

This text originates from a manuscript by Schallhart et al. (in preparation).

The PTR-TOF was used for the amine measurements because of its high mass resolution, which allows for TMA ($\text{C}_3\text{H}_{10}\text{N}_1^+$, 60.0808 Th) measurements with almost no influence of the acetone/propanal isotope ($\text{C}_2[^{13}\text{C}]_1\text{H}_7\text{O}_1^+$, 60.0525 Th) (Fig. A1). Its high measurement frequency enables to follow emissions from cattle and separate different activities such as breathing and ruminating. The PTR-TOF and CIMS TMA sensitivities were calculated by a cross calibration with impinger samples, which were analyzed by ion chromatography. The PTR-TOF calibration was done by pumping VOC free air (produced by a catalytic converter) through a semipermeable tube connected to the two instruments and the impinger. The semipermeable tube was submerged in an aqueous solution of TMA and NaOH (pH of 10.7), which was inside a temperature controlled bath. The TMA diffused through the membrane and by keeping the TMA mixture temperature and the zero air flow constant, therefore produced a continuous TMA source. The influence of the inlet-line walls, temporarily adsorbing TMA, was mitigated by using equally long tubing between the source and the PTR-TOF as well as between the source and the impinger. The PTR-TOF spectra were monitored in order to ensure that the TMA signal was stable. We integrated the signals of the mass spectrometers for the same time period as the impinger sampling. After the calibration the variation of the sensitivities, potentially caused by ambient temperature and humidity variations and changes of inlet line behavior, were considered: sensitivity changes over time were determined from several parallel ambient TMA measurements by impingers and PTR-TOF and were then used for the whole measurement period using linear interpolation. The median sensitivity was 4.2 ± 1.1 ncps/ppb.

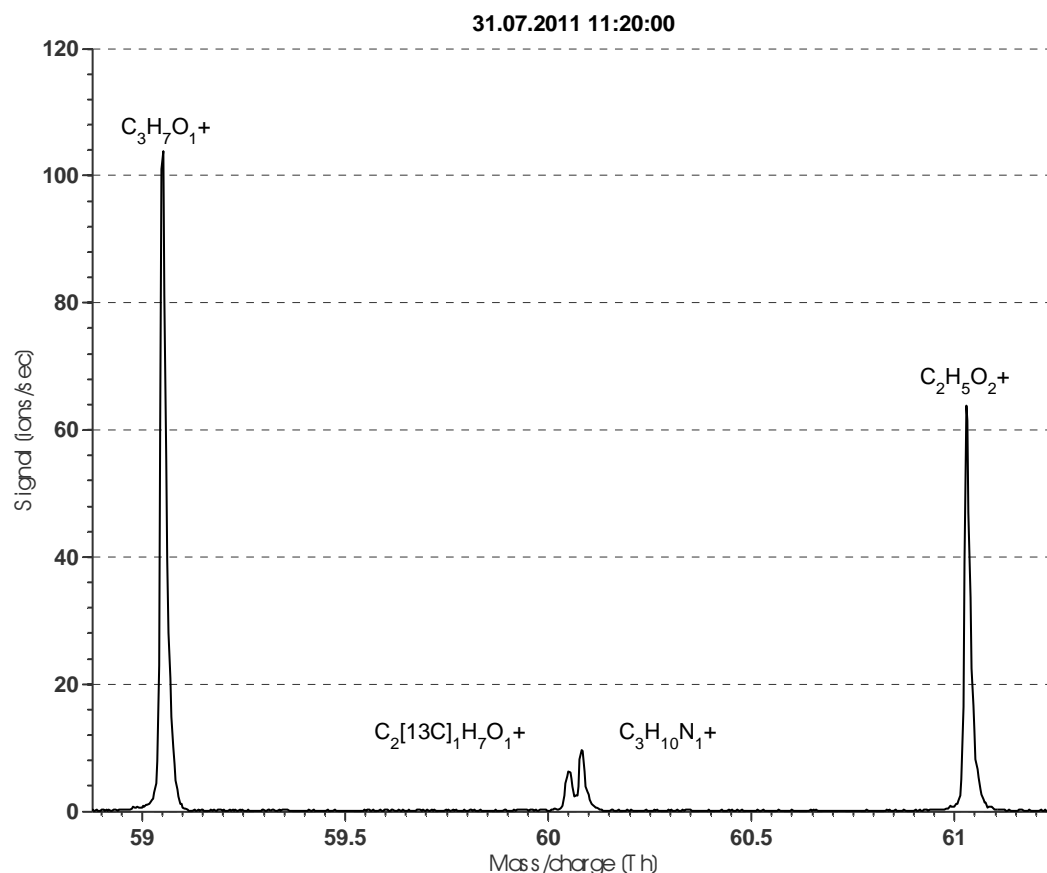


Figure A1: Part of the PTR-TOF mass spectrum with a 1 minute integration time. The high mass resolution of the instrument, allows to separate the acetone/propanal isotope peak ($\text{C}_2[^{13}\text{C}]_1\text{H}_7\text{O}_1^+$) from the TMA peak ($\text{C}_3\text{H}_{10}\text{N}_1^+$)