Characterising atmospheric volatile organic compound mixtures using soft chemical-ionisation mass spectrometry (SCIMS)

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Introduction: Why we want to do this science

Both natural[1] and anthropogenic[1, 2] processes can emit a wide variety of volatile organic compounds (VOCs), as depicted in Figure 1. Typically, many VOC compounds are emitted simultaneously, and often emissions from different sources mix into the same air. The result is a complicated mixture of VOCs, many of which have the same molecular mass, and which contain similar chemical sub-units. It is vital to know the make-up of the VOC mixture in order to trace emissions, and to calculate the production of the air pollutants ozone and particulate matter [e.g., 1, 3, 4]. Traditionally, quantification of the different VOCs has been by separation methods (usually one- or two-dimensional gas chromatography) but this has limited temporal resolution (typically about 1 chromatogram per hour) and so limits our ability to study the rapid changes in emissions, chemical reaction rates, and meteorology that can affect atmospheric VOC concentrations. Using mass spectrometry, most VOC components can be measured (almost) simultaneously, and at high temporal frequency, but it is not always clear which compounds are contributing to the observed mass spectrum because of overlapping molecular weights (compounds with the same molecular weight are said to be isobaric) and common fragmentation patterns[2, 5, 6]. Some mass spectrometers are also now sufficiently small and light to be deployed in the field more easily than gas chromatographs[7].

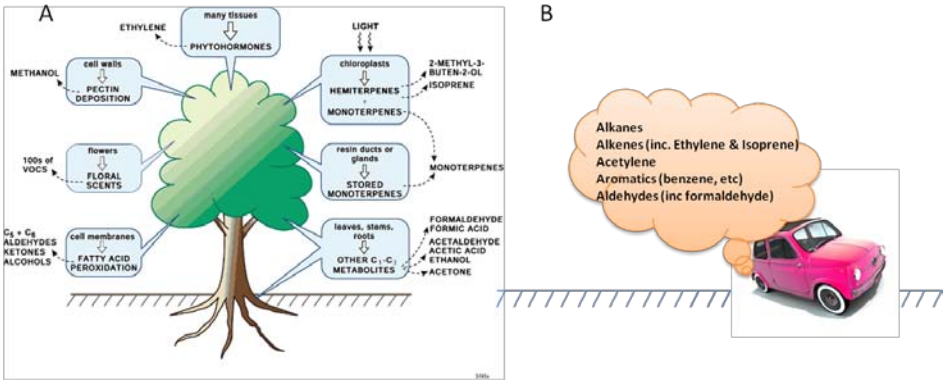

Figure 1. Sources of volatile organic compounds (VOCs) from (A) plants (image courtesy of Malcolm Possell, Lancaster University) and (B) motor vehicles.

The aim of this studentship is to develop mass spectrometric procedures that can distinguish and quantify environmentally significant VOCs in polluted (urban) and unpolluted (forest) air.
Specific initial targets for the method are to distinguish quantitatively the following isobaric compounds (i) isoprene and furan, (ii) ethyl benzene and the xylenes, and (iii) various monoterpenes such as α- and β-pinene.

Method: How we propose to do it

Mass Spectrometry can provide rapid analysis of environmental pollutants and their breakdown products. Using appropriate inlet systems, it is possible to measure atmospheric concentrations at 1 sample per second, or better, giving valuable information about the atmospheric behaviour of reactive gases.

Conventional Mass Spectrometry uses electron impact to ionise the molecules of interest but the excess energy often leads to complicated fragmentation patterns. Using Soft Chemical Ionisation Mass Spectrometry (SCIMS), the technique uses less energy to form the parent-ion molecule(s) and therefore less fragmentation. This helps to ensure that resultant mass spectra of mixtures of VOCs are less complicated to interpret.

One of the most widely used SCIMS techniques used for VOC identification in air is Proton Transfer Reaction Mass Spectrometry (PTR-MS) which involves transfer of a proton (H+) from H3O+ reagent ions generated in the hollow cathode region of the PTR-MS instrument. The VOC target molecules (M) may form protonated species (MH+) if the proton affinity of M is greater than that of water. Other reagent ions, such as O2+, NO+ etc can be used in place of H3O+ to improve the identification process, minimise ambiguity in the assignment of the neutral trace in a real-world environment and reduce interference effects[8]. The types of ion-molecule reaction processes are different (e.g. charge transfer for O2+). The use of different reagent ions is a particularly new and useful area of research with for real-time measurements.

In addition to having a range of reagent ions another useful analytical technique that can be adopted is to change the fragmentation patterns by increasing the reduced electric field, which is most easily achieved by changing the voltage applied across the drift tube[8]. The resulting product ions have the potential of helping in the assignment of trace compounds in complex chemical environments[9-11].

You will investigate ion-molecule reactions and the conditions in the drift tube, in order to seek optimal PTR-MS configurations for distinguishing the key target compound groups listed above whilst maintaining the PTR-MS advantages of high temporal resolution and relative ease of deployment. You will explore the underlying principles of PTR and seek general rules for finding the optimal settings to identify specific VOCs in complex chemical environments.

Outcomes: What's in it for you

Become an expert analytical scientist and gain experience in analytical problem-solving. Mass spectrometry is an extremely important and widely-used analytical technique, and PTR-MS is finding applications ranging from food science to the detection of explosives[10]. This studentship would give you a thorough grounding in mass spectrometry in general, and expertise in soft-ionisation techniques such as PTR-MS.

Start to become an Earth System Scientist. The project involves understanding how trace gases emitted into the atmosphere react, and how the VOCs and their reaction products impact on the

environment. You will have the opportunity to network with atmospheric chemists, ecologists, and climate scientists through our affiliation to the National Centre for Atmospheric Science (NCAS).

Develop collaborative links with Industry, National Laboratories and Governmental Regulators (Environment Agency & Health & Safety Executive). We have long-established links with PTR-MS manufacturers and a wide variety of industrial end-users, as well as with the government's Centre for Ecology and Hydrology who operate PTR-MS for analysis of a wide range of atmospheric samples. Your studentship would coincide with, and benefit from, an EC-funded Initial Training Network on Proton Ionisation Molecular Mass Spectrometry, coordinated by Dr Mayhew and involving 16 other academic, industrial and governmental partners.

Join a winning team. You will join the University of Birmingham in either the School of Geography, Earth & Environmental Sciences, or the School of Physics and Astronomy, depending on the details of your background and your intended scheme of study. This will also determine your primary supervisor. Both Schools have well-established training and support structures in place, to make sure that your time at Birmingham is fruitful and happy. You will receive training to complement your undergraduate skills and begin to move beyond undergraduate skills: studying advanced reaction kinetics and gas dynamics, for instance.

Who should apply

This unfunded studentship is available to those who have or expect to graduate with a good BSc in chemistry, physics, engineering, or a closely associated discipline. You must have demonstrable potential for creative, high-quality, PhD research and relish problem-solving. An eagerness to develop skills in instrumental analytical techniques, molecular physics, and atmospheric chemistry, is essential. We encourage students who are developing research proposals for PhD topics to contact us with a view to tailoring the science above to the research agenda of your funding agency. Some opportunities for funding for international students are listed at http://www.birmingham.ac.uk/international/students/finance/scholarships/index.aspx.

Further Reading

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9. Mayhew, C.A., et al., *Applications of proton transfer reaction time-of-flight mass spectrometry for the sensitive and rapid real-time detection of solid high explosives.* International Journal of Mass Spectrometry, 2010. **289**(1): p. 58-63.
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11. Agarwal, B., et al., *Use of proton transfer reaction time-of-flight mass spectrometry for the analytical detection of illicit and controlled prescription drugs at room temperature via direct headspace sampling.* Analytical and Bioanalytical Chemistry, 2011. **400**(8): p. 2631-2639.