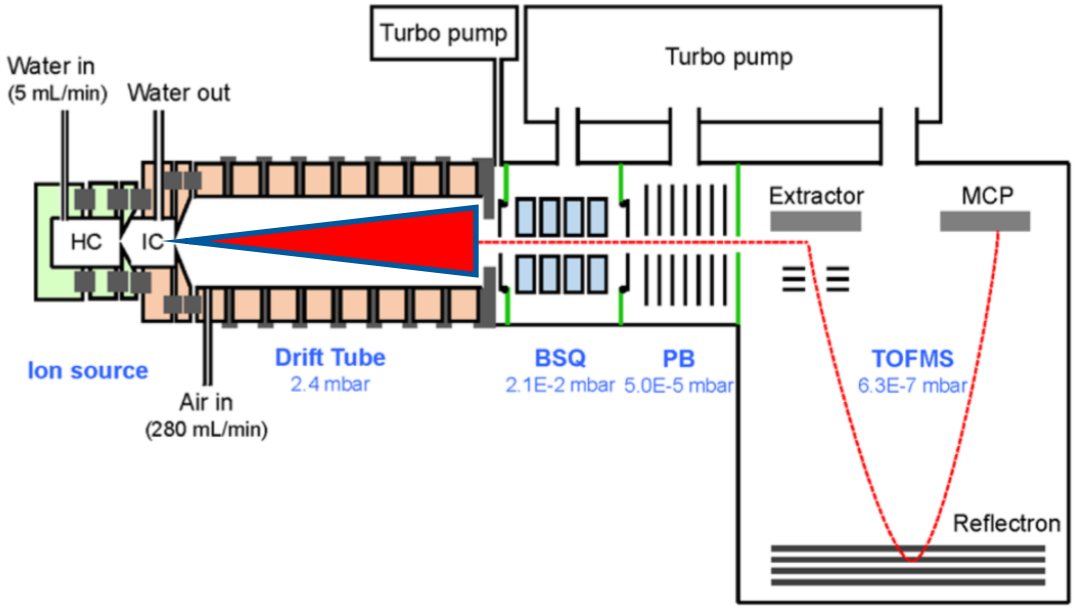
PTRMS models covered in this SOP



- **Ion Source:** H_3O^+ & traces of NO^+, O_2^+
- **Drift Tube:**

$$R + H_3O^+ \rightarrow RH^+ + H_2O$$

- **Ion Transfer Unit:** electrostatic lenses, focusing ion technologies
- **Mass Spectrometer:** QMS, ToFMS

This SOP covers only:

- ***PTR-MS equipped with conventional drift tubes*** - *simple reaction kinetics and energetics*
- ***Proton transfer using H_3O^+*** - use of other reagent ions such as O_2^+ and NO^+ not included

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Quality Assurance

3. Quality Assurance
   a. Blank measurements
   b. Calibration
   c. Figures of merit

Blank measurements

$$C_{RH^+} = C_{RH^+}^{ambient} - C_{RH^+}^{blank}$$

Zero air: VOC free air produced from ambient air using a catalyst @ 350-400°C; a VOC scrubber containing a solid sorbent, or (iii) a cylinder of dry zero air (high purity, 5.0) with a humidification system containing high purity water

Frequency: hourly blanks recommended. At least one blank every six hours to ensure that diurnal variations in instrumental blanks are well captured

Duration: several tens of minutes / check for blank stability

Ref blank values: blanks larger than reported in the table should be investigated

Table 3: Blank values for PTR-ToFMS

Species	Formula	m/z	Blank values (pptv)*
Methanol	CH_3OH	33.033	30-90
Acetonitrile	C_2H_3N	42.034	30-110
Acetaldehyde	C_2H_4O	45.033	40-270
Acetone	C_3H_6O	59.049	60-500
Isoprene	C_5H_8	69.070	20-70
Methyl Ethyl Ketone	C_4H_8O	73.065	10-70
Benzene	C_6H_6	79.054	20-80
Toluene	C_7H_8	93.070	20-140
C8-aromatics	C_8H_{10}	107.086	10-110
C9-aromatics	C_9H_{12}	121.101	5-200
Monoterpenes	$C_{10}H_{16}$	81.070 + 137.132	60-100 + 10-50

**Range of values observed on several PTR-ToFMS (m/Δm>3000). Reported values are for systems which have been running for at least several days. PTR-QMS may exhibit larger values due to the detection of isobaric species generated in the ion source and desorbing from the inlet material.*

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Quality Assurance

Calibration

Provide procedures & recommendations

3. Quality Assurance
   a. Blank measurements
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zero air and calibration gas (few ppb) sampled until a stable plateau is reached for each VOC signal
Frequency: once a week (campaign < 2 months) / twice a month (> 2 months)

Kinetic approach

$$VMR = \frac{\frac{C_{RH^+} \times IF_{RH^+} \times FF_{RH^+}}{C_{H_3O^+}}}{\left(\frac{T_{RH^+}}{T_{H_3O^+}} \times \frac{d \times k}{K_0 \times N_0} \times \frac{N^2}{E}\right)}$$

- **Use standard mixture** of VOCs w/ known proton transfer rate constants covering the whole mass range interest for ambient measurements
- **Calibrate ion transmission** at low humidity (e.g. 30% RH)
- **Evaluate whether humidity-dependent responses** are observed by varying humidity over 30-90% RH
- **Characterize fragmentation patterns** of species of interest → FF_{RH^+}

Calibration approach

$$VMR = \frac{\frac{C_{RH^+}}{C_{H_3O^+}} \times 10^6}{S_N(RH^+)}$$

- **Use standard mixture** of all VOCs targeted for ambient measurements
- **Calibrate $S_N(RH^+)$** for all VOCs
- **Evaluate whether humidity-dependent responses** are observed and, if so, apply the Following procedure for correction

$$VMR = \frac{\frac{C_{RH^+}}{C_{H_3O^+} + Xr \times C_{H_3O^+(H_2O)}}}{S_N(RH^+)} \times 10^6$$

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Quality Assurance

Calibration

Calibration standard from NPL
(Worton et al., AMT, 2023)

- SI-traceable
- 20 compounds tailored to the requirements of PTR-MS
- Expanded uncertainty: 5.1-10.8%

Component	Amount fraction / (µmol/mol)	Component	Amount fraction / (µmol/mol)
Acetaldehyde	1.35 ± 0.14	1,2,4-trifluorobenzene	0.928 ± 0.047
Methanol	1.69 ± 0.17	Toluene	0.967 ± 0.049
Ethanol	1.11 ± 0.12	Hexamethylcyclotrisiloxane	0.98 ± 0.10
Isoprene	1.13 ± 0.06	*m*-xylene	0.963 ± 0.049
Acetone	1.07 ± 0.06	Octamethylcyclotetrasiloxane	1.11 ± 0.12
Dimethyl sulfide	1.05 ± 0.06	1,2,4-trimethylbenzene	1.02 ± 0.11
Acetonitrile	1.29 ± 0.13	+3-carene	0.92 ± 0.10
Perfluorotributylamine	0.92 ± 0.10	Decamethylcyclopentasiloxane	1.11 ± 0.12
3-buten-2-one	1.14 ± 0.12	1,2,4-trichlorobenzene	1.04 ± 0.11
Butan-2-one	1.16 ± 0.06	Nitrogen	Balance
Benzene	0.845 ± 0.043	-	-

Table A2.1. Composition of the NPL standard.

Compound	Formula	Protonated mass(es)	Fragments
Nitrogen (balance)	N_2	-	-
Methanol	CH_4O	33.033	-
Acetonitrile	CH_3CN	42.034	-
Acetaldehyde	C_2H_4O	45.033	-
Ethanol	C_2H_6O	47.050	29.039
Acetone	C_3H_6O	59.049	
Dimethyl sulfide	C_2H_6S	63.030	
Isoprene	C_5H_8	69.070	41.039
Methylvinylketone (3-buten-2-one)	C_4H_6O	71.049	
Methylethylketone (Butan-2-one)	C_4H_8O	73.065	
Benzene	C_6H_6	79.054	
Toluene	C_7H_8	93.070	
m-Xylene	C_8H_{10}	107.086	
1,2,4-Trimethylbenzene	C_9H_{12}	121.101	
1,2,4-Trifluorobenzene	$C_6H_3F_3$	133.026	
3-Carene	$C_{10}H_{16}$	137.132,	81.070
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	180.937, 182.934, 184.931	
Hexamethylcyclotrisiloxane (D3)	$C_6H_{18}Si_3O_3$	223.064, 224.063, 225.061	207.032, 208.032, 209.029
Octamethylcyclotetrasiloxane (D4)	$C_8H_{24}Si_4O_4$	297.083, 298.082, 299.079	281.051, 282.051, 283.048
Decamethylcyclopentasiloxane (D5)	$C_{10}H_{30}Si_5O_5$	371.101, 372.101, 372.105, 373.098	355.070, 356.070, 357.067
Perfluorotributylamine	$C_{12}F_{27}N$	671.968	413.977

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Quality Assurance

Figures of merit

3. Quality Assurance
   a. Blank measurements
   b. Calibration
   c. Figures of merit

Provide methodologies to compute figures of merit w/ various examples

Mass resolution & accuracy

$$R_{FWHM} = \frac{(m/z)_{peak}}{\Delta(m/z)_{FWHM}}$$

Limit of detection (3σ)

$$LOD = 3 \times \frac{\sqrt{C_{AH^+}^{blank}}}{S_m(AH^+)}$$

Meas. precision (1σ)

$$\sigma_{precision} = \sqrt{C_{AH^+}^{ambient} + C_{AH^+}^{blank}}$$

Where $C_{AH^+}^{ambient}$ and $C_{AH^+}^{blank}$ are expressed in counts.

$$RSD(precision) = \frac{\sigma_{precision}}{C_{AH^+}^{ambient} - C_{AH^+}^{blank}}$$

Meas. accuracy (1σ)

$$RSD\ (accuracy) = \sqrt{\left(\frac{\sigma_{CAL}}{VMR_{CAL}}\right)^2 + \frac{1}{(F_{CAL}+F_{AIR})^2}\left(\frac{F_{AIR}^{\ 2}}{F_{CAL}^{\ 2}} \times \sigma_{F_{CAL}}^2 + \sigma_{F_{AIR}}^2\right)}$$

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Field Operation

4. Field operation
   a. Sampling
   b. Operating conditions
   c. Checking for proper field operation

Sampling

Provide recommendations on various aspects

Height: 2-3 different heights should be tested for a significant period of time

Material: coated stainless steel (Silcosteel or SilcoNert®1000 and Sulfinert or SilcoNert®2000) or polymer after a sufficient passivation time before use (PFA, PTFE)

Sampling line heating: 40-50°C

Flow rate: a few L/min to a few tens of L/min (residence time < a few seconds), turbulent flow preferred

Particle filter: mesh size < 5 µm unless low volatility compounds are targeted

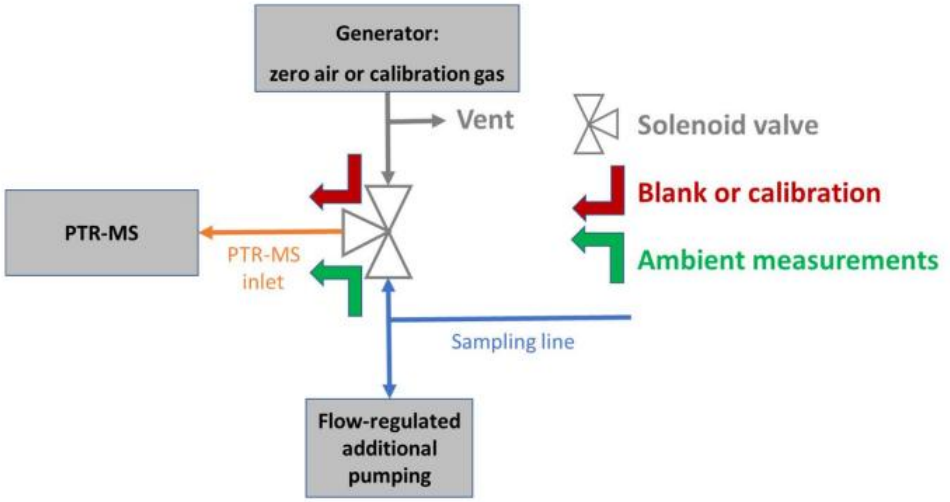

Figure 1:

PTR-MS setup for field operation

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Field Operation

4. Field operation
   a. Sampling
   b. Operating conditions
   c. Checking for proper field operation

Operating conditions

Provide settings for operating conditions & requirements for reagent ions

Table 4: Field operating conditions

Parameter	Range	Comments
Temperature (°C)	50-60 (up to 80 if IVOC & SVOC are targeted)	This temperature should be kept higher than that of the PTRMS-inlet to prevent condensation. Higher temperature: less memory effects and improved response time, less losses of semi-volatile VOCs.
Pressure (mbar)	1-4	Higher pressure reduces the diffusion of sampled air into the ion source in certain PTR-MS models, resulting in lower impurity levels of O_2^+ and NO^+
E/N (Td)	120-140	A higher E/N reduces the abundance of $H_3O^+(H_2O)$ but increases the fragmentation of protonated VOCs
PTR-MS inlet Sampling flow rate (SCCM)	50-500	A higher flow rate reduces the impact of instrument related contamination on blank signals
Sampling line flow rate	See section 4.a	A higher flow rate reduces the impact of sampling line related contamination on blank signals

Table 5: Criteria for optimum tuning of the ion source/drift tube

	Ion source
Primary ions purity	$[O_2^+ + NO^+] < 3\%$ of $[H_3O^+ + H_3O^+(H_2O)]$
Primary ions distribution	$[H_3O^+(H_2O)] < 20\%$ of $[H_3O^+ + H_3O^+(H_2O)]$

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Field Operation

4. Field operation
   a. Sampling
   b. Operating conditions
   c. Checking for proper field operation

Checking for proper field operation

Build control charts of relevant metrics to ensure that instruments are running well

Table 6: Control metrics for proper field measurements

Metric	Purpose	Criteria
H_3O^+ ion signal at m/z 21.022	Check cleanliness of reagent ion source and/or a change in detection sensitivity	Not lower than 70% of initial value at installation
$[O_2^+ + NO^+] / [H_3O^+ + H_3O^+(H_2O)]^*$	Check for reagent ions purity	As defined in Table 5
$[H_3O^+(H_2O)] / [H_3O^+ + H_3O^+(H_2O)]^*$	Check for reagent ions distribution	As defined in Table 5
R_{FWHM} (section 3c) & Peak shape	Check ToFMS tuning	R_{FWHM} not lower than 70% of initial value at installation
Blank values (sections 3a & 4b)	Check for leaks and/or contamination	Lower than 1.3 times initial values at installation
N_2H^+ ion signal at m/z 29.014	Check collision energetics in transfer region - N_2H^+ and CO_2H^+ only formed via endothermic reactions in transfer system	Minimize at selected ion-source/drift operating conditions
CO_2H^+ ion signal at m/z 44.998		
Fragmentation reference species** Ex: Diiodobenzene - ratio of m/z 203.943 over m/z 330.848	Check for abnormal ion fragmentation	Deviation lower than 30% from initial value at installation

** Ratios of transmission corrected signals. **Reference compounds continuously added to the drift tube such as diiodobezene in the PerMaScale feature of IONICON instruments*

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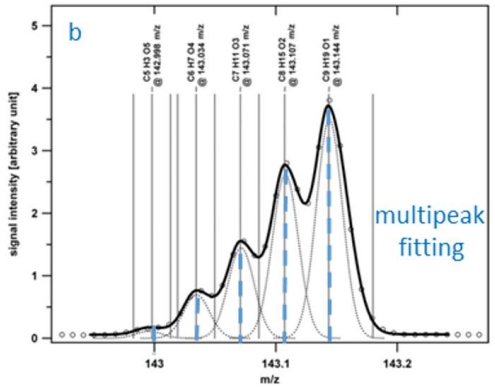
Data extraction: retrieval of ambient VMR & reporting

Provide a general ‘step by step’ procedure to process PTR-MS raw data

Software tools provided with PTR-MS (PTR-MS viewer or Ionicon Data Analyzer from IONICON Analytic GmbH, Tofware from TOFWERK) or by the scientific community (Toftool, PTRwid)

Mass scale calibration → ***Peak-shape analysis and peak-fitting*** → ***Conversion to VMR*** → ***Blank subtraction***

Grauss et al. (2010)



Kinetic approach

$$VMR = \frac{\frac{C_{RH^+} \times IF_{RH^+} \times FF_{RH^+}}{C_{H_3O^+}}}{\left(\frac{T_{RH^+}}{T_{H_3O^+}} \times \frac{d \times k}{K_0 \times N_0} \times \frac{N^2}{E}\right)}$$

Calibration approach

$$VMR = \frac{\frac{C_{RH^+}}{C_{H_3O^+}} \times 10^6}{S_N(RH^+)}$$

Table 7: Reference peaks for mass calibration

Species	Formula	m/z (Da)	Comments
Hydronium	$H_3{}^{18}O^+$	21.022	
Hydronium water-cluster	$H_3{}^{16}O^+(H_2{}^{16}O)$	37.028	May be saturated
Acetone.H^+	$C_3H_6O.H^+$	59.049	May be missing when blank measurements are performed
Diiodobenzene.H^+ and fragment	$C_6H_4I_2.H^+$	330.848	PerMaScale feature from IONICON instruments
	fragment	203.943	

Check EBAS website for templates and vocabulary updates

Additional PTRMS related activities

- Physical dedicated hands-on training to organize for small groups, or during upcoming intercomparisons with other CiGas units
- Possibility to organize intercomparisons (last one dedicated to VOC was for formaldehyde) & in 2019 for PTRMS within EUROCHAMP
- Operational for evaluation of working standards and target gas, in order to link the VOC measurement by PTRMS to primary standards and ensure the state-of-the art traceability to international scales
- Round-robin: send out a NPL PTRMS calibration standard, a dilution system, and/or an unknow target gas
- Audit and Labelling (step 1a & 1b)
- SOP for instruments equipped with new generation drift tubes ??

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