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Instrument = Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR-TOF-MS)

The following compounds are reported:

Methanol (mass 33.0335)
Acetonitrile (mass 42.0338)
Acetaldehyde (mass 45.0335)
Acetone (mass 59.0491)
DMS (mass 63.0263)
Acetic acid (mass 61.0284)
Isoprene (mass 69.0699)
Sum of methyl vinyl ketone (MVK), methacrolein (MAC) and isoprene hydroxy hydroperoxides (ISOPOOH) (mass 71.0491) (more information see Rivera-Rios et al. (2014))
Methyl ethyl ketone (MEK) (mass 73.0648)
Benzene (mass 79.0542)
Pinene fragment (mass 81.0699)
Toluene (mass 93.0699)
Total xylenes (mass 107.0855)
Total trimethylbenzenes (mass 121.1012)
Total monoterpenes (m137.1325)

Time resolution:

The data were recorded in 1 min intervals. On the server you can find the 1 min data and 10 min averages.

Spikes:

Spikes which could not be assigned to specific events were NOT cut. Only the spikes on 16 July at ca. 06:00 am (UTC) in benzene, toluene, the total xylenes and the total trimethylbenzenes were cut, because they arose from construction work at the site.

Calibration:

At the beginning and at the end of the campaign a comprehensive 4 point calibration of the instrument (spanning the measured range of compounds) was performed at 4 and 3 different humidities, respectively. An AppelRiemer gas standard was used which contained all listed compounds except for acetic acid. The acid was calibrated once during the campaign using a permeation source at two different humidities (details see below). The calibration factors were applied taking the changes in sensitivity caused by time and humidity into account. A linear interpolation was applied for the changes in sensitivity over time, while the humidity dependency was expressed by an exponential fit function. (Exceptions: Methanol and isoprene didn't show any humidity dependency; for acetic acid no interpolation over time was possible).

Calibration of acetic acid:

Acetic acid was calibrated separately by the use of a permeation source, because it was not included in the pressurized gas standard. Literature confirms that the calibration of the PTR-TOF-MS for acetic acid represents a challenge: Warneke et al. (2001) found no humidity dependency, Feilberg et al. (2010) report a linear relation while Haase et al. (2012) state that the behavior strongly depends on the instrument itself. For the acid only one calibration was performed in the field with

two different humidities. After the campaign a second calibration was done in the laboratory at three different humidities. In our case the calibration performed after the campaign is likely the more reliable, because the calibrations were performed at more humidity levels and using more calibration steps than in the field. Still, this calibration in the laboratory was done after the instrument was transported so that we cannot exclude that the sensitivity had changed. In the field as well as in the laboratory it was found that the sensitivity decreases with increasing humidity. The calibration factors obtained in the field and in the laboratory differed by a factor of ca. 2.5. Also the slope of the linear interpolations between the calibration factors of different humidities measured in the laboratory and in the field varied. Therefore the fit parameters of both linear regressions were averaged and the resulting mean fit function was used to calculate the calibration factor according to the humidity at the time. The discrepancy in the calibration factors and problems during background measurement (same as for acetaldehyde) lead to a high total uncertainty of 51%.

Acetic acid was measured at mass 61.0284 amu, but its mixing ratios must be considered as upper limits, because the PTR-TOF-MS is not able to distinguish between acetic acid and its isomer glycolaldehyde (Baasandorj et al., 2014). Furthermore, fragments of peroxyacetic acid (PAA) and ethyl acetate can also be measured on the exact mass of acetic acid (Baasandorj et al., 2014). However, it was concluded that the influence of these other compounds on mass 61.0284 amu was small during the CYPHEX campaign.

Background:

Background measurements were made every two hours for twenty minutes using platinum/palladium pellets heated to 320 °C.

The background for acetaldehyde and acetic acid did not stabilize fast enough, so that only the very last few points of the background measurement could be used. The error occurring due to a not yet stabilized background signal was estimated to 20% and added to the error calculation.

DMS:

The catalytic converter used for background measurements was emitting DMS, so that the DMS background could not be determined accurately. Therefore the baseline right next to the peak of DMS was used as background signal. Furthermore a comparison between PTR-TOF-MS and GC-MS revealed a large discrepancy in DMS data. Therefore the DMS data should be used with great caution!

Possible contamination (!!):

After a calibration performed at the 26 July a possible contamination occurred in some of the compounds:

A comparison between GC-MS, GC-FID and PTR-TOF-MS revealed that isoprene, the sum of the monoterpenes, the sum of the xylenes and the pinene fragment were contaminated from 26 July ca. 11:40 UTC until 28 July ca. 9:30 UTC. These points were cut in the dataset.

On the other hand, a comparison between the GC-FID, GC-MS and PTR-TOF-MS results for benzene and toluene showed a good agreement. Therefore it was concluded, that not all compounds were affected by the contamination.

Acetaldehyde and acetic acid showed an unnatural spike right after the calibration, which was removed from the dataset (acetaldehyde: 26 July ca. 11:30 UTC until 27 July ca. 4:10 UTC; acetic acid: 26 July ca. 10:50 UTC until 27 July ca. 4:40 UTC). No further cutting was performed, because no direct comparison with other instruments was possible. Still, the whole period from 26 July ca. 11:40 UTC until 28 July ca. 9:30 UTC needs to be regarded with great caution for all compounds, because a contamination cannot be completely excluded.

Error calculation:

1. Statistical error

For each calibration step the noise was calculated by dividing the standard deviation by the average of the step. The highest value was used as statistical error in %.

2. The Limit of Detection (LOD) is determined by calculating the standard deviation of each single background measurement (1 min time resolution). The highest value multiplied by 3 is reported (3σ). Values see Table 1.

3. Systematic error (accuracy)

$$\sqrt{a^2 + b^2 + h^2 + t^2 + c^2}$$

a = error of the mass flow controllers

b = error of the calibration gas standard

h = highest error in percent caused by humidity changes

t = highest error in percent caused by temporal changes in sensitivity.

c = error in the slope of the calibration

For acetaldehyde and acetic acid an extra term was added for problems during background measurement (20%). During a few periods of the campaign the ambient humidity was below the lower limit of the calibrated humidity range. The absence of a trend for methanol and isoprene precluded interpolation, while the exponential fit for the other compounds is afflicted with a higher error in this range. The variation in sensitivity in the range below 25% relative humidity (RH) was estimated from previous measurements in our laboratory and was given as extra error values.

4. Overall error

$$\sqrt{(stat_{error})^2 + (sys_{error})^2}$$

The values can be found in Table 1.

Table 1

Compound	Methanol	Acetonitrile	Acetaldehyde	Acetone	Acetic acid
LOD for 1 min time resolution/ ppbv	0.242	0.016	0.085	0.097	0.264
Total uncertainty >25%RH/ %	37	11	22	10	51
Total uncertainty <25%RH/ %	41	18	27	17	51

Compound	DMS	Isoprene	MVK/MAC/ ISOPOOH	MEK	Benzene
LOD for 1 min time resolution/ ppbv	0.018	0.024	0.014	0.016	0.014
Total uncertainty >25%RH/ %	12	10	11	11	14
Total uncertainty <25%RH/ %	17	11	14	16	21

Compound	Pinene fragment	Toluene	Total xylenes	Total trimethyl benzenes	Total monoterpenes
LOD for 1 min time resolution/ ppbv	0.023	0.012	0.013	0.01	0.008
Total uncertainty >25%RH/ %	16	14	14	18	16
Total uncertainty <25%RH/ %	22	20	20	24	20

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