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Supplement of

Comparison of VOC measurements made by PTR-MS, adsorbent tubes–GC-FID-MS and DNPH derivatization–HPLC during the Sydney Particle Study, 2012: a contribution to the assessment of uncertainty in routine atmospheric VOC measurements

Erin Dunne et al.

Correspondence to: Erin Dunne (erin.dunne@csiro.au)

Supplementary Information

S.1 Measurement Uncertainty Analysis

The uncertainty analysis of these measurement proceeds via the mathematical model, here called the measurement equation, for the measurement following the Guide to Expression of Uncertainty in Measurement and the law of propagation of uncertainty (JCGM, 2008) also known as the error propagation equation (Bevington and Robinson, 1992; Harris, 2003). All uncertainties in this analysis are expanded uncertainties with a coverage factor k = 2. The associated level of confidence of the uncertainty interval is typically 95%.

The equation for propagation of uncertainty for a measurement equation:
$x = f(u, v, \ldots)$ is:

$$\sigma_x^2 = \sigma_u^2 \left(\frac{\partial x}{\partial u}\right)^2 + \sigma_v^2 \left(\frac{\partial x}{\partial v}\right)^2 + \quad 2\sigma_{uv}^2 \left(\frac{\partial x}{\partial u}\right)^2 \left(\frac{\partial x}{\partial v}\right)^2 \ldots.$$

In this equation and subsequent uncertainty interpretations, variances are represented as population values. In the calculations the experimentally determined variances are used.

In this analysis, based on a knowledge of the measurement procedure, some uncertainties are set as random and can be diminished by multiple observations, whereas others are fixed. We assume that all errors evaluated here are uncorrelated.

This analysis involves more detail than is normally documented for air quality measurement uncertainty as presented in ISO 20988 (ISO, 2007).

The atmospheric units used for VOCs are parts per billion by volume (10^{-9} v/v) for the purpose of making this analysis compatible with most current studies of VOCs. The SI unit is mole fraction.

S1.1 PTR-MS Measurement Uncertainty

The basic equation for measurement by the PTR-MS includes the following terms:

C	mixing ratio in gas phase of compound measured
I	signal intensity (normalized cps)
F	flow rate in the calibration system (mL min^{-1})

With subscripts

s	the reference gas standard in the cylinder
a	ambient
z	zero mode
d	dilution (flow)

The measurement equation for PTR-MS is:

$$C_a = \frac{C_s}{(I_s - I_z)} \times \frac{F_s}{(F_s + F_d)} \times (I_a - I_z)$$

Equation S1

Represent

$I_s - I_z \quad by \qquad I_s^1$

$I_a - I_z \quad by \qquad I_a^1$

$F_s + F_d \quad by \qquad F_d^1$

Calculate the uncertainties

$\sigma_{I_s^1}$, $\sigma_{I_a^1}$, $\sigma_{F_d^1}$, σ_{C_s} , σ_{F_s}

Substitute in the following equation:

$$\sigma_{C_a}^2 = \sigma_{C_s}^2\left(\frac{C_a}{C_s}\right)^2 + \sigma_{F_s}^2\left(\frac{C_a}{F_s}\right)^2 + \sigma_{I_a^1}^2\left(\frac{C_a}{I_a^1}\right)^2 + \sigma_{I_s^1}^2\left(\frac{C_a}{I_s^1}\right)^2 + \sigma_{F_d^1}^2\left(\frac{C_a}{F_d^1}\right)^2$$

Equation S2

For the purposes of this analysis, C_a was represented by the mean VMR (ppbv) of the dataset, and I_a^1 and by the median zero corrected ion signals (ncps) of the sample data set.

We assumed:

I_s^1 , I_a^1, $\sigma_{I_a^1}$ and $\sigma_{{}_{s}^{1}I}$ were determined from the daily calibration, ambient and zero measurements.

F_s, F_d^1 and $\sigma_{F_d^1}$ $\sigma_{F_s^1}$were determined from multiple calibrations, performed before and after the field campaign, of the mass flow controllers which were used to control the flows of the dilution (F_d) and calibration gas standards (F_s).

The combined standard uncertainty, with coverage, k = 2, for an individual measurement is derived from Equation S2..

The combined standard uncertainty, with coverage, k = 2, for the mean value of a set of N measurements is derived from Equation S3.

$$\sigma_{C_a}^2 = \sigma_{C_s}^2\left(\frac{C_a}{C_s}\right)^2 + \sigma_{F_s}^2\left(\frac{C_a}{F_s}\right)^2 + \sigma_{F_d^1}^2\left(\frac{C_a}{F_d^1}\right)^2 + \frac{\sigma_{I_a^1}^2\left(\frac{C_a}{I_a^1}\right)^2 + \sigma_{I_s^1}^2\left(\frac{C_a}{I_s^1}\right)^2}{\sqrt{N}}$$

Equation S3

S1.2 AT-VOC Measurement Uncertainty

The basic equation for measurement by the AT-VOC method includes the following terms:

C	mixing ratio in gas phase of compound measured		
A	peak area		
V	volume,	V_m	molar volume, V_i = volume measured by instrument under ambient conditions
P	pressure		
T	temperature		
M	mass,	M_s	molecular mass of a compound

With subscripts

s	the reference gas standard in the cylinder, standard temp and pressure,
a	ambient

l	loop
m	molecular or standard conditions
i	instrument output
r	replicate measurements

The equation for mass injected from the loop per standard injection is:

$M_l = (V_l \times P_l \times T_s \times M_s \times C_s)/(V_m \times P_s \times T_l)$ Equation S4

The mass in an ambient sample is:

$M_a = M_l \times A_a/A_s$ Equation S5

where

A_a is the peak area of the ambient sample minus the average of the peak areas in the blanks.

A_s is the peak area of the calibration sample

Volume of an ambient sample under standard conditions

$V_a = (V_i \times P_a \times T_s)/(P_s \times T_a)$ Equation S6

The equation for concentration calculation is:

$C_a = M_a \times V_m/(V_a \times M_s)$ (units mixing ratio) Equation S7

This can be expanded by substitution.

$C_a = (C_s \times V_l) \times \left\{\frac{P_l}{A_s \times T_l}\right\} \times \left\{\frac{T_a \times A_a}{V_i \times P_a}\right\}$ (units mixing ratio) Equation S8

The uncertainty in the VOC measurement can be calculated from the uncertainties of the 3 terms on the RHS of Equation B5. The first is the uncertainty in the standard injection, the second the uncertainty in replicate measurements of the standard, and the third the uncertainty in the measurement of replicate ambient measurements. In the case of AT-VOC measurements there were two occasions when 8 sets of sampling equipment were run simultaneously and analysed on the same equipment. The repeatability of these measurements, $\sigma_{C\,r}^2$, incorporates all uncertainties due to the third term on the RHS of Equation B5 and is used for such in the uncertainty analysis. Note that in the case of C_8 aromatics allowance is made for the fact 3 peak areas (ethyl-benzene; m- + p-xylene; o-xylene) are used not one as with other compounds.

The combined standard uncertainties uncertainty, with coverage, k = 2, for an individual measurement is derived from Equation S9.

$$\sigma_{C_a}^2 = \sigma_{C_s}^2\left(\frac{C_a}{C_s}\right)^2 + \sigma_{A_s}^2\left(\frac{C_a}{A_s}\right)^2 + \sigma_{V_l}^2\left(\frac{C_a}{V_l}\right)^2 + \sigma_{T_l}^2\left(\frac{C_a}{T_l}\right)^2 + \sigma_{P_l}^2\left(\frac{C_a}{P_l}\right)^2 + \sigma_{C\,r}^2(C_a)^2$$

Equation S9

The combined standard uncertainty, with coverage, k = 2, for the mean value of a set of N measurements is derived from Equation B6.

$$\sigma_{C_a}^2 = \sigma_{C_s}^2\left(\frac{C_a}{C_s}\right)^2 + \sigma_{A_s}^2\left(\frac{C_a}{A_s}\right)^2 + \sigma_{V_l}^2\left(\frac{C_a}{V_l}\right)^2 + \sigma_{T_l}^2\left(\frac{C_a}{T_l}\right)^2 + \sigma_{P_l}^2\left(\frac{C_a}{P_l}\right)^2 + \frac{\sigma_{C\,r}^2(C_a)^2}{\sqrt{N}}$$

Equation S10

S1.3 DNPH-VOC Measurement Uncertainty

The basic equation for measurement by the DNPH method follows USEPA Method TO11A and includes the following terms:

Ca	concentration in gas phase of compound measured
Cs	concentration of standard in liquid phase
A	peak area
V	volume, V_s volume of standard injection
P	pressure
T	temperature
M	mass

With subscripts

s	the reference gas standard in the cylinder, standard temp and pressure, molecular mass
a	ambient
m	molecular or standard conditions

The instrument response factor determined from a standard injection is RF_s

$$RF_s = \frac{(A_s - A_z)}{C_s} \qquad \text{(units area/mass/unit volume)}$$ Equation S11

The mass in an ambient sample is (ng):

$$M_a = \frac{(A_a - A_z) \times V_e}{RF_s} \qquad \text{(units mass)}$$ Equation S12

Where A_a is the mass in the sample minus the average mass in the blanks; V_e is the acetonitrile extract volume.

By substitution:

$$M_a = \frac{(A_a - A_z) \times C_s \times V_e}{(A_s - A_z)}$$ Equation S13

Volume of an ambient sample under standard conditions (nL)

$$V_a = \frac{M_a}{M_s} \times (RT_a) \times \frac{P_s}{P_a}$$ Equation S14

The equation for concentration (ppbv) calculation is:

$$C_a = V_a / V_{sample}$$ Equation S15

Where V_{sample} is the total volume of air sampled (L).

The measurement equation for DNPH-VOC is:

$$C_a = \frac{C_s \times R \times P_s}{M_s} \times \frac{1}{(A_s - A_z)} \times \frac{T_a}{(P_a \times V_{sample})} \times [V_e \times (A_a - A_z)]$$

Equation S16

Note in the first term in the RHS only C_s is a variable and has uncertainty and this is associated with the standard. The second term on the RHS is associated with standard injections, the third term is associated with the volume of the ambient sample and the forth term associated with ambient sampling.

Represent

$A_s - A_z$ by A_s^1

$A_a - A_z$ by A_a^1

Calculation of the uncertainties:

$$\sigma_{C_a}^2 = \sigma_{C_s}^2 \left(\frac{C_a}{C_s}\right)^2 + \sigma_{A_s^1}^2 \left(\frac{C_a}{A_s^1}\right)^2 + \sigma_{C\,r}^2 \left(\frac{C_a}{C_r}\right)^2$$

Equation S17

The combined standard uncertainty, with coverage, k = 2, for a single measurement is derived from Equation S17.

The combined standard uncertainty, with coverage, k = 2, for the mean value of a set of N measurements is derived from Equation S18.

$$\sigma_{C_a}^2 = \sigma_{C_s}^2 \left(\frac{C_a}{C_s}\right)^2 + \sigma_{A_s}^2 \left(\frac{C_a}{A_s}\right)^2 + \frac{\sigma_{C\,r}^2 \left(\frac{C_a}{C_r}\right)^2}{\sqrt{N}}$$

Equation S18

S.2 Correction for mass interference in PTR-MS measurements

Compound identification in PTR-MS is limited due to its inability to distinguish between product ions with the same m/z (de Gouw et al., 2003; Warneke et al., 2003). In the identification of an ion signal in PTR-MS spectra of complex air mixtures such as urban air, consideration must be given to contributions from a number of reaction pathways involving constituents of the sample being analysed including (Warneke et al., 2003; Rogers et al., 2006; Inomata et al., 2008; Dunne et al., 2012; Kaser et al., 2013). :

- Protonated molecular ions –including structural isomers and isobaric compounds
- Products of fragmentation of molecular ions
- Isotopic ions including those containing ^{13}C, ^{18}O, ^{15}N, ^{37}Cl, etc.
- Products of secondary reactions with the impurity reagent ions (O_2^+, NO^+ and $H_3O^+\cdot H_2O._n$)

In the case of structural isomers, such as the C_8 aromatics (MW = 106 amu) examined in this study, the PTR-MS signal corresponding to the protonated molecular ions is regarded as a measure of the sum of the isomers (e.g m/z 107 = [ΣC_8 aromatics] = [Σ m-, p-, o- xylenes and ethylbenzene]).

Interference in the identification and quantification of a target compound in PTR-MS measurements of ambient air can and frequently does occur due to the presence of products from other reaction pathways and when comparing PTR-MS measurements to more selective VOC measurement techniques such as chromatographic methods, the presence of this interference in the target ion signal often results in an apparent positive bias in the PTR-MS reported values.

If the identity of the interferents are known, and their concentration and PTR-MS response (fragmentation patterns and instrument sensitivity) is also known or can be estimated, their contribution to the target m/z can be quantified and subtracted (Dunne et al., 2012). For the each of the seven compounds examined in this study a method was developed to correct the PTR-MS target ion signal for the presence of known and quantifiable interference. The corrected and uncorrected PTR-MS reported values are discussed for each compound in section 3 of the manuscript.

S.2.1 m/z 79: Benzene

In PTR-MS benzene undergoes non-dissociative proton transfer from H_3O^+ producing a single ion signal at m/z 79 (Gueneron et al., 2015) . There are several compounds other than benzene that are known to produce an ion signal at m/z 79 including: fragment ions from ethylbenzene, propyl- and isopropyl-benzene, butyl- and isobutyl-benzene.

The contribution to the PTR-MS signal at m/z 79 of benzene as well as the interferents: ethylbenzene , isopropyl- and propyl-benzene butyl- and isobutyl-benzene can be expressed as using the following equation based on the approach by Rogers et al (2006):

$$[m/z79] = [Benzene] + \left([EtBenz] \times \frac{S_{EtBenz}}{S_{Benz}} \times BR_{EtBenz}\right) + \left([PrBenz] \times \frac{S_{PrBenz}}{S_{Benz}} \times BR_{PrBenz}\right) + \left([iPrBenz] \times \frac{S_{iPrBenz}}{S_{Benz}} \times BR_{iPrBenz}\right) + \left([ButylBenz] \times \frac{S_{ButylBenz}}{S_{Benz}} \times BR_{ButylBenz}\right) + \left([iButylBenz] \times \frac{S_{iButylBenz}}{S_{Benz}} \times BR_{iButylBenz}\right)$$

Equation S19

Where [m/z 79] is the concentration (ppb) measured at the m/z 79 ion signal calculated using a sensitivity (S) (ncps ppbv^{-1}) determined from calibration measurements of benzene in a certified gas standard. [EtBenz], [PrBenz], [iPrBenz], and [ButylBenz] are the concentrations of the interferents: ethylbenzene, isopropyl- and propyl-benzene, butyl- and isobutyl-benzene measured in the AT-VOC samples and corrected to account for differences in the instrument sensitivity to each compound by the ratio $S_X/S_{Benz.}$ For the purposes of this analysis we will substitute the ratio of the reaction rate coefficients (k) (10^9 cm^3 sec^{-1}) k_X/k_{Benz} for proton transfer reactions between H_3O^+ and the interferent X. BR_X is the fraction of each interferent's ion signal detected at m/z 79. Therefore, if the concentration, PTR-MS sensitivity and the branching fractions are known for each interferent, the m/z 79 signal can be corrected to more accurately quantify benzene.

$$[Benzene]_{PTRMS} = [m/z79] - \left([EtBenz] \times \frac{k_{EtBenz}}{k_{Benz}} \times BR_{EtBenz}\right) - \left([PrBenz] \times \frac{k_{PrBenz}}{k_{Benz}} \times BR_{PrBenz}\right) - \left([iPrBenz] \times \frac{k_{iPrBenz}}{k_{Benz}} \times BR_{iPrBenz}\right) - \left([ButylBenz] \times \frac{k_{ButylBenz}}{k_{Benz}} \times BR_{ButylBenz}\right) - \left([iButylBenz] \times \frac{k_{iButylBenz}}{k_{Benz}} \times BR_{iButylBenz}\right)$$

Equation S20

The concentration of ethylbenzene was determined by the AT-VOC method, but not the concentrations of the propyl- and butyl- benzenes and a correction could not be determined for these interferents. The AT-VOC data for ethylbenzene and the literature values of the PTR-MS response variables for ethylbenzene and benzene - branching ratios (Gueneron et al., 2015) and ionization reaction rates (Cappellin et al., 2012) – were used to determine a correction to the PTR-MS m/z 79 data to subtract interference due to the presence of fragment ion signals from ethylbenzene. The values for the reaction rate coefficients, branching factors and relative abundance used to determine the correction to m/z 79 are presented in Table S.2.

$$[Benzene]_{PTRMS} = [m/z79] - \left([EtBenz]_{ATVOC} \times \frac{k_{EtBenz}}{k_{Benz}} \times BR_{EtBenz}\right)$$ Equation S21

S.2.3 Toluene

In PTR-MS toluene undergoes non-dissociative proton transfer from H_3O^+ producing a single ion signal at m/z 93 (Gueneron et al., 2015). Several compounds other than toluene can contribute to the PTR-MS signal at m/z 93 including α- and β-pinene, p-cymene, and several C_9 aromatics (ethyltoluenes, 1,2,3-trimethylbenzene), all of which are known to produce fragment ions at m/z 93 in PTR-MS (Warneke et al., 2003; Maleknia et al., 2007; Ambrose et al., 2010; Gueneron et al., 2015). These potential interferent compounds, with the exception of p-ethyltoluene and 1,2,3-trimethylbenzene, were measured in the AT-VOC samples.

In an analogous procedure to that outlined above for benzene, using the AT-VOC reported values for α- and β-pinene, p-cymene, and ethyltoluene isomers, as well as literature values to correct for compound specific differences in PTR-MS response (sensitivity and the branching ratios), the m/z 93 signal can be corrected to more accurately quantify toluene.

$$[Toluene]_{corr} = [m/z\ 93] - \left([\alpha Pine] \times \frac{k_{\alpha Pine}}{k_{Tol}} \times BR_{\alpha Pine}\right) - \left([\beta Pine] \times \frac{k_{\beta Pine}}{k_{Tol}} \times BR_{\beta Pine}\right) - \left([pcym] \times \frac{k_{pcym}}{k_{Tol}} \times BR_{pcym}\right) - \left([EtTol] \times \frac{k_{EtTol}}{k_{Tol}} \times BR_{EtTol}\right)$$

Equation S22

The literature values used for the reaction rates (Cappellin et al., 2010) and branching ratios (Warneke et al., 2003; Maleknia et al., 2007; Gueneron et al., 2015) are provided in Table S.2.

S.2.4 C_8 Aromatics

In PTR-MS, the signal at m/z 107 is commonly regarded as a measure of the sum of the C_8 aromatic isomers (m-, p-, o- xylenes and ethylbenzene) (de Gouw and Warneke, 2007). The sensitivity (S ncps $ppbv^{-1}$) of the PTR-MS to C_8 aromatics was from calibration measurements of a gas standard containing m-xylene. Unlike m-, p- and o-xylene, ethylbenzene undergoes fragmentation in the PTR-MS and at the operating conditions used in this study ~ 90% of the ethylbenzene ion signal occurs at m/z 107 (Gueneron et al., 2015). Consequently, using a sensitivity factor based on m-xylene alone will lead to an underestimation by PTR-MS when quantifying the sum of the C_8 aromatic isomers from the signal at m/z 107. Based on the AT-VOC data ethylbenzene comprised on average 16% of the total of C_8 aromatic isomers measured in the atmosphere during this study (Table S.2). Using this information as well as literature values of the PTR-MS response variables - branching ratios (Gueneron et al., 2015) and ionization reaction rates (Cappellin et al., 2012) – a weighted average sensitivity factor (S) was determined to account for the presence of ethylbenzene:

$$S(C_8 Aromatics)_{PTRMS} = \left(BR_{EtBenz} \times (S_{mXyl} \times \frac{k_{EtBenz}}{k_{mXyl}}) \times Rel.Abundance_{EtBenz}\right) + \left(BR_{Xyl} \times (S_{mXyl} \frac{k_{mXyl}}{k_{mXyl}}) \times Rel.Abundance_{mXyl}\right) + \left(BR_{pXyl} \times (S_{mXyl} \times \frac{k_{pXyl}}{k_{mXyl}}) \times Rel.Abundance_{pXyl}\right) + \left(BR_{oXyl} \times (S_{mXyl} \frac{k_{oXyl}}{k_{mXyl}}) \times Rel.Abundance_{oXyl}\right)$$

Equation S23

Minor contributions to the PTR-MS signal at m/z 107 may occur due to the presence of benzaldehyde (de Gouw and Warneke, 2007), which was measured by the DNPH method in this study and comprised 2% on average (Range: 0 – 5%) of the sum of the C_8 aromatics reported by AT-VOC. An additional correction was applied to the m/z 107 data to subtract the interference due to benzaldehyde:

$$[C_8Aromatics]_{PTRMS} = [m/z107] - ([Benzaldehyde]_{DNPH} \times \frac{k_{Benzald.}}{k_{mXyl}} \times BR_{Benzald.})$$

Equation S24

The literature values used for the reaction rates (Cappellin et al., 2010) and branching ratios (Spanel et al., 1997) are provided in Table S.2.

S.2.5 Formaldehyde

In PTR-MS [INSERTION: protonated] formaldehyde is detected at m/z 31 (Hansel et al., 1997). The signal at m/z 31 may also contain contributions from compounds other than formaldehyde including methanol, ethanol, and methyl hydroperoxide (Inomata et al., 2008) and glyoxal (Stonner et al., 2016). The protonated molecular ion signal of ethanol and methyl hydroperoxide cannot be unequivocally identified in the PTR-MS spectra and their concentrations were not determined independently by either the AT-VOC or DNPH method, and as a consequence their contribution to the m/z 31 signal cannot be determined in this study. Glyoxal was measured by the DNPH method in this study however due to the low PTR-MS sensitivity to glyoxal ($\leq$ 0.80 ncps ppbv^{-1}) (Stonner et al., 2016) (see section 3.2.1) it's contribution to the signal at m/z 31 was expected to be minor.

Using the PTR-MS data for m/z 33 which corresponds to protonated methanol, and laboratory measurements of the PTR-MS response variables for methanol and formaldehyde - branching ratios (BF_x) and PTR-MS sensitivity factors (S_x) - a correction was applied to the PTR-MS m/z 31 data to subtract interference in the measurement of formaldehyde due to the presence of fragment ions from methanol. Likewise, using the DNPH data for glyoxal and literature values for the PTR-MS response variables for glyoxal and formaldehyde- branching ratios (Stonner et al., 2016) and reaction rates (Cappellin et al., 2012) - a correction procedure was determine to subtract interference in the measurement of formaldehyde due to the presence of glyoxal fragment ions (Table S.2).

$$[HCHO]_{PTRMS} = [m/z31] - \left([m/z33] \times BR_{MeOH} \times \frac{S_{MeOH}}{S_{HCHO}}\right) - \left([glyoxal]_{DNPH} \times BR_{Gly.} \times \frac{k_{Gly.}}{k_{HCHO}}\right)$$

Equation S25

S.2.5 Acetone

The ion signal at m/z 59 is regarded as a measure of protonated acetone in measurements of the atmosphere however, the m/z 59 signal but may also contain contributions from propanal and glyoxal (de Gouw and Warneke, 2007; Thalman et al., 2015; Stonner et al., 2016). Acetone, propanal and glyoxal were all measured by the DNPH method in the present study. Using the PTR-MS and DNPH data for acetone, propanal and glyoxal, along literature values of the PTR-MS response variables - branching ratios (BR_x) (Spanel et al., 1997; Stonner et al., 2016) and reaction rates (Cappellin et al., 2012) (Table S.2). - a correction was applied to the PTR-MS m/z 59 data to subtract interference in the measurement of acetone due to the presence of propanal and glyoxal:

$$[Acetone]_{PTRMS} = [m/z59] - \left([m/z59] \times BR_{propanal} \times \frac{k_{propanal}}{k_{Acetone}}\right) - \left([glyoxal]_{DNPH} \times BR_{Gly.} \times \frac{k_{Gly.}}{k_{Acetone}}\right)$$

Equation S26

Table S.2: The PTR-MS calibration factors for each of the VOCs included in this work, normalised to 10^6 counts per second (cps) of H_3O^+ reagent ions per ppb (ncps $ppbv^{-1}$). The uncertainty limits represent ± the relative standard deviation of the mean. N represents the number of 30 min calibration periods used to calculate the sensitivity statistics. The average calibration for formaldehyde is presented in the Table; the ambient data processing for formaldehyde utilized a linear equation Calibration Factor = 16.08 – 0.232*[H_2O], where the water vapour concentration is in g m^{-3}.

MW	**Compound**	**m/z**	**BF (%)**	**Calibration Factor ncps $ppbv^{-1}$**	**Reaction rate (k)[a] 10^{-9} cm^3 s^{-1}**	**Rel. Abundance %**
30	Formaldehyde	31	100[d]	1.36 ± 21%	2.85	
32	Methanol	33	99[g]	4.60 ± 72%	2.29	
		31	1[g]			
58	Acetone	59		24.02 ± 7%	2.85	
	Propanal	59	100[d]	Nm	3.20	
	Glyoxal	59	10[f]	Nm	1.35	
78	Benzene	79	100[b]	17.15 ± 6%	1.93	
92	Toluene	93	100[b]	19.87 ± 6%	2.08	
106	m-xylene	107	100[b]	19.78 ± 8%	2.27	16[e]
	p- xylene	107	100[b]	Nm	2.27	43[e]
	o-xylene	107	100[b]	Nm	2.29	26[e]
	Ethylbenzene	107	91[b]	Nm	2.23	16[e]
		79	9[b]			
	Benzaldehyde	107	100[d]	Nm	3.97	
120	1,3,5-trimethyl-benzene	121	100[b]	17.72 ± 13%	2.39	
	o-ethyltoluene	121	98.5[b]	Nm	2.40	
		93	1.5[b]			
	m-ethyltoluene	121	98.5[b]	Nm	2.40	
		93	2[b]			
134	p-cymene	93	66[c]	Nm	2.50	
136	α-Pinene	93	7[c]	Nm	2.37	
	β-pinene	93	7[c]	Nm	2.46	

[a] Cappellin et al (2012) reaction rates (k) determined for E/N = 100 Td, T= 90°C.

[b] Gueneron et al (2015) values used here are the average of the BF (or % yield) determined at E/N 80 Td and 120Td in order to estimate the BF under the PTR-MS conditions of E/N 100Td used in this study.

[c] (Maleknia et al., 2007)

[d] (Spanel et al., 1997)

[e] rel. Abundance of m/z 107 isobars/isomers in the atmosphere determined from AT-VOC data

[f] (Stonner et al., 2016)

[g] (Dunne, 2016)

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