Universiteit Utrecht

CALIBRATION METHODOLGY FOR A PROTON TRANSFER REACTION MASS SPECTROMETER

Institute for Marine and Atmospheric Research (IMAU)

Master's thesis

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Climate Physics

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Abstract

Proton transfer reaction mass spectrometry (PTR-MS) is a method of measuring the volume mixing ratio (VMR) of trace components in the atmosphere based on the ionisation of molecules through proton donation. This document primarily concerns an innovative new method of gas standard addition for instrument calibration. Instead of a steady dilute flow of gas standard into the instrument, a finite, known amount of gas standard is introduced. This is a considerably faster process.

Protocols are developed here to retrieve important parameters with this method of standard addition. The compound specific calibration factor, S (the Sensitivity), is the proportionality between the intensities (in ion counts per second) that make up the output of PTR-MS and VMR's they represent. X_R, the humidity factor, is the relative rate with which compounds receive protons from water clusters in comparison to single water molecules. The retrieval of these two parameters allows for the accurate measurement of compounds contained in the gas standard (i.e. compounds for which the PTR-MS can be calibrated) independent of the humidity in an air sample.

Protocols have also been developed to increase the accuracy of the measurement of uncalibrated compounds through the application of kinetic theory. Using the same method of standard addition, the relative efficiency with which the instrument detects different masses is found. This is known as the mass dependent transmission curve.

This document also includes a collation of data processing and quality assessment techniques from other PTR-MS projects into a single, clear methodology and the introduction of new quality control and tuning protocols. These methods were developed as a contribution to a larger work concerning the implementation of a standard operating procedure for PTR-MS. The knowledge gained during this project is now being used to create a 5-minute standard addition routine that will allow for the comprehensive calibration of an instrument. Through outreach to the wider PTR-MS community via the ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure) network, it is hoped that this routine can become standard practice.

Table of Contents

1   Introduction

This document is made up of contributions to a standard operating procedure (SOP) for the operation of proton-transfer-reaction mass-spectrometers (PTR-MS) of all types and makes[1]. As such much of the content is delivered as instruction rather than commentary. This content is split into five sections:

- An introduction to the theory behind PTR-MS, covering the ion chemistry involved as well as some the main advantages and disadvantages of the technique
- Optimal settings are given for the various component sections of the instrument as well as the measurements used to find these optimal settings
- A collation of data processing and quality assessment techniques from previous PTR-MS papers into a single, clear methodology
- A description of a new method of gas standard addition and the protocols that have been developed in this project to partner it.
- Data quality assessment and tuning protocols developed in this project are detailed and evaluated

After each section a brief evaluation is included. A conclusion with thoughts on the future of the larger project is also provided along with references. An appendix is included with a basic PTR-MS schematic and the code used in the calibration protocols.

2   Theory and Ion Chemistry

Mass spectrometry of all forms is dependent on the ionisation of the molecular compounds that are being studied. Traditional electron ionization mass spectrometry suffers from strong fragmentation of molecular ionic species; the energy transfer from the impact involved is very large (Märk, 1984). Proton transfer reactions from protonated water can be used to achieve ionisation while avoiding this excessive fragmentation (Lindinger, 1993). H_3O^+ (hydronium) is created in the ion source (IS) and transferred to the drift tube of the PTR-MS. In most common PTR-MS instrument hydronium ions are produced from water vapour ionized by fast electrons in a hollow cathode plasma. Hydronium is then used as a proton donor (or primary ion) to the trace gas (R) that is being measured.

$$H_3O^+ + R \leftrightarrow RH^+ + H_2O \qquad \text{(R1)}$$
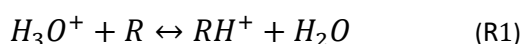
k_{19} is the net proton transfer rate constant for reaction R1. If the proton affinity[2] (PA) of R is higher than the PA of water the equilibrium position strongly shifts to the right-hand side and the steady state of R1 will almost entirely consist of the protonated compound and water. In this case the net reaction rate, k_{19}, will be practically equivalent to the collisional rate (a few times $10^{-9} cm^3$/molecules/sec) (De Gouw et al, 2007). If a compound has a PA above but close to that of water, such as formaldehyde, the exothermicity of the reverse reaction in R1 will be non-negligible (Hansel, 1998 and the dynamic equilibrium point will move further to the left-hand side. This means that the equilibrium will shift to the right side and the exact proportion will depend on the humidity and the collision energy between ions and neutral molecules. This holds for any other compound with a similar PA.

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[1] It should be noted that all the calibration measurements made in this report were performed on Ionicon instruments and therefore most specific recommendations for instrument settings are given in terms pertaining to Ionicon instruments.

[2] Proton affinity is a measure of the gas phase acidity of a compound and is the energy released when the compound bonds with a free proton (H^+). For the purposes of this paper it can be thought of a measure of the willingness of a compound to take on an additional proton (Hence proton affinity).

In table 1 the proton affinities of the most abundant constituents of the atmosphere and some commonly studied VOC's are shown. The PA of water is above that of the common atmospheric constituents. For these compounds the dynamic equilibrium point of R1 shifts strongly to the left-hand side and any ionised molecules are quickly converted back to primary ions and non-protonated compound.

The commonly studied VOC's listed in table 1 have much higher PA's and so will be ionised through equation 1. This means water is a very convenient primary ion as it will ionise only the VOC's in an air sample but not the main constituents of air. This allows such samples to be transferred to the drift tube of the PTR-MS directly, without the need of separating the VOCs from bulk air.

There are complications to this technique. Firstly, clustering water molecules can be formed and act as additional primary ions: $(H_2O)_2H_3O^+$. These can also act as proton donors to R:

$$(H_2O)H_3O^+ + R \leftrightarrow RH^+ + H_2O \qquad \text{(R2)}$$

$$(H_2O)H_3O^+ + R \leftrightarrow R(H_2O)H^+ + H_2O \qquad \text{(R3a)}$$

$$R(H_2O)H^+ + M \leftrightarrow RH^+ + H_2O + M \qquad \text{(R3b)}$$
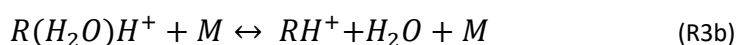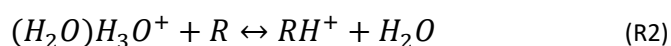
These clusters are a complication because $H_2O(H_2O)$ has a different and higher proton affinity than H_2O (see table 1). This means that compounds receive protons from clusters at a different speed and this introduces a humidity dependence into the final VMR calculation.

Compound	Formula	PA (eV)
Argon	Ar	3.8
Oxygen	O_2	4.4
Nitrogen	N_2	5.1
Carbon Dioxide	CO_2	5.7
Methane	CH_4	5.7
Nitrous Oxide	N_2O	5.9
Carbon Monoxide	CO	6.2
Butane	C_4H_{10}	7.1
Water	H_2O	7.2
Hydrogen Sulphide	H_2S	7.4
Hydrogen Cyanide	HCN	7.4
Formic Acid	HCOOH	7.8
Methanol	CH_3OH	7.8
Acetonitrile	CH_3CN	7.8
Benzene	C_6H_6	7.9
Ethanol	C_2H_6O	8.2
Propanol	C_3H_8O	8.3
Water Cluster	$H_2O(H_2O)$	8.4
Acetone	CH_3COCH_3	8.5
Ammonia	NH_3	8.9

Table 1: Proton Affinities of clean air constituents and some common VOCs
(Lias et al, 1988)(W.Jolly,1991)

The high PA means that direct proton transfer (R2) is only non-negligible for compounds that have an even higher PA than that. R3a is a much more important pathway for most VOCs. In the second step (R3b) the equilibrium between protonated VOC and the VOC-water cluster is established according to the energy conditions in the drift tube.

The availability of these clusters depends on the humidity and energy conditions in the drift tube, however for most compounds they introduce a second ionisation pathway. The net transfer rate of this second pathway will in most cases be slower than the collisional rate and this introduces a

humidity dependence in the detection of compounds. Within the recommended operating conditions in this paper only second order clusters have a noticeable effect and these can be mostly accounted for when measuring calibrated compounds (see section 5.1).

Secondly, Fragmentation is still a persistent issue; particularly with larger compounds. This can be accounted for when the m/z at which fragments are detected is known (see section 4.5.1). However, for complex samples this is not the case, the effect can be mitigated by operating in lower energy conditions. Although it should be noted that there is a lower bound to the effectiveness of operating in low energy conditions. Low energy conditions lead to increased cluster formation, the complications of which are detailed above. In addition to this there will be an increased occurrence of VOC-water clusters, which complicate the spectrum in a similar manner to fragmentation. Specific bounds on the energetic conditions in the drift tube are discussed in section 3.2 and 6.2.

3   Optimal Instrument Settings and Operating Conditions

In this section, all critical parameters that involve the ion source (IS), the reaction chamber (drift tube, DT) and ion transfer (IT) to mass spectrometer (MS) are discussed. See appendix for schematic.

3.1   Ion Source

The IS is primarily regulated with two parameters: (i) the electron current running through the hollow cathode, and (ii) the flow of water vapour into the IS from which hydronium (H_3O^+) is formed. In some (newer) models of PTR-MS the pumping efficiency of the IS can be regulated as well. The tuning of this first parameter is not covered here and it is the recommendation to keep the current in the range 3-5mA, which typically ensures stable long term operation.

Despite the pressurised nature of the separate chambers of the PTR-MS there is a mass exchange between the IS and DT (De Gouw, 2007): Water vapour leaks from the IS to the DT and air sample constituents (mainly nitrogen and oxygen) leak from the DT to the IS. This mass exchange is primarily dependent on the rate at which water vapour flows to the IS as the DT is held at constant pressure. A higher flow rate will result in higher IS pressure causing increased water vapour leakage to the DT and decreased leakage of the DT to the IS.

Both these leakages can have a critical impact on the results derived from PTR-MS analysis. Water vapour leakage will cause increased cluster formation (($H_2O)_nH_3O^+$). These clusters act as primary ions and while the effect of lower order clusters can be accounted for it is still a large source of inaccuracy (see figure 1) (see section 4.9).
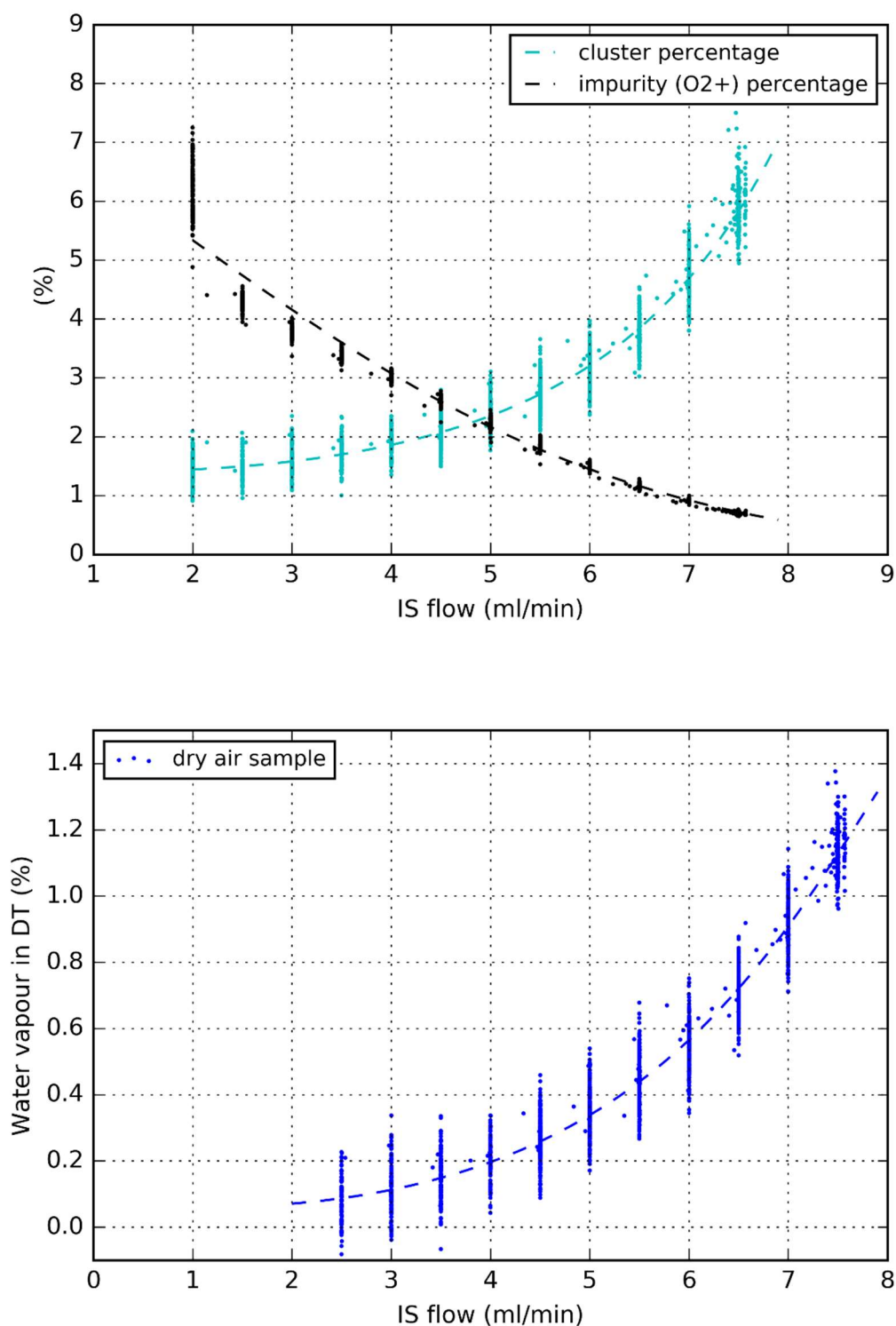
Figure 1: The top panel shows the percentage of $H_2OH_3O^+$ to H_3O^+ (cluster percentage) and percentage of O2+ to H_3O^+ at varying IS flow rates with an input of dry air to the DT. These figures were generated using E/N = 130. The bottom panel used the absolute humidity calibration introduced in section 6.1 to find the fraction of water vapour induced in the drift tube by the IS flow.

DT leakage of air causes the formation of impurities (O_2^+ and NO^+) in the ion source that are then transferred to the DT. The impurities react with atmospheric constituents and complicate the interpretation of mass spectra.

To uphold the quality of the data output of the PTR-MS boundary conditions have been set for the IS flow rate as well as a recommended value that balances both leakages:

- The leakage of water vapour from the IS to the DT should not induce an AH in the drift tube of above 1%. This value represents the amount of water vapour that would be input to the drift tube by an air sample of 50% relative humidity at 22°C (the lab temperature at which the AH calibration measurements were performed). (Instructions for calibrating for AH detection can be found in section 6.1)
- The largest non-primary ion signal (in most cases O_2^+) should less than 3% of the H_3O^+ signal. Instructions on how to properly calculate this ratio can be found in section 6.3.

For the instrument used to produce the data for Figure 1 these two conditions are met for the flow of water vapour into the ion source (F_{H2O}) in the range 4-7ml/min and the flow rate that achieves the best balance between these two leakages is 5ml/min.

3.2 Drift Tube

The ionization of trace gases in the sample occurs in the drift tube and stable conditions are essential for quantitative and accurate results. The E/N value expresses the ratio between the homogeneous electrical field across the drift tube and the number concentration of the gas in the drift tube. This parameter crucially controls the balance between H_3O^+ and water clusters $((H_2O)_nH_3O^+)$ and the fragmentation pattern of protonated organics (see figure 2). E/N values in the range 115-140 Td ($1Td=10^{-21}Vm^2=10^{-17}Vcm^2$) are adopted as standard operating conditions. In this paper an E/N value that generates a cluster ratio of approximately 10% is recommended. This provides a standard operational E/N of 125 Td. The methods by which E/N and other relevant drift tube parameters can be calculated and tuned is found in Section 6.2.
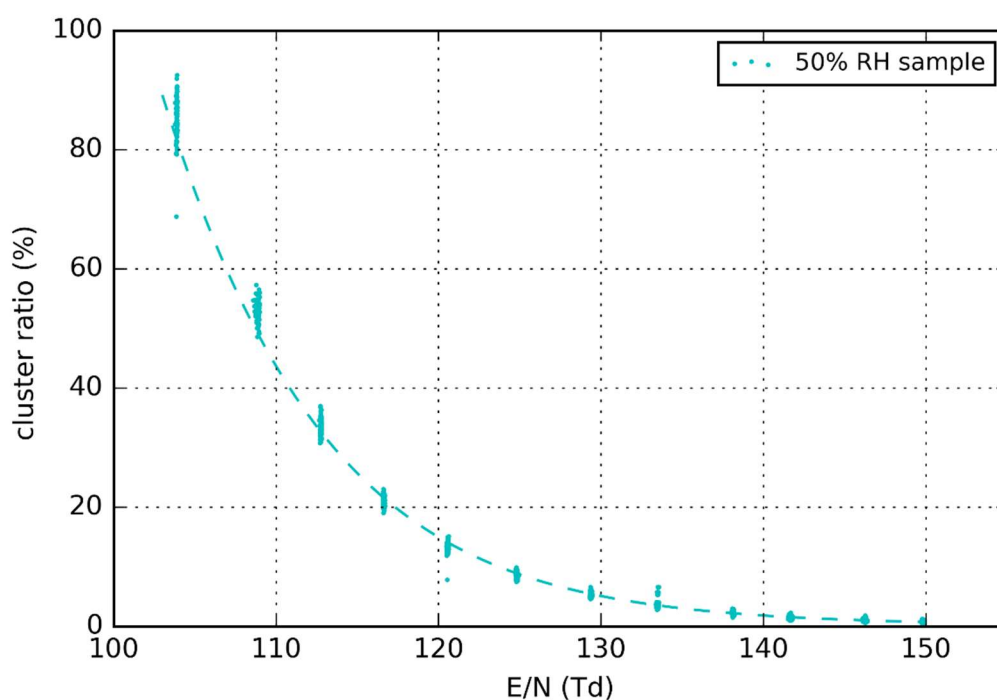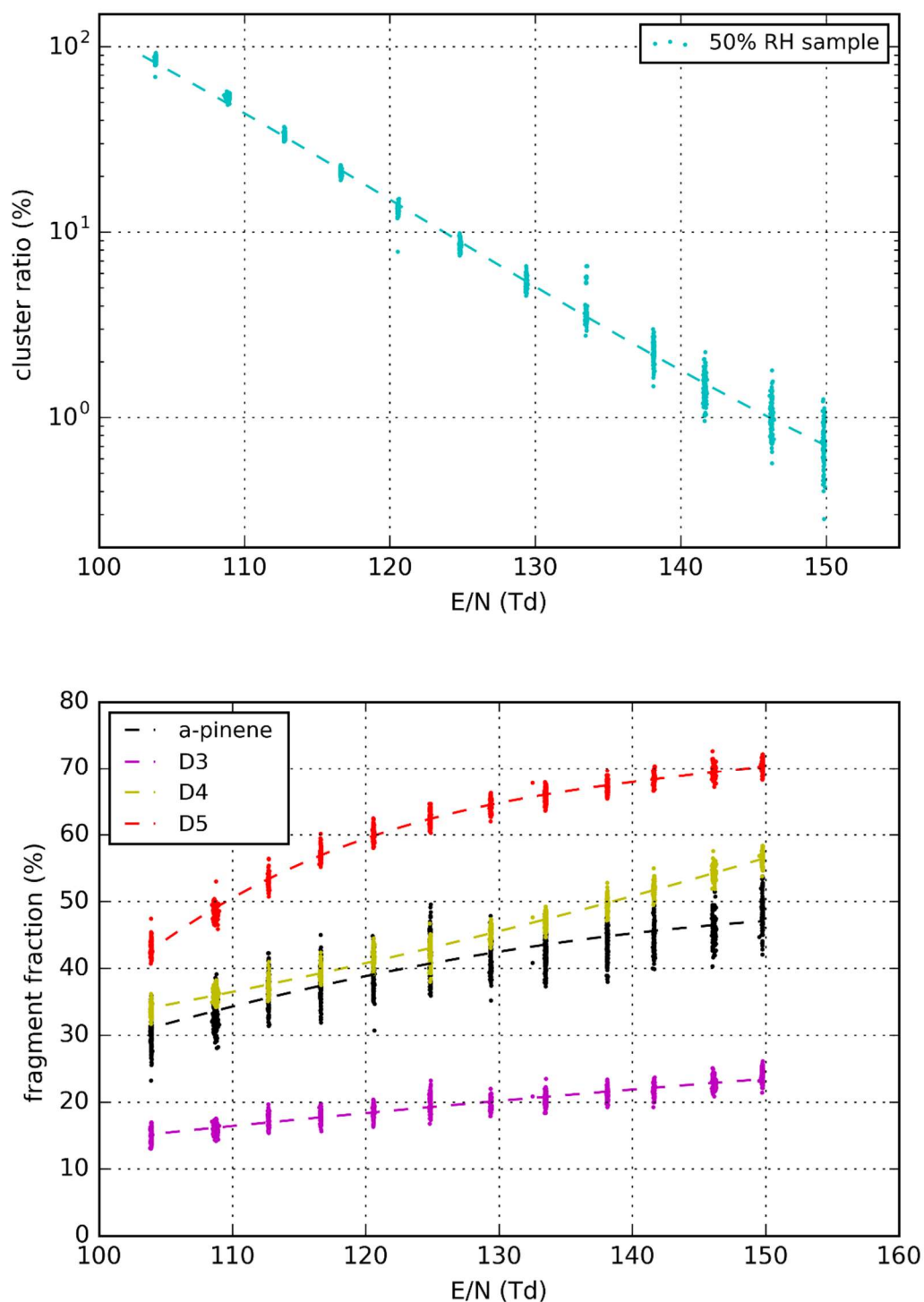
Figure 2: The top figure shows the cluster ratio ($H_2OH_3O^+/H_3O^+$) measured at different E/N values. This figure was generated by inputting an air sample of 50% Relative humidity at room temperature (295 K) into the PTR-MS and varying the voltage of the electric field in the drift tube.

In the middle figure the dependence of cluster formation is demonstrated to have an almost log-linear relationship with E/N.

In the bottom figure the intensity of the fragments of compounds found within the gas standard are shown as a percentage of the total intensity at increasing E/N values. This figure was generated by a steady dilute flow from the gas standard into the PTR-MS and varying the voltage of the electric field in the drift tube.

3.3   Ion Transfer Region

The Drift tube and mass spectrometer are connected through chambers at different pressures and ions are guided through these chambers by electrical lenses. The IT system is optimized to transfer a large fraction of ions into the mass spectrometer while keeping the kinetic energy of ions as homogeneous as possible. Sub-optimal tuning can result in additional mass dependent transmission effects and in fragmentation (or clustering) in regions where collisions between ions and molecules are still abundant. The voltage(s) at the entrance to the IT region must be tuned specifically to the E/N of the DT to avoid these effects. Instructions are provided on how to perform this tuning in section 6.5. Problems with mass dependent transmission can be avoided by following the operating instructions of the producers of the mass spectrometer being used and with protocols developed in section 5.4.

3.4   Time of Flight Mass Spectrometer (TOF-MS)

A full description of proper tuning and operation of a time of flight mass spectrometer is beyond the scope of this report. Here we adopt only a few recommendations:

The Micro Channel Plate (MCP) voltage should be raised until artefact peaks (figure 3) appear around the $H_3^{18}O^+$ signal (m/z 21.022) then set at a Maximum 20V less than this threshold voltage. Increased mass dependent discrimination will occur if operated at too low a value, as seen in figure 3. To ensure against this discrimination this simple tuning should be performed regularly.
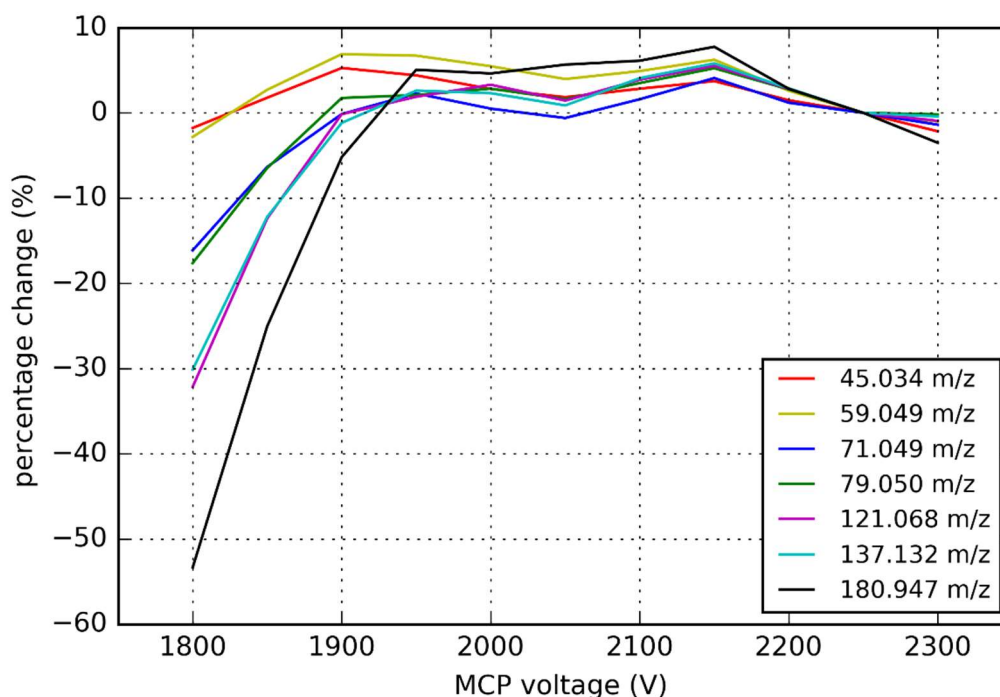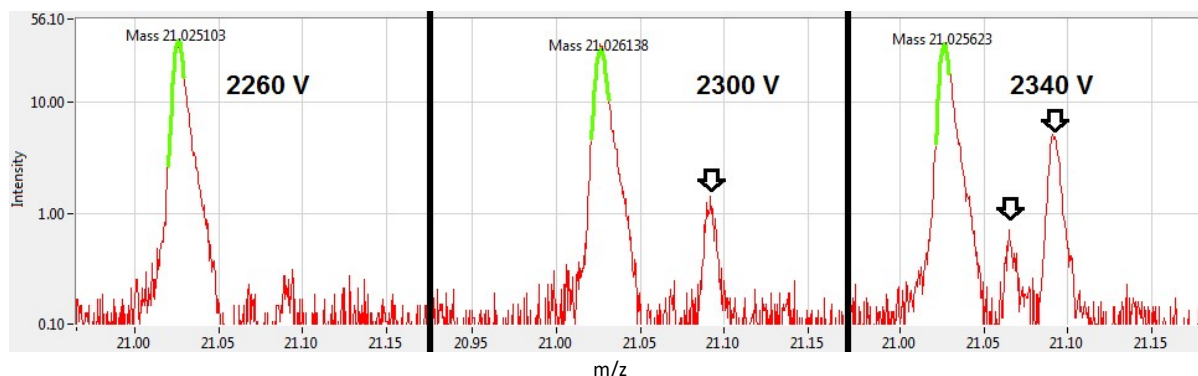
Figure 3: The top figure shows the percentage change from the operational MCP Voltage (2300V) of the normalised intensities of various compounds held at a constant mixing ratio. This plot was generated by varying the MCP voltage while inputting a constant dilute stream of gas standard into the PTR-MS.

Artefact or 'ghost' peaks are generated when the MCP voltage is too high. The bottom plot is an example of their appearance while raising the MCP voltage past a threshold maximum (in this case 2260V).

4 Collation of Data Processing and Quality Assessment Techniques

The output of the PTR-MS is a time series of intensities (that is ions counted per second, in counts per second) for an ion weight (mass to charge ratio, m/z) at which a peak is detected. As molecules are typically detected at their protonated mass, the ion weight will usually be the molecular weight+1.

4.1 Ion Counts and Ion Intensities

An ion count (C_y) is the mean intensity ($\overline{I_y}$ in counts per second, cps) detected at a chosen m/z value (denoted by the index y) multiplied by the time (t) over which the intensities were recorded. The general relationship between ion counts and intensities can be seen below:

$$C_y = t \times \overline{I_y} \qquad\qquad (4.1.1)$$

4.2 Calculating the Primary Ion Intensities

Primary ions and impurities (O_2^+, NO^+) originating from the ion source are so abundant that they cause severe saturation of ion detectors. This leads to an underestimation of primary ion intensities that cannot be corrected with available routines (Titzmann et al, 2010). To avoid this error the intensity for these ions is calculated by measuring the intensity of a less abundant isotope of the ion. For example, the ion count for hydronium with an Oxygen 18 isotope (detected at 21.023 m/z) can be measured without severe detector saturation and the intensity for total hydronium can be calculated as follows[3]:

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[3] For simplicity, the ion intensities of H_3O^+, O_2^+, and $H_2OH_3O^+$, I_{19}, I_{32} and I_{37} have been left with the subscript 19, 32 and 37. It should be noted, however, that these intensities are the intensities of all isotopologues of the primary ions and thus include I_{21}, I_{34} and I_{39} intensities, respectively.

$$I_{19} = I_{21} \frac{Tr_{19}}{Tr_{21}} \times \frac{1}{fr_{18}} \qquad\qquad (4.2.1)$$

$$I_{37} = I_{39} \frac{Tr_{37}}{Tr_{39}} \times \frac{1}{2f_{16}fr_{18}} \qquad\qquad (4.2.2)$$

$$I_{32} = I_{34} \frac{Tr_{32}}{Tr_{34}} \times \frac{1}{2fr_{16}fr_{18}} \qquad\qquad (4.2.3)$$

Here I_x denotes ion intensity, Tr_x relative transmission efficiency, and fr_x abundance of oxygen isotopes. The index denotes the integer m/z of the considered isotopologue.

4.3   Obtaining an instrumental background

Obtaining an instrumental background is essential to ensure the accuracy of data. This can be done in a variety of ways; the only necessity is that the air sample input into the PTR-MS to obtain an instrumental background does not contain any of the VOC being measured. The most popular method and the one recommended in the field set-up in this document is the use of a catalytic converter as this preserves the RH and oxygen content of the sample reading[4].

The complete operational guide to using such a catalyst is beyond the purview of these technical instructions; the make-up and length of a catalytic converter varies considerably from instrument to instrument. However, in principal all catalysts work by rapidly oxidising all VOC's in any air passing through the converter. This is usually achieved through the heating of quartz wool and platinum dust within the catalyst (Golunski, 2007).

The background count for a VOC is simply the count recorded at the m/z at which the VOC is detected when an air sample is first run through a heated catalyst. The use of the background count is detailed in section 4.4.

4.4   Calculating the Product Ion Count and Intensity

The Product Ion Intensity is calculated using the difference between the sample and background ion Intensities (de Gouw et al, 2007). The background ion Intensity for any VOC being measured will never be zero due to electronic noise and instrument contamination. To account for any offset of this kind the product ion Intensity is calculated as follows:

$$I_X = \frac{C_{X(sample)}}{t_{sample}} - \frac{C_{X(background)}}{t_{background}} \qquad\qquad (4.4.1)$$

By combining equation 4.4.1 with equation 4.1.1 we can also come to an equation for the product ion count:

$$C_X = C_{X(sample)} - \frac{t_{sample}}{t_{background}} C_{X(background)} \qquad\qquad (4.4.2)$$

I_x is the product ion intensity in cps and C_X is the product ion count in counts. $C_{X(sample)}$ is the sample ion count measured at the m/z at which compound 'X' is detected. t_{sample} is the time over which this count was measured (seconds). $C_{X(background)}$ is the count detected at the same m/z while measuring a

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[4] Although it should be noted that the resistance in a catalyst may cause pressure drop that may reduce the flow into the PTR-MS.

background intensity (see section 4.3). $t_{background}$ is the time over which this count was measured in seconds.

4.5 Calculating the Volume Mixing Ratio

Two principal approaches to calculating the volume mixing ratio (VMR) have been developed. Firstly, the 'kinetics approach' relies on well-defined conditions in the drift tube and the known kinetics of proton-transfer reactions. The VMR is calculated based on the fundamental physical conditions in the drift tube (pressure, length, E/N, ion mobility, etc.) per Hansel et al, (1995) and Lindinger et al. (1998). In later work, mass dependent transmission effects have been accounted (Holzinger et al., 2010). In section 5.4 we present a method for calculating the transmission curve from gas standard measiurements). The great strength of this approach is the ability to calculate VMR's for any compound for which reaction rate coefficients can be estimated. This method also displays none of the variability with conditions that can occur in the second method (i.e. the calibration approach) as conditions are individually accounted for within each calculation.

The 'calibration approach', (de Gouw et al, 2007,2003a) relies on gas standard measurements from which compound specific sensitivities (in units of normalized counts per second per mol/mol, ncps/ppb) are calculated. VMR's are calculated by dividing the ion signal (normalized to the same primary ion signal as the sensitivity) by the sensitivity. This method has two main advantages: better constrained accuracy and user friendliness. The inaccuracy inherent in using calculated reaction rate coefficients and transmission efficiencies is not incurred. The measured sensitivity includes the mass dependent transmission efficiency, possible fragmentation, and automatically accounts for isotope peaks and possible fragmentation. This is mitigated by the fact that only compounds for which the PTR-MS is calibrated can be evaluated. Thus, this method is limited to the compounds contained within the gas standard used for calibration. Corrections and rules have been developed to properly account for compounds that react with both the H_3O^+ and the $(H_2O)H_3O^+$ primary ions (de Gouw et al, 2003a). [5]

4.5.1 Kinetic Method

(Holzinger et al 2010, Hansel et al 1995 and Lindinger et al 1998)

The kinetic method relies on well-defined drift tube conditions and known kinetics of proton transfer reactions to determine a final volume mixing ratio (VMR). The first step is to calculate the reduced primary ion mobility (μ_0). μ_0 is the reduced ion mobility of both H_3O^+ and $H_3O(H_2O)^+$; it is their weighted average[6]. This is representative of the fact that during its journey through the drift tube a hydronium ion may gain and lose an H_2O ligand several times (Warneke et al 2003b, de Gouw et al, 2007). The primary ion mobility is calculated as follows:

$$\mu_0 = \frac{I_{19}}{I_{19}+I_{37}}\mu_{0,19} + \frac{I_{37}}{I_{19}+I_{37}}\mu_{0,37} \qquad\qquad (4.5.1)$$

I_{19} and I_{37} are the primary intensities in cps. $\mu_{0,19}$ (2.7 cm^2/Vs) and $\mu_{0,37}$ (2.3 cm^2/Vs) are the reduced ion mobility's of H_3O^+ and $H_3O(H_2O)^+$ respectively.

Now the drift velocity of primary ions (v_d) can be found with the following formula:

$$v_d = \frac{E \times \mu_0 \times p_0 \times T_{drift}}{p_{drift} \times T_0} \qquad\qquad (4.5.22)$$

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[5] These two paragraphs, while edited and added to by myself, were originally from a draft paper by Holzinger et al.

[6] Note that the dependency of the reduced ion mobility on humidity is not fully accounted for in the calibration method. This gives the Sensitivity a slight dependency on the humidity.

Here T_{drift} and p_{drift} are the temperature (K) and pressure (mbar) respectively in the drift tube, while T_0 is 273.15K and p_0 is standard atmospheric pressure (1013.25 mbar). E is the electric field over the drift tube (V/cm). This can then be used to calculate the residence time of primary ions in the drift tube (t_{react})

$$t_{react} = \frac{d}{v_d} \qquad (4.5.33)$$

Where d is the length of the drift tube in cm. Next, the number density of the sample gas in the drift tube must be calculated:

$$N = \frac{N_0 \times p_{drift} \times T_0}{p_0 \times T_{drift}} \qquad (4.5.44)$$

N_0 (2.69×10^{19} molecules/cm³) is the number density of an ideal gas held at p_0 and T_0. N is the number density of the air sample in molecules/cm³. Now the product and primary ion Intensity can be converted into a volume mixing ratio for the measured VOC:

$$VMR = I_X \frac{Tr_{19}}{fr_X Tr_X} \frac{1}{\left[\left(I_{19} \times k_{19} + \frac{Tr_{19}I_{37}k_{37}}{Tr_{37}}\right) \times t_{react} \times N\right]} \qquad (4.5.5)$$

I_X is the product intensity in cps (see equation 4.4.1). Tr is the relative transmission factor of the ion which is detected at the integer m/z given in the index of the symbol i.e. Tr_X is the relative transmission factor of the ions detected at the m/z X (Note that Tr_{19} is 1 as defined in section 5.4). k_{19} and k_{37} are the reaction rate coefficients of the VOC being measured.

fr_X is included to account for the presence of common isotopologues of the measured VOC[7]. The final VMR is in mole per mole. When using the kinetic method, it is vital to account for the fragmentation of certain VOC's, for example α-pinene (detected at m/z = 137.132). Fragments of a-pinene are detected at m/z = 81.070 so to find the VMR of α-pinene the kinetic method must be used for intensities generated at both m/z = 81.070 and m/z = 137.132. The true product ion intensity of α-pinene will be the sum of these two product intensities.

4.5.2 Calibration method

(de Gouw et al, 2007,2003a)

The calibration method works on the principal that the VMR of a VOC is proportional to a normalised intensity via a calibration factor. This method uses the same reasoning as the kinetic method however all the steps in the previous section are combined into two experimentally determined values: X_R and S (methods to calculate/measure X_R and S are presented in sections 5.1 and 5.3). The first step in this method is to calculate the Normalised Intensity, NI (normalised counts per second, ncps) using the equation below:

$$NI_X = \frac{I_X}{I_{19} + X_R \times I_{37}} \qquad (4.5)$$

Here I_{19} and I_{37} are the two primary intensities in counts per second (section 2). I_X is the product intensity in cps (section 4.4) and X_R is the humidity factor (section 5.1). The NI is practically independent of the humidity due to X_R and from its definition is proportional to the VMR. In other words, if compound X exhibits the same VMR in a dry and a humid sample, equation 4.5.6 will

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[7] To evaluate this final part of the kinetic method the chemical formula of the VOC being measured must be known. In the case where the chemical formula is not known so that fr_X must be estimated an error not usually larger than a few percent will be induced.

produce the same normalised intensity, NI_X. Therefore, the second and final step in calculating the VMR is to divide NI_X by a calibration factor: the sensitivity, S.

$$VMR = \frac{NI_X}{S} \qquad (4.5.76)$$

The unit of the VMR is dependent on the units of S. Commonly S is given in ncps/ppb, this would mean that the final VMR is given in parts per billion (ppb).

4.6 Calculating Signal to Noise Ratio

The signal of the PTR-MS output is the total ion count for the VOC being measured (see equation 4.1.1 and 4.4.2)

$$Signal = C_X = C_{X(sample)} - \frac{t_{sample}}{t_{background}} C_{X(background)} \qquad (4.6.1)$$

The clear majority of error is generated in the counting statistics of product ions (de Gouw et al 2003a). As shown in section 4, the product intensity (I_x) is a combination of two sets of data, the background intensity, and the sample intensity (equation 4.4.1). Therefore, the error inherent in the PTR-MS output (or noise) is simply the addition of the standard deviation of both data sets (de Gouw et al 2007, de Gouw et al 2003). Both follow a Poisson distribution so the noise is described by:

$$Noise = \sqrt{C_{X(sample)}} + \frac{t_{sample}}{t_{background}} \sqrt{C_{X(background)}} \qquad (7)$$

C_X(sample) and C_X(background) are the sample and background ion counts (equation 4.1.1 and section 4.3). The dwell time ratio in the second term of the above equation is to account for the possibility of different dwell times when measuring sample and background ion counts. The signal to noise ratio (4.6.3) is simply the ratio of the signal calculated in equation 4.6.1 to the noise calculated in equation 4.6.2.

$$\frac{Signal}{Noise} = \frac{C_{X(sample)} - \frac{t_{sample}}{t_{background}} C_{X(background)}}{\sqrt{C_{X(sample)}} + \frac{t_{sample}}{t_{background}} \sqrt{C_{X(background)}}} \qquad (4.6.3)$$

4.7 Calculating the limit of detection

The limit of detection (LOD) is determined by the minimum signal to noise ratio required by the individual experiment/measurement The LOD is given by how many times larger the signal is required to be larger than the noise. A value of three has been commonly used and in this case the LOD is given by:

$$LOD = \frac{3}{\frac{Signal}{Noise}} \times VMR \qquad (4.7.18)$$

The LOD is a quality assessment of the VMR. If the VMR is below the LOD then the result loses validity. The minimum signal to noise ratio chosen depends on the level of precision required for the measurements being made. The value will determine the chance, at the limit of detection, of the signal falling below the noise and losing meaning. If 1 is chosen there is a probability of 32%, if 2 is chosen this drops to 5% and if 3 is chosen (as above) 0.3% is the probability of the signal losing meaning. The probabilities are given assuming that ion counts are normally distributed, which is allowable in cases of over ~10 counts.

4.8 Calculating the precision

The precision of the PTR-MS data is best described by the standard deviation of the output. This is the same as the signal to noise ratio multiplied by the VMR calculated equation 4.6.3.

$$Precision = \frac{VMR}{\frac{Signal}{Noise}} \qquad\qquad (4.8.19)$$

The precision is given here by one standard deviation and thus there is a 68.2% chance the true VMR is no further from the calculated VMR than the value calculated for the precision.

4.9 Determining the Accuracy

The accuracy of the results derived from PTR-MS output is dependent on the method used to convert the ion counts to a VMR. The accuracy of the calibration method is largely dependent upon the accuracy of the gas standards used to obtain the value of S, this can vary but is usually around 5%. Additional error is generated from the transmission efficiency of the $H_2O(H_3O)^+$ ion count. Energy input into the clusters during the measurement process can cause the bond to the H_2O ligand to break (see section 6.3). This error is not well constrained but can be minimised by keeping the I_{37}/I_{19} intensity ratio as low as possible.

The accuracy of the kinetic method is dependent on the uncertainty in the values of all the parameters used. These can be analysed in three distinct groups: drift tube conditions, transmission factors and reaction rate coefficients. The values of parameters that describe drift tube conditions are taken directly from in situ measurements that are highly accurate and so the uncertainty is negligible. Transmission factors are experimentally determined as described in section 5.4. The inexact nature of determining the polynomial curve that defines these factors leads to a level of inaccuracy of up to 25% (de Gouw et al 2007).

The uncertainty in the k_{19} reaction rate coefficient is estimated at around 30-40% (k_{19} = 1.7-2.5×10^{-9} cm^{3}s^{-1}), k_{37} varies significantly depending on the VOC being measured (k_{37} = 0.0-4.0×10^{-9} cm^{3}s^{-1} and the uncertainty is therefore difficult to quantify. Most estimates of the uncertainty of k_{37} are higher than that of k_{19} (Holzinger et al 2010). The poorly constrained uncertainty in the k_{37} reaction rate coefficient can be mitigated by again keeping the I_{19}/I_{37} intensity ratio low. The error in this group of parameters is far larger than the previous two groups which have very small uncertainties therefore most error inherent in the kinetic method is due to the calculated reaction rate constants.

5 Gas Standard Injection Methodology and Associated Protocols

Most PTR-MS users measure gas standards by providing a steady dilute flow from a gas standard tank (see figure 4a) (de Gouw et al, 2003a). This has several disadvantages. The dilution of the flow requires precisely known flow rates (both from the gas standard and the dilution agent) to preserve the accuracy of the known VMR of the compounds contained in the gas standard. These two flows need to be well mixed and fully equilibrated with tubing walls. Especially the latter will take time to stabilise. These disadvantages can and have been overcome but in doing so this method becomes very time consuming.

In this project a new method is introduced. Instead of a steady dilute flow of gas standard into the instrument, a finite, known amount of gas standard is introduced. This is a considerably faster process. A sample loop filled from a gas standard is injected into a mixing volume which is then fed into the PTR-MS (see figure 4b). A standard measurement can thus be completed in a matter of a few econds. Using this method, it is possible to calculate all the calibration coefficients required as well as a transmission curve.
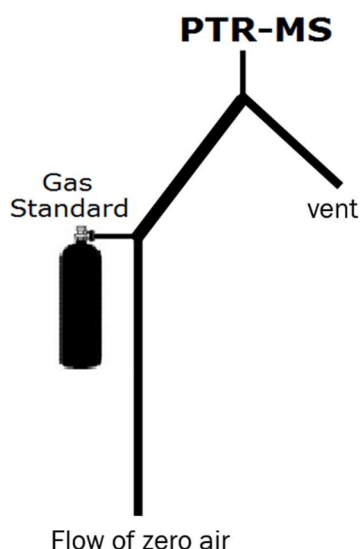
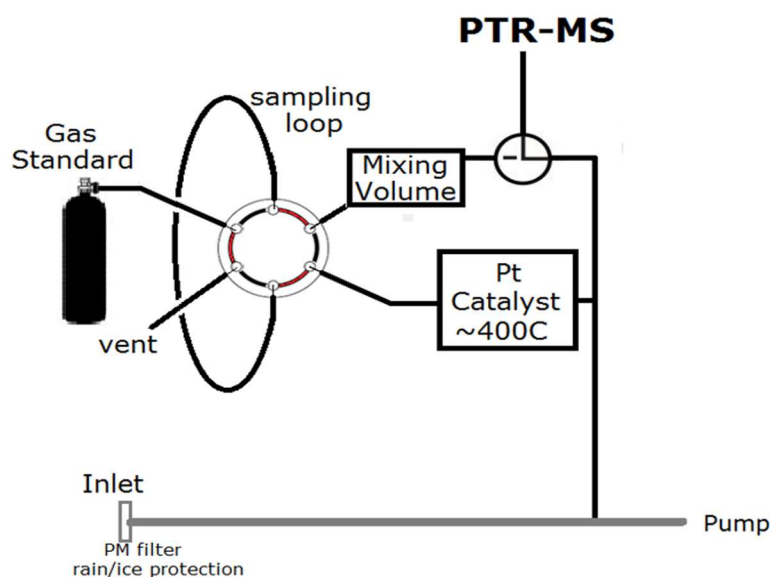Figure 4a   Figure 4b

Figure 4: The left-hand figure is an example schematic of the common method of gas standard addition with zero air (meaning air run through a catalyst) used as the dilution agent. The vent is used for runoff from the strong flow from the gas standard and zero air.

The right-hand figure shows a schematic of the new set-up. The sample loop is filled by the gas standard then injected into the mixing volume via a six-port valve. The catalyst is included to provide zero air as carrier gas and to allow for measuring of a background signal.

5.1   Calculating the Humidity Factor

By the definition of the NI it is proportional to the VMR of the compound it is generated for (see equation 4.5.7) and independent of the cluster ratio (I_{37}/I_{19}), which is a proxy for humidity in the drift tube. An X_R value must be found for each compound that validates this definition of the NI.

The Humidity Factor is an experimentally determined compound specific coefficient that accounts for the presence of $H_2O(H_3O)^+$ clusters and the fact that product ions may be formed at a different rate with these second primary ions. X_R is dependent on two ratios. Firstly, the ratio of reaction rates of compound X with the primary ions H_3O and $H_3O(H_2O)^+$ (equation 5.1.1) This ratio is the relative rate at which this compound, R reacts with protonated water clusters with respect to hydronium. Second, the ratio of the instrument specific transmission factors for H_3O and $H_3O(H_2O)^+$ (equation 5.1.2; also, see section 5.4 for instructions for calculating transmission curves) [8].

$$X_{R0} = \frac{k_{37}}{k_{19}} \qquad\qquad (5.1.1)$$

$$X_R = X_{R0} \frac{Tr_{19}}{Tr_{37}} \qquad\qquad (5.1.2)$$

X_{R0} is the ratio of reaction rate coefficients. This value is not instrument specific; it is then converted to X_R by accounting for the transmission factors of the primary ions. X_R is experimentally determined as follows:

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[8] This definition is derived by combining definitions from De Gouw et al, 2007 and Holzinger et al, 2010

Method

1. We set E/N to a low value (e.g. 100 Td) to favour the production of cluster ions. The ion source flow should be set to a low value (e.g. 2.5 ml/min) ensure low humidity in the drift tube.
2. Inject the sample loop filled by the gas standard into the PTR-MS. Use dry air as carrier gas.
3. Raise the ion source flow in increments of 1 to 7.5 ml/min to increase the humidity in the drift tube. For each increment repeat the injection and record the output.

Data management:

An injection from the sample loop will cause peaks in recorded intensities these represent the compounds in the sample loop passing through the PTR-MS (see figure 5).
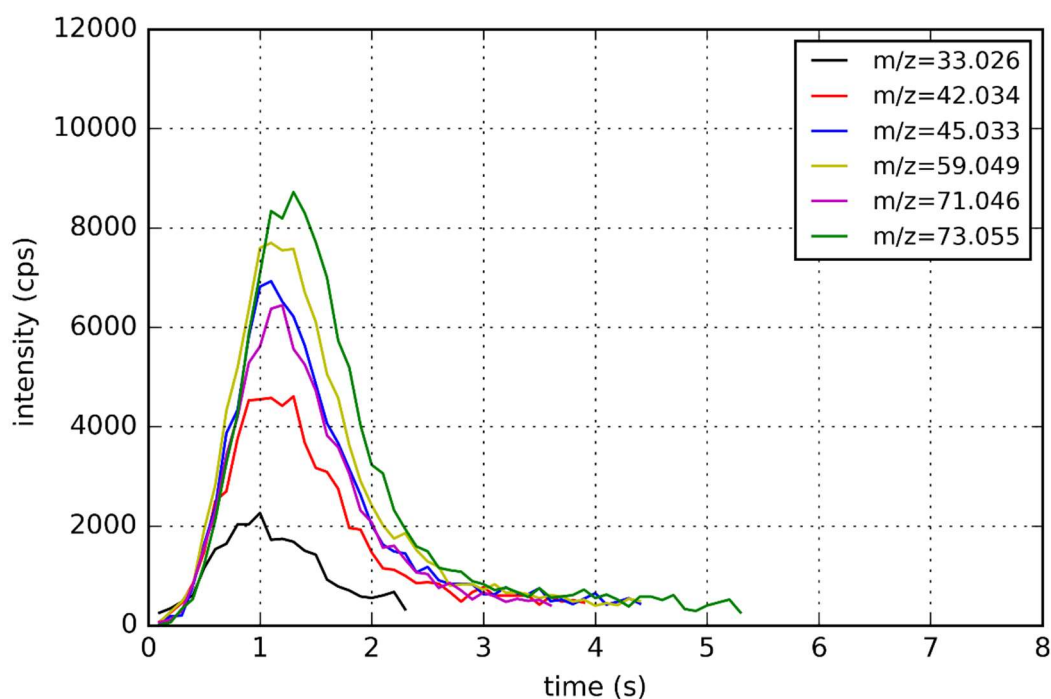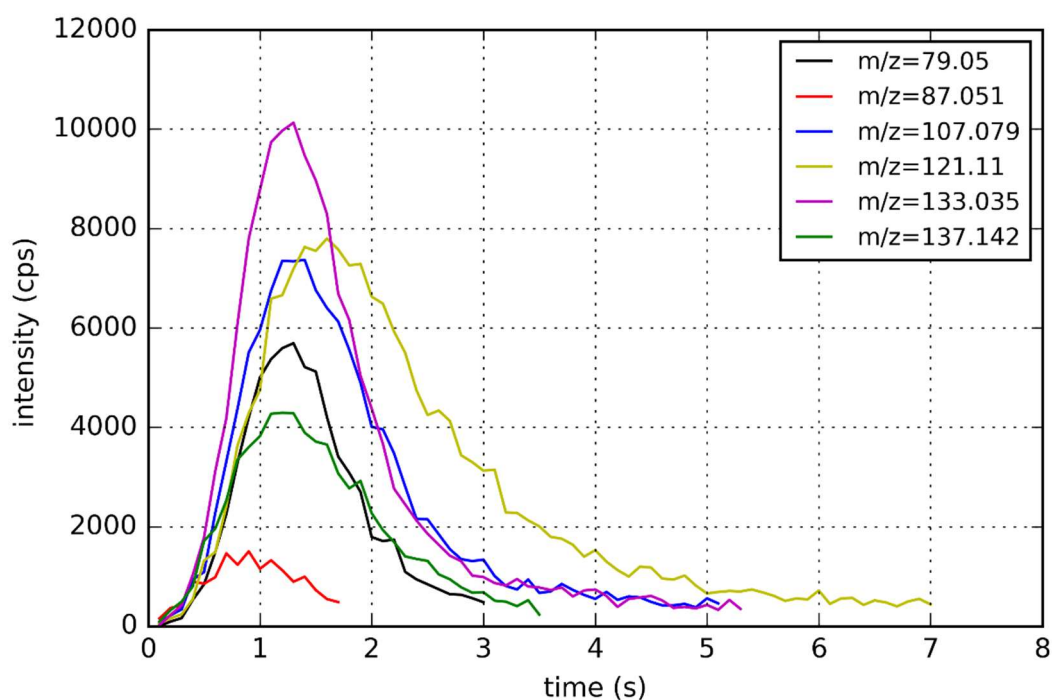
Figure 5: The peaks generated by an injection of gas standard are given from time of injection to time of depletion. Which is the first and last time the product intensity time series hits a certain counts threshold.
The counts threshold used for these calculations was 100 cps. This allows the vast majority of the peak to be found while not including unnecessary tailings. All injections were corrected by the mean intensity of the first 4 seconds of the measurement, before the injection. This corrects for any contaminant VOCs in the mixing volume.
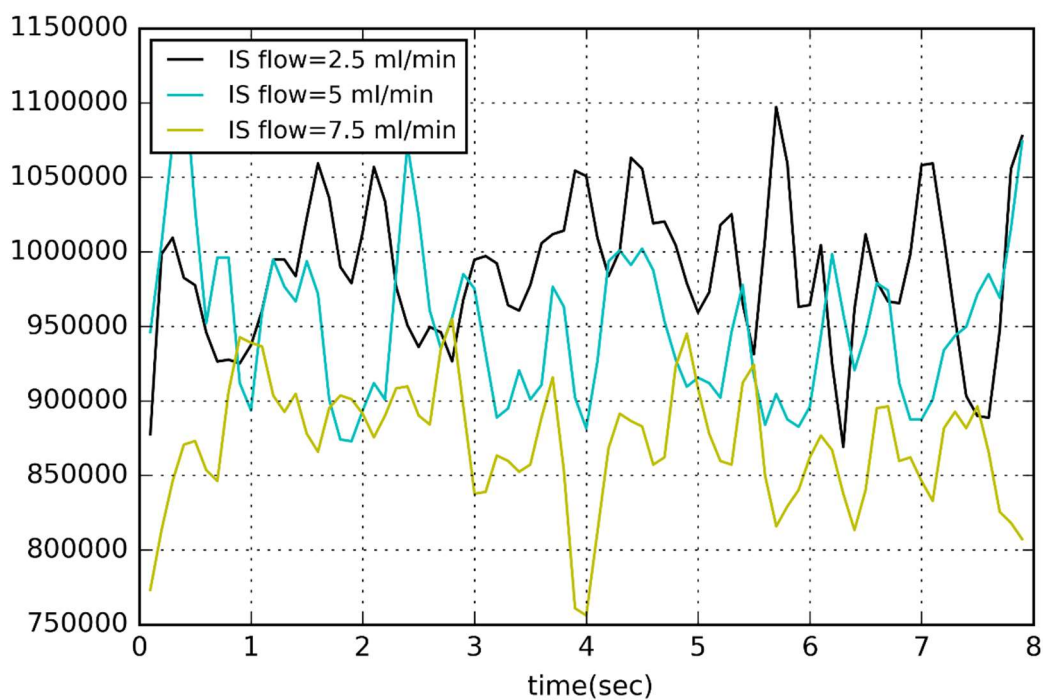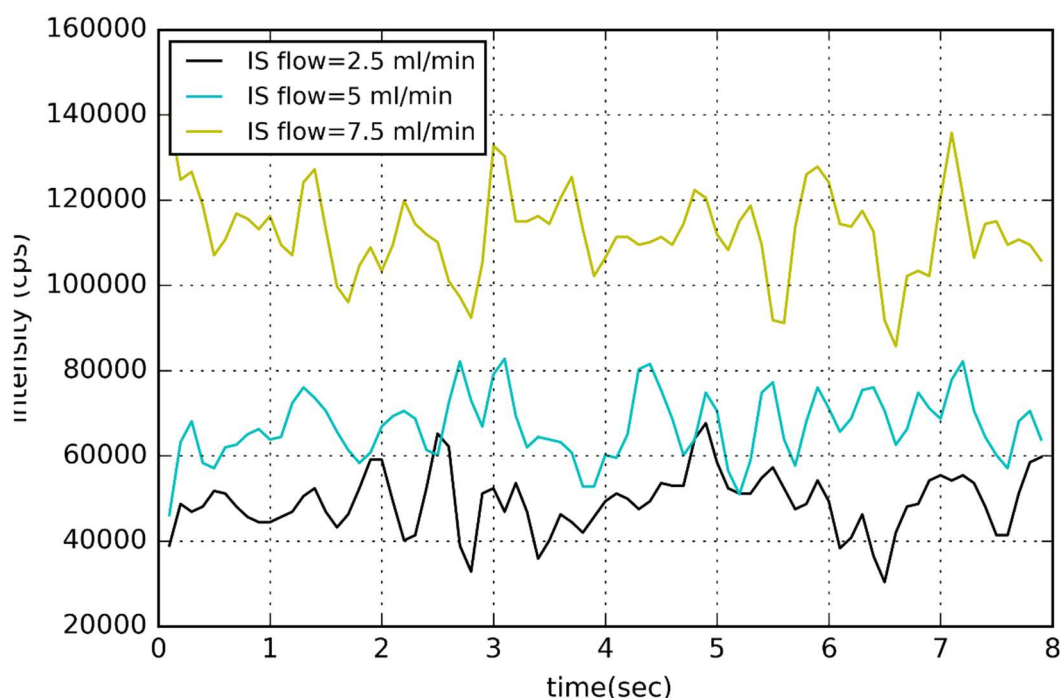
Figure 6: Here the I_{19} intensity (top figure) (equation 4.2.1) is shown over the same period as figure 5. These demonstrate the high variability of the primary intensities. Which is not to say that either intensity has a high signal to noise ratio and in fact over longer time periods the I_{37}/I_{19} ratio shows good stability (in stable conditions.
On the bottom figure the I_{37} intensity is shown over the same period. These 2 figures also demonstrate the effect that varying the IS flow has on the primary intensities and therefore the cluster ratio. This is due to leakage from the IS to the DT (see figure 1).

If the intensities within each peak are normalised using primary ion intensities and a compound specific X_R (as in equation 5.6) then each normalised intensity will be proportional to the VMR that generated it. Here it is convenient to introduce the idea of 'Normalised Counts' (NCs). Similar to equation 4.1.1, an NC is the mean of all normalised intensities measured in a certain period, multiplied by the time over which they were measured.

$$NC_X = t \times \overline{NI_X} \qquad (5.1.3)$$

Here NC_X is the normalised count, t is the time over which a peak occurs and $\overline{NI_X}$ is the mean of all normalised intensities measured within a peak. Following the previous line of reasoning, the NC within a peak is dependent on the amount the amount of substance that generated it, while by its definition independent of the humidity level. This implies that the NC generated at different humidity levels, with the same amount of a compound, will be the same. With this information, it is possible to calculate an X_R value using the data generated by following the instructions above.

For each IS flow value, generate a time series of primary and product ion intensities, figures 5 and 6 display the typical behaviour of these series. In each time series locate the peaks generated by the gas standard injection. The X_R value cannot be determined analytically. This is because the conserved quantity from which X_R is derived (NC_X) is in fact the sum of the ratio of three different time series (see equation 5.1.4). Equation 5.1.4 is not solvable with respect to X_R.

$$NC_X = \frac{t}{D}\sum_{i=0}^{i=D} NI_{Xi} = \frac{t}{D}\sum_{i=0}^{i=D} \frac{I_{Xi}}{I_{19i}+X_R \times I_{37}} \qquad (5.1.4)$$

Here i=0 and i=D represent the time of injection and depletion respectively in the time series. These may vary slightly from compound to compound (see figure 5)[9]. Using equation 5.1.4, An NC_X can be generated for a range of potential X_R values at each ion source flow value.

An NC value needs to be generated for each IS flow rate, for each compound, with a range of potential X_R values. To find the correct X_R value for each compound simply choose the one that gives a linear line of best fit between the NCs at different IS flow rates a zero gradient. Figure 7a shows a non-zero gradient for calculations assuming X_R=0. Figure 7 shows the progression of the gradient of the line of best fit as the X_R value is changed.
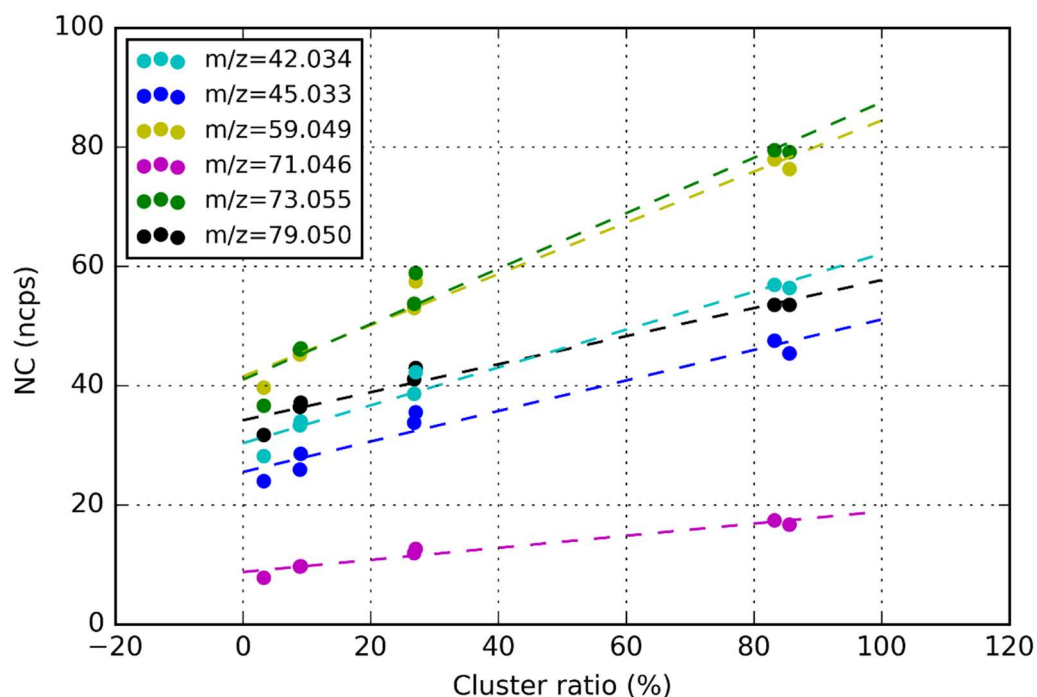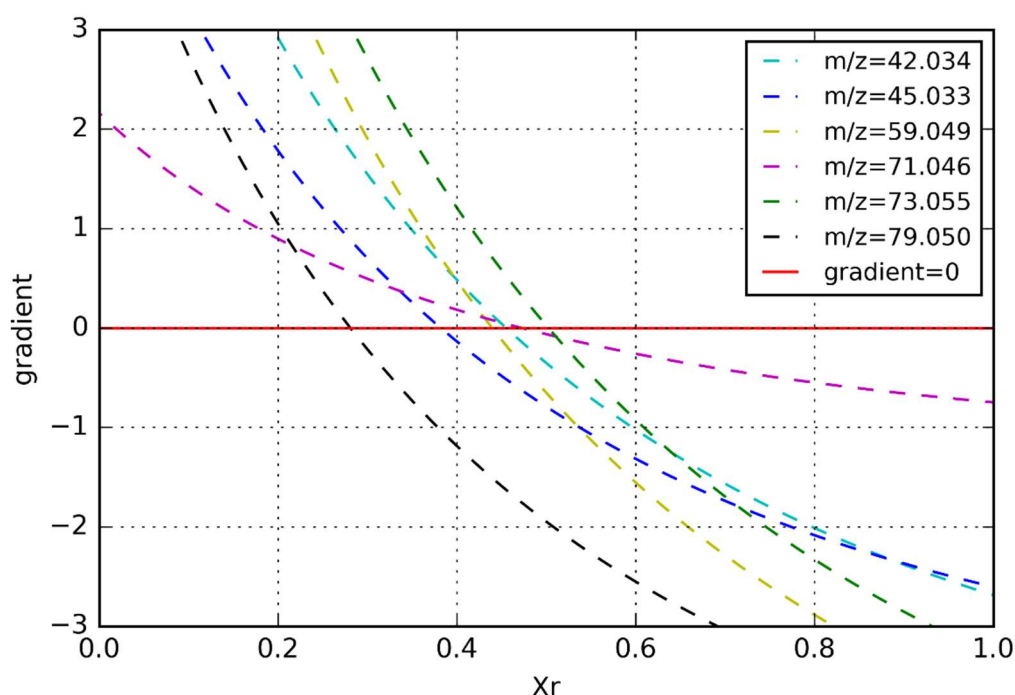

Figure 7: The top figure shows the sums of normalised intensity if X_R=0 is assumed for all compounds. The difference in the lines of best fit in this figure demonstrate the compound specific nature of X_R. This figure was developed by varying the E/N parameter rather than the flow rate. In practice, any wide variation of cluster ratios between injections will allow for X_R calculation but the method described above will have the least problems with fragmentation.
The bottom figure shows the progression of the gradients of the lines of best fit with changing X_R is displayed. The X_R value at which these lines intersect the red line (these X_R values produce slopes of zero) is the chosen X_R value.

X_{R0} is a constant and X_R a function of stable conditions in the PTR-MS, so in principle, X_R can be calculated by comparing any two outputs from the different IS flow rates. These represent largely identical measurements with only difference being the H_3O to $H_3O(H_2O)^+$ ratio. However, using a larger spread of IS flow rates (and therefore a larger range of H_3O to $H_3O(H_2O)^+$ ratios) mitigates the possibility of error in individual measurements affecting the final generated X_R value.

5.2   Measuring the flow rate into the PTR-MS

The flow rate into the PTR-MS needs to be known to calculate the Sensitivity and transmission curve with the recommended field set up. This can be achieved by using the flow controller installed via a T-junction with the fore line of the PTR-MS[10] (see Figure 8; this flow controller is standard with Ionicon models and is denoted 'FC-inlet' in the software interface). The flow generated by this flow controller will be referred to as 'bypass flow' for simplicity. For a clearer idea of where these flows are taking place within the PTR-MS a labelled schematic diagram can be found in the appendix.

The total flow at the inlet will be the bypass flow added to the flow going into the PTR-MS, which is yet to be determined. When a gas standard sample is injected into the mixing volume, a fraction of it is lost to run-off (i.e. is lost to the T-junction section in which the bypass flow is generated). This fraction equals the fraction of the bypass flow to the total flow. As discussed in the previous section the amount of a compound contained in the standard in moles going into the PTR-MS is proportional to the NC_X generated, between time of injection and time of depletion.

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[10] The flow into the PTR-MS can also be found by using a flow meter. However, the method presented here allows retrieving this flow without physically changing the field setup. Therefore, this method is essential to automated calibrations using the sample loop.
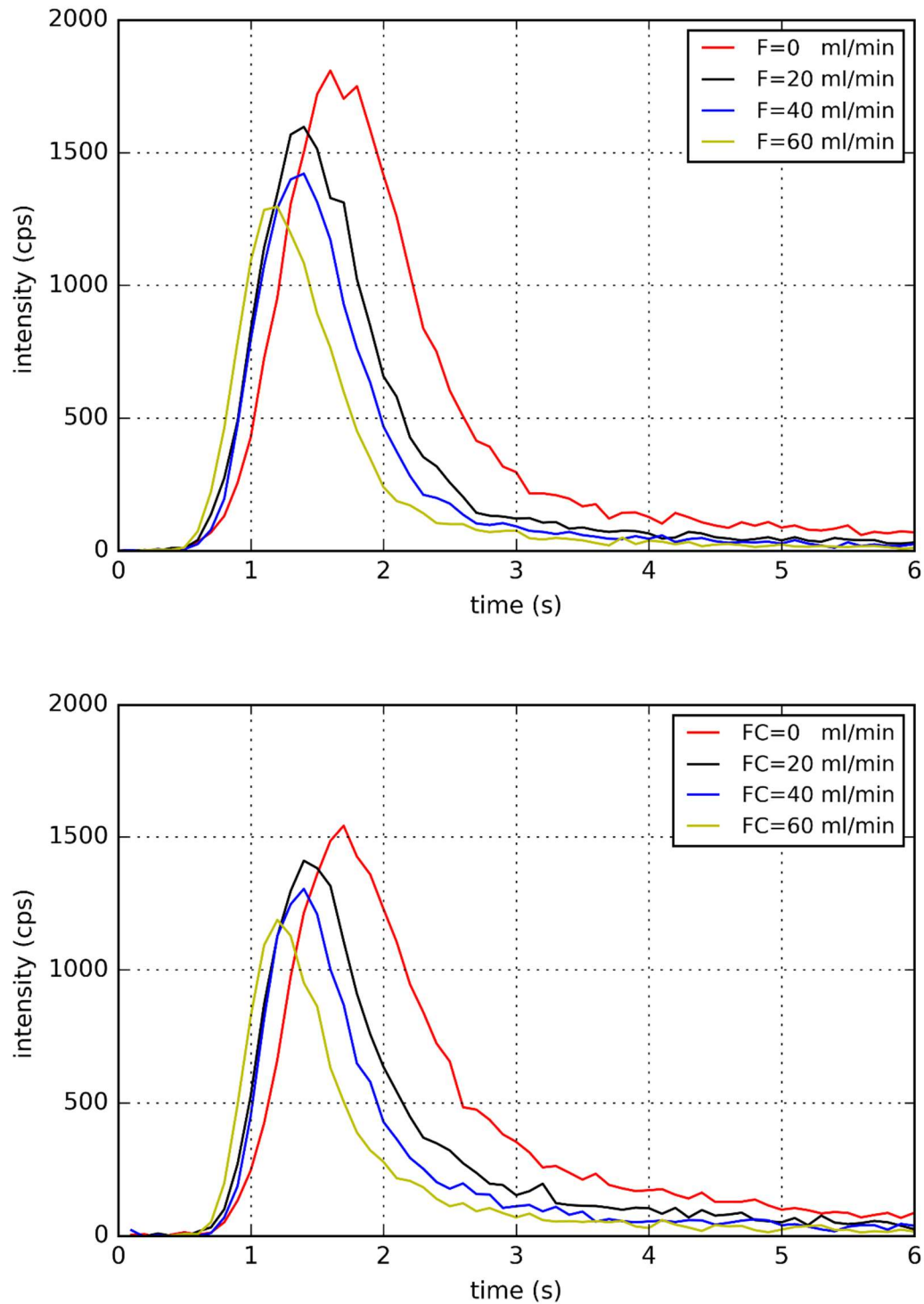
Figure 8: The development of the intensity of MEK (detected at m/z=73.065) (top figure) during a gas standard injection into the PTR-MS. It can be seen that the integrated curves will be smaller for higher values of F.
Acetaldehyde (detected at m/z=45.033) has the same behaviour as MEK. Note the accelerated approach to the intensity maximum that is caused by a higher total flow at the inlet.

Therefore, the ratio of two NCs generated from injections of sample gas with two different bypass flows will be equal to the ratio of total flows at those two FC flow settings. With this knowledge, it is possible to calculate the flow into the PTR-MS as follows

Method

Data acquisition:

1. Ensure the bypass flow is set to zero
2. Inject the sample loop filled with the gas standard into the mixing volume and record the PTR-MS output.
3. Raise the FC flow[11], repeat the injection and record the output.

Data Management:

Calculate an NC_X value for a VOC included in the gas standard (equation 5.1.4) from time of injection to time of depletion for each bypass flow increment. The choice of compound is not important.

The inlet flow (F_{PTR}) can now be calculated using the following equation:

$$F_{PTR} = \frac{F_1 NC_1 - F_2 NC_2}{NC_2 - NC_1} \qquad (5.2.1)$$

This is a general formula showing that the flow that F_{PTR} can be found using any two, different bypass flows, F_1 and F_2, (not necessarily bypass = 0ml/min). When using $F_2=0$ and following the method above this simplifies to:

$$F_{PTR} = \frac{F_1 NC_1}{NC_2 - NC_1} \qquad (5.2.2)$$

In these equations F_1 and F_2 are bypass flow values, NC_1 and NC_2 are the total normalised counts measured during the sample injection of each bypass flow value.

5.3 Calculating the Sensitivity

The Sensitivity (S, ncps/ppb) is the experimentally determined coefficient used to convert the NI_X to a VMR and is in situ obtained from gas standard measurements. S is specific to the VOC being measured and is representative of the steps taken in the kinetic method (see section 4.5.1) condensed into a single value. In principle S is equal to (de Gouw 2007):

$$S = \frac{k_{19} d}{\mu_0 N_0} \times \frac{N^2}{E} \times Tr_X \times (1 - FR_X) \times fr_X \qquad (5.3.1)$$

Here k_{19} is the reaction rate coefficient of compound X with hydronium (cm^3/molecules/sec). μ_0 is the reduced primary ion mobility (cm^2/Vs, see equation 4.5.1), d is the drift tube length in cm and N_0 is the number density of an ideal gas held at standard atmospheric conditions (2.69×10^{19} molecules/cm^3). N is the number density of gas in the drift tube (molecules/cm^3), E is the electric field across the drift tube (V/cm - see equation 6.2.2). Tr is the relative transmission factor of the ion which is detected at the m/z given in the index of the symbol i.e. Tr_X is the relative transmission factor of the ions detected at the m/z=X (see section 5.4 for instructions on how to calculate a transmission curve). fr_X is the relative isotopic abundance of the compound being measured. FR_X is

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[11] The value the FC is raised to will depend on the instrument and inlet configuration. The method yields the most accurate result if the bypass flow is set so that the total flow into the PTR-MS is split into equal parts at the T-junction.

the fragmentation fraction, which is 0 for VOCs that produce ions only at the protonated mass and values between 0 and 1 if more than one ion is produced during ionization (equation 6.4.1).

Method

Data acquisition:

Inject the sample loop filled with the gas standard into the mixing volume and record the PTR-MS output.

Data management:

There are several variables that need to be computed, first the number of moles of the VOC in the sample loop for which the transmission factor is being calculated. This can be found using the ideal gas law:

$$n = \frac{pV}{RT} * VMR_{VOC} \qquad (10)$$

Here n is the amount of the VOC in moles. T is the ambient temperature (K), p is atmospheric pressure in Pascal and R is the gas constant (Jmol^{-1}K^{-1}). VMR$_{VOC}$ is the mixing ratio of the VOC in the gas standard; given in mol per mol. V is the volume of the sample loop (m^3).

Next, the number of moles per second being taken into the PTR-MS, which is also computed using the ideal gas law:

$$F_{PTR\_mol} = \frac{pF_{PTR}}{RT} \qquad (11)$$

F$_{PTR\_mol}$ is the inflow rate in moles per second of the PTR-MS. T and p are the temperature (K) and pressure (Pascal) respectively. R is again the gas constant. These three variables are used in the same way in equation 5.3.2. F$_{PTR}$ is the flow rate into the PTR-MS in m^3 per second. This variable was calculated in the previous section in units of ml per minute, the change in units needs to be accounted for.

The next step is calculating an NC$_X$ value for the peaks generated by the gas standard injection (equation 5.1.4). In the process of computing NC$_X$ a time series of normalised intensities will also be generated. This will run from time of injection (i=0) to time of depletion (i=D).

The amount of VOC in moles that generates each normalised intensity needs to be calculated. Assuming a steady flow into the PTR-MS, this this proportional to the NI. This implies that the proportion of VOC from the total in the sampling loop will be the same as the proportion of the counts in each normalised intensity from the total NI:

$$n_i = n \frac{NI_{Xi}}{f \, NC_X} \qquad (5.3.4)$$

Here n is the total amount of VOC in the sampling loop in moles, as calculated in equation 5.3.2. n$_i$ is the amount of VOC in moles that generates the NI recorded at the ith measurement. f is the sampling frequency in Hz. To determine the Sensitivity, these amounts must be converted to volume mixing ratios. These VMR's can be calculated as follows:

$$VMR_i = \frac{f \, n_i}{F_{PTR\_mol}} \qquad (5.3.5)$$

F$_{PTR\_mol}$ is the inflow into the PTR-MS in moles per second; f is the sampling frequency in Hz.

For each measurement, a VMR and a NI have been found and a Sensitivity can be found that validates its definition given in section 4.5 (equation 4.5.6). However each individual calculation of the Sensitivity using this method will have weakly constrained accuracy due to poor counting

statistics in product intensities. To counteract this we effectively take the mean of all calculated Sensitivities over the duration of the peak data being used:

$$S = \frac{1}{D} \sum_{i=0}^{i=D} \frac{NI_{Xi}}{VMR_i} \qquad (5.3.612)$$

Here D represents the number of measurements recorded from time of injection to time of depletion and i is indicative of which measurement the NI and VMR are calculated from. Equations 5.3.4 to 5.3.6 can be combined to give:

$$S = \frac{F_{PTR\_mol}}{n} NC_X \qquad (5.3.7)$$

Equation 5.3.7 gives the Sensitivity in units of ncps/(mol/mol) and represents a convenient way to calculate the sensitivity (S) that is equivalent to the definition from De Gouw 2007 (equation 4.5.6).

5.4 Calculating a Transmission Curve

The transmission factor for a value of m/z is the mass-dependent efficiency with which the PTR-MS detects that ion mass. The transmission curve corrects for this mass dependent effect; it is a vital component of interpreting PTR-MS output. In this document, all transmission factors are given relative to m/z =19 i.e. Tr_{19}=1.

The transmission curve is the relationship between the m/z at which an ion is detected and the mass-dependent transmission factor for that ion (see figure 9). This curve can be found with the following method:

Method

Data acquisition:

Inject the sample loop filled with the gas standard into the mixing volume and record the PTR-MS output.

Data management

From the definition of the Sensitivity (equation 5.3.1) the definition of an individual transmission factor can be found:

$$\frac{Tr_x}{Tr_{19}} = \frac{\mu_0 N_0 E}{fr_X k_{19} N^2 d} S \qquad (5.4.1)$$

This equation is simply a deconstructed definition of the Sensitivity (S, ncps/ppb). E is the electric field strength in the drift tube (V/cm, see equation 6.2.2); μ_0 is the reduced ion mobility of hydronium in cm^2/Vs (see equation 4.5.1). N is the number density of the gas in the drift tube and N_0 is the number density an ideal gas held at 273.15K and standard atmospheric pressure, both given in 10^9molecules/cm^3. Finally, d is the drift tube length in cm and k_{19} is the reaction rate coefficient of the VOC with hydronium in cm^3s^{-1}molecules^{-1}. fr_X is its isotopic fraction. The values of these parameters are either in the engineering data of the measurements taken or can be found in the table of variables in the Appendix.

By combining equations 5.3.4 and 5.4.1 a definition of individual transmission factors independent of previously calculated Sensitivities can also be found:

$$\frac{Tr_x}{Tr_{19}} = \frac{\mu_0 N_0 E}{fr_X k_{19} N^2 d} \frac{F_{PTR\_mol}}{n} NC_X \qquad (5.4.2)$$

Here n is the total amount of VOC in the sampling loop in moles, as calculated in equation 5.3.2. F_{PTR_mol} is the inflow into the PTR-MS in moles per second. NC_X is the total normalised counts during

the peak generated by the sample injection (see equation 5.1.4). For each compound in the gas standard calculate an individual transmission factor using equation 5.4.2.
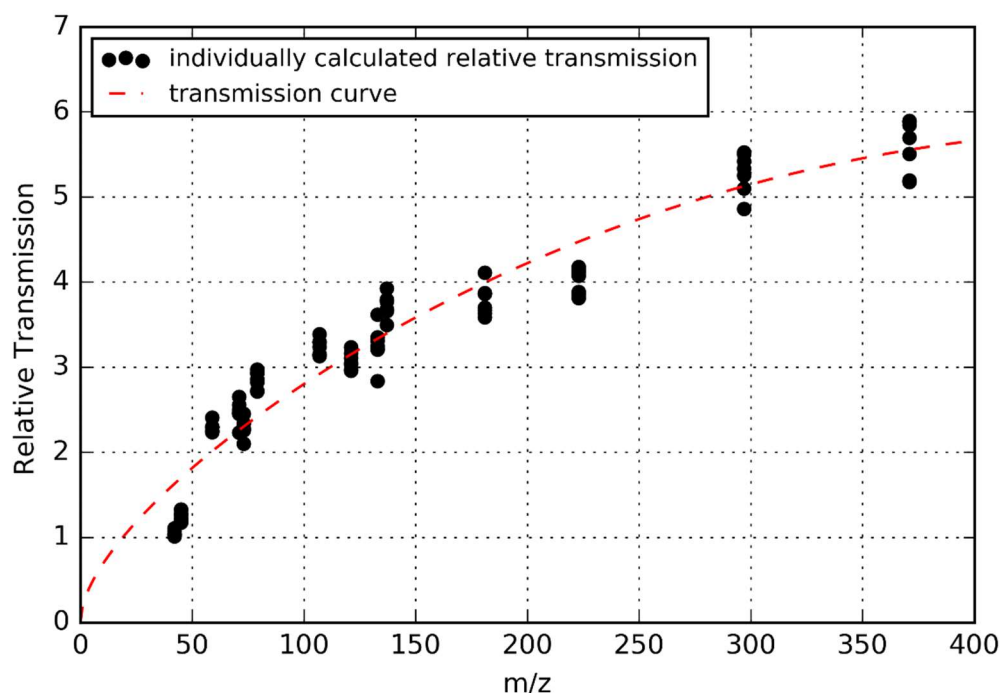

Figure 9: This transmission curve was developed using the methods described in this section, with data from 7 different injections at varying E/N values. The equation is $0.0012x - 0.00002x^2 + 0.18x^{0.5}$.

Once all relative transmission factors are obtained plot them against their corresponding m/z values and approximate the relationship with a curve of the form $Tr(x)=a(x^2) + b(x) + c(x^{0.5})$. This form allows for a monotonically increasing curve with a monotonically decreasing derivative that intersects the y axis at 0. This function is the mass dependent transmission curve. Figure 9 shows a transmission curve calculated using this method with seven injections taken at differing energetic conditions. Note that this transmission curve is instrument specific and needs to be updated regularly to account for instrument degradation.

5.5 Evaluation

In general, all the protocols developed here delivered good results. What follows is a comparison of the initial output with calibration coefficients reported in the literature.

5.5.1 Humidity Factor

Compound	Measured X_R	Literature value (de Gouw et al, 2003a)
Methanol	0.46 ± 0.07[12]	0.38
Acetonitrile	0.55 ± 0.04	0.54
Acetaldehyde	0.46 ± 0.04	0.48
Acetone	0.53 ± 0.04	0.58
Benzene	0.36 ± 0.08	-0.2

Table 2

[12] Error estimates are given as the highest difference between the two sets of results generated and further testing will be required to give better defined error estimates

The measured X_R values for the first four compounds deliver a good match up to the values taken from literature. No more than a difference of 0.08 and some variation is to be expected because of the different mass spectrometers used (time of flight in this project, quadruple in the literature values). The big difference is in the values found for benzene. Here I would argue that the X_R value from this project is more physical. In equation 5.1.2, X_R is seen to be a ratio of universally positive parameters so this negative value from the literature is unexpected, and de Gouw et al. (2003) suspected that tuning issues in the ion transfer region may have caused this artefact. Additional problems may be due to the fact that de Gouw et al. (2003) used only two levels of humidity in their calculations. This means that any mistake or natural variation in either measurement will radically alter the calculated value.

Whatever the case, the initial values delivered by the protocols developed in this project are all in the right range and may in fact be of better quality than previously calculated X_R values.

5.5.2   Sensitivity

Compound	Protonated mass	Measured Sensitivity (ncps/ppb)	Literature Value (de Gouw 2003a)
Acetonitrile	42.034	57.7 ± 6.6	48.8
Acetaldehyde	44.033	49.06 ± 4.8	26.6
Acetone	59.049	78.88 ± 7.2	64.0
Methyl Ethyl Ketone	73.065	78.18 ± 6.6	42.6
Benzene	79.054	62.27 ± 11.1	33.8
Tri Methyl Benzene	121.101	82.63 ± 13.4	30.2
Monoterpene	137.132	79.46 ± 8.3	29.2

Table 3

The Sensitivity values found here are of the right order but show significant variation from the literature values. There are mitigating factors for this, however. The different mass spectrometers used have a greater effect here as the transmission factors for larger masses will differ significantly (in favour of the modern time of flight MS). In addition, many of the literature values were calculated from estimated or negative X_R values. These factors combined with the slight variation of the Sensitivity with conditions explain most of the discrepancy in table 3. The difference in the acetaldehyde may be due to superior materials manufactured in modern drift tubes. Especially viton O-rings used in old instruments (de Gouw et al. 2003) turned out to be very problematic because they absorbed many polar VOCs and have therefore been replaced by Teflon rings in newer instruments. These are initial calculated values and need further testing and evaluation. The comparison here is more to see whether the output of these protocols is in the right physical range; which it is.

5.5.3   Transmission Curve

The transmission curve calculated here is entirely instrument specific so a comparison with literature is impractical. The main points to consider when evaluating the output of this protocol is that it displays the expected behaviour and the function chosen is a good fit to the individually calculated transmission factors. The real result is that a transmission curve can be calculated from a single gas standard injection, allowing for a curve to be calculated regularly. This should allow the user to see how the curve changes over time (i.e. with instrument degradation).

6   Data Quality Control and Tuning Protocols

The methods detailed here consist are varied in their application. Calibrating for absolute humidity allows for greater insight into the effect of humidity on data output as well as providing a way for

the PTR-MS to accurately measure the moisture content of air samples. Also, provided here are the methods used to find the recommended settings shown in section 2 and protocols for evaluating whether further tuning or recalibration is necessary.

6.1   Calibrating for absolute humidity in the drift tube

The cluster ratio in the drift tube (I_{37}/I_{19}) is determined by the absolute humidity (AH) and the energetic conditions in the drift tube (in most cases the latter is best described by E/N see figure 11). The AH determines the amount of H_2O available to form clusters. The energetic conditions determine the rate of formation and the lifetime of hydronium water clusters in the drift tube. This means that with the drift tube held at a specific value of E/N the AH can be deduced from the cluster ratio (Ammann et al, 2006).

In order to calibrate the PTR-MS for AH a way of regulating the AH of air samples fed into the PTR-MS such as a dew point generator is required. Additionally, the input of moisture into the drift tube from the ion source must be minimised (by reducing F_{H2O}) as this artificially raises the AH of the air sample being measured.

Method

1. Connect a charcoal filter that will remove all moisture from the airflow to the PTR-MS inlet. Decrease the flow of H_2O to the ion source (F_{H2O}) in increments of 0.5 ml/min. Continue until the I_{19}/I_{37} ratio approaches zero. [13]
2. Connect a dew point generator and provide air samples into the PTR-MS with RH ranging from 10% to 80% in increments of 10%. Take note of the ambient temperature so that these relative humidity values can be converted to absolute humidity.
3. At each increment take measurements of the intensity of protonated water and the clusters. Calculate values of I_{37}/I_{19} for each increment per equations 4.2.1 and 4.2.2.

The AH has a roughly quadratic relationship with the cluster percentage (C. Ammann et al, 2006). Now that a value of this percentage has been obtained for each increment fitting a quadratic curve to the graph between AH and I_{37}/I_{19} will approximate this relationship. Figure 8 shows the results of this method carried out for 3 different E/N values at 2 drift tube temperatures.

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[13] Note that the O_2^+/H_3O^+ ratio will increase, however the higher O_2^+/H_3O^+ ratio will not cause any difficulty in interpreting the relevant PTR-MS output although the flow should not be too low to ensure there are enough H_3O^+ generated in the ion source. For most Ionicon instruments the lower limit should be around 2.5 ml/min.
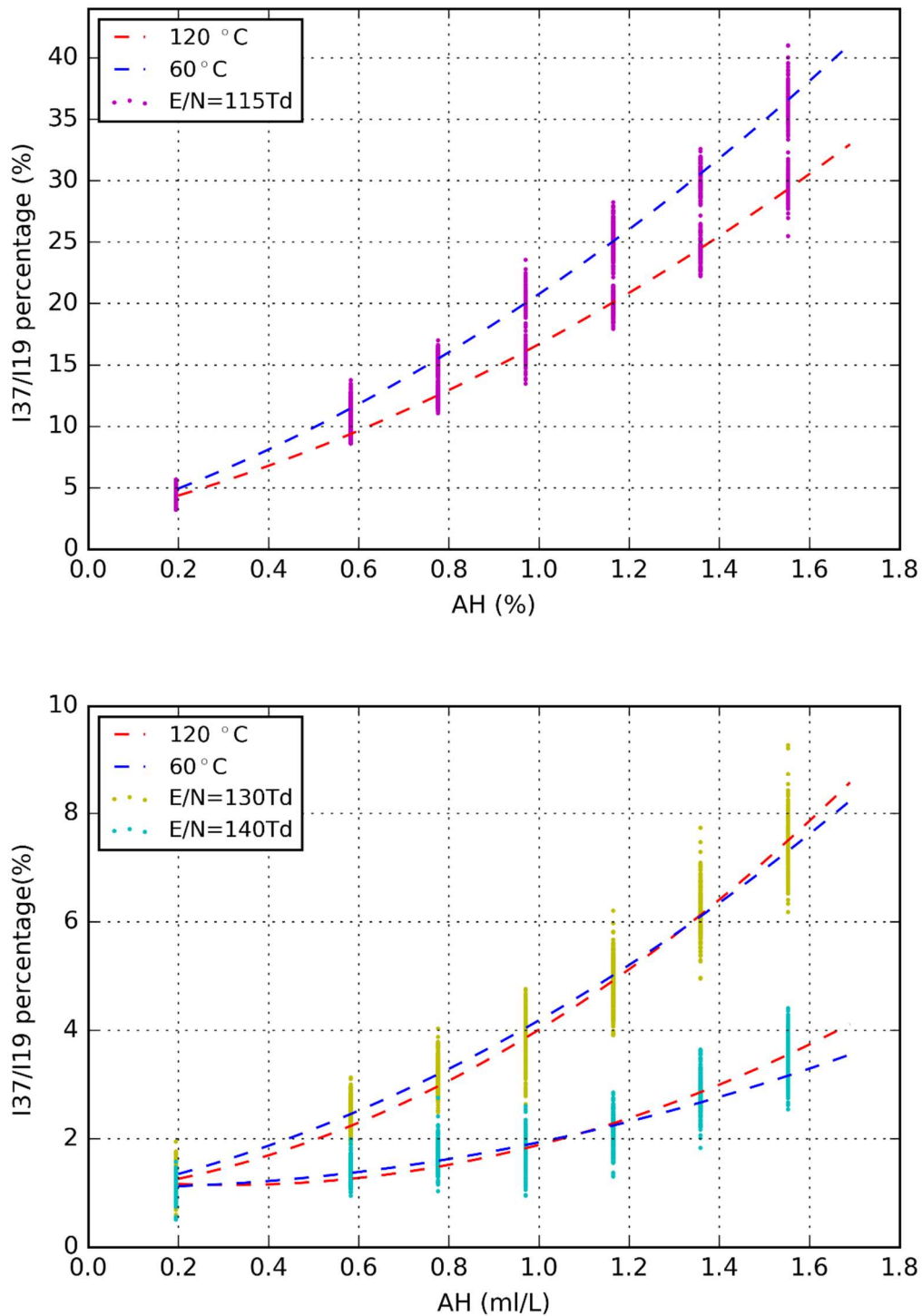
Figure 10: The red and blue lines show the quadratic relationships generated at different drift tube temperatures. The dependence on drift tube temperature is only apparent at low E/N values and high absolute humidity's. For higher values of E/N the relationships generated are independent of drift tube temperature. This behaviour is explored in figure 11

Figure 10 highlights the fact that any relationship generated is only valid for the E/N at which the measurements were taken. Figure 10 also shows that at lower E/N values (and therefore higher cluster ratios) there is a dependence on the drift tube temperature. Equation 6.1.1 (taken from de

Gouw et al, 2007) shows an energy balance for an ion, with effective ion temperature (T_{eff}) serving as a proxy for energy input to the ion during a collision with a molecule:

$$\frac{3}{2}k_b T_{eff} = \frac{1}{2}m_b v_d^2 + \frac{3}{2}k_b T_{drift} \qquad (6.1.1)$$

Here k_b is the Boltzmann constant ($1.38*10^{-23}$). m_b is the molecular mass of air and v_d is the drift velocity of the ion (see 6.1.2). T_{drift} is the drift tube temperature in Kelvin. The constants in front of the terms represent the dimensions that the energy from that term is applied in. The temperature term constants are 3 times as large as the velocity term because they cause motion in 3 dimensions rather than 1. This equation is a modified version of the Wannier expression (Viggiano and Morris, 1996). Combining equations 4.5.2 and 4.5.4, v_d can be shown to be primarily dependent on the E/N:

$$v_d = \frac{E \times \mu_0 \times N_0}{N} \qquad (6.1.213)$$

E is the electric field strength in the drift tube (V/cm), N_0 (2.69×10^{19} molecules/cm^3) is the number density of an ideal gas held at 1 atmosphere and 0°C. N is the number density of the air sample in molecules/cm^3 and μ_0 is the reduced primary ion mobility (see equation 4.5.1). From figure 11 it can be seen that the first term on the right-hand side of equation 6.1.1 usually dominates (de Gouw, 2007), so E/N is generally the largest factor in the energy balance. However, at low E/N values the temperature dependent term will have a non-negligible effect as can be seen in figure 10. At higher E/N values this term becomes negligible.
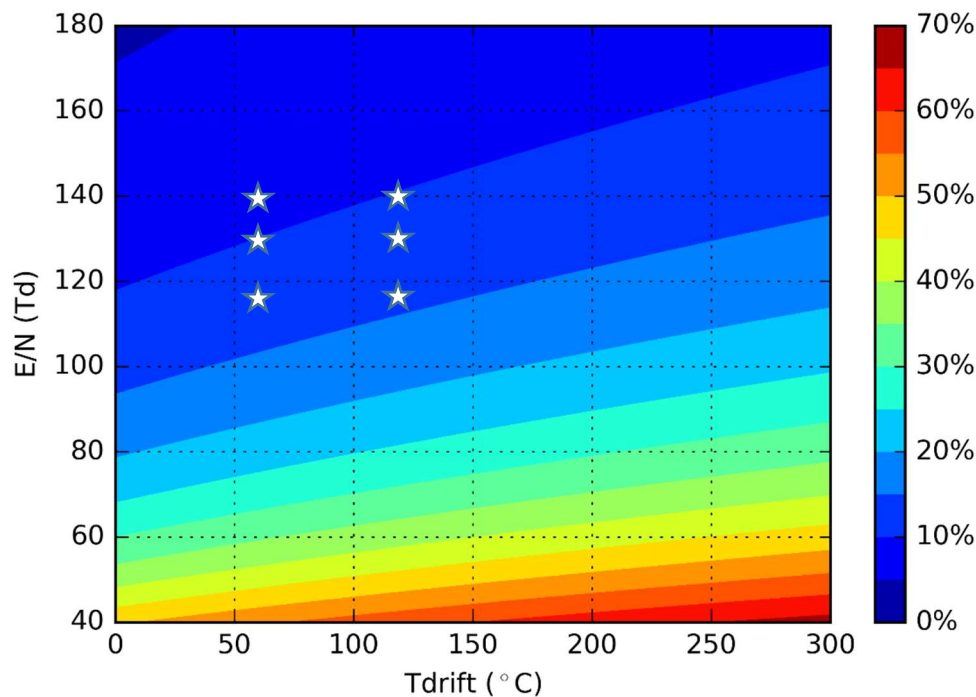

Figure 11: These results are based on a 1-dimensional analysis of equation 13.1 as the temperature term will only have a significant impact on ion fragmentation when it is causing motion opposite to the velocity represented in term 1. Thus, the percentages shown here are generated by one third term 2 as a percentage of term 1 plus one third term2 (i.e. the percentage input of temperature into fragmentation driving energy). For simplicity, it is assumed that reduced ion mobility is constant with humidity (see equation 4.5.1). The white stars indicate the conditions the measurements shown earlier were subject to, this should give some explanation of the different behaviours in figure 10.

The measurements displayed in figure 10 have been used to generate quadratic relationships between cluster ratio and AH for each data set. These have then been used to create contour plots that visualise these relationships within the two temperatures used (figure 12):

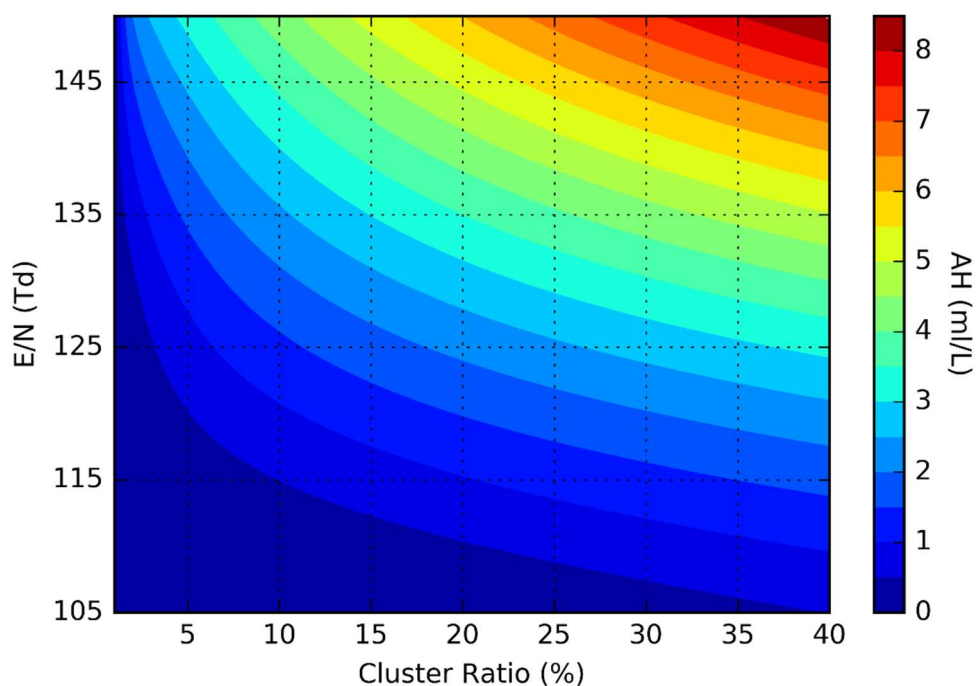| AH (ml/L) = a$(I_{37}/I_{19})^2$ + b(I_{37}/I_{19}) + c		$(I_{37}/I_{19}$ is given as a percentage rather than a ratio)		
E/N (Td)	T_{drift} (°C)	a	b	c
115	120	-7.52*10^{-4}	7.83*10^{-2}	-9.77*10^{-2}
130	120	-1.67*10^{-2}	3.52*10^{-1}	-1.46*10^{-1}
140	120	-1.51*10^{-1}	1.18	-7.34*10^{-1}
115	60	-4.41*10^{-4}	6.02*10^{-2}	-6.02*10^{-2}
130	60	-1.51*10^{-2}	3.51*10^{-1}	-2.03*10^{-1}
140	60	-1.82*10^{-1}	1.39	-1.01

Table 4

60 °C
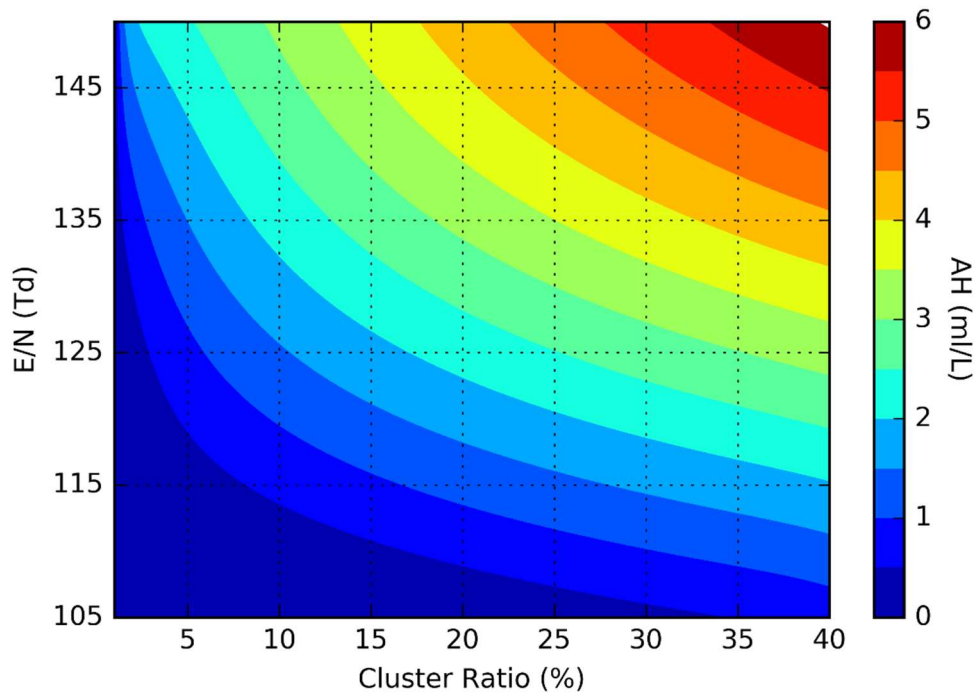
120 °C

Figure 12: From the relationships listed in table 4 it is possible to extrapolate an overall relationship between the AH, the cluster ratio and E/N for a given temperature. On the top is that relationship demonstrated for 60°C and on the bottom 120°C

6.2   Optimizing drift tube conditions

E/N, given in Townsends (1Td=10^{-21}Vm^2=10^{-17}Vcm^2), is a measure of the induced collision energy between ions and neutral buffer gas molecules (mostly N_2 and O_2 from the sample gas). E is the strength of the electric field (V/cm) and N is the number density of the sample gas (molecules/cm^3). N can be calculated as follows:

$$N = \frac{N_0 \times p_{drift} \times T_0}{p_0 \times T_{drift}}$$
(6.2.1)

Here T_{drift} and p_{drift} are the temperature (K) and pressure (mbar) respectively in the drift tube, while T_0 is 273.15K (0°C) and p_0 is standard atmospheric pressure (1013.25 mbar). N_0 (2.69×10^{19} molecules/cm^3) is the number density of an ideal gas held at p_0 and T_0.

E is calculated using the drift tube voltage, the lens voltage(U_{lens}) extracting the ions from the drift tube to the mass spectrometer (the IT region; this voltage is tagged U_{ds} in Ionicon instruments) and the length of the drift tube (cm):

$$E = \frac{U_{drift} + U_{lens}}{d}$$
(6.2.2)

Here E is the electric field strength (V/cm), U is the voltage of the different parts of the drift tube (V) and d is the length of the drift tube (cm). E/N is simply the ratio of E and N multiplied by 10^{17} to convert it Townsends (Td).

The level of fragmentation of molecules and clusters in the drift tube is primarily dependent on E/N. The value of E/N should be decided on with two important factors taken into consideration.
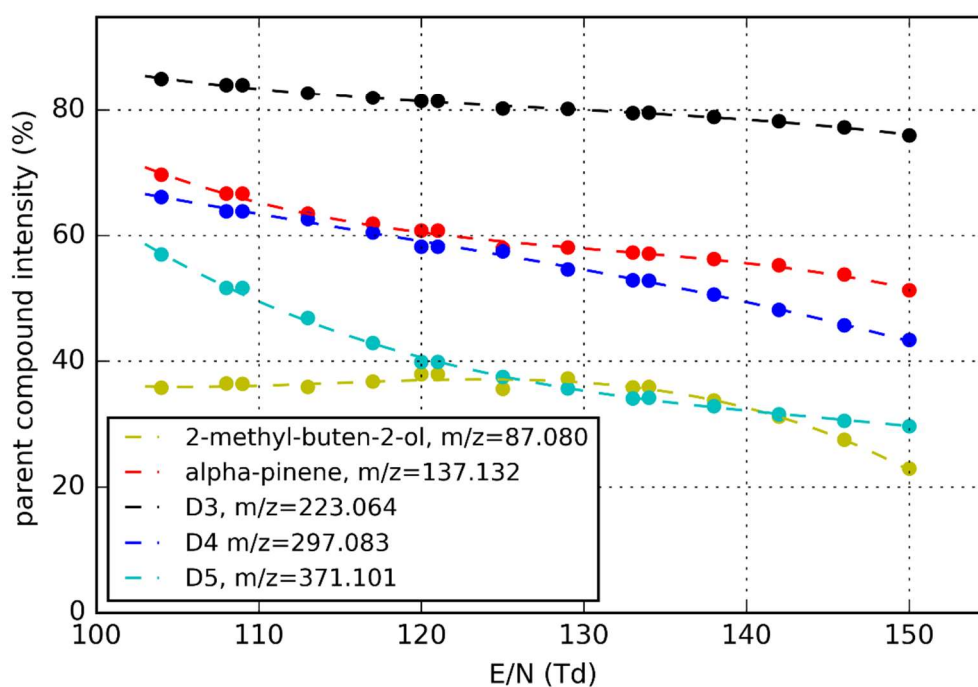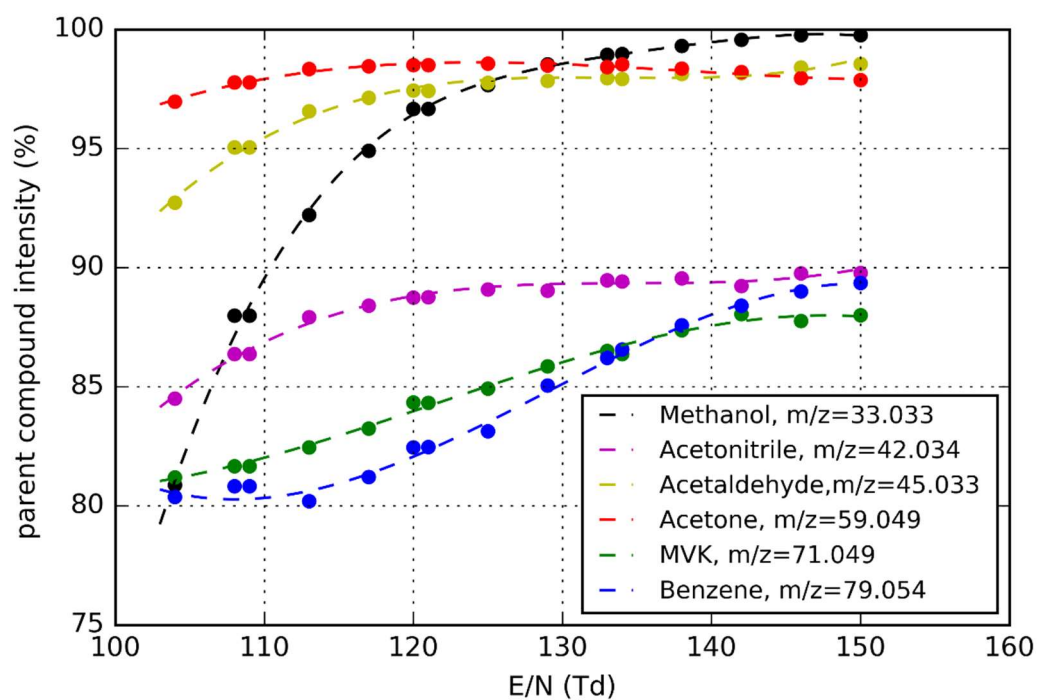
Figure 13: In the top panel, the fragmentation patterns of compounds contained within the gas standard that are not prone to fragmentation are shown at rising E/N values. The percentages shown are the contribution of the intensity detected at the protonated mass of the compound to the overall signal of that compound. In this top figure the other components of the signal are all the VOC clustered with a water molecule, these become less common as the energy in the drift tube rises. This is seen in the rising contribution of the parent compound.

In the bottom panel the same data is shown for compounds known to be prone to fragmentation. As the energy in the drift tube increases the intensity detected at the protonated mass of these compounds falls as fragmentation becomes more common. These figures demonstrate the need to keep within the recommended operating conditions given in section 3. Otherwise, mass spectra will be very difficult to properly interpret.

Firstly, at lower values of E/N higher order $H_3O^+(H2O)_x$ clusters form. These clusters have a higher proton affinity than the hydronium (H_3O^+)(W.Jolly, 1991) and so react with VOC's in the drift tube at a different rate. The error this causes when calculating mixing ratios is difficult to account for and leads to inaccuracy. Clustering can also occur with lighter compounds, i.e. $RH^+(H_2O)$. This reduces the prominence of the signal detected at the protonated mass of a compound and complicates interpretation of mass spectra (see figure 13).

Secondly, higher values of E/N can cause fragmentation of VOC's being measured (see figures 2 and 13). For known or lighter VOC's this is less of a problem. Lighter molecules are less prone to fragmentation and if the m/z of the fragments of a VOC are known then fragmentation can be accounted for when calculating the VMR (see section 4.5 – Calculating the VMR). For larger VOC's with unknown fragmentation patterns, a lower E/N value is essential to minimise the inaccuracy caused by fragmentation.

The value of E/N chosen when using the PTR-MS should be thought through carefully. E/N must be kept as high as possible to avoid higher order clusters but mustn't cause excessive fragmentation of VOC's being measured, particularly if they have unknown fragmentation patterns. In Figure 13 the effect of E/N on the prominence of the parent compound's signal is clearly demonstrated. The affinity of lighter compounds for clustering with water is demonstrated by the lower parent compound signals at low E/N values. Methanol as the lighter compound has a pronounced upward curve at these E/N values. Fragmentation prone compounds (mainly in the lower panel of figure 13) have less prominent parent signals at higher E/N values as expected. A recommended range and optimal value are provided for regular measurements in section 3.2.

6.3 Measuring and tuning the ratio O_2^+/H_3O^+

O_2^+ ions are caused by oxygen in the air sample being input into the PTR-MS diffusing back into the ion source and becoming positively charged. Another production pathway is associated with ions that are initially produced in the hollow cathode discharge (e.g. H^+, OH^+, H_2^+, O^+), and are dragged into the drift tube before they reacted with neutral H_2O to form hydronium ions. It is important to keep these ions to a minimum as they react with VOC's in the air sample that would otherwise be reacting with primary ions as well as VOC's that have too low a proton affinity to react with primary ions (de Gouw et al, 2007). This makes it difficult to accurately interpret mass spectra. The ratio O_2^+/H_3O^+ is a measure of the abundance of these unwanted ions relative to hydronium ions. It is given simply by the ratio of their intensities (given by I_{19} and I_{32}, see equations 2.1 and 2.3) multiplied by their relative transmission factors (Tr_{19} and Tr_{32}, see section 5.4):

$$\frac{O_2^+}{H_3O^+} = \frac{Tr_{19}}{Tr_{32}} \times \frac{I_{32}}{I_{19}} \qquad\qquad (6.3.1)$$

Blow back of oxygen into the ion source can be minimised by increasing the flow of H_2O into the ion source, and the voltages pulling the ions into the drift tube need to be low enough that the initial ions produced in the hollow cathode have sufficient time to complete the production of hydronium ions. Increasing the flow of H_2O, however, will cause higher relative humidity in the drift tube which

itself can be a source of inaccuracy, and the extraction voltages need to be at a certain level to obtain sufficient ion signal. Figure 1 shows the effect of varying the flow into the ion source on this impurity ratio.

6.4 Retrieving drift tube conditions from a gas standard

In this section, two relationships are generated between compound specific parameters and drift tube conditions. These relationships can then be used to retrieve the drift tube conditions from a connected gas standards. Both these methods are more easily applied when this gas standard is connected via a steady dilute flow rather than the injection set up detailed in previous sections. When applied, these retrieval methods serve as excellent quality control tools. Any difference between the retrieved and drift tube conditions calculated from basic engineering data (p_{drift}, U_{drift} etc.) is an indication that further instrument tuning or re-calculation of calibration constants is needed.

The first relationship is between the level of fragmentation and E/N. This relationship can be used to infer the E/N in the drift tube from the level of fragmentation (Fr_x). Fr_x is given by:

$$Fr_X = \frac{\frac{I_X}{Tr_X}}{\frac{I_X}{Tr_X} + \frac{I_{Fr}}{Tr_{Fr}}} \qquad (6.4.1)$$

Where I_x is the product intensity of the parent compound (i.e. the compound that is fragmenting) and Tr_x is its relative transmission factor (section 5.4). I_{fr} and Tr_{Fr} represent respectively the product intensity (equation 4.1) and transmission factor of the fragment. This equation gives Fr_x as a ratio.

Fr_x calculated using equation 6.4.1 will be primarily dependent on the E/N [14]at which the measurements were performed and independent of the PTR-MS with which it was found (once transmission factors have been accounted for). By calculating Fr_x at a range of E/N values a quadratic relationship between the two parameters has been developed. The compounds used (alpha-pinene, D3, D4 and D5, see figure 2c) here were chosen for their simple fragmentation patterns.

E/N (Td) = a(fr$_x$)^2 + b(fr$_x$) + c (fr$_x$ given as a percentage (%))					
Compound	Protonated m/z	m/z of fragment	a	b	c
Alpha pinene	137.132	81.070	0.105	-5.524	176.134
Hexamethylcyclotrisiloxane (D3)	223.064	207.032	0.099	1.702	55.325
Octamethylcyclotetrasiloxane (D4)	297.083	281.051	-0.020	3.860	-3.943
Decamethylcyclopentasiloxane (D5)	371.101	355.070	0.064	-5.801	240.315

Table 5

These relations can be used to check whether further tuning of the PTR-MS is required; if the E/N inferred by the level of fragmentation seen differs greatly from the value calculated from PTR-MS engineering data then further tuning is required. This will likely be in the ion transfer region, the procedure for which is shown in the following section.

The second relationship is more complicated. By deconstructing the definition of the Normalised Intensity and the Sensitivity, the product intensity normalised by only the first primary intensity

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[14] at low E/N the temperature may have some effect but within the recommended range provided in this text its contribution will be small. These relations were derived at 60 °C and if this quality assessment technique is performed at a significantly different temperature then some regular deviation is to be expected.

(I_X/I_{19}), the Sensitivity (S) and the humidity factor (X_R) can be used to infer the cluster ratio of an air sample.

From the definition of the NI (equation 4.5.6) it is easy to see that:

$$\frac{\frac{I_X}{I_{19}}}{NI_X} = \frac{I_{37}}{I_{19}}X_R + 1 \qquad \text{(6.4.2)}$$

If the definition of the sensitivity (S=NI/VMR) as the calibration factor between the VMR and the NI is inserted into this equation, with some rearrangement equation 6.4.2 becomes:

$$\frac{I_{37}}{I_{19}} = \frac{I_X}{I_{19}}\frac{1}{VMR*S*X_R} - \frac{1}{X_R} \qquad \text{(6.4.3)}$$

Here VMR is the mixing ratio of the compound X in the gas standard. Mathematically, equations 6.4.2 and 6.4.3.3 are simple. Conceptually equation 6.4.2 is derived from the idea that the amount by which the product intensity normalised by only I_{19} differs from the NI is dependent upon the cluster ratio. Figure 14 demonstrates very clearly that I_X/I_{19} and NI_X evolve very differently with the cluster ratio.
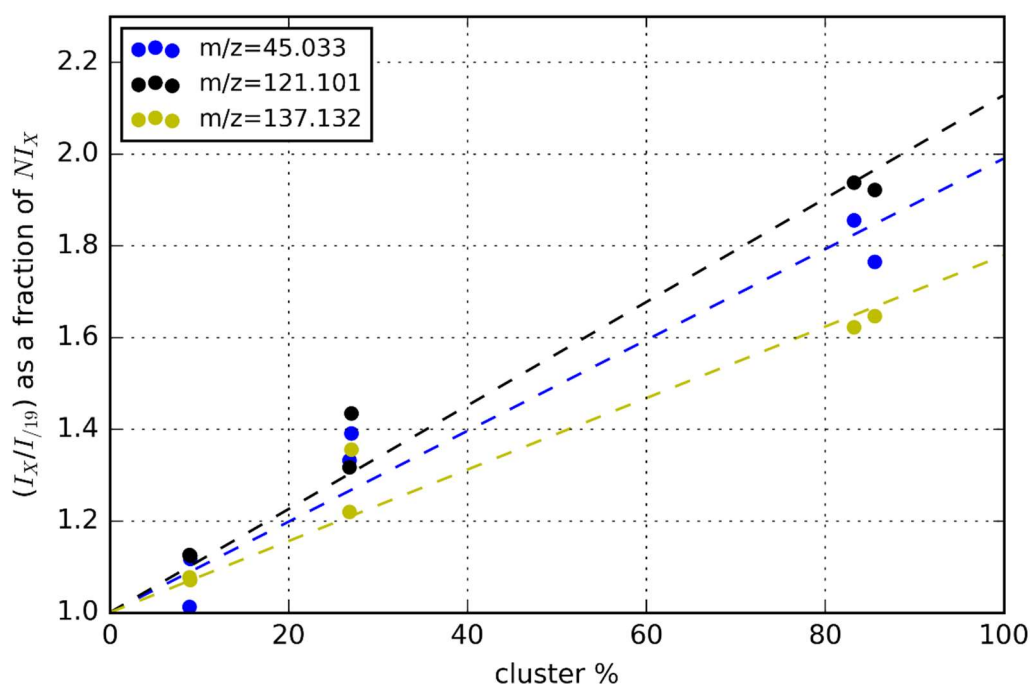

Figure 14: Values of I_X/I_{19} are taken and divided by NI_X. This is a physical demonstration of equation 6.4.2. Compounds are Acetaldehyde, Trimethylbenzene and alpha-pinene (in ascending order of protonated atomic mass).

Using equation 6.4.3 an inferred cluster ratio can be found using S, X_R, I_{19}, I_X and the known VMR of compound x in the gas standard from a gas standard measurement. If this inferred cluster ratio differs significantly from the calculated value (found using equations 4.2.1 and 4.2.2) then tuning of the ion transfer region may be required. If the tuning process is completed and there is still a difference between the inferred and calculated values, then recalculation of X_R and S is required. The problem may also be the needle valve regulating the pumping power of the IS (the SV valve for Ionicon Instruments).

6.5   Tuning the Ion Transfer region

This protocol is necessary for PTR-MS systems that require tuning of the ion transfer region between the drift tube to the high vacuum region of the mass spectrometer. In Ionicon instruments the variable to be tuned is U_{dx}. In this region, there is potential for additional fragmentation or production of $H_3O^+(H2O)_x$ clusters if this area has a different E/N value to the rest of the drift tube, figure 15? highlights the impact of this effect. To avoid these unwanted effects the voltage must be tuned relative to local geometry and the number density (N) of the area (which may be smaller than the general drift tube N). To find the correct voltage the following method is suggested:

Set up

Steady dilute flow from the gas standard into the PTR-MS

Set the voltage of U_{dx} to the lowest value that still produces reasonable ion intensities (that is a fraction of ~20-30% of the maximum signal obtained with an optimized U_{dx}). This may be around 15V for many instruments.

Method

Raise the voltage in small increments (~2V) to no more than 60V and record the intensity of a compound within the standard that is prone to fragmentation along with the intensities of its fragments. The compound chosen in the testing of this method was tert-Amyl alcohol or 2-methylbutan-2-ol, detected at m/z=87.080. This compound was chosen because it is very susceptible to fragmentation and has complicated fragmentation patterns (see figure 11). The results of other compounds as well as cluster ratios can be found in the appendix.

Data management:

Compute the percentage contribution (PC) of each intensity recorded to the total intensity generated by the compound. This will be the intensity recorded as a percentage of the sum of all intensities:

$$PC_y = \frac{\frac{I_y}{Tr_y}}{\sum_{i=1}^{A}\frac{I_i}{Tr_i}} \qquad (6.5.1)$$

Here I is the intensity with the subscript denoting the m/z at which it was detected. A is the total number of intensities recorded and Tr is the transmission (see section 5.4).

These PC will change as U_{dx} rises. There will be two regimes of behaviour: first the composition will change steadily as raising U_{dx} raises the overall E/N (equation 6.2.2), then the IT region will reach an E/N higher than that of the rest of the drift tube and there will be a distinct change in the way in which the intensity composition evolves with rising U_{dx}. The value of U_{dx} at which there is a regime change is just above the required value. Figure 15 shows this method in practice for 3 different E/N values.

Figure 15
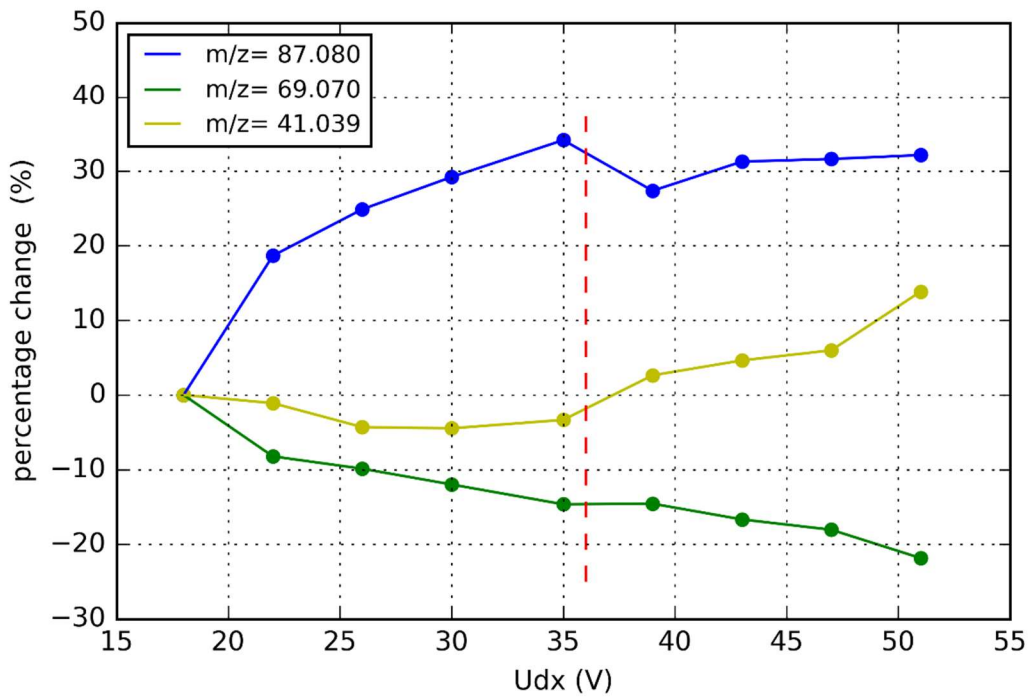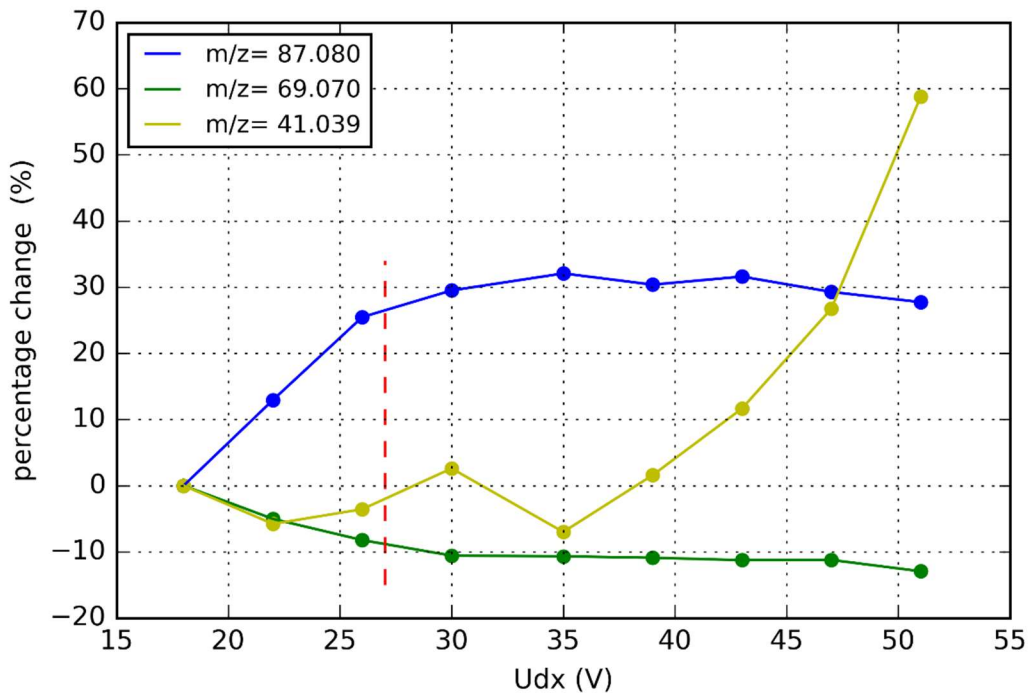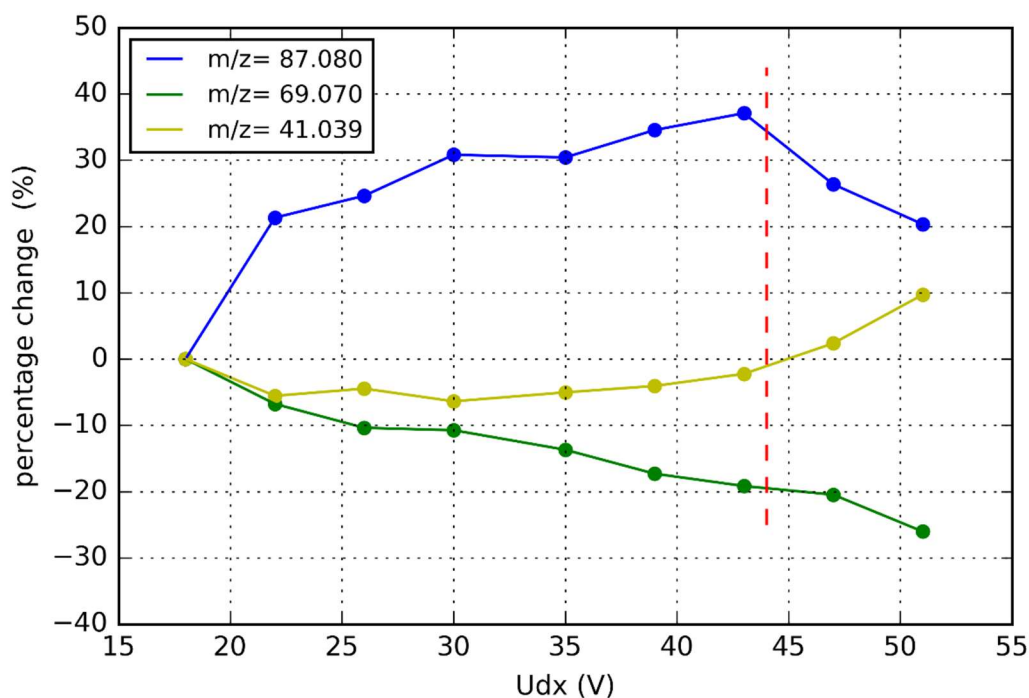
Top figure: Tuning procedure for E/N= 115 Td. The component detected at m/z = 41.039 starts to increase in PC at Udx = 25. This marks the regime change and implies that for this E/N value Udx should be set to approximately 24V. Middle figure: Tuning procedure for E/N= 130 Td. In this figure, there is a rise in the PC at m/z = 41.039 at Udx = 35. This again marks a regime change and so the Udx for this E/N is approximately 34V
Bottom figure: Tuning procedure for E/N= 140 Td. Here the is a distinct drop in the PC of the parent component at Udx = 43 V. Here Udx is tuned to 42V.

It should be noted that this tuning is specific to the E/N in the drift tube and will need to be repeated if a different E/N value is required.

7   Conclusions and Outlook

Section 3, Optimal Instrument Settings and Conditions, fulfilled its objective. The data presented gives reasonable upper and lower bounds to most of the important parameters that need to be considered when performing measurements. One weakness of this section is that all the data was collected from Ionicon instruments with time of flight mass spectrometers. This data can give an idea of good operating conditions for other types and makes of PTR-MS but in order to make this section truly comprehensive more measurements need to be taken on a wider variety of instruments. Ideally, this can be done with the input of the wider PTR-MS community.

The collation of data processing and quality assessment techniques also fulfilled its objectives (Section 4). The methodology is straight forward and has a logical through-line. Both methods of converting counts data to volume mixing ratios are included and the hope is that if this section is adopted as standard operating practice (SOP) then results comparison between different groups will be considerably easier.

 Section 5 is progressive. The new calibration methodology and associated protocols produce promising results. The evaluation within that section has a more complete review of those results. The output is of similar or better quality than some previous methods. The exiting aspect of this is the speed with which the calibration can be carried out. The knowledge gained during this project is now being used to create a 5-minute standard addition routine that will allow for the comprehensive

calibration of an instrument. While these results are promising, it needs to be remembered that this is only a first step and will require further refinement and testing on a wider variety of types and makes of PTR-MS. Again, this will be easier with the input of the wider PTR-MS community.

Finally, the data quality control and tuning section is a partial success. The methods in the first half of the section have been used by previous campaigns and show good results. Again, the methodologies given are clear and concise and should be of great use to anyone wanting to use these techniques. The second half of the section requires more development, at the moment, it is mostly a theoretical basis. The data collected for these protocols is not yet sufficient to justify their use in an SOP. In order to justify the uptake of these methods by PTR-MS users much more testing needs to be done as well as some refinement of the method, particularly in the tuning of the ion transfer region which is as of now not exact enough. I do think that these protocols will work, they just need more development.

Overall, I'm pleased with results of this project. The most important content is the protocols developed for the new method of gas standard addition and these show excellent initial results. This paper is an important contribution towards creating an SOP for PTR-MS.

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9 Appendix

9.1 PTR-MS schematic
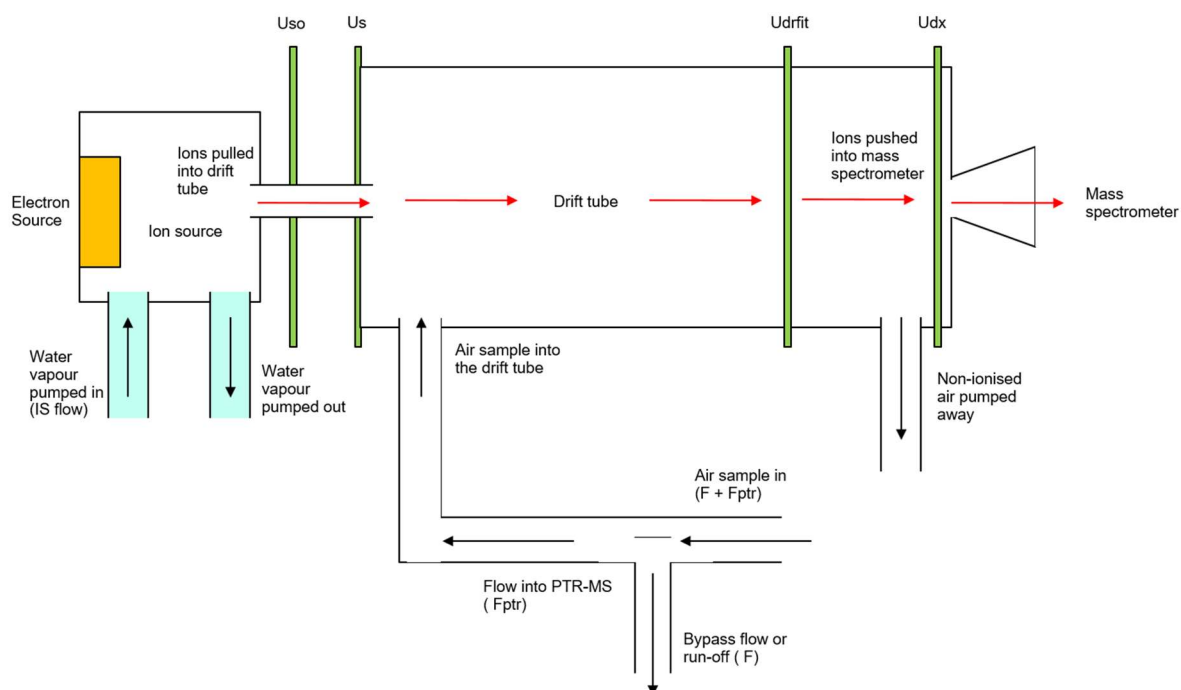
Presented for clarity; a scematic of a PTR-MS. Red arrows represent movement of ion while black arrows repesent non ionised flow. Drift rings are in green and the electron source is in orange.

9.2 Table of variables

List of variables	
C_{21}	Total ion count for ^{18}O hydronium
C_{39}	Total Ion count for ^{18}O $H3O(H2O)^+$ clusters
$C_{X(sample)}$	Total Ion count at the m/z for the measured VOC (R).
$C_{X(background)}$	Total Background Ion count at the m/z for the measured VOC (R).
t	Total length of time over which measurements are evaluated (s)
t_{sample}	Length of time over which sample measurements are evaluated (s)
$t_{background}$	Length of time over which background measurements are evaluated (s)
I_{21}	Intensity for ^{18}O Hydronium (cps)
I_{39}	Intensity for ^{18}O $H_3O(H_2O)^+$ clusters (cps)
I_{19}	Total primary ion intensity of Hydronium (cps)
I_{37}	Total primary ion intensity of $H_3O(H_2O)^+$ clusters (cps)
NI_X	Normalised intensity for VOC X (ncps)
$I_{X(sample)}$	Sample product ion intensity for the VOC being measured (cps)
$I_{X(background)}$	Background product ion intensity for the VOC being measured (cps)
I_X	Background corrected product ion Intensity for the VOC being measured (cps)
fr_{16}	Fractional isotopic abundance of ^{16}O (0.99757)
fr_{18}	Fractional isotopic abundance of ^{18}O (0.00205)
fr_X	Fractional isotopic abundance of the principal isotopologue of the VOC being measured
FR_X	Fragment fraction of the considered ion. If a compound does not fragment upon ionization FR_X equals 0.
X_{R0}	Experimentally determined humidity factor
X_R	Experimentally determined instrument specific humidity factor
S	Experimentally determined instrument specific sensitivity (normalised counts/second/ppb)
d	Drift tube length (cm)
E	Electric field strength in the drift tube (V/cm)
N	Number density of sample gas in the drift tube (10^9molecules/cm3)
N_0	Number density at p_0 and T_0 (10^9molecules/cm3) (2.69×10^{10})
k_{19}	Reaction rate constant of VOC with Hydronium (see appendix B for specific values)
k_{37}	Reaction rate constant of VOC with $H_3O(H_2O)^+$ (see appendix B for specific values)
μ_0	Reduced Ion mobility of primary ions ($2.7cm^2$/Vs)
$\mu_{0,19}$	Reduced Ion mobility of hydronium ($2.7cm^2$/Vs)
$\mu_{0,37}$	Reduced Ion mobility of protonated water clusters ($2.3cm^2$/Vs)
T_{drift}	Temperature in the drift tube (K)
T_0	273.15K
p_{drift}	Pressure in the drift tube (hPa or mbar)
p_0	1013.25 hPa or mbar
Tr_{19}	Transmission Factor for hydronium (set equal to 1 in this paper)
Tr_{37}	Transmission Factor for $H_3O(H_2O)^+$
Tr_X	Transmission Factor for compound X
v_d	Drift velocity of H_3O^+ (cm/s)
t_{react}	Residence time of primary ions in the drift tube
F	Flow controller generated (bypass) flow (ml/min)
V	Sample loop volume (ml or cm^3)
F_{PTR}	Flow into the PTR-MS (ml/min, ml/s or cm^3/min)
n	Amount of sample gas in sample loop (mol)
F_{PTR_mol}	Amount of sample gas passing through the inlet (mol/min)
R	gas constant (8.3144598 $JK^{-1}mol^{-1}$)
f	sampling frequency (Hz), e.g. f= 0.2 if a spectrum is saved every 5 seconds.
U_{so}	Voltage in first drift ring for extracting ions from the ion source (V)
U_s	Voltage in second drift ring for extracting ions from the ion source (V)
U_{drift}	Voltage across the drift tube (V)

U_{dx}	Voltage across the ion transfer region (V)
IS_{flow}	Flow of water vapor into the ion source (ml/min)

9.3 Transmission Curve Data

All intensities for compounds with known fragments were calculated as the intensity recorded at the protonated mass of the compound added to the intensity recorded at the protonated mass of the fragment.

9.3.1 Environmental values used

| |
|---|
| P = 101325   atmospheric pressure in Pascals |
| V = 250e-9   sample loop volume in m^3 |
| R = 8.31441   gas constant |
| T = 259.15   ambient temperature in K |
| MR = 1e-6   mixing ratio of VOC in standard |
| F = 0.97e-6   inlet flow in m^3/s |
| T_0 =237.15 |
| p_0 =1013.25 |
| n=(p*V*MR)/(R*T)   moles of VOC |
| Fmol=(p*F)/(R*T)   inlet flow in moles per second |
| N_0=2.69e19   standard number density in cm-3 |
| d=10   drift tube length in cm |

9.3.2 Compound specific values used

| Compound	Protanated Mass	Isotopic fraction	X_R value	k_{19} (10^{-9}cm^{3}s^{-1}molecules^{-1})
Acetonitrile	42.034	0.974	0.46	4.74
Acetaldehyde	45.033	0.976	0.38	3.38
Acetone	59.049	0.965	0.44	3
MVK	71.049	0.955	0.47	0.6
MEK	73.065	0.955	0.5	3
Benzene	79.054	0.936	0.28	1.97
Xylene	107.086	0.915	0.4	2.25
Trimethylbenzene	121.101	0.905	0.38	2.5
Trifluorobenzene	133.026	0.936	0.51	2.8
Alpha-pinene	137.132	0.642	0.46	2.8
Trichlorobenzene	180.937	0.407	0.34	1.5
D3	223.064	0.730	0.35	0.4
D4	297.083	0.657	0.37	1.7
D5	371.101	0.591	0.22	1.2

9.4 Additional Lens tuning Plots
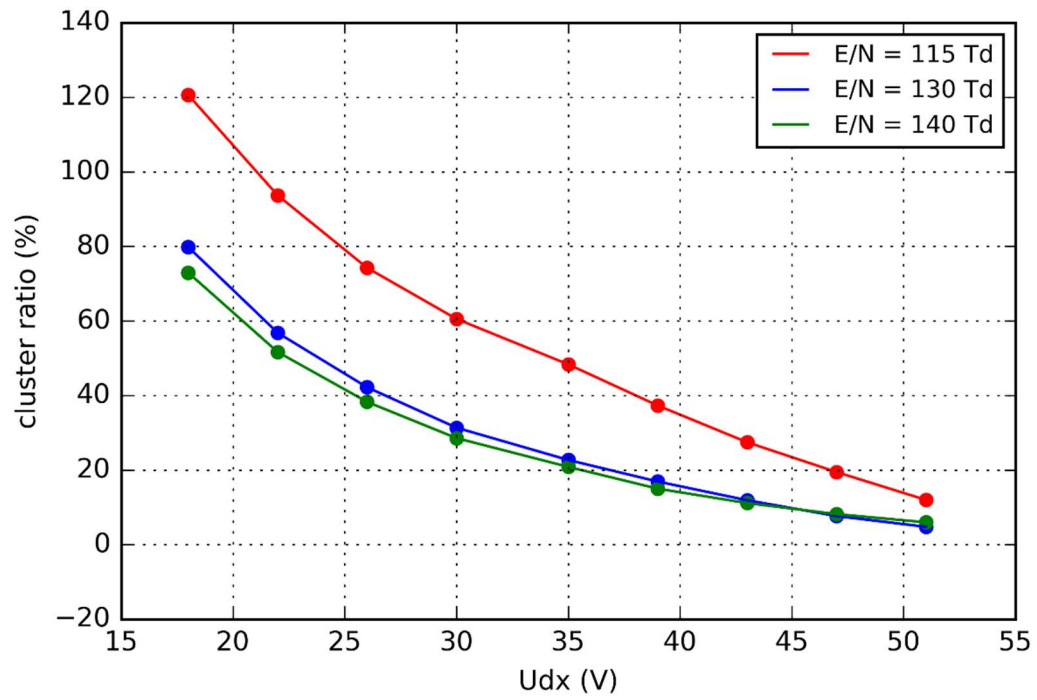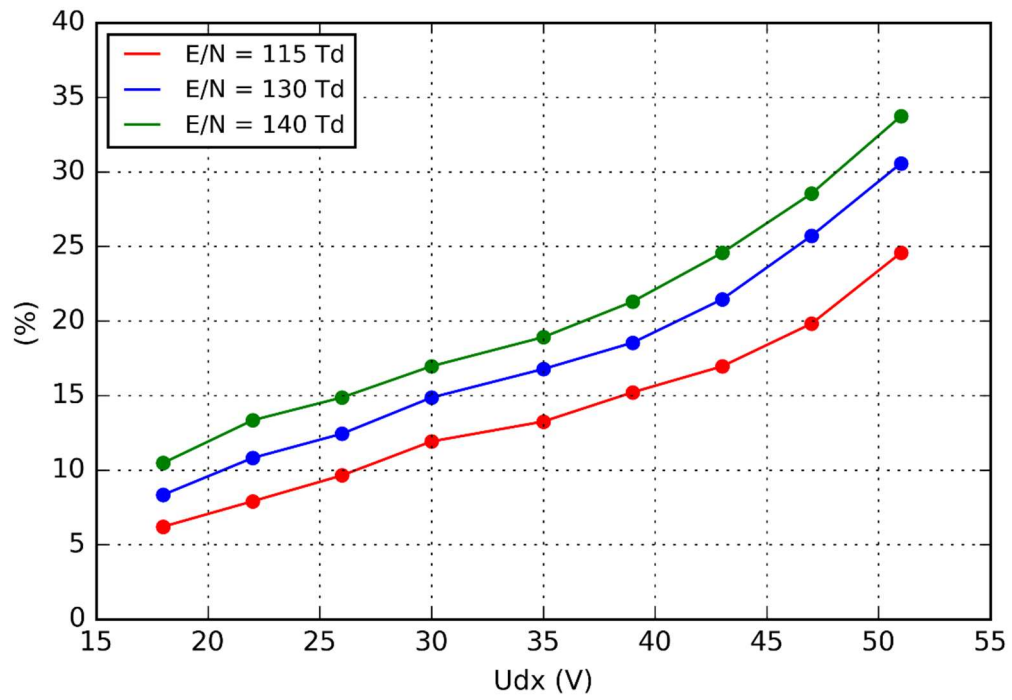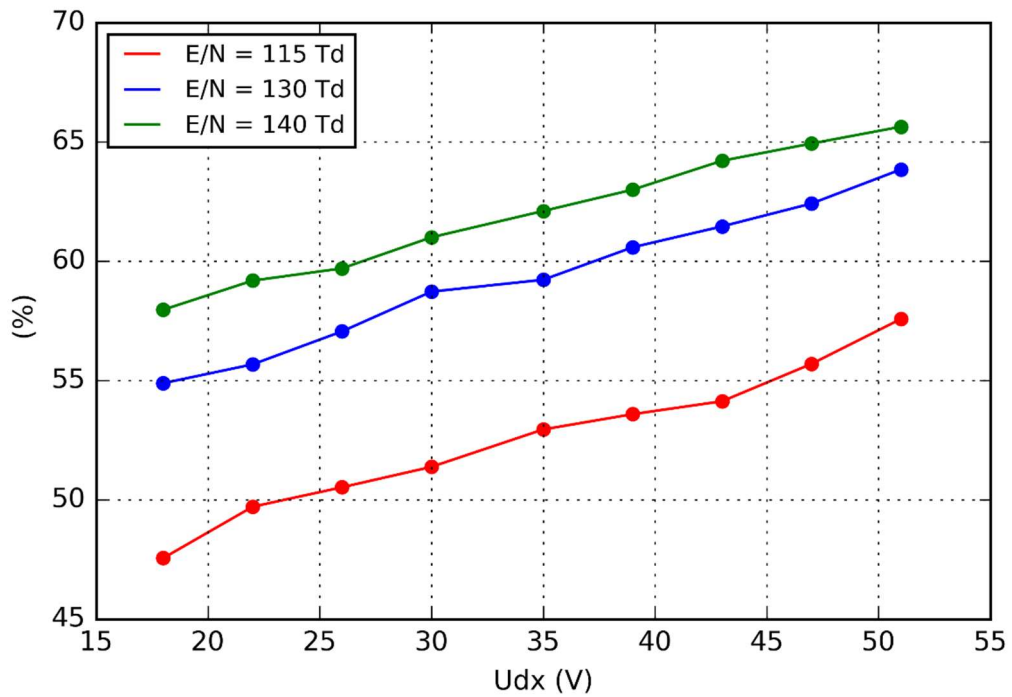
Cluster ratio (I_{37}/I_{19})
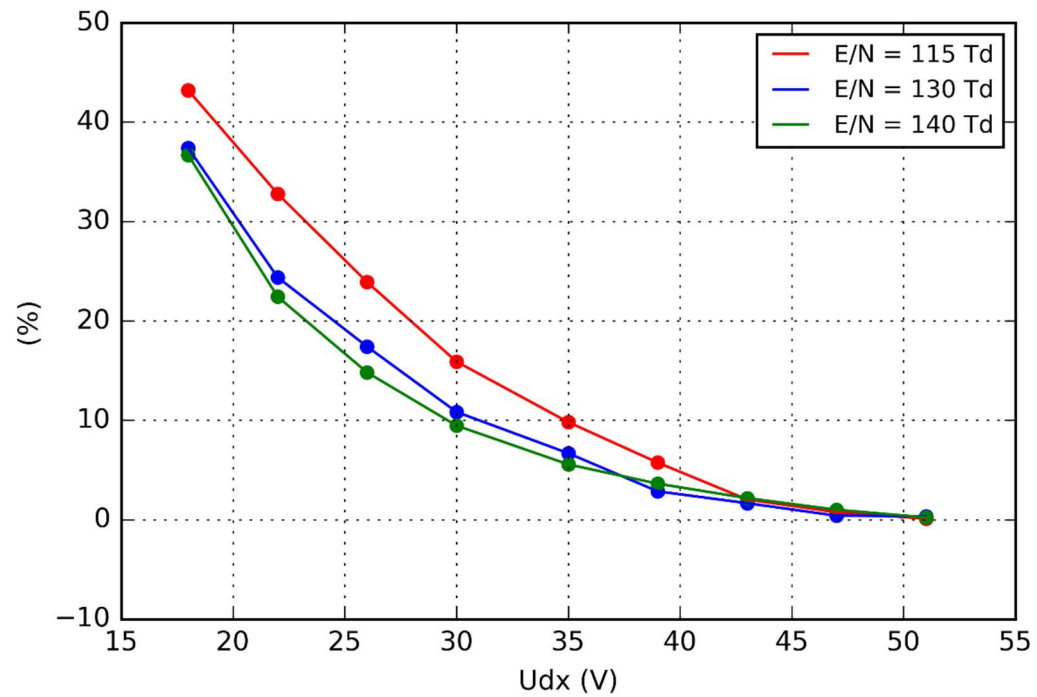
Percentage of water clustered methanol ($I_{51}/I_{33}+I_{51}$)
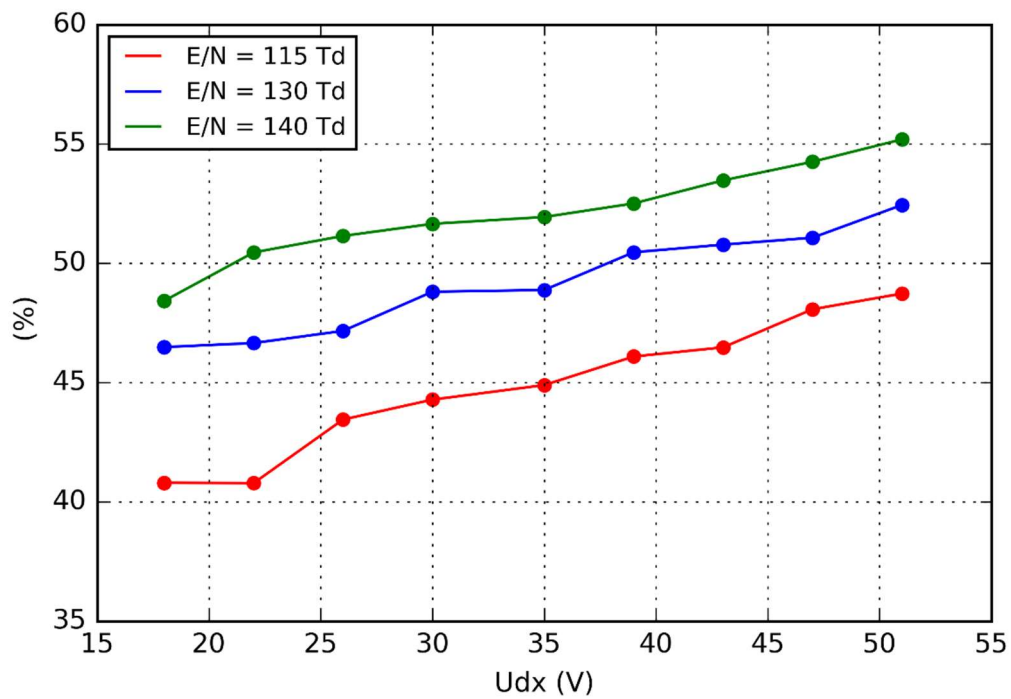
Alpha pinene fragmentation ($I_{81}/I_{137}+I_{81}$)
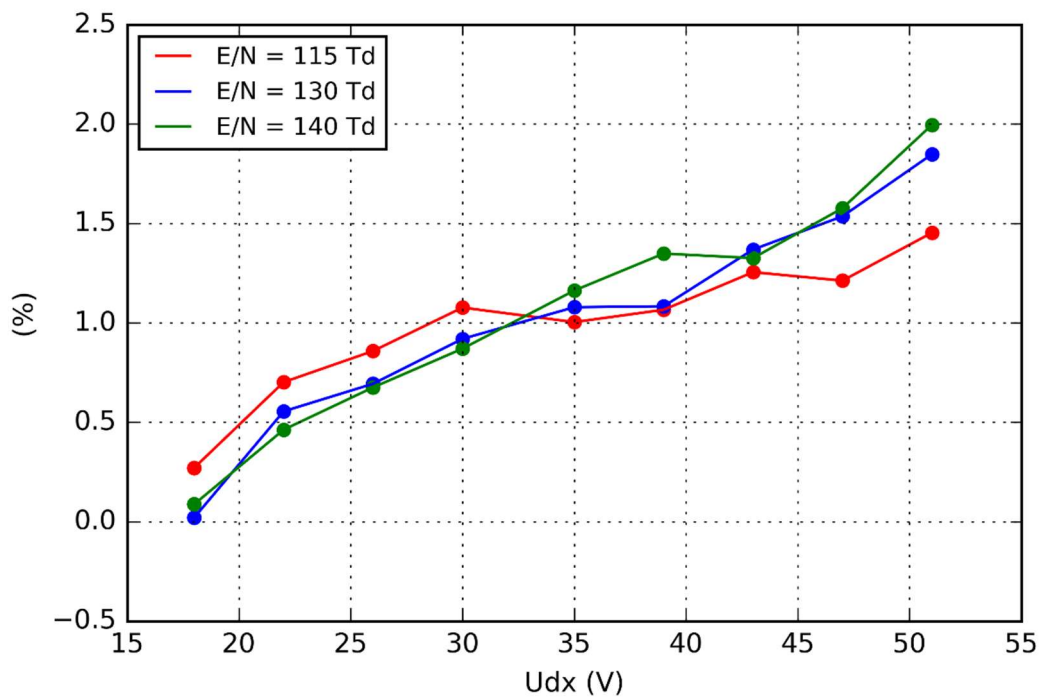
D3 fragmentation ($I_{207}/I_{223}+I_{207}$)

D4 fragmentation ($I_{281}/I_{297}+I_{281}$)

D5 fragmentation ($I_{355}/I_{371}+I_{355}$)