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# Inter-comparison between airborne measurements of methanol, acetonitrile and acetone using two differently configured PTR-MS instruments

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## Abstract

Proton-transfer-reaction mass spectrometry (PTR-MS) has emerged as a useful tool to study the atmospheric chemistry of volatile organic compounds (VOCs). The technique combines a fast response time with a low detection limit, and allows atmospheric measurements of many important VOCs and their oxidation products. Here, we inter-compare the results obtained with two differently configured PTR-MS instruments operated onboard a Falcon aircraft during the Mediterranean Intensive Oxidants Study (MINOS) campaign in the Mediterranean region. One PTR-MS was operated at a drift tube pressure of 2.3 mbar and an electric field divided by gas number density value ($E/N$) of 120 Td for the detection of VOCs and aromatic hydrocarbons. The other PTR-MS was operated at an increased pressure of 2.8 mbar and a reduced $E/N$ of 97 Td for the detection of peroxyacetyl nitrate (PAN). As a consequence, more $H_3O^+(H_2O)_n$ cluster ions were present in the drift tube, which undergo proton-transfer reactions with VOCs similar to $H_3O^+$ ions. The results for methanol ($CH_3OH$), acetonitrile ($CH_3CN$) and acetone ($CH_3COCH_3$) obtained with the instruments compared very well. The agreement between the two results was relatively independent of the ambient mixing ratio of water, which influences the $H_3O^+(H_2O)_n$ cluster ion distribution, and of ozone, which has been implicated in the artificial formation of aldehydes and ketones.

*Keywords:* Proton-transfer-reaction mass spectrometry; Volatile organic compounds; Earth's atmosphere

## 1. Introduction

Volatile organic compounds (VOCs) are released to the earth's atmosphere from a wide variety of sources, both of natural and man-made origin [1]. Although some sources are reasonably well quantified, many uncertainties remain about the ultimate fate of these compounds in the atmosphere. Most VOCs react with hydroxyl radicals (OH), many react with ozone and at night with nitrate radicals ($NO_3$), and some can be photolyzed. The products of the reactions may react further or may be lost from the atmosphere by deposition at the earth's surface or through uptake by clouds and aerosols followed by rainout. The magnitude of the different loss processes is largely unknown, and hence the atmospheric budget of organic carbon remains very uncertain. Resolving the uncertainties is one of the main problems in our understanding of the chemistry of the lower atmosphere. It is an important issue, since the photo-oxidation of VOCs is implicated in the formation of ozone and aerosols in polluted air, which are

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both major air pollutants, have adverse health effects to humans, and are significant factors in the earth's climate system [2].

Proton-transfer-reaction mass spectrometry (PTR-MS) is a technique for measuring trace amounts of VOCs in air, and was developed by Lindinger et al. at the University of Innsbruck [3,4]. In PTR-MS, air is continuously pumped through a drift-tube reactor, and the VOCs are ionized by proton-transfer reactions with $H_3O^+$ ions. The $H_3O^+$ and product ions are extracted from the gas flow, and are mass analyzed and detected with a quadrupole mass spectrometer. Clustering of the $H_3O^+$ and product ions with water molecules in the drift reactor is prevented to a large extent by applying a longitudinal electric field in the drift tube. This simplifies the ion chemistry in the drift tube reactor considerably and allows the detection of a wide variety of VOCs independently of the water content of the sampled air.

Since 1998, PTR-MS has been used in a number of airborne measurements of the atmospheric composition. PTR-MS and other instruments were used onboard a Dutch Citation research aircraft to study the composition of the atmosphere over the tropical rain forest in Surinam [5,6], and the outflow of polluted air from India during Indian Ocean Experiment (INDOEX) [7]. A second PTR-MS system was used during INDOEX onboard the NCAR C-130 aircraft [8]. More recently, a PTR-MS system was used onboard the NCAR Electra aircraft in a regional air quality study in the Houston area during the 2000 Texas Air Quality Study (TEXAQS) [9], and onboard a NOAA WP-3 aircraft during the Intercontinental Transport and Chemical Transformation experiment in 2002 (ITCT2k2) [10].

In PTR-MS, only the mass of the product ions is determined, which is a valuable but certainly not a unique indicator of the identity of trace gases. It is clear that different isomers cannot be separated in this manner. Moreover, the interpretation of the mass spectra can be complicated by the fragmentation of product ions, which may lead to further mass overlap [6]. It is necessary, therefore, to investigate the possible interferences in the measurements, and in general to inter-compare the measurements with alternative techniques. Measurements of benzene and toluene in urban air have been inter-compared with GC-FID measurements of canister samples and the two measurements were found to be in good agreement [11]. The results for acetone ($CH_3COCH_3$) and acetonitrile ($CH_3CN$) during INDOEX were inter-compared with those obtained with an atmospheric-pressure chemical ionization mass spectrometer (AP-CIMS) and were also found to agree well [8]. The specificity of the measurements has been investigated by combining a gas-chromatographic separation of the VOCs in individual air samples with PTR-MS detection of the column effluent (GC-PTR-MS) [12]. GC-PTR-MS analyses of air samples from urban air and from the free troposphere indicated that PTR-MS measurements of several VOCs were free from significant interference [13,14]. Recently, a detailed inter-comparison between a PTR-MS instrument and several other techniques for VOC measurements was performed during the New England Air Quality Study (NEAQS) [15].

Here we inter-compare measurements of methanol ($CH_3OH$), acetonitrile and acetone that were made using two differently configured PTR-MS instruments onboard a Falcon research aircraft as part of the Mediterranean Intensive Oxidants Study (MINOS) [16]. The MINOS campaign was focused on the chemistry of tropospheric ozone in the Mediterranean region and on the long-range transport of pollutants to the global atmosphere. Global models have shown that summertime ozone levels over the Mediterranean are continuously elevated with mean mixing ratios in excess of 80 ppbv [17]. A three-dimensional chemistry transport model reproduced the seasonal trend of ozone levels observed at Crete Island, but consistently underestimated the ozone mixing ratios by 10–20 ppbv, pointing out the need for more comprehensive information on the VOC and $NO_x$ emission sources in the region and a better understanding of the VOC chemistry [18]. The MINOS campaign was organized in August 2001 to study these and other issues, and involved ground-based measurements from Finokalia at Crete Island and airborne measurements using a Falcon aircraft operated by the DLR (Deutsches Zentrum fur Luft und Raumfahrt).

Two PTR-MS instruments were part of the instrument payload of the DLR Falcon. One instrument, hereafter referred to as the Utrecht PTR-MS, was set up to measure a variety of VOCs (methanol, acetonitrile, acetone, benzene and toluene), whereas the other PTR-MS, the Mainz PTR-MS, was used at a reduced value of the parameter electric field divided by gas number density ($E/N$) in the drift tube for the detection of peroxyacetyl nitrate (PAN) [19]. The Mainz PTR-MS was also used to detect methanol, acetonitrile and acetone. Benzene and toluene were not measured by this instrument: at the reduced value of $E/N$ in this instrument, the ion chemistry in the drift tube does not permit these species to be ionized efficiently [11]. Results from both instruments have been used in several papers about the MINOS experiment [20–22].

As a consequence of the lower $E/N$ in the Mainz PTR-MS, there was a relatively high fraction of $H_3O^+(H_2O)_n$ cluster ions in the drift tube, which undergo proton-transfer and ligand switching reactions with VOCs. The question arises whether the sensitivity depends on the humidity of the sampled air, because this changes the $H_3O^+(H_2O)_n$ cluster ion distribution. Secondly, the gas inlets used for the two systems were different. The inlet for the Mainz PTR-MS was equipped with a heated scrubber to selectively remove PAN from the sample flow by thermal dissociation, and with an additional pump to increase the inlet flow. The question is addressed whether or not the gas inlet caused a difference between the two measurements. Inlet effects could affect the determination of background impurities in the system, which is done in both systems by removing VOCs from the sample flow with a catalytic converter. Also, the effect of ozone in the sample flow is investigated. The presence of ozone has been implicated in the artificial formation of aldehydes and ketones [23].

## 2. Airborne measurement set-up

Lindinger et al. have described the PTR-MS technique in detail [3,4], and therefore only a brief description is given here. Ions are produced in a hollow-cathode discharge in water vapor, which forms an intense source of $H_3O^+$ ions. A water vapor flow of 4–8 STP $cm^3$ $min^{-1}$ (STP: standard temperature of 273.15 K and pressure of 1 atm) is pumped through the source. From the source, ions are extracted into the drift tube reactor, in which the proton-transfer reactions between $H_3O^+$ and the VOCs take place. A flow of ∼15 STP $cm^3$ $min^{-1}$ of ambient air is continuously pumped through the drift tube. About 5% of the water flow in the source also reaches the drift tube, leading to an increased humidity of the sampled air [11]. The drift tube was operated at 2.3 mbar in the Utrecht PTR-MS instrument and at 2.8 mbar in the Mainz PTR-MS. A homogeneous, longitudinal electric field of 66 V $cm^{-1}$ is applied in the drift tube to prevent the clustering of $H_3O^+$ and product ions with primarily water molecules. The sample air and a fraction of the ions exit the drift tube through an orifice and enter a small intermediate chamber, which is pumped by a turbo pump (Pfeiffer TPD 022). The intermediate chamber separates the pressure of 2.3/2.8 mbar in the drift tube from the high vacuum in the mass spectrometer chamber ($10^5$ mbar). In the intermediate chamber, ions are focused onto the opening of the quadrupole mass spectrometer (Balzers QMG422).

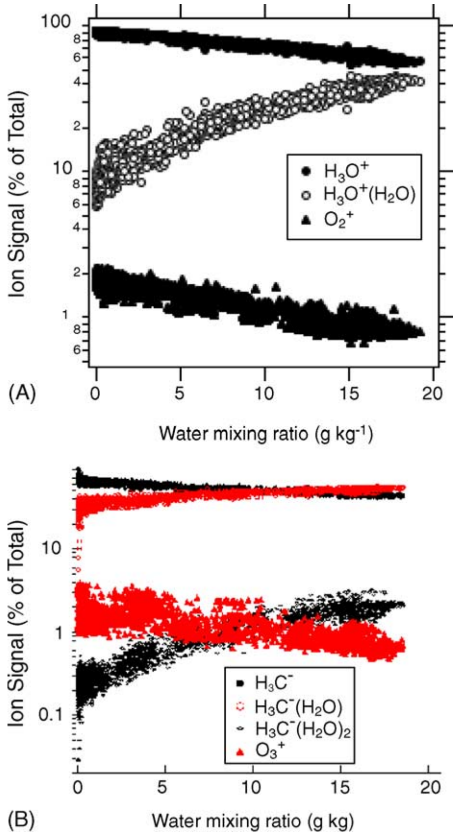

Fig. 1. Distribution of reagent ions in (A) the Utrecht and (B) the Mainz PTR-MS as a function of the water content of the sampled air. Data were taken in-flight during MINOS and represent the results from all the research flights.

The parameter $E/N$, the ratio of the electric field and the gas number density in the drift tube, determines the mean kinetic energy of ions in the drift tube and the degree of clustering with (primarily) water molecules [13]. $E/N$ is expressed in units of Townsend or Td (1 Td = $10^{-17}$ V $cm^2$). The parameter $E/N$ is weakly dependent on the temperature and the values reported in this paragraph were calculated for 298 K. During research flights the operating temperature of the instruments was in most cases significantly higher and, consequently, the value of $E/N$ was a few percent increased. In the Utrecht PTR-MS, $E/N$ was approximately 120 Td (at 298 K) and the resulting distribution of the main ions in the drift tube versus the ambient mixing ratio of water, measured during the MINOS flights, is given in Fig. 1A. It is clear that in the dry, upper troposphere $H_3O^+$ is the dominant reagent ion in the drift tube, whereas in the humid conditions near the surface there is a significant fraction of $H_3O^+(H_2O)$ ions. Also present are $O_2{}^+$ ions, possibly formed in the source by back streaming of air, or in the drift tube from $H_2O^+$ ions or UV photons from the ion source. In the drift tube $O_2{}^+$ ions react slowly with water to form, in the end, $H_3O^+$, which explains why the fraction of $O_2{}^+$ decreases with the humidity. The presence of $O_2{}^+$ ions in the drift tube is in general not a significant problem. One of the main consequences for the measurements presented here is the fact that the mass of one of the $O_2{}^+$ isotopes ($^{17}O^{16}O^+$) coincides with the mass of protonated methanol and, therefore, forms a background to the measurements, which needs to be subtracted. In the Mainz PTR-MS, $E/N$ is approximately 97 Td (at 298 K) and the cluster ion distribution measured during MINOS is given in Fig. 1B. It is clear that in this case the average cluster size is larger. In humid conditions, the most abundant ion is $H_3O^+(H_2O)$ and there is also a small fraction of $H_3O^+(H_2O)_2$ ions at mass 55 amu. Apart from the pressure and electric field in the drift tube, the distribution of cluster ions as shown in Fig. 1 is significantly influenced by the potentials applied to the electrostatic lenses in the intermediate chamber between the drift tube and the quadrupole MS. Collision-induced dissociation (CID) in this intermediate chamber may cause $H_3O^+(H_2O)_n$ ions to be detected as $H_3O^+(H_2O)_m$ with $m < n$ [11]. It is possible, therefore, that the cluster ion distribution was significantly larger in the drift tube than shown in Fig. 1.

It is clear from Fig. 1 that the distribution of reagent ions depends on the humidity of the sampled air in both the Utrecht and the Mainz PTR-MS. The question arises how to account for this. The drift tube pressure recommended by Ionicon is 2.0 mbar, in which case $H_3O^+$ is the only significant reagent ion in the drift tube regardless of the humidity. Under these circumstances it is possible to calculate the sensitivity with a good accuracy from the proton-transfer rate coefficient, the transit time of the $H_3O^+$ ions in the drift tube, and the difference in detection efficiency between the $H_3O^+$ and the $RH^+$

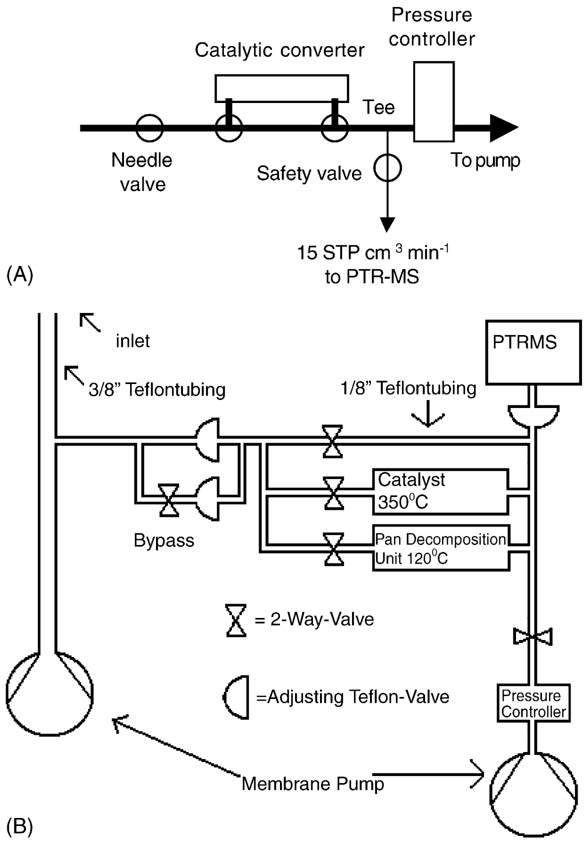

Fig. 2. Gas inlets used for (A) the Utrecht and (B) the Mainz PTR-MS during MINOS.

Table 1

Background mixing ratios (in ppbv) of methanol, acetonitrile and acetone in the Utrecht and Mainz PTR-MS instruments measured during flight 6 on August 14, 2001

| Compound | Utrecht | Mainz |
|---|---|---|
| Methanol | 4.3 | 4.1 |
| Acetonitrile | 0.15 | 0.14 |
| Acetone | 1.7 | 1.8 |

product ions [3,13]. In principle, it is possible to calculate the conversion efficiency of $H_3O^+(H_2O)_n$ into $RH^+$ ions, but this requires many more parameters such as the rate coefficients of the proton-transfer and ligand switching reactions between $H_3O^+(H_2O)_n$ ions and R, and the relative detection efficiencies of the $H_3O^+$, $H_3O^+(H_2O)$ and $RH^+$ ions. Not all of these parameters are accurately known. Moreover, it is possible that CID in the intermediate chamber leads to the observation of smaller $H_3O^+(H_2O)_n$ cluster ions than are actually present in the drift tube [11]. For these reasons, the calculated sensitivities are deemed less reliable in this work, and we have used calibrations instead. Calibrations for both instruments were performed during MINOS using a standard mixture prepared by Apel and Riemer, and were compared before and after the mission to other standards. The standard mixture was diluted in dry and wet air to account for the change in the reagent ion distribution. The accuracy of the calibrations is estimated to be around 20%.

A schematic diagram of the gas inlet system used for the Utrecht PTR-MS is shown in Fig. 2A. A diaphragm pump is used to pump the gas inlet. The inlet pump is the first stage of the three-stage diaphragm pump that is used to back the two turbo pumps of the PTR-MS. A pressure controller (Bronkhorst) regulates the inlet flow (approximately 50–500 STP $cm^3\ min^{-1}$), such that the pressure upstream of the controller is kept at a constant value. In this way, the pressure in the drift tube of the PTR-MS is independent of the ambient pressure. The sample flow is exposed to Teflon parts only, which minimizes inlet losses, memory effects and the build-up of impurities in the inlet system. The gas inlet for the Mainz PTR-MS is shown in Fig. 2B. Similarly to the Utrecht PTR-MS, the inlet contained a pressure controller to maintain the pressure in the inlet, and thus in the drift tube, at a constant value during the flights. A Teflon needle valve was used, or could be by-passed, to control the inlet flow and to make sure that the set-up would work at all altitudes. Apart from a catalytic converter, the sample flow could be directed through a scrubber heated to 120 °C for the selective removal of PAN by thermal decomposition.

The measurements of VOCs in ambient air are corrected for the backgrounds in the system. In PTR-MS, methanol, acetonitrile and acetone are detected at masses 33, 42 and 59 amu, i.e. their respective protonated masses. The backgrounds at these masses are shown in Table 1 and are influenced by (i) the presence of these compounds in the vacuum system and gas inlet even when sampling zero air, (ii) impurity ions from the source, for example the $O_2^+$ isotope at 33 amu, and (iii) to a lesser extent the dark counts of the electron multiplier. The background levels were determined by diverting the sample flow through a catalytic converter (see Fig. 2). The converter consists of a stainless steel chamber with Pt-coated quartz wool (Shimadzu) heated to 350 °C, which efficiently removes the VOCs from the sample. The catalytic converter does not remove water vapor from the sample, which is important because the background impurities may depend on the humidity of the sampled air. Moreover, the proton-transfer reactions in the PTR-MS can be influenced by the humidity.

## 3. Results and discussion

### 3.1. Inter-comparison between Utrecht and Mainz

In Fig. 3 the results for methanol, acetonitrile and acetone are shown as obtained with the Utrecht and Mainz PTR-MS instruments during MINOS flight 6 on August 14, 2001. During this flight the Falcon took off from Heraklion at Crete, flew at high altitude towards Greece and made a vertical profile down to the surface several tens of kilometers away from Athens. Elevated levels of ozone, CO, NO and $NO_y$, and

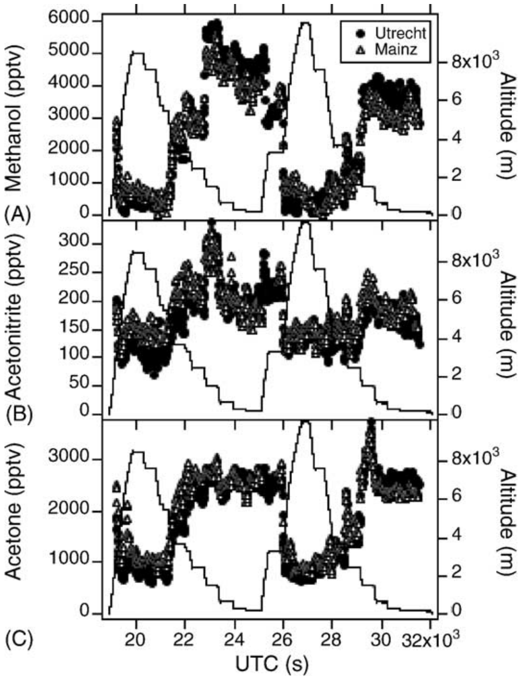

Fig. 3. Mixing ratios of (A) methanol, (B) acetonitrile and (C) acetone measured using the Utrecht and Mainz PTR-MS during flight 6 on August 14, 2001.

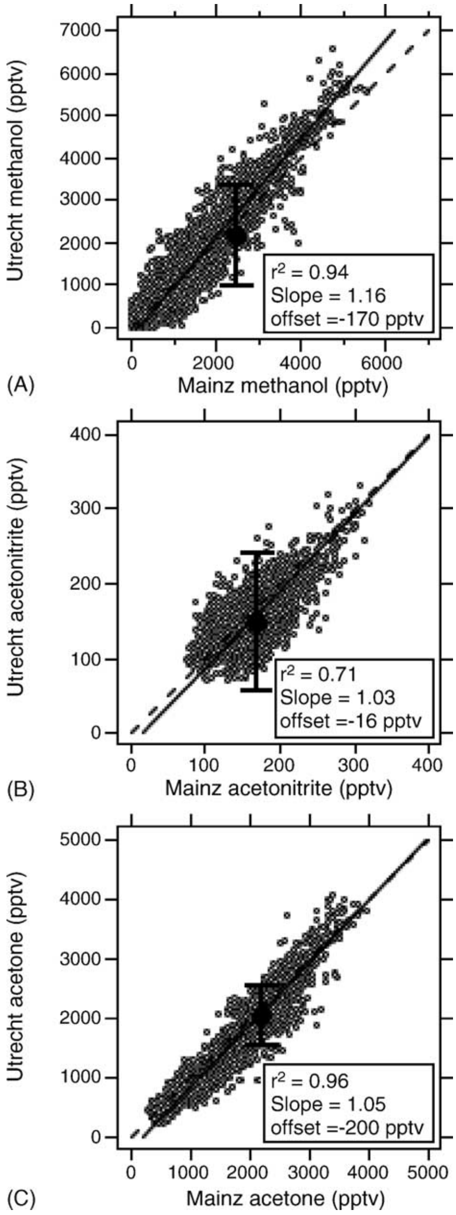

Fig. 4. Inter-comparison between the Utrecht and Mainz data from all MINOS flights for (A) methanol, (B) acetonitrile and (C) acetone. The solid lines show the results of the ODR analyses and the dashed lines are the 1:1 relationship.

VOCs were observed in the lowest 3 km of the profile. After that, the Falcon returned towards Crete at high altitude and made a similar altitude profile north of Crete. Again, the lowest 3 km showed a strong influence of pollution, although the levels were somewhat lower than during the first profile. It is clear from Fig. 3 that the agreement between the results from Utrecht and Mainz is in general quite good. Almost all of the features are reproduced in the two data sets.

Fig. 4 shows scatter plots of the Utrecht versus the Mainz results. Data from all measurement flights are included. The frequency of the Mainz measurements was somewhat lower and, therefore, the Utrecht data have been interpolated linearly on the time basis of the Mainz data. It is clear that the correlation between the two measurement results is good. The linear correlation coefficient ($r^2$) is 0.94 and 0.96 in the case of methanol and acetone, respectively. Only in case of acetonitrile is the correlation coefficient lower (0.71). This is due to (1) the higher statistical error in the results caused by the small mixing ratio, and (2) the smaller range of the acetonitrile mixing ratios as a result of its long atmospheric lifetime. To give an idea of the uncertainty in the individual data points, Fig. 4 shows for one randomly chosen data point the statistical error (Fig. 3A) estimated from the raw count rates for ambient and background measurements [24]. It is clear that the estimated error bar describes the scatter in the data point reasonably well.

Also included in Fig. 4 are the results of computing an orthogonal distance regression (ODR) to the data as indicated by the solid lines. We prefer to use an ODR instead of a standard linear regression (SLR): in an ODR the orthogonal distance between the data and the fitted line is minimized, whereas in an SLR only the distance in the *y*-direction is minimized [25]. Thus, in an SLR the two data sets do not have an equal influence on the outcome of the fit, and hence the slope and offset depend on the arbitrary choice of which data to treat as *x*- and which as *y*-values. If the statistical scatter in the data is high, such as for the acetonitrile data in Fig. 4B, then the difference between an ODR and an SLR can be significant: in this case an [Utrecht]/[Mainz] ratio of 0.72 is obtained from the SLR if the Mainz data are treated as *x*-values, whereas the [Utrecht]/[Mainz] ratio is 1.45 if the Utrecht data are treated as *x*-values, i.e. a difference of a factor of 2. From the ODR, the [Utrecht]/[Mainz] ratio was determined to be 1.03. In the ODR calculations, all data points are taken with equal weights. The precision of a PTR-MS measurement improves at higher mixing ratios, because it is limited by Poissonian ion counting statistics [15,24], and thus the higher values could carry more weight in the ODR analysis. On the other hand, weighting the higher values more leads to artificial skewing of the ODR fit, because the data at low mixing ratios are basically ignored. For these reasons, equal weights are used for the individual data points.

It is clear from Fig. 4 that the quantitative agreement between the Utrecht and Mainz data is good for acetonitrile and acetone, and reasonable in case of methanol. For the first two compounds the result of the ODR (the solid line) is hard to distinguish from the 1:1 relationship (the dashed line). In the case of methanol, the slope from the ODR is 1.16 and significantly different from 1. In the following, the remaining discrepancies are studied as a function of the humidity and the mixing ratio of ozone in the sampled air.

Finally, it should be mentioned that the inter-comparison was done in an informal fashion: there was interaction between the two groups about the results during the MINOS experiment, and both instruments used the same standard to calibrate their response. In between the MINOS experiment and the reporting of final data by the Utrecht and Mainz groups, there was no more interaction, and no further corrections to the data reported here were made.

### 3.2. *Influence of humidity*

In Fig. 5 the data obtained with the Utrecht and Mainz PTR-MS instruments are compared for dry conditions (Fig. 5A–C), in which the water vapor content was lower than 5 g $\text{kg}^{-1}$, and for wet conditions (Fig. 5D–F), in which it was higher than 5 g $\text{kg}^{-1}$. An ODR has been calculated for all of these cases, and the results are shown in Fig. 5 and Table 2. From Fig. 1 it is clear that the reagent ion distribution is different depending on the humidity of the sampled air. Nevertheless, the inter-comparison between the Utrecht and Mainz data is not significantly worse in wet or dry conditions, which demonstrates that the humidity is properly taken into account.

In the case of methanol, the inter-comparison is excellent in dry conditions, but less good in wet conditions: the Utrecht data seem to be somewhat higher than the Mainz data by an average of 291 pptv (see Table 2). Combined with the fact that on average the methanol mixing ratio is higher in wet than in dry conditions, this explains why the slope from the inter-comparison between all the data was slightly higher than 1 (1.16; see Fig. 4A). The offset of 291 pptv may be due to an overestimate of the Utrecht data possibly caused by a release of methanol from the walls of the inlet system, which is indeed expected to be more significant in wet conditions. Another reason for the discrepancy could be that the reactions of $H_3O^+(H_2O)_n$ ions with methanol are not perfectly accounted for in the analysis.

Table 2
Results from the inter-comparison between the Utrecht and Mainz data sets for methanol, acetonitrile and acetone

| | # Points | Correlation | Slope | Offset (pptv) |
|---|---|---|---|---|
| Methanol | | | | |
| All data | 5023 | 0.94 | 1.16 | −170 |
| Water 0–5 g $\text{kg}^{-1}$ | 3913 | 0.89 | 0.98 | −56 |
| Water >5 g $\text{kg}^{-1}$ | 1110 | 0.94 | 1.07 | 291 |
| Ozone > 100 ppbv | 754 | 0.87 | 0.85 | 100 |
| Ascents | 451 | 0.88 | 1.23 | −437 |
| Descents | 637 | 0.91 | 1.11 | −161 |
| Acetonitrile | | | | |
| All data | 5016 | 0.71 | 1.03 | −16 |
| Water 0–5 g $\text{kg}^{-1}$ | 3906 | 0.43 | 0.94 | −4 |
| Water >5 g $\text{kg}^{-1}$ | 1110 | 0.83 | 0.90 | 16 |
| Ozone >100 ppbv | 753 | 0.28 | 2.21 | −177 |
| Ascents | 450 | 0.55 | 1.20 | −48 |
| Descents | 638 | 0.73 | 1.05 | −21 |
| Acetone | | | | |
| All data | 5018 | 0.96 | 1.05 | −200 |
| Water 0–5 g $\text{kg}^{-1}$ | 3909 | 0.94 | 0.89 | −36 |
| Water >5 g $\text{kg}^{-1}$ | 1109 | 0.91 | 1.03 | 28 |
| Ozone >100 ppbv | 752 | 0.95 | 0.85 | 30 |
| Ascents | 449 | 0.92 | 0.99 | −222 |
| Descents | 637 | 0.94 | 1.03 | −210 |

In the case of acetonitrile, the correlation between the Utrecht and Mainz data is good in wet conditions ($r^2 = 0.83$) and from Fig. 5E the slope seems not significantly different from 1, even though a value of 0.90 is obtained from ODR. In dry conditions – upper tropospheric air – the range of acetonitrile values is small due to its long lifetime in the atmosphere, and the scatter-plot is therefore dominated by statistical noise. Still, the fit calculated from the ODR agrees reasonably well with the 1:1 relationship.

In the case of acetone, the agreement between the Utrecht and Mainz data is excellent in wet conditions, whereas in dry conditions the Mainz data seem to be somewhat reduced by a constant factor: the slope calculated from the ODR is 0.89. The reason could be a proportional loss of acetone in the inlet system of the Utrecht PTR-MS, or an inaccuracy in the calibration factors used.

### 3.3. *Influence of ozone*

The data obtained with the Utrecht and Mainz systems are inter-compared for conditions in which ozone was higher than 100 ppbv and the results are shown in Fig. 5G–J. The presence of ozone has been implicated in the artificial formation of aldehydes and ketones in VOC measurement setups [23], and it is therefore investigated here. It is clear from Fig. 5G–J that in high ozone conditions, influenced by stratospheric air, the agreement between the Utrecht and Mainz data is still reasonable. In the case of methanol and acetone, the slope calculated from the ODR is lower than 1, and the difference seems significant from Fig. 5G–J, in particular in the case of acetone (Fig. 5J). The highest ozone values are correlated

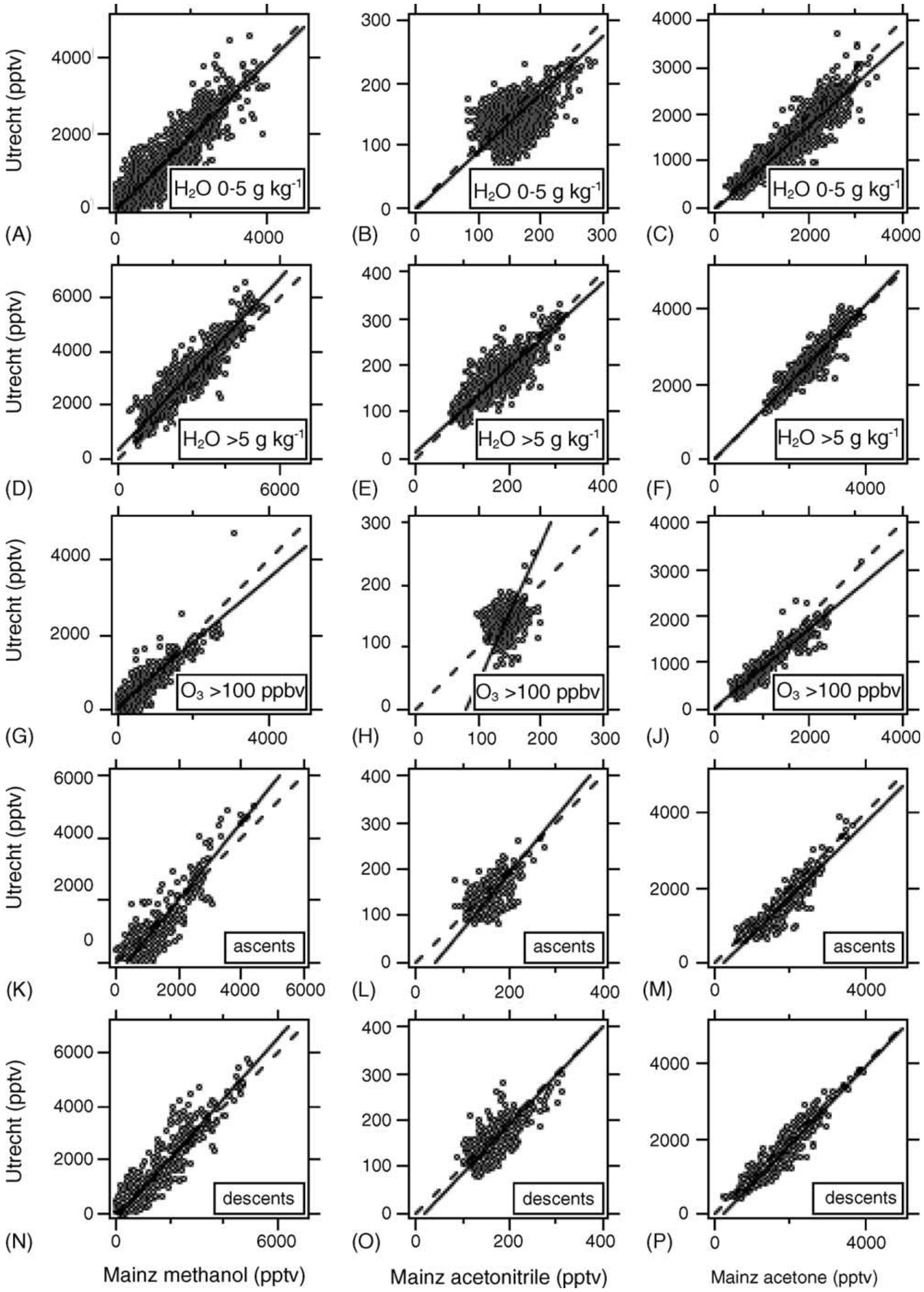

Fig. 5. Inter-comparison between the Utrecht and Mainz data for methanol (first column), acetonitrile (second column) and acetone (third column) for five different sub-categories: water vapor content between 0 and 5 g kg$^{-1}$ (first row), water vapor content >5 g kg$^{-1}$ (second row), ozone mixing ratios >100 ppbv (third row), data taken during ascents (fourth row) and during descents (fifth row). The solid lines show the results of the ODR analyses and the dashed lines are the 1:1 relationship.

with the lowest methanol and acetone values in Fig. 5, and it is not evident that the artificial formation from wall reactions of ozone is a problem. It should be noted that the ozone-rich air encountered during MINOS was in all cases influenced by the stratosphere and therefore extremely dry. The problem for acetone could thus be the same as the one observed in dry conditions. In the case of acetonitrile, again, the scatter in the correlation plot is dominated by statistical noise and the correlation between the Utrecht and Mainz results is poor.

### 3.4. Ascents and descents

The most challenging conditions for VOC measurements occur during ascents and descents, when the ambient pressure, temperature and humidity change dramatically on a

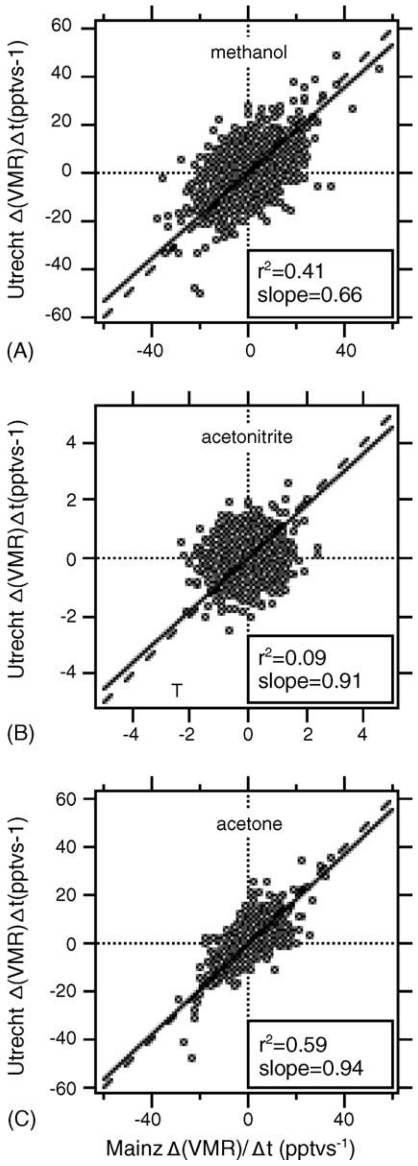

Fig. 6. Inter-comparison between the rates at which the observed mixing ratios changed with time. (panel A) The results for methanol; (panel B) for acetonitrile; and (C) for acetone. The solid lines show the results of the ODR analyses and the dashed lines are the 1:1 relationship.

timescale of minutes. Potential problems include the condensation of water vapor (and possibly VOCs) in the inlet, the uptake of VOCs by the condensed water, and degassing of VOCs from the inlet material. The data obtained during ascents and descents are therefore studied separately. Fig. 5 shows the inter-comparison between the Utrecht and Mainz data for methanol, acetonitrile and acetone for the ascents ($v_{\mathrm{vertlcal}} > 5\,\mathrm{m\,s^{-1}}$) in Fig. 5K–M and descents ($v_{\mathrm{vertlcal}} < -5\,\mathrm{m\,s^{-1}}$) in Fig. 5N–P. The results from the ODR analyses are shown in Fig. 5K–P and in Table 2. It is clear that the agreement between the Utrecht and Mainz data during ascents and descents is similar to that of the entire data set in Fig. 4.

### 3.5. *Response time*

Memory effects in the inlet system and drift tube can adversely affect the response time of the measurement. Memory effects are studied here by comparing the rates at which the measured volume mixing ratios (VMR) changed with time. The rate $\Delta\mathrm{VMR}/\Delta t$ at time $t_i$ is defined as:

$$\frac{\Delta\mathrm{VMR}}{\Delta t} = \frac{\mathrm{VMR}_{i+1} - \mathrm{VMR}_{i-1}}{t_{i+1} - t_{i-1}},$$

where $\mathrm{VMR}_{i+1}$ and $\mathrm{VMR}_{i-1}$ are defined as the volume mixing ratios measured at times $t_{i+1}$ and $t_{i-1}$, respectively. The rates $\Delta\mathrm{VMR}/\Delta t$ are calculated for all the points in the Utrecht and Mainz data sets where times $t_{i+1}$ and $t_{i-1}$ were less than 40 s apart, and are inter-compared in Fig. 6. It is clear that in the case of methanol and acetone there is a good quantitative agreement between the values of $\Delta\mathrm{VMR}/\Delta t$ derived from the measurements. Evidently, the response times of the two instruments were both short enough to resolve variations in the ambient mixing ratios at time scales shorter than the sampling frequency of the measurements (around 15 s). In the case of acetonitrile, there is no correlation between the $\Delta\mathrm{VMR}/\Delta t$ derived from the Utrecht and Mainz data (Fig. 6B): the short-term variation in the data is dominated by statistical noise.

## 4. Conclusion

The airborne measurements of methanol, acetonitrile and acetone with two differently configured PTR-MS instruments are compared. The correlation between the two data sets is good for methanol and acetone, and reasonable for acetonitrile, which is explained in large part by the statistical noise in the measurement due to low ion count rates. The quantitative agreement between the two data sets is excellent for acetone and acetonitrile, but in the case of methanol the Utrecht data are consistently higher than the Mainz data, possibly caused by the release of methanol from the walls of the inlet system in wet conditions or to reactions of $H_3O^+(H_2O)$ cluster ions with methanol. Despite the small discrepancies, the overall agreement between the two data sets clearly demonstrates the viability of atmospheric measurements of methanol, acetonitrile and acetone using PTR-MS.

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