TNA User Report

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Project title	Intercomparison of instruments for the measurement of small oxygenated organics
Name of the accessed chamber	EUPHORE
Number of users in the project	2
Project objectives (max 100 words)	The measurement intercomparison of concentrations of oxygenated Volatile Organic Compounds (OVOCs) of atmospheric relevance.
Description of work (max 100 words):	Work involved establishing whether a new state of the art commercially available Selected Ion Flow Tube Mass Spectrometer (SIFT-MS, Syft technologies) had adequate mass resolution and analyte sensitivity for atmospheric applications. The SIFT-MS results from this project will be compared to other OVOC measurement techniques such as PTR-MS and FTIR.

Principal Investigator's and group's information	
First name	Marvin
Family name	Shaw
Nationality	British
Activity domain[1]	Chemistry
Home institution	University of York
Institution legal status[2]	UNI
Email	Marvin.shaw@york.ac.uk
Gender	Male
User status[3]	RES
New user	yes

User 1 Information[4]	
First name	Martyn
Family name	Ward
Nationality	British
Activity domain	Chemistry
Home institution	University of York
Institution legal status	UNI
Email	Martyn.ward@york.ac.uk
Gender	male
User status	RES
New user	yes

User 2 Information	
First name	
Family name	
Nationality	
Activity domain	
Home institution	
Institution legal status	
Email	
Gender	
User status	
New user	

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[1] Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

[2] UNI= University and Other Higher Education Organisation;
RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);
SME= Small and Medium Enterprise;
PRV= Other Industrial and/or Profit Private Organisation;
OTH= Other type of organization.

[3] UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

[4] Reproduce the table for each user who accessed the infrastructure

Trans-National Access (TNA) Scientific Report

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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Dr Marvin Shaw
Chamber name and location: Fundación CEAM
Campaign name and period: OVOC Intercomparison 2018

Introduction and Motivation

Volatile organic compounds (VOCs) are emitted from a variety of anthropogenic and natural sources to the earth's atmosphere with their concentrations in air being affected by numerous chemical and physical processes. An ability to selectively quantify VOC concentrations in both urban and rural environments is of importance to understand and characterise the sources and sinks for individual VOCs.

To provide a real-time analytical method for the detection of a wide range of VOCs which compliments Gas Chromatographic (GC) based techniques Spanel and Smith pioneered the analytical application of selected ion flow tube mass spectrometry (SIFT-MS) in 1976 [1]. SIFT-MS utilizes known ion-molecule reactions of mass-selected reagent ions with an analyte. The mass-selected reagent ions (H_3O^+, NO^+, and $O_2{}^+$) are introduced into a flow tube at low energy into a carrier gas (typically helium) where they undergo chemical reactions with analytes in the gas sample that is drawn directly into the SIFT-MS flow tube at a known mass flowrate. These reagent ions are directed through a quadrupole mass filter where one is selected for reaction with the sample enabling clean reaction between one reagent ion and the analyte as well as rapid switching between reagent ions. The availability of NO^+ and $O_2{}^+$ enables the measurement of compounds that do not react with H_3O^+ (e.g., light hydrocarbons, halogenated and inorganic species) and also facilitates the identification of compounds that cannot be differentiated on the basis of H_3O^+ reactions alone. Whereas H_3O^+ almost always reacts by proton transfer, $O_2{}^+$ usually reacts by charge transfer or dissociative charge transfer and NO^+ reacts be a number of mechanisms including charge transfer, adduct formation and hydride abstraction. The switching time of the reagent ion mass filter is sufficiently fast that essentially simultaneous measurements with all three of these reagent ions can be carried out. The ensuing reagent ion-analyte ion-molecule reaction enables identification of the analyte in seconds and provides quantitation from the ratio of counts of the analyte product ion(s) relative to the reagent ion [2].

The ionisation of anaytes is softer in a SIFT-MS reactor (flow tube) than in a PTR-MS reactor (drift tube). PTR-MS product ion distributions measured for a range of compounds [3-5] reveal different fragmentation patterns and generally a higher degree of fragmentation than observed for the same compounds when analysed using SIFT-MS. The increased fragmentation observed in PTR-MS arises due to the higher collision energies in the drift tube (appox 0.2 eV), which are substantially greater than the thermal collision energies (approx. 0.038 eV) observed in a SIFT-MS flow tube. Hera et al.[29] extended the use of SIFT-MS from helium to nitrogen carrier gas and observed enhanced association reactions may occur such as the reactions converting H_3O+ to $H_3O+.(H_2O)n$ where n is 1-3. To my knowledge, despite the considerable advantages SIFT-MS has to offer over particularly PTR-MS, it has never been used extensively for air quality research.

Scientific objectives

The objectives of the project are :

1) Evaluate the performance of the SIFT-MS technique against recognized technologies (PTR-MS and FTIR) for VOC concentration determination under controlled conditions.

2) Evaluate the performance of the supporting autonomous sampling systems, zeroing and calibration over the 2 week experimental period.

3) To utilize the power of the near simultaneous 3 reagent ion switching to identify and quantify a wide range of OVOCs formed under controlled conditions from precursors and compare these compounds to estimates from the Master Chemical Mechanism (MCM, Andrew Rickard, University of York).

Reason for choosing the simulation chamber

The EUPHORE (Fundación CEAM) chamber was chosen to conduct this research due to the wide range of certified gas calibration standards, gas phase reference measurements and the high level of analytical expertise available within the facility. Also the Euphore chamber is a natural light photochemical reactor which is advantageous for this research.

Method and Experimental Set-up

Pressure Controlled Gas Inlet System

The experimental design was as shown in figure 1. The SIFT-MS had a gas selector valve box which allowed the instrument to autonomously switch between sample, zero gas and calibrant (sol 1, 2 and 3 in figure 1). Chamber air was sampled using a 2 metre PFA line (swagelok) at 2L min^{-1} using a stainless steel diaphragm pump (KNF). Sample gas pressure was controlled using back pressure controller (Alicat) prior to introduction to the SIFT-MS at 100sccm through Solenoid 1. The remainder of the sample gas was scrubbed using a zero air generator (platinum catalyst) and introduced at a constant flowrate to solenoid 2. Calibrant gas generated (see below) was introduced to solenoid 3 as required at a flowrate of 1L/min^{-1}. All gas lines used were 1/8 inch OD PFA heated to 70ºC.

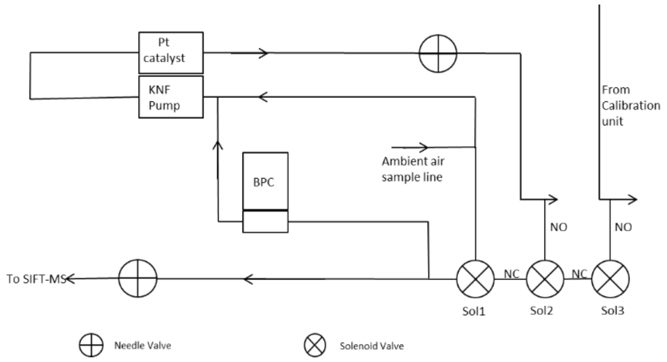

Figure 1. Pressure controlled gas inlet system

Automated Calibration System

A Latte Panda based automated calibration system was developed capable of generating a multipoint VOC calibration from a NPL certified 9 component gas mixture and a range of %RH without user input. The NPL calibrant contained 1ppm of methanol, ethanol, isoprene, MVK, MEK, Benzene, Toluene, Xylene, Trimethylbenzene. The system was autonomously triggered prior to and after every experiment SIFT-MS on-board microcontroller linked with the instruments Batch Scanner software. This allowed sequential calibration without any operator input.

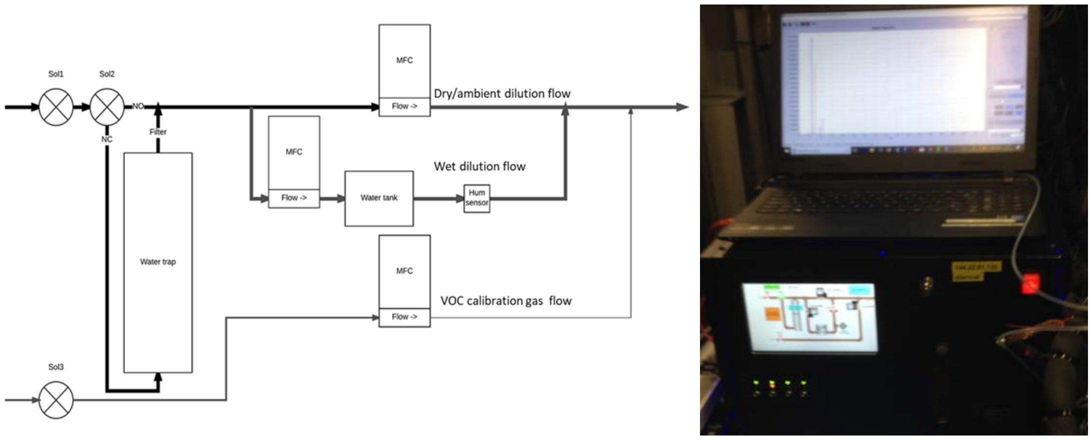

Figure 2. University of York Gas Calibration Unit (GCU).

Preliminary results and conclusions

As shown in figure 3, SIFT-MS determined isoprene, methacrolein, MVK and formaldehyde concentrations compare reasonabley well with MCM estimates for experiment 5. There seems to be a minor divergence of modelled and measured concentrations for methacrolein during the early stages of the experiment which is currenly being investigated.

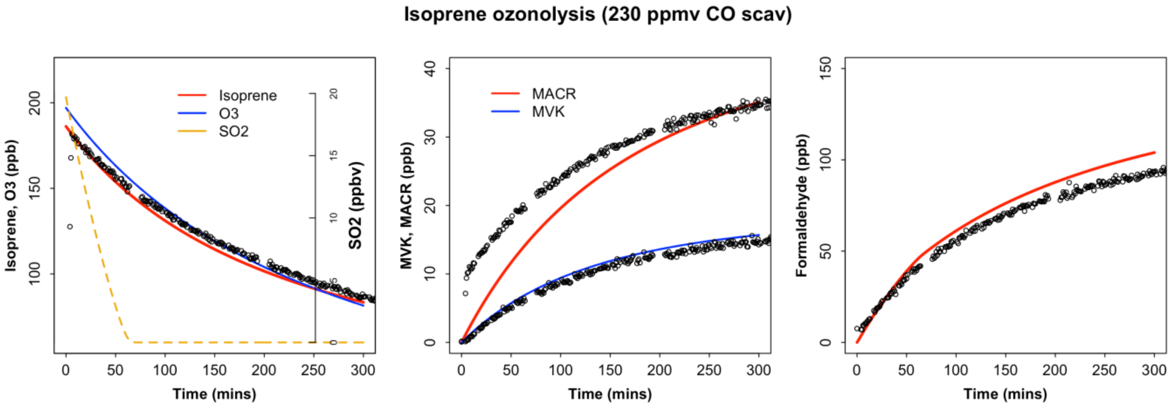

Figure 3. Evolution of concentrations of Isoprene, methacrolein, methylvinylketone and formaldehyde during experiment 5. Black dotted lines; SIFT-MS. Coloured solid lines ; MCM estimates for experimental conditions (M. Newland and A. Rickard, University of York).

Outcomes and Future Studies

The SIFT-MS and all supporting hardware operated succesfully during the 10 days of chamber experiments. From the data acquired i am able to identify a number of VOC oxidation products and track their evolution during the course of all 8 experiments conducted at the EUPHORE chamber. Some of the compounds currently identified are unlikely to be detected using either PTR-MS or FTIR. Further planned work involves comparison of the measurement data to the MCM OVOC estimates to evaluate model accuracy. We are also considering deployment of the SIFT-MS to the HELIOS Chamber (Centre National de la Recherche Scientifique - Institut de Combustion Aérothermique Réactivité et Environnement (CNRS-ICARE) during next years EUROCHAMP Intercomparison excercise.

References

1) Spanel, P.; Smith, D. Selected ion flow tube: A technique for quantitative trace gas analysis of air and breath.Med. Biol. Eng. Comput. 1996, 34, 409–419
2) Smith, D.; Spanel, P. Selected ion flow tube mass spectrometry (SIFT-MS) for on-line trace gas analysis. Mass Spec. Rev. 2005, 24, 661–700.
3) Aprea E, Biasioli F, Mark TD, Gasperi F. Int. J. Mass. Spectrom. 2007; 262: 114.7
4) Buhr K, van Ruth S, Delahunty C. Int. J. Mass. Spectrom. 2002; 221: 11.8.
5) Warneke C, de Gouw JA, Kuster WC, Gordan PD, Fall R. Environ. Sci. Technol. 2003; 37: 2494