

### [OVOC measurements at the Hohenpeissenberg Meteorological Observatory]

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- Introduction and motivation

NCAS, University of York have operated and maintained a gas chromatograph for the measurement of a wide range of volatile organic compounds, including oxygenated compounds, at the Cape Verde Atmospheric Observatory since 2006. The observatory is one of a handful of GAW global sites and provides data for use by the wider atmospheric science community via submission to the world data centre for greenhouse gases (WDCGG) and also the British Atmospheric Data Centre (BADC). In order for scientists to evaluate and draw conclusions from the data from different observatories around the globe, one must be sure that the data produced are on the same calibration scales and that good quality control measures are in place. The gas chromatograph used to measure VOCs has partaken in a number of comparison studies led by the GAW VOC world calibration centre (WCC) which have thus far focused their efforts on the measurement of non-methane hydrocarbons (NMHCs). Accurate and precise measurements of oxygenated VOCs in the atmosphere are more difficult to achieve due to loss to surfaces and other factors including changing humidity and levels of ozone (known to cause interferences). NCAS, University of York have made and reported observations of OVOCs for a number of years and continue to strive for better characterization of the instrument in order to report the best possible data.

The system use to preconcentrate the samples prior to GC analysis has recently been changed to a commercially available unit, a move that was necessary due to the older components no longer being readily available. While the behaviour of NMHCs is found to be much the same between the different systems, the response to oxygenated compounds is more difficult to evaluate. The intercomparison activity at the Hohenpeissenberg Meteorological Observatory provided a great platform to help improve our understanding of the instrument and how it behaves under a variety of conditions.

- Scientific objectives

The main objectives of this study are to evaluate the performance of the NCAS GC-FID instrument and methods when measuring oxygenated volatile organic compounds. We will evaluate the interferences caused by humidity and changing levels of ozone. The exercise will also allow us to exchange ideas with other groups concerning the operation, calibration and quality of the instrument and the data produced.

- Reason for choosing station

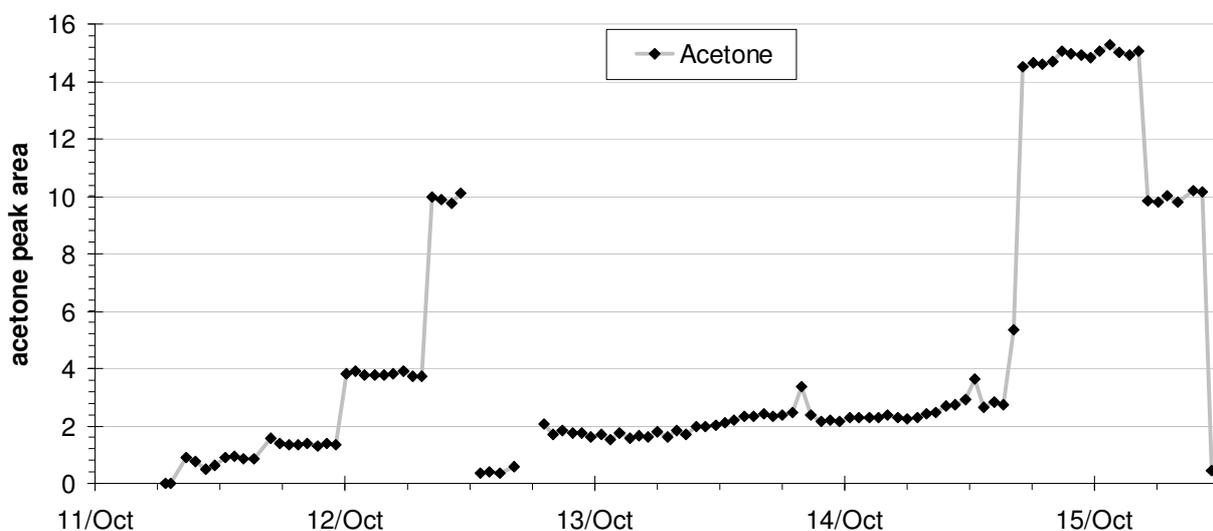
The Hohenpeissenberg Meteorological observatory was chosen because it has a long history of VOC observations and a well-respected reputation. Hohenpeissenberg is well-equipped with appropriate lab space and calibration equipment. The exercise involved ten different instruments being operated side by side and sampling from a common manifold. This was setup within ACTRICS WP4.

- Method and experimental set-up

The Dual Channel Gas Chromatograph with Flame Ionisation Detectors is capable of reporting mixing ratios of a wide range of volatile organic compounds in the atmosphere. Full details of the instrument and its operation can be found in Hopkins *et al.* (2003 and 2011). Briefly, Samples of air are drawn through a condensation trap (a glass tube held at -30 °C), to remove moisture from the sample, and then pre-concentrated on a dual-bed adsorbent trap held at sub-ambient temperature (typically -20°C). Sample volumes of up to one litre of air are acquired and then the trap is resistively heated during desorption within a stream of helium (or hydrogen) and injected into the GC oven for analysis. The eluent is split in approximately equal portions between a Na<sub>2</sub>SO<sub>4</sub> deactivated aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) porous layer open tubular (PLOT) column (50 m, 0.53 mm id, Varian Netherlands) for analysis of the less polar NMHCs and a LOWOX column (10 m, 0.53 mm id, Varian Netherlands) for analysis of the more polar VOCs including monoterpenes and oxygenated species. Flow restrictors are placed upstream of the LOWOX column in order to provide a balance in back pressure such that the sample split between columns is maintained at, or close to, the desired 50:50. Observations of toluene, baseline resolved on both channels of the system, are used to measure the exact split ratio during each run. Analytes elute from the GC columns into two flame ionisation detectors for detection. The GC oven has been programmed for optimal separation of all compounds of interest.

- Preliminary results and conclusions

Data from the intercomparison are still under evaluation. The plot shows a time-series of the system response to changing levels of acetone within the manifold. “Blank” values (lowest points on the 11<sup>th</sup>, 12<sup>th</sup> and 15<sup>th</sup> October) were found to be non-zero and have to be accounted for in the final data set. The step-changes in the data around the 12<sup>th</sup> October show the instrument responding to changing levels of calibration gas while data between the 13<sup>th</sup> – 15<sup>th</sup> October are from ambient air sampling. These data will be compared directly with the other instruments taking part in the comparison.



- Outcome and future studies

The results from the intercomparison exercise will prove useful in determining the performance of the instrument in the measurement of oxygenated VOCs in the atmosphere. Working closely with colleagues during the intercomparison has also proved extremely useful in sharing ideas and knowledge of instruments and equipment which will be applied in the near future and help to improve the robustness of the instruments and measurement systems.

- References

A dual channel gas chromatograph for atmospheric analysis of volatile organic compounds including oxygenated and monoterpene compounds. Hopkins, J. R., C. E. Jones, A. C. Lewis. J. Environ. Monit., **2011**, 13 (8), 2268 - 2276. DOI: 10.1039/c1em10050e.

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