



U.S. DEPARTMENT OF
ENERGY | Office of
Science

DOE/SC-ARM-TR-160

Proton Transfer Time-of-Flight Mass Spectrometer Instrument Handbook

TB Watson

March 2016



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Work supported by the U.S. Department of Energy,
Office of Science, Office of Biological and Environmental Research

Acronyms and Abbreviations

amu	atomic mass units
cps	counts per second
GoAmazon	Green Ocean Amazon 2014/15 campaign
IOP	intensive operational period
LOD	limit of detection
PA	proton affinity
ppbv	parts per billion by volume or molar mixing ratio
ppm	parts per million
pptv	parts per trillion by volume or molar mixing ratio
PTR-MS	Proton Transfer Reaction Mass Spectrometer
PTR-TOF-MS	Proton Transfer Reaction Time-of-Flight Mass Spectrometer
TOF	time of flight

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1.0 Instrument Title

Proton Transfer Time-of-Flight Mass Spectrometer (PTR-TOF-MS).

2.0 Mentor Contact Information

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FN:172007b|LandesgerichtInnsbruck

Instrument manual available from manufacturer <http://www.ionicon.com/>

4.0 Instrument Description

The Proton Transfer Reaction Mass Spectrometer (PTR-MS) measures gas-phase compounds in ambient air and headspace samples before using chemical ionization to produce positively charged molecules, which are detected with a time-of-flight (TOF) mass spectrometer. This ionization method uses a gentle proton transfer reaction method between the molecule of interest and protonated water, or hydronium ion (H_3O^+), to produce limited fragmentation of the parent molecule. The ions produced are primarily positively charged with the mass of the parent ion, plus an additional proton. Ion concentration is determined by adding the number of ions counted at the molecular ion's mass-to-charge ratio to the number of air molecules in the reaction chamber, which can be identified according to the pressure levels in the reaction chamber. The PTR-MS allows many volatile organic compounds in ambient air to be detected at levels from 10–100 parts per trillion by volume (pptv). The response time is 1 to 10 seconds.

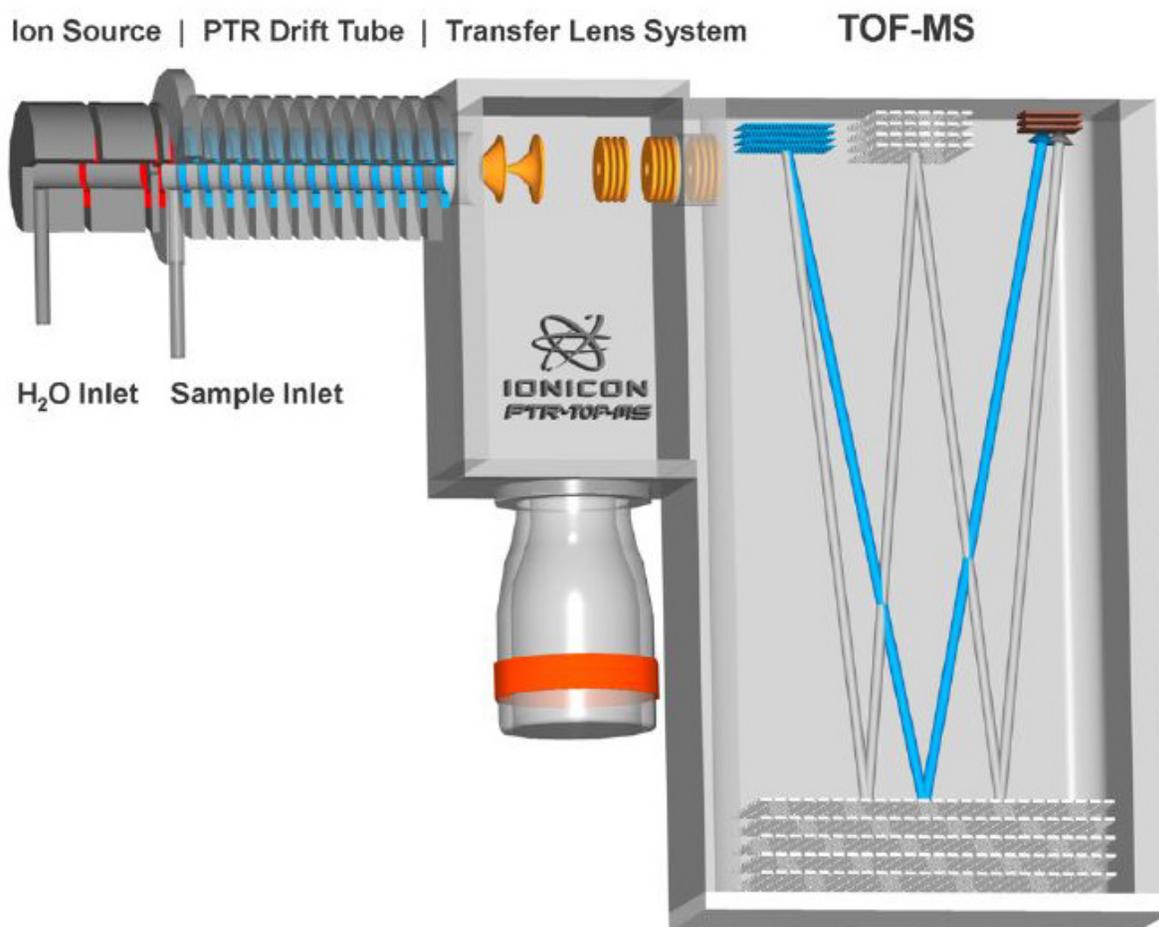


Figure 1. Schematic of PTRMS components.

5.0 Measurements Taken

The PTRMS measures molecules that can be ionized through a proton transfer reaction using the following equation:



where H_3O^+ is produced in the ion source of the instrument, R^+ is the analyte molecule, and H_2O has a proton affinity (PA) of 166.5 kcal/mol.

Most common organic molecules have PAs ranging from 171–207 kcal/mol. If the PA of the sampled molecule is less than the proton affinity of H_2O , however, the molecule will not be detected or ionized. Proton affinities of primary air components are less than that of H_2O and, therefore, not detected by the instrument. Examples of molecules with PAs < H_2O are:

- N_2
- O_2

- A_r
- CO_2
- CH_4
- alkanes with less than eight carbons.

If the PA of the molecule in the sample is greater than the PA of H_2O , there will be a proton transfer and a detectable ion will be produced. Most unsaturated hydrocarbons, substituted hydrocarbons, hydrocarbon derivatives, and some inorganic species such as HNO_2 and HNO_3 have PAs greater than H_2O . Some examples of molecules with PAs $> H_2O$ are:

- alkenes such as C_3H_6
- alkanes such as n-Octane n-Decane and n-Dodecane
- cycloalkanes
- alkynes
- isoprene and atmospheric reaction products.

For more comprehensive summaries of proton affinities, visit webbook.nist.gov/chemistry. A summary of product ions detected by PTRMS in atmospheric samples (de Gouw and Warneke 2007) can be found in Table 1.

6.0 Data

6.1 Object Description

The PTRMS generates two types of raw data files. These are designated “a1” in the ARM archive and contain data in different formats.

The first format is specific to the Ionicon Analytik PTRMS Viewer software and is known as hdf5 files. They use the following format: DataFile_yyy.mm.dd-xxhyymzss_AS.h5; where “DataFile” refers to the location or intensive operational period (IOP) in which work was conducted, “xx” specifies the time in hours, “yy” the time in minutes, and “zz” the time in seconds. (For example: DataFile_2012.06.26-14h34m53s_AS.h5). When using this format, the information is typically stored daily.

The second format stores data as text files, which can be imported directly into a spreadsheet program such as Excel. These files are named with the convention: DataFile_yyy.mm.dd-xxhyymzss.txt, using the same placeholders as above. The structure of these files can be seen in Appendix A.

6.2 Data Ordering

To order data, please visit <http://www.arm.gov/xdc>.

Table 1. Summary of product ions detected by PTR-MS in atmospheric air, taken from de Gouw and Warneke (2007).

Mass (amu)	Compound	Reference
28	HCN	(Karl et al., 2003)
30	HONO	(Wisthaler et al., 2003)
31	Formaldehyde	chapter III
33	Methanol	id.
42	Acetonitrile	id.
43	Multiple species	id.
45	Acetaldehyde	id.
47	Formic acid	(Williams et al., 2001; Karl et al., 2004)
54	Acrylonitrile	(Karl et al., 2003)
57	Butenes, MTBE, butanol	(Karl et al., 2003)
59	Acetone	chapter III
61	Acetic acid	id.
63	DMS	id.
69	Isoprene	id.
	Furan	id.
71	MVK + MACR	id.
73	MEK	id.
75	Hydroxy acetone	(Williams et al., 2000; Williams et al., 2001)
77	PAN	chapter III
79	Benzene	id.
81	Monoterpenes	id.
	Hexenal	(Karl et al., 2001c; Karl et al., 2001d; Warneke et al., 2002)
83	Hexenol, hexanal, hexenyl acetate	(Karl et al., 2001a; Karl et al., 2001c; Karl et al., 2001d; Karl et al., 2001e; Williams et al., 2001)
	Methyl furan, isoprene hydroxy carbonyls	(Williams et al., 2001)
85	Ethyl vinyl ketone	(Karl et al., 2001a)
87	MBO	(Holzinger et al., 2005a)
	C ₇ -carbonyls, methacrylic acid	(Williams et al., 2001)
91	PPN	(Hansel & Wisthaler, 2000)
93	Toluene	chapter III
95	2-vinyl furan	(Williams et al., 2001)
	Phenol	(Rinne et al., 2005)
99	Hexenal	(Karl et al., 2001a; Karl et al., 2001d; Williams et al., 2001; Warneke et al., 2002)
101	Isoprene hydroperoxides	(Crutzen et al., 2000; Williams et al., 2000; Warneke et al., 2001a; Williams et al., 2001)
103	MPAN	(Hansel & Wisthaler, 2000)
105	Styrene, PiBN	chapter III
107	C ₈ -aromatics	id.
115	Heptanal	(Karl et al., 2001a)
121	C ₉ -aromatics	chapter III
129	Octanal	(Karl et al., 2001a)
	Naphthalene	(Karl et al., 2003)
135	C ₁₀ -aromatics	(Karl et al., 2001b; Beauchamp et al., 2004)
137	Monoterpenes	chapter III
139	Nopinone	(Holzinger et al., 2005a)
143	Nonanal	(Karl et al., 2001a)
149	C ₁₁ -aromatics	(Karl et al., 2003)
	Methylchavicol	(Holzinger et al., 2005a)
151	Pinonaldehyde	(Holzinger et al., 2005a)
163	C ₁₂ -aromatics	(Karl et al., 2003)

7.0 Technical Specification

Technical operational specifications for the PTRMS are as follows.

1. Operating voltage 100–240V
2. Operating frequency 47–63 Hz
3. Power consumption <1000 watts
4. Operating pressure 600–1200 mbar
5. Mass spectrometer Tofwerk time of flight
6. Mass resolution approximately 5000m/Δm (FWHM)
7. Response time 100 ms
8. Detection threshold 10 pptv at 1 minute averaging

7.1 Units

Data is stored as counts per second (cps), while calculated molar mixing ratio is typically expressed as parts per billion (ppbv).

7.2 Range

Concentration levels can range from 1 pptv to 10 parts per million by volume, depending on the compound of interest, while the range for mass is typically 0 to 450 atomic mass units (amu).

7.3 Accuracy

The PTRMS mass accuracy reflects the degree to which the measurement result and the true value measurement agree. Measurement accuracy, based on calculated concentrations, is determined by propagating the errors from all parameters used in the calculation, which usually comes out to about 30–50%. De Gouw and Warneke (2007) report that several published inter-comparisons between the PTRMS and other methods agree within a range of 1–20%. A summary of scatter plot inter-comparisons of PTRMS and other instruments is illustrated in Table 2. Direct calibration of specific compounds eliminated the uncertainty in the concentration calculation parameters, thus increasing accuracy to more than 10%.

7.4 Precision

PTRMS precision depends on the instrument settings and is defined as the standard deviation in the product ion counts, which is a function of the dwell time at any given concentration. It is therefore estimated using a Poisson distribution:

$$\sigma = \sqrt{N} \quad (2)$$

where σ is the precision and N is the number of product ion counts.

Based on this equation, 600 counts at a particular mass-to-charge ratio (m/z) will have a precision of 24 cps, or 4%.

7.5 Detection Limit

The theoretical detection limit, or PTRMS, can be calculated by determining the number of collisions with molecules of interest in the drift tube, which yields a 25 pptv limit of detection (LOD).

Another way to determine the LOD is through measurement. The PTRMS LOD can also be defined as three times the noise. Noise is determined by measuring the background signal when the instrument is supplied with zero air. The counts measured under these conditions depend on the time over which counts at each mass are collected, or the dwell time. Therefore, the LOD is three times the background noise, compound-dependent, and somewhat concentration-dependent. De Gouw and Warneke (2007) report a detection limit of 35 pptv for benzene.

Table 2. Summary of scatter plot inter-comparisons of PTR-MS with other instruments from de Gouw and Warneke (2007).

VOC	Mass (amu)	Reference	Other method	Slope	Intercept (pptv)
Formaldehyde	31	(Steinbacher et al., 2004)	Hantzsch		N/A
Methanol	33	(de Gouw et al., 2003a) (de Gouw et al., 2004b)	on-line GC-MS PTR-MS	1.028 1.16	-110 -170
Acetonitrile	42	(Sprung et al., 2001) (de Gouw et al., 2003a) (de Gouw et al., 2004b)	AP-CIMS on-line GC-MS PTR-MS	0.86 0.91 1.03	40 -3 -16
Propylene	43	(Kuster et al., 2004)	on-line GC-FID	0.9	2700
Acetaldehyde	45	(Kuster et al., 2004) (de Gouw et al., 2003a)	on-line GC-ITMS on-line GC-MS		N/A -170
Acetone	59	(Sprung et al., 2001) (Kuster et al., 2004) (de Gouw et al., 2003a) (de Gouw et al., 2004b) (Ammann et al., 2004)	AP-CIMS on-line GC-ITMS on-line GC-MS PTR-MS on-line GC-FID	1.18 0.95 1.002 1.05	63 0 -50 -200 N/A
DMS	63	This work	GC canisters	0.64	-3.2
Isoprene	69	(de Gouw et al., 2003a) (Kuster et al., 2004) (Kuster et al., 2004) (Kuster et al., 2004) (Ammann et al., 2004) (Kato et al., 2004) This work	on-line GC-MS on-line GC-ITMS on-line GC-FID on-line GC-QMS on-line GC-FID on-line GC-FID GC canisters	0.97 1.1 1.2 0.96 2.15 0.888	14 100 100 120 N/A 212 19
MVK+MACR	71	(de Gouw et al., 2003a) (Ammann et al., 2004) This work	on-line GC-MS on-line GC-FID GC canisters	1.01 0.967	6 N/A 1
MEK	73	(de Gouw et al., 2003a) (de Gouw et al., 2006)	on-line GC-MS GC canisters	2.51 0.85	16 57
PAN	77	(de Gouw et al., 2003a)	GC-ECD	0.72	60
Benzene	79	(Warneke et al., 2001b) (Kuster et al., 2004) (Kuster et al., 2004) (de Gouw et al., 2003a) (de Gouw et al., 2004a) (Ammann et al., 2004) (Kato et al., 2004) (de Gouw et al., 2006)	GC canisters on-line GC-ITMS on-line GC-QMS on-line GC-MS GC canisters on-line GC-FID on-line GC-FID GC canisters	0.82 0.85 0.91 1.12 1.04 0.82 1.08	106 0 0 1 15 N/A 26 12.8
Toluene	93	(Warneke et al., 2001b) (Kuster et al., 2004) (Kuster et al., 2004) (de Gouw et al., 2003a) (de Gouw et al., 2004a) (Kato et al., 2004) (de Gouw et al., 2006)	GC canisters on-line GC-ITMS on-line GC-QMS on-line GC-MS GC canisters on-line GC-FID GC canisters	1.18 0.97 0.81 1.08 0.83 0.52 0.88	-66 0 100 10 23 158 4.3
Styrene	105	(Kuster et al., 2004)	on-line GC-ITMS	0.9	40
C ₈ -aromatics	107	(Kuster et al., 2004) (de Gouw et al., 2003a) (Steinbacher et al., 2004) (Kato et al., 2004) (de Gouw et al., 2006)	on-line GC-ITMS on-line GC-MS GC filters on-line GC-FID GC canisters	1.02 3.2 0.78 ^a 0.58 0.856	0 11 150 0.7 -0.5
C ₉ -aromatics	121	(Kuster et al., 2004) (de Gouw et al., 2003a) (Kato et al., 2004) (de Gouw et al., 2006)	on-line GC-ITMS on-line GC-MS on-line GC-FID GC canisters	2.01 1.35 0.98 1.03	0 33 93 24.6
Monoterpenes	137	(de Gouw et al., 2003a) (Kato et al., 2004) (Lee et al., 2005) This work	on-line GC-MS on-line GC-FID GC-FID bags GC canisters	0.80 0.96 1.30 1.93	19 33 0 5.6

gas. The constant and well-defined conditions in the drift region, and the high purity of the primary ion (H_3O^+) signal, make the calculation of absolute concentrations possible without the use of gas standards.

10.0 Operation

There is currently one PTR-MS system operating in ARM installations, located in the Mobile Aerosol Observing System chemistry container.

11.0 Software

Two programs are used in the operation of the PTR-MS: the PTR Manager and the TPS-Controller.

The PTR Manager controls ion production in the drift tube and monitors temperatures, flow and pressure controllers, turbo pumps, and the instrument's overall operational state. It also controls the data acquisition settings, including the averaging time and length of data records. It is used for mass calibration, to select the peaks to be saved in data files, and to measure and store transmission factors.

The TPS-Controller, conversely, is used to control the settings of the TOF mass spectrometer. It also optimizes the multi-channel plate detector's performance.

Data can be viewed and manipulated using the PTR-MS Viewer, which reprocesses data stored by the PRT Manager. It can also be used to change the mass calibration and organize files, and can change the peak integration, mass calibration, and concentration calculations.

12.0 Calibration

12.1 Mass Calibration

Mass calibration ensures an ion's exact mass reflects the mass identified by the instrument. It is usually sufficient to select one mass in the lower range of the spectra and a second in the higher range. Ambient air is a sufficient medium to accomplish this, because several signals are present in all air samples. NO^+ at m/z 30 is usually chosen as the low range mass, because no mass exists at m/z 29; thus, there are no interfering compounds in this region. The calibration is accomplished in the TofDaq viewer by entering the correct value in the mass calibration window. The same procedure is then performed on another peak at a higher mass range such as acetone- H^+ , $\text{C}_3\text{H}_7\text{O}$; at mass 59. Acetone is convenient because it is always present in significant concentrations in ambient air. If using calibration gas and a suitable dilution system is available, a higher mass can be used. Mass calibration can be checked and changed in post-processing, using the PTR-MS Viewer.

12.2 Transmission Factors

Ions are not transported through the lens system and ion extractor with the same efficiency. Lighter ions are transported more effectively than heavier ions. It is necessary to quantify this effect. Transmission factors are determined using a gas standard containing compounds with varying mass ranges. The TO-14 Aromatics standard is typically used in ARM calibrations and is provided in Table 3. Compounds with more than one mass reflect the presence of isotopes. All components in this standard are nominally 1 parts per million (ppm), so the standard must be diluted to reduce the concentration to approximately 1 ppbv. The concentrations can be entered into software provided by the manufacturer to generate a transmission factor curve, similar to that shown in Figure 3. These data are stored and used to calculate concentration levels.

Table 3. TO-14A aromatics mix composition. All components are at a nominal 1 ppm.

Component	CAS Number	Protonated Molecular Weight (amu)
Benzene	71-43-5	79
Chlorobenzene	108-90-7	113
<i>m</i> -Dichlorobenzene	541-73-1	147
<i>o</i> -Dichlorobenzene	95-46-7	147 and 149
<i>p</i> -Dichlorobenzene	106-46-7	147 and 149
Ethyl benzene	100-41-4	107
Styrene	100-42-5	105
Toluene	108-88-3	93
1,2,4-Trichlorobenzene	120-82-1	181
1,2,4-Trimethylbenzene	95-63-6	121
1,3,5-Trimethylbenzene	108-67-8	121
<i>m</i> -Xylene	108-38-3	107
<i>o</i> -Xylene	95-47-6	107
<i>p</i> -Xylene	106-42-3	107

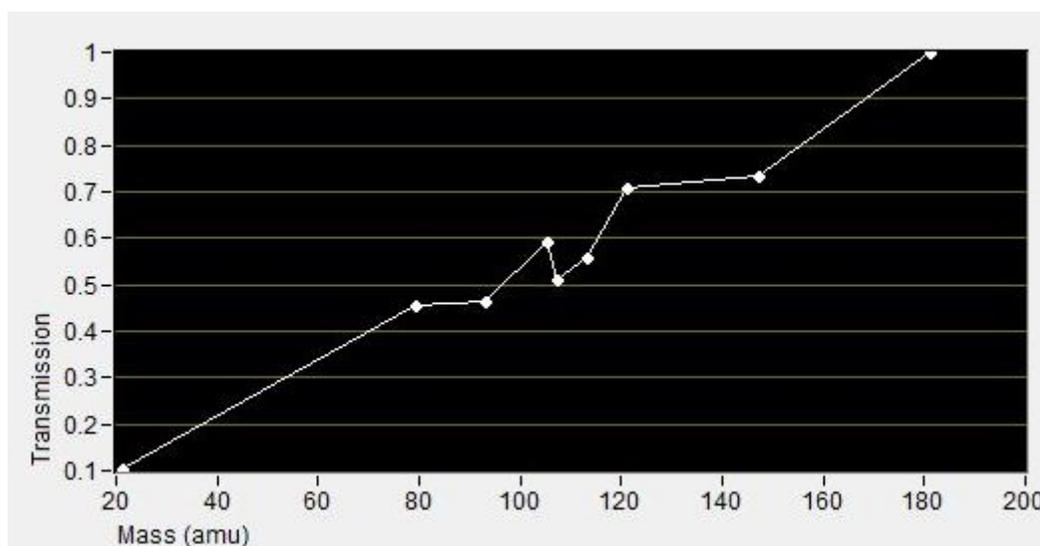


Figure 3. Transmission factor curve.

12.3 Response Factors

Response factors can also be calculated directly for compounds present in the calibration mixture. A dynamic dilution system provides a range of concentrations to the instrument based on the levels expected in ambient air samples. The results are response factors measured in units of cps ppbV^{-1} . An example taken from Singer et al. (2007) is given in Figure 4.

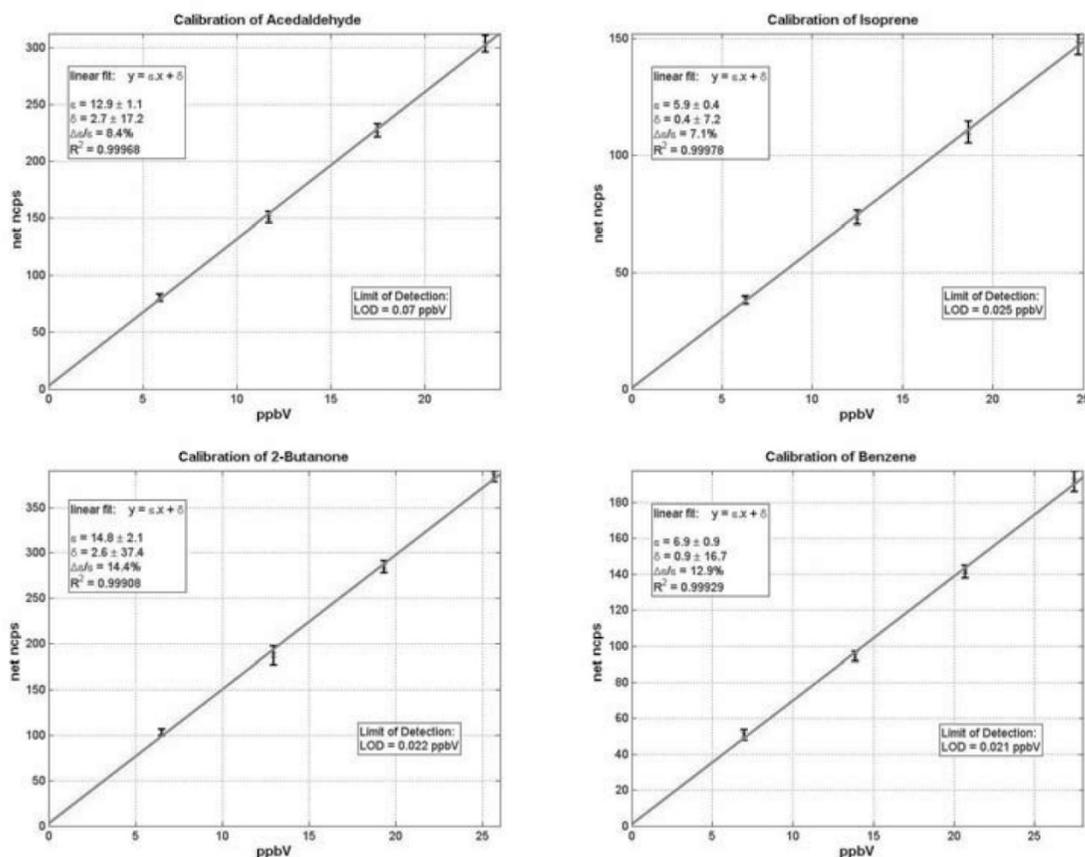


Figure 4. Calibration curves for four compounds. Plots from Singer et al. (2007).

12.4 Calibration Frequency

Calibration is performed at the beginning, end, and as needed, throughout all deployments. Mass calibration can easily be completed during post-processing of the data. Determination of transmission and response factors requires an on-site operator. The frequency depends on deployment length, number of mentor visits, and measurement goals. Calibrations during the Green Ocean Amazon (GoAmazon) 2014/15 campaign were performed daily because a post-doctoral scientist was present continuously.

13.0 Inlet System

Ambient aerosol-laden air is brought to the instruments through an 8-in. diameter external stack nominally 10 in. above the roof of the enclosure at 800 lpm, as pictured in Figure 5. Inside the stack, sample air flows through a 2-in.-diameter stainless steel pipe in the center of this larger flow at 120 lpm. This flow is split into four 30 lpm sample lines; one of which supplies air to the PTR-MS, as well as other instruments. The PTR-MS is connected to this line with a “T”, insulated to prevent condensation accumulation in the air-conditioned interior of the instrument enclosure.



Figure 5. AOS instrument enclosure with 10-m sampling stack.

Upstream of instruments connected to this line is a calibration system that supplies diluted calibration gas to all the instruments. A TO-14 Aromatic calibration standard is connected to this system and is used for PTR-MS calibration.

MAOS C Aerosol and Trace Gas Inlets

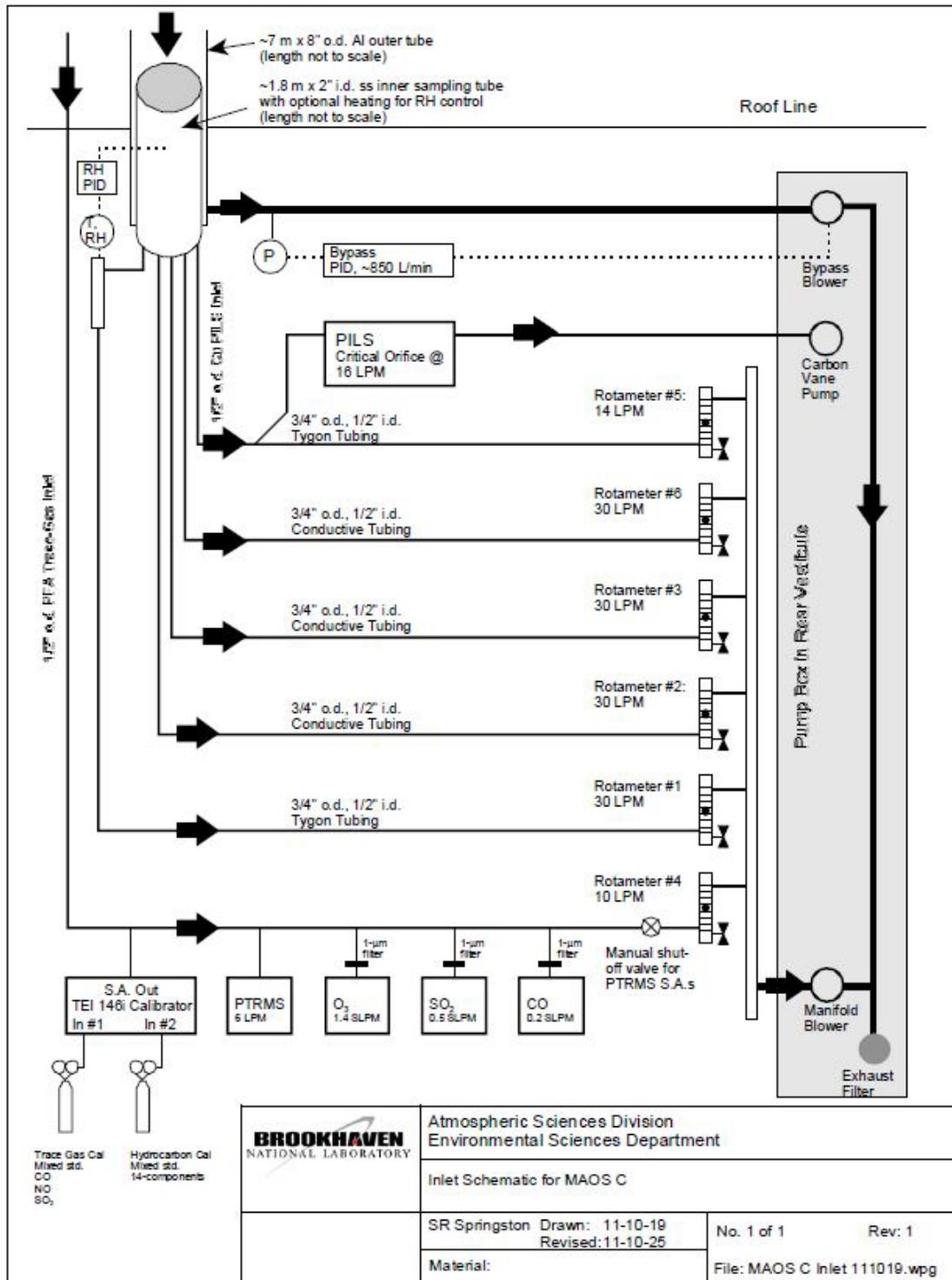


Figure 6. Schematic of inlet system.

14.0 Maintenance

The ion source should be cleaned after six months to a year of continuous operation. The PTR-MS is equipped with a PKR pressure sensor that monitors the detection chamber. If the detection chamber turbo pump draw is in the usual range, but the displayed pressure value is above 1 E-3 mbar, it means the sensor is dirty, which can impair or stop instrument function. When this occurs, the gauge must be cleaned.

15.0 Safety

Standard safety protocols should be followed for working on the PTR-MS. The instrument should be disconnected from all power before attempts should be made to service any element.

16.0 Citable References

de Gouw J, C Warneke, T Karl, G Eerdekens, C van der Veen and R Fall. 2003. "Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry." *International Journal of Mass Spectrometry* 223-224: 365-382, [doi:10.1016/S1387-3806\(02\)00926-0](https://doi.org/10.1016/S1387-3806(02)00926-0).

de Gouw J, and C Warneke. 2007. "Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry." *Mass Spectrometry Reviews* 26(2): 223-257, doi:10.1002/mas.

Singer W, J Beauchamp, J Herbig, J Dunkl, I Kohl and A Hansel. 2007. "Dynamic gas dilution system for accurate calibration of analytical Instruments such as PTR-MS." In *3rd International Conference on Proton Transfer Reaction Mass Spectrometry and Its Applications*, pp. 232-237. January 27-February 1, 2007, Obergurgl, Austria. Innsbruck University Press.

Appendix A: Text File Column Headings

Column #	Parameter
1	Abs time
2	Abs Time [sec]
3	Rel Time [sec]
4	Cycle
5	PrimIonInfo
6	Us V
7	Uso V
8	Udrift V
9	Udx V
10	Ihc mA
11	Source On/Off
12	p-Foreline mbar
13	p-Drift mbar
14	p-Toflens mbar
15	p-Tof mbar
16	PC-Inlet mbar
17	FC-Inlet sccm
18	FC-H2O sccm
19	FC-O2 sccm
20	FC-NO sccm
21	SV %
22	E/N Td
23	T-Drift?C
24	T-Inlet?C
25	T-Opt1?C
26	T-Opt2?C
27	TPdrift-I A
28	TPdrift-rot Hz
29	TPdet-I A
30	TPdet-rot Hz
31	DO 1
32	DO 2
33	DO 3
34	DO 4
35	N [cps]
36	CH2 [cps]

Column #	Parameter
37	HN [cps]
38	CH3 [cps]
39	O [cps]
40	H2N [cps]
41	HO [cps]
42	H3N [cps]
43	H2O [cps]
44	H4N [cps]
45	H3O [cps]
46	H3(O17) [cps]
47	H2(H2)O [cps]
48	H3(O18) [cps]
49	C2H3 [cps]
50	N2 [cps]
51	CH2N [cps]
52	HN2 [cps]
53	NO [cps]
54	HN(N15) [cps]
55	(N15)O [cps]
56	HNO [cps]
57	CH3O [cps]
58	O2 [cps]
59	O(O17) [cps]
60	HO2 [cps]
61	CH5O [cps]
62	O(O18) [cps]
63	H2O2 [cps]
64	H4NO [cps]
65	HO(O18) [cps]
66	H3O2 [cps]
67	H6NO [cps]
68	H5O2 [cps]
69	H5O(O17) [cps]
70	H4(H2)O2 [cps]
71	C3H3 [cps]
72	H5O(O18) [cps]
73	C3H5 [cps]
74	C2H2O [cps]
75	C2H4N [cps]
76	C3H6 [cps]

Column #	Parameter
77	C2H3O [cps]
78	C3H7 [cps]
79	N2O [cps]
80	CH2NO [cps]
81	CHO2 [cps]
82	C2H5O [cps]
83	NO ₂ [cps]
84	CH4NO [cps]
85	CH3O2 [cps]
86	C2H7O [cps]
87	H2NO2 [cps]
88	CH4O2 [cps]
89	H3NO2 [cps]
90	CH5O2 [cps]
91	H2O3 [cps]
92	C4H3 [cps]
93	C3O [cps]
94	C3HO [cps]
95	H5O3 [cps]
96	C4H5 [cps]
97	C3H3O [cps]
98	H7O3 [cps]
99	C4H7 [cps]
100	Fe [cps]
101	C3H5O [cps]
102	H7O2(O18) [cps]
103	C4H9 [cps]
104	C2H4NO [cps]
105	C4H10 [cps]
106	C3H7O [cps]
107	C2H6NO [cps]
108	C2H5O2 [cps]
109	CH4NO2 [cps]
110	C2H6O2 [cps]
111	CH3O3 [cps]
112	CH5O3 [cps]
113	C5H7 [cps]
114	C4H5N [cps]
115	C5H8 [cps]
116	C4H5O [cps]

Column #	Parameter
117	C5H9 [cps]
118	H10N2O2 [cps]
119	C3H3O2 [cps]
120	C4H7O [cps]
121	C5H11 [cps]
122	FeO [cps]
123	C3H6NO [cps]
124	C4H8O [cps]
125	FeHO [cps]
126	C3H5O2 [cps]
127	H9O4 [cps]
128	C4H9O [cps]
129	FeH2O [cps]
130	C2H4NO2 [cps]
131	C3H8NO [cps]
132	C6H3 [cps]
133	C2H5NO2 [cps]
134	C3H7O2 [cps]
135	C2H5O3 [cps]
136	C6H7 [cps]
137	C5H5O [cps]
138	C6H9 [cps]
139	C5H7O [cps]
140	C6H11 [cps]
141	CFeO [cps]
142	C4H6NO [cps]
143	C5H8O [cps]
144	CFeHO [cps]
145	C4H5O2 [cps]
146	C5H9O [cps]
147	C6H13 [cps]
148	CFeH2O [cps]
149	C4H8NO [cps]
150	C4H7O2 [cps]
151	C5H11O [cps]
152	C6H15 [cps]
153	FeO2 [cps]
154	FeH2NO [cps]
155	FeHO2 [cps]
156	FeH3NO [cps]

Column #	Parameter
157	C3H5O3 [cps]
158	C2H5N2O2 [cps]
159	C4H9O2 [cps]
160	FeH2O2 [cps]
161	FeH4NO [cps]
162	FeH3O2 [cps]
163	C7H9 [cps]
164	C7H11 [cps]
165	C5H5O2 [cps]
166	C4H4NO2 [cps]
167	C4H3O3 [cps]
168	C5H7O2 [cps]
169	C6H11O [cps]
170	C4H6NO2 [cps]
171	C5H10NO [cps]
172	CFeHO2 [cps]
173	C4H5O3 [cps]
174	C5H9O2 [cps]
175	CFeH2O2 [cps]
176	CFeH3O2 [cps]
177	C4H7O3 [cps]
178	FeH2NO2 [cps]
179	C8H9 [cps]
180	FeH2O3 [cps]
181	FeH3O3 [cps]
182	C8H11 [cps]
183	FeH4O3 [cps]
184	FeH5O3 [cps]
185	ClFeH4O [cps]
186	C6ClH4 [cps]
187	C2FeO2 [cps]
188	C5(C13)ClH4 [cps]
189	C5H6NO2 [cps]
190	C6(Cl37)H4 [cps]
191	C5H5O3 [cps]
192	C5H5O3 [cps]
193	C5(C13)(Cl37)H4 [cps]
194	C5H8NO2 [cps]
195	C5H7O3 [cps]
196	C5H7O3+ [cps]

Column #	Parameter
197	C5H9O3 [cps]
198	CFeH3O3 [cps]
199	C9H13 [cps]
200	FeH4O4 [cps]
201	FeH5O4 [cps]
202	FeH6O4 [cps]
203	C5H5O4 [cps]
204	C5H7O4 [cps]
205	C5H9O4 [cps]
206	C10H15 [cps]
207	C10H17 [cps]
208	C9H15O [cps]
209	C10H19 [cps]
210	C6Cl2H4 [cps]
211	C6Cl2H5 [cps]
212	C6Cl(Cl37)H4 [cps]
213	C5(C13)Cl2H5 [cps]
214	C6Cl(Cl37)H5 [cps]
215	C6(Cl37)2H4 [cps]
216	C5(C13)Cl(Cl37)H5 [cps]
217	C9H13O2 [cps]
218	C10H17O [cps]
219	C10H19O [cps]
220	C12H23O [cps]
221	C15H25 [cps]
222	N [ppb]
223	CH2 [ppb]
224	HN [ppb]
225	CH3 [ppb]
226	O [ppb]
227	H2N [ppb]
228	HO [ppb]
229	H3N [ppb]
230	H2O [ppb]
231	H4N [ppb]
232	H3O [ppb]
233	H3(O17) [ppb]
234	H2(H2)O [ppb]
235	H3(O18) [ppb]
236	C2H3 [ppb]

Column #	Parameter
237	N2 [ppb]
238	CH2N [ppb]
239	HN2 [ppb]
240	NO [ppb]
241	HN(N15) [ppb]
242	(N15)O [ppb]
243	HNO [ppb]
244	CH3O [ppb]
245	O2 [ppb]
246	O(O17) [ppb]
247	HO2 [ppb]
248	CH5O [ppb]
249	O(O18) [ppb]
250	H2O2 [ppb]
251	H4NO [ppb]
252	HO(O18) [ppb]
253	H3O2 [ppb]
254	H6NO [ppb]
255	H5O2 [ppb]
256	H5O(O17) [ppb]
257	H4(H2)O2 [ppb]
258	C3H3 [ppb]
259	H5O(O18) [ppb]
260	C3H5 [ppb]
261	C2H2O [ppb]
262	C2H4N [ppb]
263	C3H6 [ppb]
264	C2H3O [ppb]
265	C3H7 [ppb]
266	N2O [ppb]
267	CH2NO [ppb]
268	CHO2 [ppb]
269	C2H5O [ppb]
270	NO2 [ppb]
271	CH4NO [ppb]
272	CH3O2 [ppb]
273	C2H7O [ppb]
274	H2NO2 [ppb]
275	CH4O2 [ppb]
276	H3NO2 [ppb]

Column #	Parameter
277	CH5O2 [ppb]
278	H2O3 [ppb]
279	C4H3 [ppb]
280	C3O [ppb]
281	C3HO [ppb]
282	H5O3 [ppb]
283	C4H5 [ppb]
284	C3H3O [ppb]
285	H7O3 [ppb]
286	C4H7 [ppb]
287	Fe [ppb]
288	C3H5O [ppb]
289	H7O2(O18) [ppb]
290	C4H9 [ppb]
291	C2H4NO [ppb]
292	C4H10 [ppb]
293	C3H7O [ppb]
294	C2H6NO [ppb]
295	C2H5O2 [ppb]
296	CH4NO2 [ppb]
297	C2H6O2 [ppb]
298	CH3O3 [ppb]
299	CH5O3 [ppb]
300	C5H7 [ppb]
301	C4H5N [ppb]
302	C5H8 [ppb]
303	C4H5O [ppb]
304	C5H9 [ppb]
305	H10N2O2 [ppb]
306	C3H3O2 [ppb]
307	C4H7O [ppb]
308	C5H11 [ppb]
309	FeO [ppb]
310	C3H6NO [ppb]
311	C4H8O [ppb]
312	FeHO [ppb]
313	C3H5O2 [ppb]
314	H9O4 [ppb]
315	C4H9O [ppb]
316	FeH2O [ppb]

Column #	Parameter
317	C2H4NO2 [ppb]
318	C3H8NO [ppb]
319	C6H3 [ppb]
320	C2H5NO2 [ppb]
321	C3H7O2 [ppb]
322	C2H5O3 [ppb]
323	C6H7 [ppb]
324	C5H5O [ppb]
325	C6H9 [ppb]
326	C5H7O [ppb]
327	C6H11 [ppb]
328	CFeO [ppb]
329	C4H6NO [ppb]
330	C5H8O [ppb]
331	CFeHO [ppb]
332	C4H5O2 [ppb]
333	C5H9O [ppb]
334	C6H13 [ppb]
335	CFeH2O [ppb]
336	C4H8NO [ppb]
337	C4H7O2 [ppb]
338	C5H11O [ppb]
339	C6H15 [ppb]
340	FeO2 [ppb]
341	FeH2NO [ppb]
342	FeHO2 [ppb]
343	FeH3NO [ppb]
344	C3H5O3 [ppb]
345	C2H5N2O2 [ppb]
346	C4H9O2 [ppb]
347	FeH2O2 [ppb]
348	FeH4NO [ppb]
349	FeH3O2 [ppb]
350	C7H9 [ppb]
351	C7H11 [ppb]
352	C5H5O2 [ppb]
353	C4H4NO2 [ppb]
354	C4H3O3 [ppb]
355	C5H7O2 [ppb]
356	C6H11O [ppb]

Column #	Parameter
357	C4H6NO2 [ppb]
358	C5H10NO [ppb]
359	CFeHO2 [ppb]
360	C4H5O3 [ppb]
361	C5H9O2 [ppb]
362	CFeH2O2 [ppb]
363	CFeH3O2 [ppb]
364	C4H7O3 [ppb]
365	FeH2NO2 [ppb]
366	C8H9 [ppb]
367	FeH2O3 [ppb]
368	FeH3O3 [ppb]
369	C8H11 [ppb]
370	FeH4O3 [ppb]
371	FeH5O3 [ppb]
372	ClFeH4O [ppb]
373	C6ClH4 [ppb]
374	C2FeO2 [ppb]
375	C5(C13)ClH4 [ppb]
376	C5H6NO2 [ppb]
377	C6(Cl37)H4 [ppb]
378	C5H5O3 [ppb]
379	C5H5O3 [ppb]
380	C5(C13)(Cl37)H4 [ppb]
381	C5H8NO2 [ppb]
382	C5H7O3 [ppb]
383	C5H7O3+ [ppb]
384	C5H9O3 [ppb]
385	CFeH3O3 [ppb]
386	C9H13 [ppb]
387	FeH4O4 [ppb]
388	FeH5O4 [ppb]
389	FeH6O4 [ppb]
390	C5H5O4 [ppb]
391	C5H7O4 [ppb]
392	C5H9O4 [ppb]
393	C10H15 [ppb]
394	C10H17 [ppb]
395	C9H15O [ppb]
396	C10H19 [ppb]

Column #	Parameter
397	C6Cl2H4 [ppb]
398	C6Cl2H5 [ppb]
399	C6Cl(Cl37)H4 [ppb]
400	C5(C13)Cl2H5 [ppb]
401	C6Cl(Cl37)H5 [ppb]
402	C6(Cl37)2H4 [ppb]
403	C5(C13)Cl(Cl37)H5 [ppb]
404	C9H13O2 [ppb]
405	C10H17O [ppb]
406	C10H19O [ppb]
407	C12H23O [ppb]
408	C15H25 [ppb]



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