

VOC measurements at the Hohenpeissenberg Meteorological Observatory by SRI-PTR-TOF-MS (PTR-TOF@HPB)

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Introduction and motivation

Since its inception in the mid-1990ies, proton-transfer-reaction mass spectrometry (PTR-MS) has become the most important tool in atmospheric chemistry for real-time monitoring of volatile organic compounds (VOCs). The PTR-MS technique does, however, suffer from a lack of specificity which is particularly pronounced in the first-generation, quadrupole-MS (QMS) based instruments. PTR-QMS instruments detect a large number of signals in tropospheric air but – with the exception of about a dozen signals – it is not possible to identify their VOC precursors. Recently, a high mass resolution proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) instrument has become available which identifies the exact atomic composition of the analyte ions (Jordan et al., 2009a; Graus et al., 2010). In its high-end version, the PTR-TOF-MS instrument is equipped with the “Switchable Reagent Ion” (SRI) technology based on the use of different chemical ionization (CI) agents (H_3O^+ , NO^+ , O_2^+) for specific detection of VOCs (Jordan et al., 2009b). The use of NO^+ CI ions has, for example, been suggested for differentiating between aldehydes and ketones which are not distinguishable in the H_3O^+ CI mode. The use of different CI modes combined with high mass resolution analysis may potentially result in a higher specificity of SRI-PTR-TOF-MS measurements but this remains to be assessed and validated in laboratory and field measurements.

Scientific objectives

The scientific objectives of the two-week measurement campaign at the Hohenpeissenberg Meteorological Observatory in Germany were as follows

- i) to assess the operational performance of an SRI-PTR-TOF-MS instrument in ground-based measurements of atmospheric VOCs
- ii) to assess the analytical capabilities and limitations of the SRI-PTR-TOF-MS technique through challenges with different test gas atmospheres
- iii) to validate the analytical performance of an SRI-PTR-TOF-MS instrument in atmospheric VOC measurements by comparison with gas chromatographic techniques and routinely operated PTR-TOF instruments

Reason for choosing station

The location and facilities at the Hohenpeissenberg Meteorological Observatory in Germany are ideal for conducting validation exercises of atmospheric composition measurement techniques. Sufficient lab space is available in a guest laboratory to host a number of different analytical instruments which can all be connected to a common sampling manifold. The sampling manifold can be either fed with an artificially generated test gas atmosphere (e.g. purified air with variable levels of humidity and ozone and defined concentrations of VOCs) or with ambient air at rural background or low pollution levels. The location and available infrastructure thus allow to design and execute a series of challenges for analytical method validation.

Method and experimental set-up

A commercial PTR-TOF 8000 instrument (Ionicon Analytik, Innsbruck, Austria) was used for the measurements. The reader is referred to the literature for a description of the PTR-MS measurement principle (de Gouw and Warneke, 2007), of the PTR-TOF 8000 instrument (Jordan et al., 2009a; Graus et al., 2010) and of the SRI mode of operation (Jordan et al., 2009b). The instrument was interfaced to the common sampling manifold in the guest laboratory via a temperature-stabilized 1/8" PFA Teflon tube. The ion source was alternately operated in the H_3O^+ and the NO^+ mode, for 45 and 15 minutes, respectively. No measurements were carried out with other CI agents (O_2^+ , Kr^+ , Xe^+) which are considered not to be suitable for atmospheric VOC measurements. The instrumental background was determined by diverting the sampling air through a noble metal catalyst for VOC destruction. A dynamically diluted (0-20 ppb) multi-component VOC standard (Apel-Riemer Environmental Inc., Denver, USA) was used for instrument calibration. Periodic zero measurements and standard additions to the analyte air were carried out. The PTR-TOF 8000 instrument in the guest laboratory of Hohenpeissenberg Meteorological Observatory is shown in Figure 1.

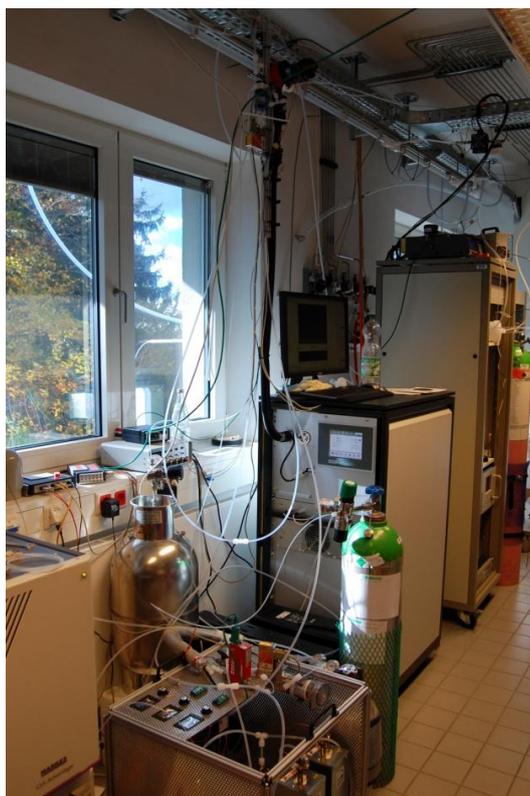


Figure 1: PTR-TOF 8000 instrument in the guest laboratory of the Hohenpeissenberg Meteorological Observatory. The sampling manifold is shown in the upper part of the photograph.

Preliminary results and conclusions

The PTR-TOF 8000 instrument was fully functional during the entire measurement period, with the exception of one overnight software failure. Alternating between the H_3O^+ and the NO^+ modes of operation appeared to be a feasible approach for ground based measurements of atmospheric VOCs. A final assessment can, however, only be made after the data analysis has been completed. Real-time data visualization was hampered by large signal changes induced by alternating operation modes. Quick in-field data analysis was also not possible with the currently available software tools for data analysis. The test campaign made evident that data post-processing efforts will significantly increase and that the interpretation of results will become more difficult and time consuming. As for now, only data obtained in the H_3O^+ mode can be reported. Figure 2 shows preliminary acetone data as measured by a variety of

techniques in ambient air. Measurements by three PTR-TOF-MS were in excellent agreement, while significant discrepancies between GC measurements were observed. It is noted that all data shown are preliminary.

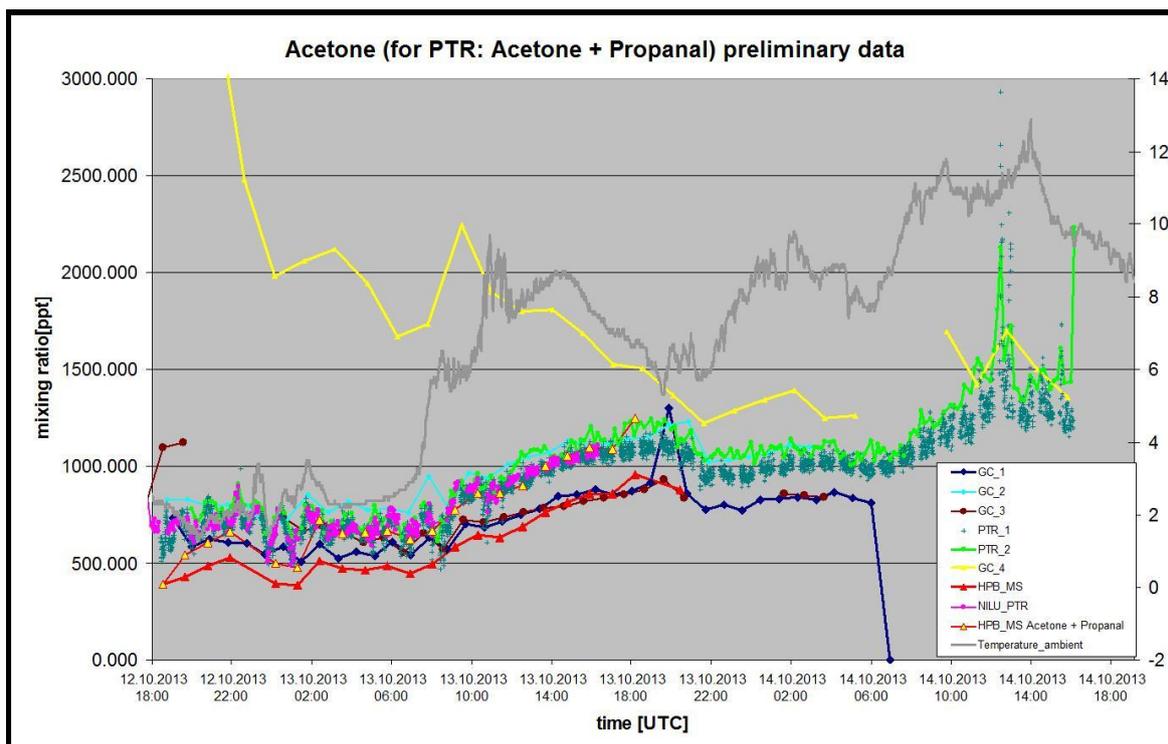


Figure 2: Acetone mixing ratios in ambient air at Hohenpeissenberg on October 13 and 14, 2013 as measured by a series of different instruments. (figure courtesy: A. Werner, DWD)

Outcome and future studies

Data processing and interpretation will take several months which is when final data from other analytical techniques will also become available for comparison. Only thereafter it will be possible to assess if the use of different operation modes (SRI) is a valuable approach for improving the specificity of atmospheric VOC measurements by PTR-TOF-MS.

References

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