

Measurement Improvements for moNitoring of OVOCs**MINOVOC****S. Sauvage, S. Dusanter, T. Leonardis****• Introduction and motivation**

Volatile Organic Compounds (VOCs) include a wide range of atmospheric species that are difficult to measure due to their reactive nature and their low mixing ratios (ppt-ppb). Belonging to the VOC family, non-methane hydrocarbons (NMHCs) and Oxygenated Volatile Organic Compounds (OVOCs) are important tracers of anthropogenic, biogenic, and photochemical processes. In addition, VOCs play a key role in atmospheric chemistry as precursors of photochemical pollutants such as ozone and secondary organic aerosols. For this reason, long term monitoring of VOCs is included in EMEP and GAW programs to study temporal and spatial trends, to use these species as inputs in atmospheric models, and to improve our understanding of their sources and sinks. In France, NMHCs and OVOCs are currently monitored at 3 remote sites using off-line methods. In addition, on-line methods (TD/GC/FID-MS and PTR-ToFMS) can be deployed for intensive observation periods. While measurements of NMHCs are now performed with confidence, methods are more sparse and uncertain for OVOCs. Several issues still need to be addressed, including calibration procedures, matrix effects, interferences, and calculations of uncertainties.

• Scientific objectives

A first objective was to compare several OVOC instruments from Mines Douai (TD/GC/FID-MS, PTR-ToFMS, active sampling on DNPH cartridges) to instruments from other scientific groups to assess the accuracy of ambient OVOC measurements. The latter can only be demonstrated by comparing instruments based on fundamentally different techniques using samples of complex composition with mixing ratios ranging from a few ppt to several ppb.

A second objective was to optimize the performances and the reliability of our different OVOC instruments, based on comparison experiments performed using synthetic air as well as real ambient air. Several groups of experts in OVOC measurements attended this intercomparison and transfer of knowledge between the different participants will help to define standard operating procedures, which in turn will help us to meet the second objective.

• Reason for choosing station

The Hohenpeissenberg station is well known as a reference station for trace gas measurements in background air. The team in charge of the station has a long experience in monitoring low VOC levels and in managing intercomparison studies. In addition, this station includes space and facilities needed for in situ comparison exercises, including a long manifold that can be used to feed all instruments with the same air masses, either synthetic mixtures or external ambient air.

• Method and experimental set-up

Three instruments from Mines Douai were deployed during the comparison exercise:

- a TD/GC/FID-MS instrument designed to measure approximately 40 species (OVOCs and NMHCs) with a time resolution of 91 minutes. Air is sampled without an ozone scrubber through a trap made of Carpack B and Carpack X. The sample humidity is reduced through dilution with dry zero air

(50:50) and a trap purge with He before the desorption step. A polar CP-Lowox column is used to get a good separation of OVOCs. Detection limits were in the range 2-50 ppt.

- a PTR-ToFMS instrument from Kore Technology (UK) was used to measure 6 NMHCs or sum of NMHCs (acetonitrile, isoprene, benzene, toluene, C8-aromatics, monoterpenes) and 5 OVOCs or sum of OVOCs (methanol, acetaldehyde, acetone+propanal, methacrolein + methylvinylketone, methyl ethyl ketone) with limits of detection in ranging from 10-80 ppt, except for methanol whose limit of detection was in the range 250-300 ppt. The measurement time resolution was set to 10 minutes.

- an automatic sampler was used to perform off-line measurements of 15 OVOCs (aldehydes + ketones) using DNPH cartridges that are post-analyzed by HPLC/UV in the laboratory. A KI scrubber was used on the sampling line to remove ozone. Detection limits ranged from 30-60 and 5-10 ppt for measurement durations of 40 and 240 minutes respectively.



Figure 1 : PTR-ToFMS (left) and TD/GC/FID-MS (right) instruments deployed by Mines Douai in the guest lab

Above mentioned instruments were calibrated using a NPL standard mixture (TD/GC/FID-MS, PTR-ToFMS, DNPH cartridges), an Ionimed Gas Calibration Unit (GCU) (PTR-ToFMS), and traceable mass flowmeters (Bios Definer).

Three people from Mines Douai were involved in this study: an expert in GC techniques (T. LEONARDIS) and two scientists involved in research activities and VOC monitoring programs (S. SAUVAGE, S. DUSANTER).

- **Preliminary results and conclusions**

The three instruments from Mines Douai were operated for 8 days from 10/10/2013 to 10/17/2014 and successfully measured data during dry and humid zero air tests (with and without ozone), dilution series of OVOCs (from approximately 50 ppt to 10 ppb), and ambient air sampling. In addition, tests were performed by adding common standards, as well as NMHCs with and without ozone, to the manifold.

Scatter plots of preliminary GC and PTR-ToFMS measurements are displayed in Figure 2 for acetone, acetaldehyde, methyl ethyl ketone (MEK), and methacrolein (MAC) + methyl vinyl ketone (MVK). A reasonable agreement (within 25%) is observed for acetone, MEK, and MAC+MVK. However, a large discrepancy is observed for acetaldehyde, likely due to a calibration issues on the GC instrument. Comparison of the GC and PTR-ToFMS data to DNPH measurements, as well as measurements from other groups, is ongoing for all experiments mentioned above.

An example of time series for ambient measurements of MEK is shown in Figure 3. This figure displays measurements from the three PTR-ToFMS instrument involved in this study. This preliminary data indicate a good agreement for ambient monitoring of MEK using PTR-ToFMS. Similar results have been observed for other OVOCs such as acetone + propanal, methanol, and MAC + MVK.

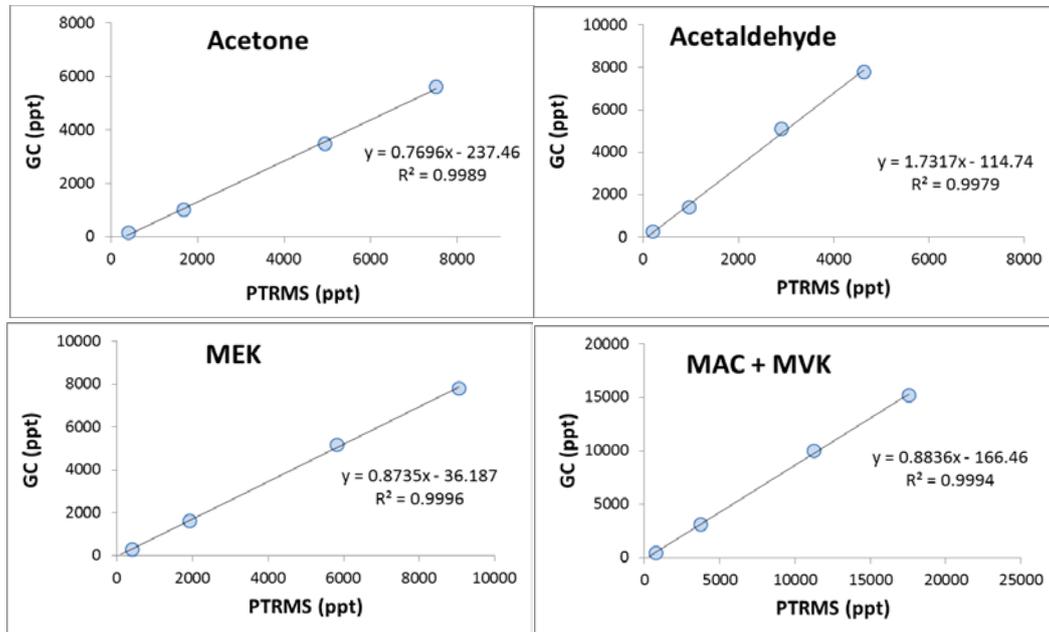


Figure 2: Preliminary OVOC measurements from Mines Douai during the Hohenpeissenberg side by side intercomparison - Scatter plots of GC vs. PTR-ToFMS measurements for dilution series of synthetic mixtures

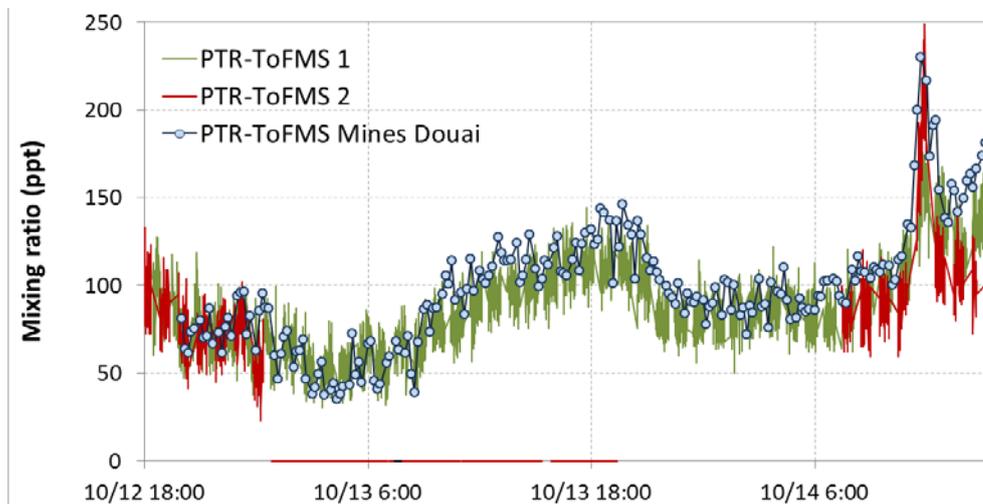


Figure 2 : Preliminary time series of MEK mixing ratios in ambient air during the Hohenpeissenberg side by side intercomparison

- **Outcome and future studies**

As mentioned above, data analysis is ongoing to compare measurements from the 5 GCs, 3 PTR-ToFMS, and 2 cartridge samplers that were involved in this intercomparison study. This study will provide unvaluable information to assess the accuracy of our OVOC instruments and to determine whether it is necessary to improve some of their characteristics.