This is a description about how PTR-QMS works, and how it is used in the SMEAR II station

Proton Transfer Reaction – Quadrupole Mass Spectrometer (PTR-QMS) is an instrument for monitoring various volatile orcanic compounds (VOC). Detection limit is low, while quantification of compounds is real-time and no sample preparation is needed. Ionization is chemical using H_3O^+ as primary ions. The whole measurement system consists of PTR-QMS - instrument, sampling system and calibration system. The instrument used at Smear II is an earlier version from the beginning of the 21st century, but there are no major differences between that and the newer ones.

This is a short and comprehensible description of PTR-QMS techniques and applications used at Smear II. Further information about use and maintenance of PTR-QMS can be found for example from the manual of the instrument. Further information about applications and their use in ecophysiological and atmospherical sciences can be found from research papers listed at the end of this text.

Part I: Techniques

PTR-QMS instrument looks outside like a gray box with dimensions about one meter high and somewhat less in other directions. Inside the metal sheet are the main parts of the instrument. However, in addition one needs sample lines, calibration system and a computer with appropriate software. The core of the instrument is naturally vacuum section (fig 1), but besides it instrument contains various electronics, pumps and flow controllers, which are introduced when necessary. In this part the focus is mainly on vacuum section.
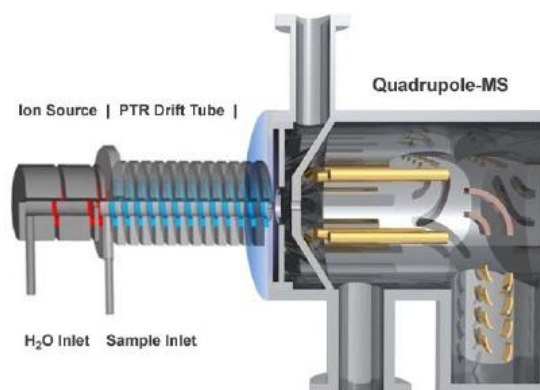

Fig 1. Vacuum section. Picture from PTR-QMS operating instructions V1.9, Ionicon Analytik.

The vacuum section consists of ion source, PTR drift tube and quadrupole mass spectrometer (figs 1, 2). This wholeness is called with term vacuum section, because it is differentially pumped with two (standard version) or three (high sensitivity version) turbo pumps. Typical values for pressures in drift tubes and quadrupole-MS are 2,0 mbar and 10^{-5} mbar, respectively. Differential pumping sustains the flow of gases through the device. Inlet system outside the drift tube is also pressure controlled and, added to this, heated, which guarantees a constant and accurate injection of sample and allows response times down to 100 ms.

The ion source (fig 1) produces H_3O^+ ions. One nice and simple advantage of PTR-QMS is that ions are made from pure water. Water vapour is protonated to H_3O^+ primary ions with a hollow cathode. This process provides an intense source of primary ions. Flow of water is controlled and before drift tube excess water is dumped out. By varying voltages after hollow cathode (fig 2, V5 and V4) the signal of H_3O^+ can be increased, but that also leads to higher fractions of O_2^+ and NO^+ ions, which in turn means much harder ionization in drift tube. Basically the distinction

between soft and hard ionization is that the softer ionization method is used the less fragmentation is caused for target compounds.
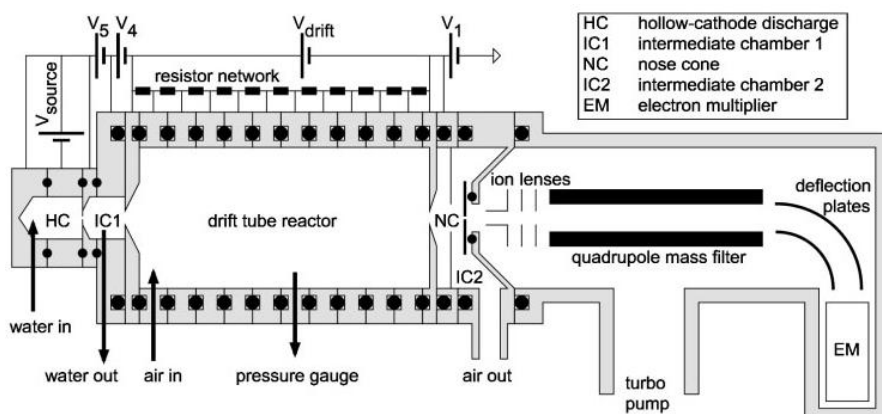

Fig 2. Vacuum section with higher details. Picture from de Grouw & Warneke 2006.

The drift tube consists of stainless steel rings with intervening Teflon rings to seal and isolate the steel rings electrically. Lens units (fig 2, marked with V) guide the ions to the reaction chamber and are responsible for an efficient primary ion signal. Overall drift voltage is controlled with resistor network (fig 2). In drift tube sampled air is exposed to primary ions (H_3O^+), which along with homogeneous electric field causes proton transfer reaction. This reaction means that compounds with high enough proton affinity take one proton out of primary ion. Major components of clean air have too low proton affinities so they can't be exposed to proton transfer. This is considered as an advantage because sampled air can be used as a buffer gas. It also improves the relative signal of preferred trace gases. The proton affinity of water (7,2 eV) is the limiting factor. If proton affinity of a compound is lower than that of water (e.g. $O_2 \rightarrow$ 4,4 eV, $N_2 \rightarrow$ 5,1 eV, $CO_2 \rightarrow$ 5,7 eV, $CO \rightarrow$ 6,2 eV), no proton transfering occurs. However, most of the target compounds have proton affinities high enough so they can be protonated (table 1). After proton transfer reaction the molecular mass of the protonated compound is molecular mass of the target compound + 1 because of transfered proton. The unit of molecular mass is amu (atomic mass unit).

At the other end of drift tube is a separate chamber connected to reactor with a small orifice. Most of the sampled air is pumped away by a turbo molecular pump (fig 2). A small fraction of ions is funnelled through the nose cone of quadrupole mass spectrometer. The mass spectrometer consists of a quadrupole mass filter, deflection plates and an electron multiplier. Quadrupole mass filter is used to select ions with certain m/z ratios (mass-to-charge -ratio). Selection is done by rf- and dc- voltages of rods of quadrupole. Those voltages causes oscillation of ions. By changing the rf-field it is possible to select only a certain m/z ratio to pass through the quadrupole mass filter. Usually quadrupole mass filter is used to find

Table 1. Proton affinities of different compounds. Masses are non-protonated molecular masses. Table from PTR-QMS operating instructions V1.9, Ionicon Analytik.

compound	mass/mol [g]	proton affinity [kcal/mol]	proton affinity [eV]
helium	4	42.5	1.84
argon	40	88.6	3.85
O_2	32	100.9	4.38
H_2	2	101.3	4.40
N_2	28	118.2	5.13
CO_2	44	130.9	5.68
CO	28	141.9	6.16
H_2O	18	166.5	7.23
formaldehyde	30	171.8	7.46
formic acid	46	178.8	7.76
methanol	32	181.9	7.89
acetaldehyde	44	186.6	8.10
methanthiol	48	187.4	8.13
ethanol	46	188.3	8.17
methylformeat	60	188.4	8.18
propionaldehyde	58	189.6	8.23
acetic acid	60	190.2	8.25
aceton	58	196.7	8.54
methylethylketone	72	199.8	8.67
dimethylsulfide	62	200.6	8.70
...	...	...	...

selected ions rather than scanning over the mass range. The whole mass range is 1-512 amu. Measuring of different masses is done one at a time. Integration time of one mass highly effects on the precision of the result. Integration time varies e.g. due the sampling system properties and target compound, but is usually within seconds or tenths of seconds. The whole measurement cycle lasts thereby from couple of seconds to dozens of seconds depending on the mass list measured.

After quadrupole mass filter selected ions arrive via deflection plates to electron multiplier. Bowed deflection plates are needed to eliminate the background signal from ion source. In electron multiplier the hits of single ions is counted. That countrate is a starting point for calculating the mass concentrations of target compounds in sampled air. However, besides countrate one needs also data of many other factors for calculations. Some of this information is recorded by device itself (pressures etc.), but case-specific some external data may be needed. One interesting point is that calculating mass concentrations of compounds present in standard gas is quite straightforward, while calculating mass concentrations of other compounds is somewhat more complex and not so easy to perceive. The latter calculation is done with relative transmission curves based on relative transmission coefficients of different compounds present in standard gas (fig 3). Transmission curves are calibration-specific, so
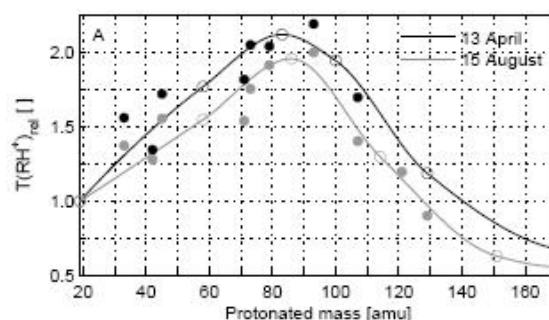

Fig 3. Examples of relative transmission curves at Smear II in Hyytiälä. Circles are relative transmission coefficients of compounds present in standard gas. Lines are transmission curves solved based on transmission coefficients. Different colors mark two different calibration times. Relative transmission of water (protonated mass 19 amu) is set to one. Relative transmission of masses around 80 amu has much lower loss in drift tube than water. Masses over 130-140 amu has higher loss than water. Figure from Taipale et al. 2008.

proper calibration made in due order has high impact on precision of whole measuring and calculation system. The calibration system consists of zero air generator and standard gas cylinder with reasonable pumps and lines. Calibration gas is diluted with zero air close to ambient concentrations and then masses of compounds involved in standard gas are measured (fig 4). At Smear II calibrations are conducted once or twice in two weeks. Raw data of one or two weeks is betweentimes saved to 'Timo'.

For calculation one needs information about primary ion signal. It could be got by measuring mass 19 amu, which is the mass of protonated water, but the signal of that is so high it would detoriorate the electron multiplier very fast. By measuring mass 21 amu (protonated mass of water isotope H_2O^{18}) instead of mass 19 amu one gets same information with much lower signal. With knowledge about fraction of this isotope in water it is possible to solve the primary ion signal. Mass concentrations of measured masses can be solved on by way of transmission coefficients/curves and primary ion signal.

It's sometimes discussed that measuring mass concentrations of masses is an unbalanced way to study concentrations of target compounds. This problem is two-sided: First off the signal of one mass can consist of several compounds which happen to have same protonated mass. And on the second place same compound can turn up by different masses e.g. because of fragmentation. Fragmentation patterns of different compound can vary within seasonal cycle. Therefore

application-spesific research of these phenomena is required to get reliable results. Monitoring certain masses also raises a requirement that one needs solid basic understanding about a phenomenon to decide which masses are useful to monitor.

The instrument must be maintained regularly. Maintenances can be divided in three parts. First part consists of various cleaning and optimization processes, and there is no need to do them coexistent but when ever there seems to be need for them. The last two parts are small and large services, conducted by a trained people with a high knowledge level about PTR-QMS technology. These maintenance procedures consist of various exchanges, checks, calibrations and updates. Again there is no need to do all maintenance processes at a same time, but a trained people can do one or several of them when there seems to be need for them. Transportation and also many of aforesaid maintenance processes require shutting down the instrument. This shut down can be done on three different level: stand-by mode, idle mode and power-down completely. If instrument is transported or certain maintenance processes are done, complete power-down is needed. This is mainly because of turbo pumps, which do not tolerate any mechanical shocks when rotating. If power-down time lasts longer than two weeks, the vacuum section is recommended to be filled with non-oxidant gas (e.g. N_2) to avoid oxidations. Besides correct shutting down also switching on the instrument must be done correctly (see manual for further instructions concerning shutting down and switching on).
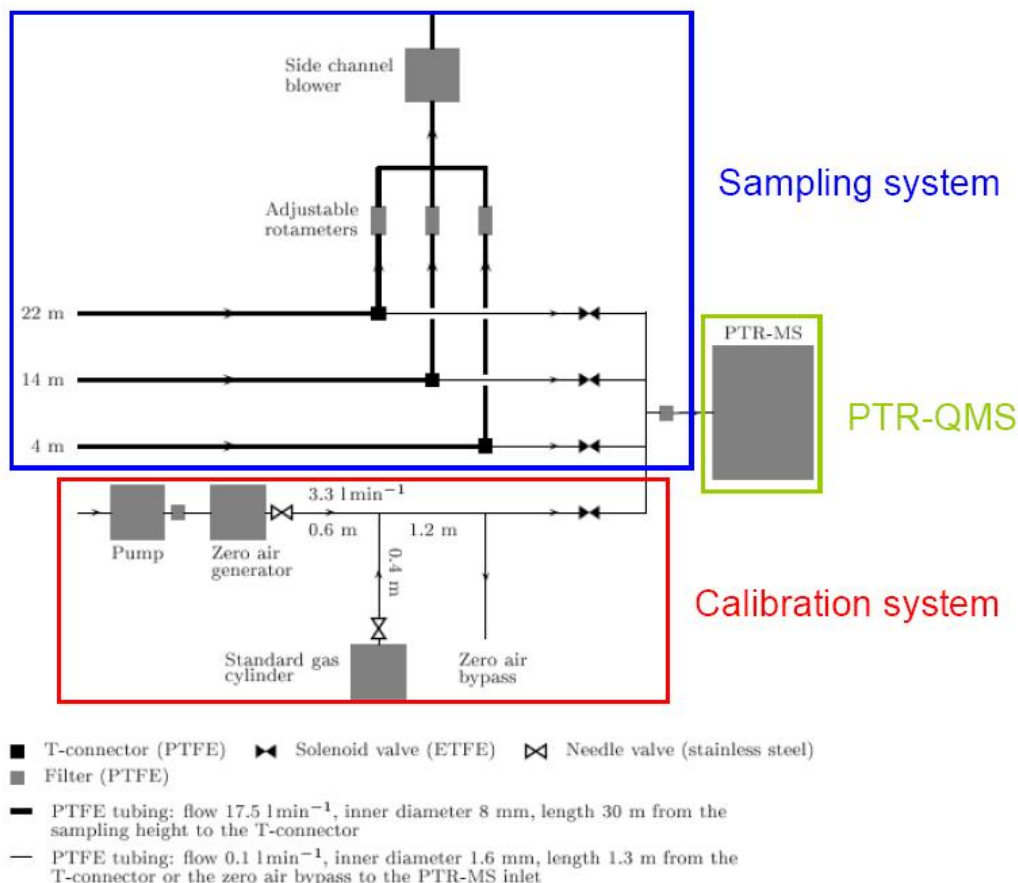

Fig 4. Schematic picture of measurement system used in Hyytiälä at Smear II for measuring VOC-concentrations from different altitudes, valid 2007-2009. PTR-QMS and calibration system are same for also other kind of measurements including cuvette measurements. Flows may differ from those mentioned in picture. Picture from Taipale et al. 2008. Starting from 2010 there has been sampling from 6 heights, and from 2013 from 8 heights.

Part II: Applications

PTR-QMS is an instrument for monitoring various volatile orcanic compounds (VOC). Basically it measures countrate, which can be converted into mass concentration. Among atmospheric and ecophysiological sciences PTR-QMS is usually used for monitoring atmosphere-biosphere interactions. This means various flux measurements based on mass concentrations and monitoring concentration profiles in biosphere-atmosphere –continuum.

A measure set-up for monitoring concentration profiles is presented in fig 4. This set-up is used at the Smear II. Concentrations of different compounds (masses) are monitored on different altitudes, which provides a profile of concentrations. When combined with information about other environmental factors it is possible to study how compounds act in biosphere-atmosphere continuum.

Tubings from various measurements (mast: concentrations, photo tower: shoot chambers, catchment: soil chambers) are ran to main cabin. Sample flows in tubings may be different from mentioned in fig 4. Flows are kept up with pumps and regulated and controlled with rotameters and magnetic valves.

For understanding processes of VOC synthesis and emissions various chamber measurements are needed. At the Smear II both soil (summertime 3 chambers, wintertime no measurements) and shoot (typically 2 in Scots pine shoots and 2-4 four in Scots pine stem) chambers are used. The calibration system (see fig 4) is same for all PTR-QMS measurements. The PTR-QMS is located to main cabin. Shoot chambers are cylindrical, volume 3.5 or 4.5 dm^3. The chambers are made of acrylic plastic and their internal surfaces are coated with Teflon FEP sheeting. Measurements of VOCs in chambers are conducted in three hour cycles (8 cycles per day), with no measurements during the last hour of each cycle. Every cycle consists of several closures (typically four for shoot and stem chambers, and one for soil chambers), which last few minutes each (210 seconds for the shoot chambers, somewhat less for stem chambers, and 810 seconds for soil chambers). PTR-QMS measurements coupled with every closure include both measuring when chamber is open (ambient consentrations) and when chamber is closed. In addition to PTR-QMS sampling also CO_2 and H_2O samples are analysed. Also PAR and temperature in chamber are measured. Some of the details mentioned above may be valid only with shoot chambers. Detailed information of flux measurement system and calculations can be found from research papers listed at the end and from resbonsible persons (Pasi Kolari, Juho Aalto).

Effect of chambers and tubing for measuring VOCs with PTR-QMS has been tested at Smear II. Testing has been proceeded by feeding chamber or tubing with standard gas, which composition is known. Teflon tubing (64 meter long + some meters inside the cabin) has no effect on results. Resulting from materials used in chambers even couple of dozens per cent of VOCs can get lost (absorbed by chamber walls and other surfaces). Therefore also shoot chambers are covered with Teflon FEP sheeting. After all, some proportion of VOCs will always get lost inside the system before PTR-QMS instrument. At Smear II this portion can be estimated as minor, 5-30 %. More details in Kolari *et al.* 2012.

Since March 2009 the mass list of PTR-QMS chamber measurements has been like represented in table 2, and since November 2013 in table 3. Mass list used to be somewhat longer, but limited time resources led to short integration time which increased the noise level. With a shorter mass list and more data points the solving of mass balance equation is on more reliable basis.

Table 2. Mass list of chamber measurements with PTR-QMS at Smear II, 2009-2012.

Mass	Primary compound
M21	Water isotope
M33	Methanol
M39	Water cluster ($H_2O+H_3O^+$)
M45	Acetaldehyde
M59	Acetone
M69	Isoprene + MBO
M79	Benzene
M81	Monoterpene fragment
M99	Hexenal
M101	Hexanal, 3-hexenol
M137	Monoterpene
M153	Methyl salicylate

Table 3. Current (2013) mass list of chamber measurements with PTR-QMS at Smear II.

Mass	Primary compound
M21	Water isotope
M33	Methanol
M39	Water cluster ($H_2O+H_3O^+$)
M45	Acetaldehyde
M59	Acetone
M69	Isoprene + MBO
M81	Monoterpene fragment
M87	Methylbutenol
M93	Toluene
M137	Monoterpene

Next the measurement system of PTR-QMS with shoot chambers is illustrated with some photos.
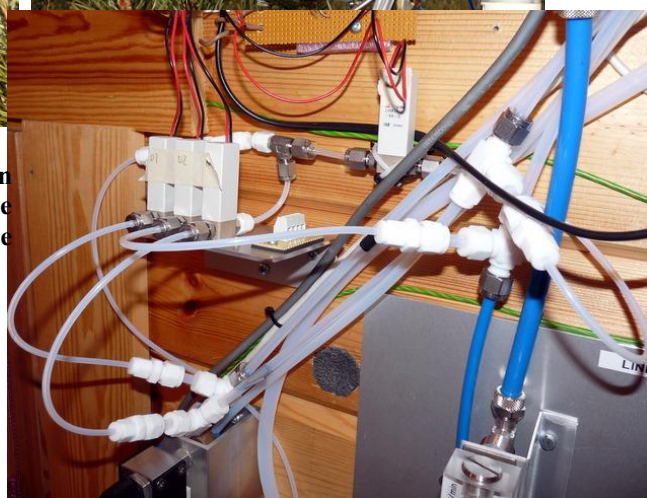
Shoot chambers for VOC-measurements. Left one is on normal position, right one in upward position, only the terminal bud inside the chamber to allow the growth of the shoot inside the chamber.

PTR-QMS instrument.

Some controls and displays of PTR-QMS are placed on front panel of instrument. Further information can be found from manual.

Part III: Files

This part of documentation concerns only chamber measurements conducted with PTR-MS. Raw files recorded by PTR-QMS are saved to 'Timo' every week or every second week. Files ch*yymmdd*.asc contain raw measurements, ze*yymmdd*.asc information about zero air. Raw measurements consist of time colums (A-D in excel), countrate colums (E-P, use mass list mentioned above as header), and pressures and voltages (Q-U). Last four columns (V-Y) show if the line of the chamber in question is measured or not.

Calculation of mass concentrations is done as below (for further information see Taipale et al. 2008):

Molecular concentration of target compound inside reaction:

$$[R] = \alpha \left[\frac{I(\mathrm{RH}^+)}{I(\mathrm{H_3O}^+) + I(\mathrm{H_3O}^+\mathrm{H_2O})} - \frac{p_{\mathrm{drift}}}{p_{\mathrm{drift,\,zero}}} \frac{I(\mathrm{RH}^+)_{\mathrm{zero}}}{I(\mathrm{H_3O}^+)_{\mathrm{zero}} + I(\mathrm{H_3O}^+\mathrm{H_2O})_{\mathrm{zero}}} \right]$$

Unit of $[R]$ is m^{-3}.
α is calibration coefficient $[m^{-3}]$.
$I(RH^+)$ is countrate of target compound [cps].
$I(H_3O^+) = 500 \cdot I(M21)$ is countrate of primary ion [cps].
$I(H_3O^+ H_2O) = 250 \cdot I(M39)$ countrate of primary ion cluster [cps].
p_{drift} is pressure inside reaction chamber [Pa]. Unit in raw data is mbar.
Index zero means zero air.

Turning molecular concentration into mixing ratio:

$$VMR = \frac{[R]}{N} \cdot 10^9 = \frac{[R]}{N_A \frac{p_{drift}}{RT_{drift}}} \cdot 10^9$$

Unit of VMR is ppbv ($\rightarrow 10^9$).
N is concentration of air inside reaction chamber $[m^{-3}]$.
$N_A = 6.0221367 \cdot 10^{23} \ mol^{-1}$ Avogadro constant.
$R = 8.314510 \ J \ mol^{-1} \ K^{-1}$ is gas constant.
$T_{drift} = 323.15$ K is temperature inside reaction chamber.

Turning mixing ratio into mass concentration:

$$C = M \cdot VMR \cdot 10^{-9} \cdot C_{tot, molar} \cdot 10^6 = M \cdot VMR \cdot 10^{-9} \cdot \frac{p_{ambient}}{RT_{ambient}} \cdot 10^6$$

Unit C is $\mu g \ m^{-3}$ ($\rightarrow 10^6$).
M molecular weigth of target compound $[g \ mol^{-1}]$.
$C_{tot, molar}$ is concentration of ambient air $[mol \ m^{-3}]$.
$p_{ambient} = 101325$ Pa is pressure of ambient air.
$T_{ambient} = 293.15$ K is temperature of ambient air.

For chamber measurements this calculation is normally done with a Mathematica code programmed by Pasi Kolari, for further details of the calculation see Kolari *et al.* 2012. This code calculates also CO2 exchange and transpiration. These calculations need raw chamber gas exchange files for background information. Also URAS calibration file is needed.

References

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