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DNPH cartridge / HPLC analysis - a still relevant method for OVOC monitoring: a contribution to the assessment of uncertainty in current atmospheric VOC measurements

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Oxygenated volatile organic compounds (OVOCs) are a class of VOCs affecting various chemical processes in the atmosphere. They represent the most abundant VOCs in ambient air, they have important role in processes leading to the formation of ozone and secondary organic aerosol (SOA), and can potentially influence climate change. Adding to that, OVOC measurement is important for source understanding, verification of atmospheric models and exposure evaluation. Therefore, there is a high demand for accurate and reliable carbonyl measurement methods. OVOCs measurement is challenging in atmospheric samples due to OVOC low mixing ratios (ppt to ppb range), their high water solubility, and their polarity. Nevertheless, measurement techniques are evolving but the uncertainties and the shortcomings associated with these measurements are often poorly understood. Off-line OVOC measurement using active air sampling through a 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbent cartridge followed by high-performance liquid chromatography (HPLC) analysis is the most extensively used method for OVOCs monitoring.

In this presentation, we will first give a summary of inter-comparison with other technics from either the ACTRIS side by side held in 2015 or from field campaigns. Secondly, we will present results of an on-going study dedicated to the optimization of the DNPH method. Several standards were compared: the liquid ones (SUPELCO, ACSD) and gaseous ones (Apel Riemer, NPL, and PRAXAIR). The results show some discrepancies varying between 5 and 20% for most of the compounds. From two cartridges back to back, we estimated the collection efficiencies (CE) of over 10 OVOCs at different concentrations and at different relative humidity (RH). The CEs were nearly 100% for most of the OVOCs, except for ketones (acetone and MEK) over 50% RH, where the CEs are inversely related to RH. The use of KI scrubber for ozone was also assessed as well as the impact of NO_2 which can interfere with the accurate detection of carbonyls. Based on the results and following a rigorous protocol, the method shows very good repeatability and reproducibility. The uncertainty is then estimated following the ACTRIS guide for NMHCs namely by considering the different parameters like standard uncertainty, sampling efficiency, volume, blank, selectivity, humidity, and precision.

Finally, these findings were used to support the long term measurements of OVOCs at two EMEP sites in France. The results show high levels of methanal, ethanal, and acetone mainly, and a clear seasonal variation pointing out the impact of primary and secondary sources for such compounds especially in summer.

The consolidation of this method is crucial because OVOC data are reported without acknowledgment of the method short-comings or how to best address them, and in order to provide a valid path forward for accurate OVOC measurement.