Simultaneous analysis of organic gases and particles by chemical ionisation mass spectrometry

Supervisors (including Title; Dr, Prof etc): Dr. James Allan, Dr. David Topping, Prof. Hugh Coe

External supervisors and institution (including Title): Prof. Doug Worsnop (Aerodyne Research/ University of Helsinki)

Primary Contact Name and Email: James Allan james.allan@manchester.ac.uk

Introduction:

A large portion (around half) of fine particulate matter in the atmosphere is organic in nature, which is a diverse mixture of typically hundreds of thousands of compounds, both naturally occurring and anthropogenic. The majority of this mass is secondary organic matter, which means that the particulate matter is the product of volatile organic compounds (VOCs) after being subjected to chemical reactions. These chemical processes are complex and in many cases very poorly understood because we currently lack the instrumentation to comprehensively measure the myriad of chemical compounds present in both the gas and particulate phases. To further complicate matters, some chemical species are semivolatile, which means they exist in equilibrium between the particle and gas phases, which makes measuring them using traditional techniques difficult, as most methods of collecting and analysing samples assume the material to be either completely volatile or involatile. However, a new instrument, the Filter Inlet for Gases and Aerosols Chemical Ionisation Mass Spectrometer (FIGAERO-CIMS), is capable of not just comprehensively analysing the organic matter but can also perform quantitative measurements on both phases.

Project Summary:

This project is concerned with the development and application of the FIGAERO-CIMS. This utilises a new design of sampling inlet design that can be used to study both gases and particles simultaneously; while the mass spectrometer performs measurements on the gas phase, particles are collected on a filter. When sufficient sample is collected, the particulate matter is then transferred to the instrument through vaporisation by an inert carrier gas. The analysis is performed using time-of-flight CIMS, which is capable of delivering data on a very wide range of chemical compounds simultaneously and resolving them according to their elemental composition. Because the analysis is performed in situ, this means data can be generated on the time scale of an hour, which presents a significant advantage over offline techniques such as analysing filters manually in a laboratory, where samples are typically collected over the course of a day. The Manchester Centre for Atmospheric Science (CAS) is a very strong position to push this development forward, as we have a very strong track record in the optimisation of CIMS systems and application to quantitative atmospheric and laboratory measurements.

As part of a PhD, the development work will include the optimisation of the iodide ionisation method to a range of organic compounds and the development of calibration methodologies. The instrument will

generate a very large quantity of data and you will develop methods to handle the data in an automated fashion using cheminformatics tools. You will also be in a unique position to test the capability of the instrument to deliver quantitative data on semivolatile behaviour, as we are involved in an international network of scientists performing vapour pressure measurements and developing models of fundamental properties (see UManSysProp http://umansysprop.seaes.manchester.ac.uk/).

This PhD will involve a large amount of laboratory work at Manchester, measuring authentic standards and aerosols and gases produced by the Manchester Aerosol Chamber (MAC). There will also be opportunities to participate in field experiments in conjunction with other CAS aerosol instruments such as the Aerosol Mass Spectrometer (AMS) and also potentially aboard the Facility for Airborne Atmospheric Measurements (FAAM) BAe-146 research aircraft. These projects are generally collaborative, involving a large number of partners working in related areas of air quality, atmospheric chemistry, meteorology and climate science. In addition, you will be expected to participate in the international network of Aerodyne time-of-flight CIMS users, so this PhD will present an excellent opportunity for networking.

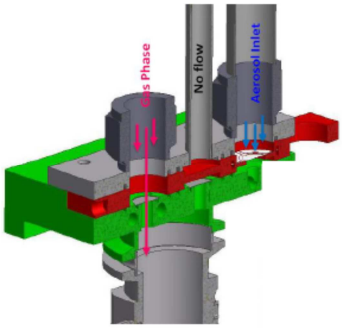

Image 1 *A schematic of the FIGAERO inlet system*

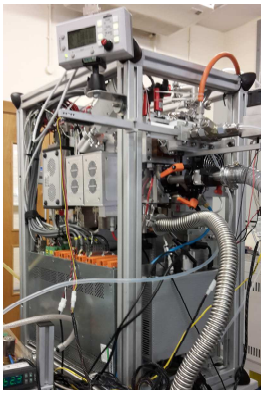

Image 2 *The Time of Flight Chemical Ionisation Mass Spectrometer (TOF-CIMS)*

References

Lopez-Hilfiker et al. (2014): A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROsols (FIGAERO), http://dx.doi.org/10.5194/amt-7-983-2014

Bannan et al. (2014): Importance of direct anthropogenic emissions of formic acid measured by a chemical ionisation mass spectrometer (CIMS) during the Winter ClearfLo Campaign in London, January 2012, http://dx.doi.org/10.1016/j.atmosenv.2013.10.029

O'Meara et al. (2014): An assessment of vapour pressure estimation methods, http://dx.doi.org/10.1039/C4CP00857J

Nozière et al. (2015): The Molecular Identification of Organic Compounds in the Atmosphere: State of the Art and Challenges, http://dx.doi.org/10.1021/cr5003485