Spectrometry for Security Applications

First International Workshop

Programme and abstracts

Foreword

Welcome to the First International Workshop on Spectrometry for Security Applications! It is our very great pleasure to welcome you to FH Vorarlberg University of Applied Sciences, Dornbirn, in the beautiful Vorarlberg region of Austria.

Following two very successful one-day workshops at the University of Birmingham in 2015 and 2016, this first International Workshop has been organized by the Chemical Sciences Security Group (CSSG) of the Royal Society of Chemistry, the UK Defence Science and Technology Laboratory (Dstl), Universität Innsbruck Institute for Breath Analysis, and FH Vorarlberg University of Applied Sciences. Our aim is to bring together scientists and technologists from academia, industry and government in an informal setting to network and share recent advances in ion mobility and mass spectrometry, and related fields, for applications including (but not limited to) explosives, chemical agent and narcotics detection; forensic science; counterfeiting; food and water security; emergency response; and border protection.

We invite you to engage with an excellent programme of talks and posters, and forge new links and partnerships. We are very grateful to the Royal Society of Chemistry Analytical Division for a generous grant to support graduate student travel to the Workshop.
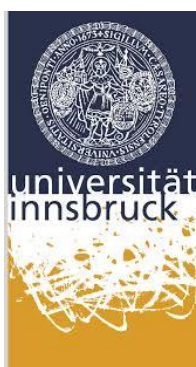
We look forward to your contribution!

The Organising Committee

Dr Matthew Brookes (Chair), Energetics Analysis Group, Defence Science and Technology Laboratory, UK

Prof. Chris Mayhew, Universität Innsbruck, Institut für Atemgasanalytik**,** Austria, and Birmingham University, UK

Prof. Karl Unterkofler, FH Vorarlberg, University of Applied Sciences, Austria

Times	Sunday 10th February	Monday 11th February	Tuesday 12th February	Weds 13th February
0700 – 0815		Breakfast (hotels)	Breakfast (hotels)	Breakfast (hotels)
0815 – 0830		**Welcome and introductory remarks**		
0830 – 0930		**Keynote** Forensic science and security: the importance of meaning *Ruth Morgan*	**Keynote** The state of trace detection: retrospective and future *Dave Atkinson*	**Keynote** Reactive Multi-stage Ion Mobility Spectrometry (IMS) for Advanced Selectivity with Explosive Trace Detectors and for Molecular Identification with General Chemical Analyses *Gary Eiceman*
0930 – 1030		**Forensic Science** 1. A Procedure for the determination of selectivity in High Resolution Mass Spectrometry *Thomas Conner* 2. Computational Modelling in the Forensic Context *Pooja Goddard*	**Chemical Warfare Agents** 1. Real-time monitoring of chemical warfare agents with PTR-MS *Philipp Sulzer* 2. Engineering the casualty journey at a nerve agent attack simulation in Greece *Andria Hadjithekli*	**Novel concepts** 1. Enhancing optical signatures in liquids using open microcavities *Aurélien Trichet* **MS-based fieldable explosives detection (1)** 1. High throughput detection of explosive particle and vapor by mass spectrometry *Shun Kumano*
1030 – 1100		**Official Opening and coffee break** Rector FHV - Prof. (FH) Dr. Tanja Eiselen	**Coffee break**	**Coffee break**
1100 – 1200		**Analysis and detection methods** 1. A Thermal Extraction Ionisation Source (TEIS) for the Direct Analysis of Organic Compounds in Real Time *Carl Fletcher* 2. Evolution and Developments of Proton Transfer Reaction-Mass Spectrometry for Security Applications *Ramón González-Méndez* 3. Headspace analysis of inorganic materials *Dstl, presenter to be confirmed*	**Sampling and preconcentration** 1. Silicon Nanowire Arrays for Preconcentration and Partial Separation Coupled to Mass Spectrometry and Ion Mobility Spectroscopy *Braden Giordano* 2. Novel passive samplers for explosives vapour detection *Leon Barron*	**MS-based fieldable explosives detection (2)** 2. Threat detection using Scenthound™ platform *Jani Hakala* 3. Fast carry-on luggage screening method for explosive detection *Gonzalo Fernandez de la Mora*
1200 – 1230			**Workshop photograph**	**Closing remarks and workshop ends**
1230 – 1800		**Networking / free time**	**Networking / free time**	
1800 – 1900	**Registration** Hotel Krone	**Food and Border Security** 1. Enhancing Food Safety and Authentication through Training and Implementation of Advanced Mass Spectrometry Techniques in Asia and the Pacific *Stewart Walker* 2. Detection of human traces for reduction of people's illegal transport *Veronika Ruzsanyi*	**Poster session**	
1930 – 2200	**Networking**	**Evening meal** EventGastro inatura	**Workshop Dinner** Hotel Krone	

ORAL PRESENTATIONS

Spectrometry for Security Applications - First International Workshop
FH Vorarlberg, Dornbirn, Austria, 10th – 13th February 2019

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KEYNOTE: Forensic science and security: the importance of meaning

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Abstract

The innovations and developments in analytical approaches in the last 10 years have been phenomenal. The capacity for accuracy, precision and reliability in measurements, combined with the ability to interrogate larger datasets than ever before has created significant opportunities to identify and understand trends, relationships and networks.

Good data quality and analysis integrity is without doubt foundational, however it is also important that we ensure that the basis for robust and transparent inferences about the meaning of the data in different contexts is valid. Forensic science operates in a highly complex environment, with different stakeholders, competing timeframes and critically in the UK, a strong driver in terms of financial costs. Against this backdrop there is a need to be pioneering research that not only develops our technological capabilities for the detection of traces, but also the foundational research that is needed to underpin our understanding of what a trace material means when it is identified. Grappling with questions of uncertainty and how inherent uncertainty can be communicated within a high stakes security environment has never been more important, and developing our understanding of the role of human decision making at each phase of the forensic reconstruction process is critical. Examples of research seeking to address some of these challenges will be presented and the broad questions this research raises as we look to the future will be discussed.

A Procedure for the determination of selectivity in High Resolution Mass Spectrometry

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Abstract

The Forensic Explosives Laboratory has developed a new sample processing procedure to optimise analyte recoveries for subsequent analysis of explosives using two newly developed Liquid Chromatography coupled with High Resolution Mass Spectrometry (LC-HRMS) analytical methods. Coupling chromatography with HRMS increases selectivity compared to using either technique in isolation: chromatography can offer separation of isobaric species and HRMS can offer more confident identification of the analyte, due to precise analyte identification according to mass (± 3 parts per million); which can be used to determine probable molecular formulae. The number of possible molecular formulae that fit a given mass is, typically, very low, because of the high mass accuracy. Molecular structure is asserted based on the molecular formulae, where usually the formula with lowest mass error (the difference between the theoretical and measured mass) is the true identity of the analyte. However, in some cases, a single molecular formula can be linked to different structural arrangements that correspond to different analytes (isomers).

Guidance produced by the European Union [1] for the interpretation of results from analytical methods, alongside several papers (*e.g.* [2][3][4][5]) that have been published on the subject, detail the use of 'identification points' to identify a molecule. These papers acknowledge the increased mass resolution of HRMS versus traditional MS, and correspondingly, the technique earns more 'identification points' per ion. Generally, however, at least two ions are recommended to identify a molecule, which causes problems for the analysis of small molecules by mass spectrometry; in many cases two ions are not produced, or the second ion is produced at low levels, significantly impacting limit of detection.

An assessment of mass spectral uncertainty was undertaken; whereby, isobaric species that could potentially generate false positive results on the basis of mass analysis alone were interrogated. Factors such as bonding rules, functional group chemistry, molecular structure and general availability were considered. This led to the justification that the accurate mass of a single ion was sufficient to identify certain analytes, when combined with retention time comparison to a known standard, as well as other considerations (solubility, ionisation *etc.*).

References

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Computational Modelling in a Forensic Context

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Abstract

Quantum mechanical-based calculations are increasingly becoming a useful tool for chemists to both explain and predict chemical behaviour of molecular systems. However, the potential of computational modelling in chemicals forensic chemistry has been relatively unexplored.

This present study focuses on 2,2-Dihydroxyindane-1,3-dione (Ninhydrin), a widely-used reagent to develop latent fingerprints on porous surfaces such as paper. Despite being a popular choice in forensic investigations, a search for more efficient development reagents is ongoing, with most previous attempts being purely synthetic and based on a trial and error approach.

The use of Density Functional Theory (DFT) simulations offer a complementary approach, through which new, novel development reagents may be designed, and their effectiveness predicted before chemical synthesis thereby reducing the cost and effort in discovering effective fingerprint development reagents.

Results presented here highlight the chemical processes that occur immediately after the application of Ninhydrin to fingerprint residue. Various candidate development compounds with predicted fluorescence behaviour are studied and compared to identify an explanation for the discrepancies in the observed fluorescence activity.

This project takes a large step towards enabling a less-labour intensive, more economical method to the modelling informed rational design of new and effective fingerprint development reagents.

A Thermal Extraction Ionisation Source (TEIS) for the Direct Analysis of Organic Compounds in Real Time

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Abstract

Ambient Ionisation-Mass Spectrometry (AI-MS) is a rapidly growing field of interest as the need for direct analysis and minimal sample preparation becomes increasingly desirable. Presented here is a thermal extraction ionisation source (TEIS) for mass spectrometry which enables the direct analysis of solids, liquids and gases with little to no sample preparation and produces results in real-time. Samples can be introduced by swabs, vapours or direct injection, resulting in a versatile technique for analysing substances of forensic interest such as drugs and explosives to sub-nanogram detection limits.

The TEIS has been used to examine drug contamination on currency for many years and has been involved in many UK court cases up to the UK Court of Appeal. Furthermore, the ability to directly analyse swabs allows the TEIS to be used for analysis of items such as clothing, phones, cars and more, adding to the informative power of a particular case.

The TEIS is very capable of detecting explosives from many functional groups i.e. nitroamines, nitroesters, nitroaromatics and peroxides and features an option to introduce adducts such as chloride to aid detection. Additionally, the TEIS has shown great potential for other security applications, such as food testing and environmental monitoring. Finally, the TEIS demonstrates impressive reproducibility; making quantification possible without chromatography within minutes.

Headspace methods and their application to inorganic explosives

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Abstract

The detection of explosive vapours is a key capability in security screening in both military search operations and civil security screening. Unlike particle detection, which indicates the recent handling of explosives, explosive vapours are directly attributable to the presence of a bulk quantity.

Understanding the vapour phase properties of threat materials is crucial for characterisation of scenarios and identification of target compound(s) for vapour detection. The vapour signature of organic explosives can contain components from the explosive material, associated composition materials, taggants or decomposition products and techniques to characterise these signatures are well developed. In contrast explosives compositions based on inorganic compounds are far less well understood.

Here we describe our ongoing work to develop and assess broad spectrum headspace characterisation methods providing greater knowledge of vapour signatures of both organic and inorganic explosive materials.

Evolution and Developments of Proton Transfer Reaction-Mass Spectrometry for Security Applications

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Abstract

Proton Transfer Reaction-Mass Spectrometry (PTR-MS) is a broad-based technique that has proved its analytical use for fast trace explosives detection.[1,2] It has been almost a decade since the first publication for explosives detection came to light.[1] From that moment on, the PTR-MS technique has developed into a more multidimensional technique, overcoming the challenges for achieving fast, selective and sensitive detection of threat agents for security applications. For such a journey to be sucessful, hardware developments had been necessary. Among these, this talk will revise the developments of a)- new inlet unit based on commercial swabs allowing no (or minimun) memory effects; and new methodologies for improving selectivity, based in enhancing collisional induced dissociation in a controlled way by manipulating the ion-molecule chemistry within the drift tube of a PTR-MS, through b)- the use of a radio frequency ion-funnel (RFIF) DT,[3] and c)-rapid switching (less than a microsecond at a frequency of 0.1-10 Hz) of the reduced electric field.[4] All these improvements translate into allowing identification of a compound of interest with higher specificity in complex chemical environments.

Finally, all these recent developments have been combined and recently applied to the detection of organic additives used in smokelss powders,[5] expanding thus the range of compounds and applications where PTR-MS can be used as the detection tool.

References

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Enhancing Food Safety and Authentication through Training and Implementation of Advanced Mass Spectrometry Techniques in Asia and the Pacific

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Abstract

The right of everyone to sufficient food and water is enshrined in Article 25(1) of the United Nations Universal Declaration of Human Rights[1]. Food and Water also feature highly in lists of the greatest challenges facing humanity.[2] The provision of sufficient good food and water assists in solving some of the other challenges – protecting the environment, reducing disease, reducing conflict and coping with our population (including starvation and infant mortality). This presentation will outline the key roles that mass spectrometers have in ensuring that food is safe, contains what it is supposed to (organic MS) and comes from where is stated (IRMS and ICPMS) and does not have contaminants – either accidental e.g. pesticide residues or deliberate adulteration - (GCMS and LCMS).

A four-year project – "Enhancing Food Safety and Supporting Regional Authentication of Foodstuffs through Implementation of Advanced Analytical Techniques" - has been funded by the United Nations Development Program and International Atomic Energy Agency through the Regional Cooperative Agreement for Research and Development and Training Related to Science and Technology for Asia and the Pacific. New Zealand is leading the project through Lead Country Coordinator Prof. Russell Frew (Otago) with Assoc. Prof. Stewart Walker as the Australian counterpart as National Project Coordinator (Australia).

In this project international mass spectrometry experts from - Australia, China, India, Japan, Malaysia, New Zealand, Pakistan, Singapore and South Korea will provide expertise to scientists from Bangladesh, Cambodia, Fiji, India, Indonesia, 'Jordan', Laos, Malaysia, Mongolia, Myanmar, Nepal, Pakistan, Palau, Philippines, Sri Lanka, 'Taiwan', Thailand and Vietnam.

In the first exercise rice from various countries were analysed in Japan. However, to paraphrase the saying about giving a man a fish - 'Take a mass spectrum for someone and they will have a mass spectrum. Teach them to take their own mass spectra and they become mass spectrometrists....'

References

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Detection of human traces for reduction of people's illegal transport

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Abstract

Within Europe there has been an increase of illegal human trafficking, which has resulted in the current migrant and refugee crisis. People locked in trucks and shipping containers are taking risks with their health and even their lives. Mobile tracking systems to find people hiding inside containers and trucks would help to protect smuggled people and greatly aid the border control police. Requirements for such systems are that they can be used without breaking the seal on containers, and that they provide rapid analysis with low false positives and negatives, thereby enabling a higher control rate. Analytical instruments that provide a chemical fingerprint of volatile compounds associated with the human body can potentially fulfil that role.

The development of gas sensors that achieve a good selectivity for specific compounds or substance groups and at the same time have sensitivities in the ppt-ppb range, represents a major challenge. However, ion mobility spectrometry (IMS) has these capabilities, and importantly owing to its size and power consumption can be integrated into portable systems.

In a recent study we have used an IMS coupled with fast gas chromatography (GC-IMS) to monitor the volatile compounds emitted by humans enclosed in a body plethysmography *chamber*. Altogether 35 ion mobility peaks were observed which could be linked to a human being present. From these peaks, 17 compounds were identified and then quantitatively monitored during 2 hours in the chamber. These volatiles include 7 aldehydes, 5 esters, 3 ketones, and acetic acid.

In addition to determining the key volatile compounds to monitor, we have developed a backpack system which includes an aspiratory IMS in combination with an electrochemical aldehyde sensor and three metal oxide sensors. The device has been characterized using test gas mixtures based from the knowledge gained from the chamber experiment and also using human samples such as urine, breath, sweat, etc. Measurements of surrounding air in containers and confounder compounds, such as air pollutants and fragrances, including various test scenarios (such as trucks and containers with and without cargo, and with and without persons) are currently being investigated. With our partners in the Federal Ministry and Johanniter, Austria, this prototype instrument is currently being validated in field trials and optimized for connectivity to current systems. Ultimately, we envisage that this system and data analysis will be controlled using smart phones and tablets.

The development of our system and its subsequent deployment will strengthen the effectiveness and speed of search operations to find people who are being illegally.

KEYNOTE: The State of Trace Detection: Retrospective and Future

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Abstract

Trace detection methods were developed in earnest for aviation security after the Lockerbie event in 1988. Thirty years later, the methods used are eerily similar to those first deployed into airports in the 1990s. There has been a large assortment of research on sampling and detection since that time, but major changes in deployment have not occurred, both for operational and technical reasons. Recent research and advancements have the potential to transform the future of trace detection for use in security operations. Techniques such as mass spectrometry based vapor detection and non-contact sampling are emerging as potential cornerstone technologies.

KEYNOTE: The State of Trace Detection: Retrospective and Future

Real-time monitoring of chemical warfare agents with PTR-MS

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Abstract

Proton-Transfer-Reaction – Mass Spectrometry (PTR-MS) has already been utilized for the investigation of various threat agents, such as Chemical Warfare Agent (CWA) analogues, toxic industrial chemicals, explosives, illicit drugs, etc. (compare [1] for a comprehensive overview). However, work on "real" CWAs is limited so far due to legal restrictions and extremely high safety requirements when working with these compounds. Here, we present results from a recent measurement campaign at a facility specialized and licensed for CWA handling, where nine of the most important CWAs (including sarin, tabun, soman, VX, etc.) have been investigated with the latest time-of-flight based PTR-MS technology.

Figure 1 shows a photograph of the experimental setup with the PTR-MS instrument on the left and the operator manipulating the sample inlet hose close to the CWA samples under a fume hood on the right. Most importantly, a novel method of producing NH_4^+ reagent ions has been employed, which enabled NH_4^+ production from N_2 and H_2O source gas without the need of any toxic and corrosive NH_3. Particularly organophosphates showed extremely high sensitivity, selectivity and considerably lower fragmentation compared to ionization via H_3O^+. Surface contamination tests revealed limits of detection down to 1 ng/cm^2.

Figure 1 CWA detection tests at specialized facility

References

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Engineering the casualty journey at a nerve agent attack simulation in Greece

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Abstract

TOXI-triage, a multi-million pound Horizon 2020 funded European Project, brings together 18 teams from 8 different countries on a research project to develop and field/trial an advanced medical care and site management during triage within rescue efforts in a CBRN incident. In a time where chemical, biological, radiological and nuclear (CBRN) terrorism is a real threat, TOXI-triage is developing new technologies, analytical methods and is suggesting a novel pathway hot zone assessment using an integrated digitalised system to provide rapid diagnosis and a revolutionary approach to CBRN incident management.

A field trial took place at a Greek Air Force base in October 2018 during which the 7 technologies developed within the project were demonstrated and tested. The scenario was based on a nerve agent attack at an airport, where a CBRN simulant and a breath volatile organic compound (VOC) standard were used to target 53 casualties; 50 civilians, 1 fireman and 2 blue light responders. In total 723 targets were evaluated across all demonstrated technologies. The casualties were 'tagged and traced' and then taken through the two CBRN decontamination triage lines based on the symptoms developed from their level of simulant exposure. Two analytical platforms, a hybrid air Ion Mobility Sensor (IMS) and breath analyser based on Gas Chromatography-Ion Mobility Spectrometry (GC-IMS) were used to screen casualties. 11 casualties were severely exposed and taken through medical decontamination, whereas 21 individuals did not show signs of exposure to the chemical. A breath analyser was set up at each decontamination line and samples were collected from all individuals taken through. 5 cm^3 of single breath was collected using a disposable sampler and analysed immediately with rapid detection within 40 seconds. The results were available to a trained operator determining whether the casualty was exposed or not to the chemical. The air IMS sensor was used at the end of the medical decontamination process where the alarm was activated in case of not-successful decontamination, suggesting repetition of the procedure. The ability to rapidly screen the casualties was demonstrated enabling decision making within minutes.

The field exercise in Athens was the first time multiple advanced methods and technologies were combined to test a CBRN incident response. The full dataset collected is yet to be processed and the outcomes of the field exercise in Athens and to a greater extend of TOXI-triage, are expected to be of a great interest to emergency services, military and government policy makers. The CBRN triage systems developed by TOXI-triage will continue to evolve and potentially be adopted by emergency responders across the world.

Silicon Nanowire Arrays for Preconcentration and Partial Separation Coupled to Mass Spectrometry and Ion Mobility Spectroscopy

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Abstract

Silicon nanowire (SiNW) arrays are a suitable platform for the preconcentration of trace nitroaromatic compounds and subsequent desorption via Joule heating of the array. Arrays are fabricated from Si wafers containing an epitaxially grown layer of low conductivity intrinsic Si sandwiched between layers of high conductivity p-type Si. Passage of current through the nanowires results in nanowire temperatures in excess of 200°C during heating of the arrays. Analyte vapor preconcentration and partial separation is achieved on the array at analyte concentrations nearly two orders-of-magnitude below saturated vapor concentrations at room temperature. Successfully coupling of the arrays to mass spectrometry and ion mobility spectrometry are demonstrated. In addition, the use of chemometric tools leveraging the multichannel detection (e.g. the mass channels in MS detection) is demonstrated as a tool to identify and quantify partially resolved analytes.
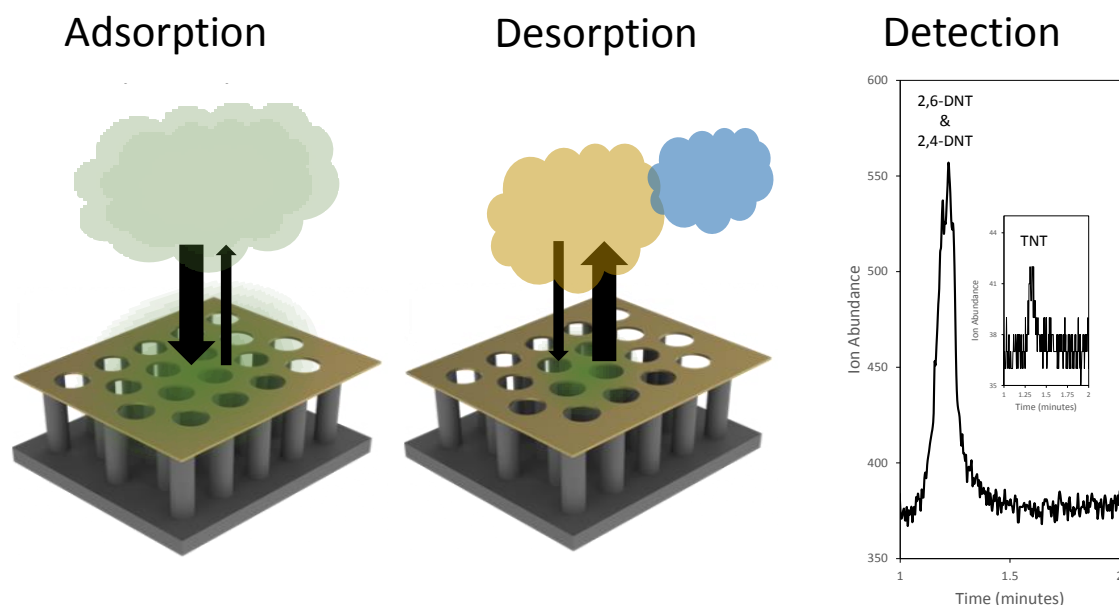
Figure 2. Depiction of the adsorption and desorption process using SiNW arrays. Detection panel shows the total ion chromatogram associated with the desorption of 2,6-DNT, 2,4-DNT, and TNT achieved after 10 minutes of sampling at 180 mL/min from a vapor stream consisting of 800 ppt_v 2,6- and 2,4-DNT and 65 ppt_v TNT. Inset presents the m/z 210 ion unique to TNT.

Novel passive samplers for explosives vapour detection

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Abstract

A new thin-film passive sampler is presented as a low resource dependent and discrete continuous monitoring solution for explosives-related vapours. Using fifteen mid-high vapour pressure explosives-related compounds as probes, combinations of four thermally stable substrates and six film-based sorbents were evaluated. Analysis was performed using liquid chromatography-high resolution accurate mass spectrometry, ion mobility spectrometry and thermal desorption mass spectrometry. Uptake kinetics experiments revealed equilibrium was reached between 3-5 days. Compounds used in improvised explosive devices, such as triacetone triperoxide, were detected within 1 hour of exposure and were stably retained on the sampler over 7 days. The results from several trials with bulk materials is also presented. Ethylene glycol dinitrate (EGDN) was detected within 4 h in a container holding a suitcase packed with 0.2 kg Perunit 28E. Within a 22,000 dm^3 room, 1 kg of concealed Seguridad was detected within 24 h and in an adjoining room within 7 days. Exposed samplers also successfully captured components of 1 kg TNT after 72 h and 1 kg concealed Perunit 28E after 24 h in both a furnished room and a large, partially-filled shipping container. A one-week trial at three operationally relevant venues including a university, a theatre and a government building revealed a nuisance positive rate of <1.4 % (n=72). High-security monitoring for concealed explosives using such cost-effective and discrete passive samplers can add extra assurance to search routines while minimising any additional burden on personnel or everyday site operation.

KETNOTE: Reactive Multi-stage Ion Mobility Spectrometry (IMS) for Advanced Selectivity with Explosive Trace Detectors and for Molecular Identification with General Chemical Analyses

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Abstract

Ion mobility spectrometry has been a selective detector of explosives with capabilities for picogram detection limits across a range of demanding environments and with extended periods of use. High speed, convenience of use, stable calibration, and simplicity of spectral interpretation have been strong attractions for embodiments of IMS technology at Explosive Trace Detectors (ETDs). Limitations or difficulties in these same ETDs are found from matrix influences in chemical ionization at ambient pressure and from resolving powers, commonly, of ~20 to 40. Suppression of ionization is a low level nuisance for explosives detection with commercial ETDs in while false positive rates from spectral interferences constitute a more significant concern. Differences in chemical properties of gas phase ions derived from explosives and their interferents have provided, for little increase in complexity of technology or methodology, a pathway towards increased selectivity of response using a reactive stage within a tandem drift tube. Subjecting ions (principally $M \cdot Cl^-$) at ambient pressure to electric fields of 100+ Td in a wire grid assembly over drift tube cross sections provides another dimension of control in an IMS measurements, with enhanced selectivity of response and reduced rates of false positives, even with analyzers of low resolving power.

The lack of structural information in mobility spectra owing to ion formation near thermal energies has limited ion mobility spectrometers throughout all of chemical measurements regardless of particular application. Recent advances in fragmentation of gas phase ions at ambient pressure in reactive multi-stage drift tubes has permitted recognition of spectra by chemical class, even with unfamiliar chemicals. Patterns of fragmented ions are being explored as additional structural detail in spectra to transform IMS, as a method, from the historic category of selective detector into a new level of performance as molecular identifier. Supporting studies will be described for protonated monomers from a range of organic compounds including alcohols, esters, aldehydes, and others.

Enhancing optical signatures in liquids using open microcavities

Dean James, Aurélien Trichet, Jeremy Warren, Claire Vallance and Jason Smith

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Abstract

Oxford HighQ is a spin-out company from the University of Oxford which aims at producing a new range of micro-optical sensors. Our technology is based on a combination of optical microcavity and microfluidics chips. We are currently developing table-top devices for liquid characterisation and have demonstrated a colourimetric detection limit around 10-100's nM within a detection volume of few 10's of fL. This unique combination offers the long term possibility to perform a large number of measurements with minutes quantity of reagents and therefore has a potential for highly multiplexed measurements.

High throughput detection of explosive particle and vapor by mass spectrometry

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Abstract

we developed two types of mass spectrometry-based explosive trace detectors (ETDs), namely, a high-throughput ETD which detects explosive particles using non-contact sampling, and a compact ETD which detects explosive particles and their vapor by one sampling unit. Based on the prototype of high-throughput ETD [1], the non-contact sampling system was improved using a fluid dynamic simulation. A mass spectrometer was downsized, leading to the downsizing of overall system. As the other type of ETD, we combined such mass spectrometer with both a vapor introduction port and swab sampling function. We confirmed that the high-throughput ETD detected a few ng TNT within 3 sec after the start of measurement. The compact ETD with a weight of around 60 kg has a function of continuous monitoring of surrounding gas and swab sampling. Experimental results suggested that the compact ETD detected vapor of TATP at a concentration of below 0.1 ppm and TNT particle at ng level. Use of those ETD as a security gate and an area monitoring system is considered to increase the security level in a wide area of the city.
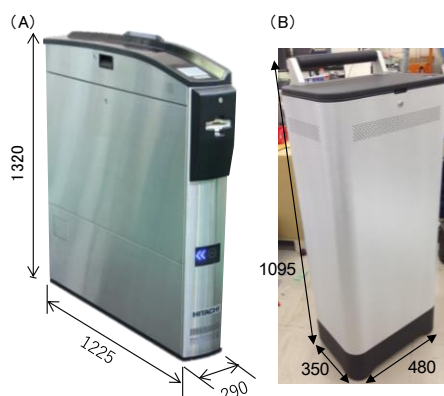
Figure 3 Two types of mass spectrometry based trace explosives detection system. (A) High-throughput ETD. (B) Compact ETD.

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Threat detection using Scenthound™ platform

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Abstract

Scenthound™ (Karsa LTD, Helsinki, Finland) is a new ultrasensitive threat detection platform based on atmospheric pressure chemical ionization time-of-flight mass spectrometry (APCI-ToF-MS). The target threats can be explosives, narcotics, chemical warfare agents and toxic compounds, or other chemicals of interest. Scenthound™ consists a hand-held high volume sampler, a selection of filter cassettes for sample collection, a cassette desorber inlet, a high resolution time-of-flight mass spectrometer, and an automated system control, threat detection and analysis software. Scenthound™ is capable of collecting and analyzing target vapors, liquid micro-injections, filters containing particulate target material and swabs. The platform is also capable of online vapor and particle analysis. Scenthound™ can reach low ppq sensitivity for target vapors. We will present technical particularities and test results in our presentation.

Figure 1. *Illustration of the Scenthound™ platform. Please find out more at karsa.fi*

Fast carry-on luggage screening method for explosive detection

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Abstract

A fast carry-on luggage screening method for explosive detection has been designed and tested, allowing screening rates similar to the X-Ray scanners at airport security checkpoints. Vapours emanated from the sampled item are captured in a TENAX-GR filter by aspirating the surrounding air volume during six seconds; then the filter is transferred to the analyser where after another six seconds results are presented. The analyser is based on SEADM TD-DMA-MS platform (Thermal Desorption - Differential Mobility Analysis - Mass Spectrometry) [1].
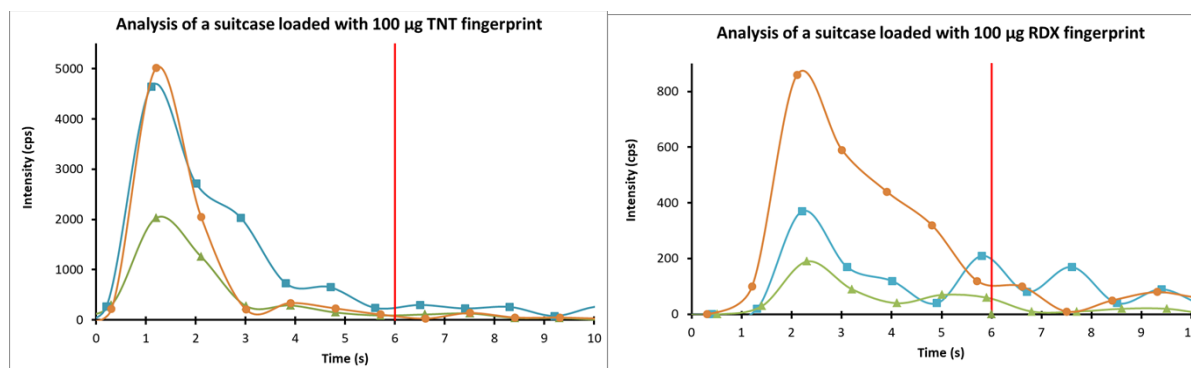
Figure 4 Analysis of fingerprint, explosive-loaded suitcases. Left: TNT; right: RDX.

Samples from two suitcases were taken with different aspiration volumes. One suitcase was loaded with TNT and RDX by simulating single transferred fingerprints of each explosive on the outside [2]; the other one was used as a blank reference. Both fingerprints were loaded with 100 ug of explosive. Figure 1 shows the results of these tests. TNT detection from a single fingerprint was easily achieved. RDX detection was weaker than TNT, however, to the author's knowledge, this was the first test reported worldwide where RDX from a single fingerprint had been detected through vapour analysis.

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POSTERS

Understanding explosive vapour signatures: TNT and RDX vapour evaluation using GC-MS and GC-ECD analysis

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Abstract

The diverse and varying nature of explosive threats confined in different containers and conditions forms a big challenge for their adequate detection and identification. Understanding the phenomena involved in the evaporation of explosives in confined spaces enables the development of effective explosives vapour detection systems for a variety of applications, like aviation security and critical infrastructure protection.

The relation between explosive material (mass and morphology), soak time, confined volume and confinement material was investigated in elementary simulated operational conditions for RDX, TNT and C4

Bare explosives samples were placed in closed glass and folded cardboard containers, left for evaporation and then repeatedly sampled with tenax adsorbent and SPME fibres and subsequently analysed.

Figure 5: Experimental setup showing the glass containers (left) and cardboard containers (right)

TNT, RDX and their common residues, greatly differing by their vapor pressures, have been observed and described using gas chromatographic analysis (GC) with Mass Spectrometry (MS) and Electron Capture Detection (ECD).

The vapor signatures were measured for the explosives prepared in different forms: TNT material was studied as flakes and in its casted form, RDX was examined as pure, powdered material and as a plasticized C4 cylinder

The evaporation profiles were analysed and described both qualitatively and in a (semi) quantitative way. Different evaporation (soak) times and sampling times were studied for an extensive description of the behaviour of explosive vapours.

The Characterisation of Fluorescence-based Amino Acid-Sensitive Fingerprinting Reagents - A Combined Theoretical and Experimental Study

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Abstract

In this work, we report a combined computational and experimental study using both Density Functional Theory (DFT) calculations and fluorescence spectroscopy to grade the efficiency of fluorescent fingerprinting reagents, working towards the design of new and more effective reagents.

Fluorescent fingerprinting reagents are a powerful forensic tool, routinely used for the identification of individuals. It is therefore of interest to improve both their sensitivity and development contrast. The majority of previous work has been on synthesising analogues of existing compounds, and comparing their effectiveness against the original, which has proved to be time-consuming and in some cases wasteful. Therefore, our approach is to focus on well-known development compounds, 1,8-Diazafluoren-9-one (DFO), 1,2-Indanedione, and 2-hydroxy-1,4-naphthoquinone (Lawsone). We will experimentally determine the quantum yield, which is a direct measure of the fluorescent product. This is compared with the theoretically-predicted fluorescence properties calculated from excited state transition *Ab Initio* calculations and Natural Transition Orbital (NTO) analysis. To complement this, the grading of a range of fingerprints developed by each of the three reagents was carried out using the Bandey scale [1], a method which grades each fingerprint based on judgement by eye.

In this study, we aim to propose an improved method to determine the efficiency of fluorescent fingerprinting reagents. Furthermore, we will validate the chosen computational method of choice (DFT and Time dependent DFT) for the design of new, more-effective reagents.

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ION MOBILITY STUDIES ON THE NEGATIVE ION-MOLECULE CHEMISTRY OF PENTACHLOROETHANE

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Abstract

An investigation of the negative ion-molecule chemistry of pentachloroethane (PCE) in air based Ion Mobility Spectrometry and Ion Mobility Spectrometry-Mass Spectrometry systems has been undertaken. The observed product ions are Cl^-, produced by dissociative electron attachment, and $Cl^-.HOO$ resulting from a reaction with O_2^-. Based upon the moisture content of the system, these ions can be observed as a doublet in a 'dry' system or as a singlet in a 'wet' system. The nature of the $Cl^-.HOO$ product ion was investigated by using isoflurane as a probe to monitor the changing ratios of Cl^- and $Cl^-.HOO$ as the PCE concentration decreased. This confirmed the origins of the two product anions. Electronic structure calculations have aided to the understanding of the reaction processes observed.

Proton transfer reaction – mass spectrometry and its applications to homeland security: detection of cocaine and its metabolites

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Abstract

PTR-MS has already proved to be a useful tool for the detection of drugs. It has successfully been used to detect rape drugs even when mixed in drinks [1] and ion-molecule processes can be manipulated to differentiate between isomeric substances [2]. Cocaine is one of the most consumed illicit drugs. A recent study has shown that only the use of cannabis is higher than that of cocaine [3]. Often, cocaine users are heavy drinkers of alcohol. When both cocaine and ethanol are present in the bloodstream, the metabolite cocaethylene is produced in the body [4], which in itself is a recreational drug.

Law enforcement agencies need to rapidly detect cocaine or similar compounds rapidly and with a high level of confidence. One real time analytical technique that can provide this is PTR-MS. To be able to use this instrument in the field, we first need to determine and understand the protonation and fragmentation processes that cocaine and related compounds undergo as a function of the key operational parameter, namely the reduced electric field, which is the ratio of the electric field strength to the gas number density in the drift (reaction) tube. Here we present a study of the reactions of cocaine, methyl ecgonine and cocaethylene with hydronium ions as a function of the drift tube voltage and the reduced electric field.

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Interface of an atmospheric flow tube ionization source to a time-of-flight mass spectrometer for vapor detection of explosives

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Abstract

Direct vapor detection of explosive compounds has been achieved with the development of atmospheric flow tube-mass spectrometry (AFT-MS). The AFT-MS has demonstrated the detection of low parts-per-quadrillion levels with a quadrupole based mass spectrometer using selected ion monitoring (SIM). [1,2,3] This presentation presents the results of interfacing the AFT to a time-of-flight (TOF) mass spectrometer. The TOF provides two major advantages over a quadrupole system: 1) the TOF provides higher resolution resulting in accurate mass determination potentially reducing false positives and 2) the TOF provides an entire mass spectrum at once compared to the peak hopping of SIM in a quadrupole. The increased resolution provided by the TOF was expected, however, the relative sensitivity of the TOF compared to SIM in a quadrupole was unknown. This comparison was the main objective of this endeavor. In this study, an AFT developed at the Pacific Northwest National Laboratory (Richland, Washington USA) was interfaced to an L-TOF Time Of Flight mass spectrometer at Karsa (Helsinki, Finland). The result of this integration will be presented. The greater than expected sensitivity is due in part to the increased resolution of the TOF-MS which collects the ion signal within a much smaller mass distribution, thus increasing the signal-to-noise. In summary, the AFT-TOF-MS provided explosive vapor detection sensitivities similar to (and possibly better than) a quadrupole based system in SIM mode, even with a smaller orifice in the TOF-MS.

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3D-printed, multi-sorbent solid phase extraction and high-resolution trace chemical analysis for explosives in complex matrices

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Abstract

Complex sample types often contain significant matrix interferences that can challenge routine trace explosives detection. The aim of this work was to design and optimise a 3D-printed solid phase extraction (SPE) array to be used both in the lab or at scene, to simultaneously remove unwanted matrix from a range of sample types, whilst efficiently extracting target explosives prior to analysis with liquid chromatography-high resolution mass spectrometry (LC-HRMS). A fritless, 3D-printed SPE cartridge was designed and optimised without sorbent bleed or leaking (Fig. 1). Blocks could be 'clicked together' in series, enabling rapid assembly of sample-dependent, multi-sorbent SPE approaches for multiple different sample types. Recoveries in model solutions using these cartridges packed with Biotage Isolute® ENV+ sorbent showed promising results, with recoveries in the range 15 – 69 % for 14 selected explosives analytes, including peroxides, nitramines, nitrate esters and nitroaromatics, and a 20-fold concentration factor. In terms of precision, relative standard deviations for replicate extractions were from 2-12 %. The method was then applied to three selected complex matrices; dried blood, cooking oil residues and soil. By removing additional matrix components, a dual or triple combined-sorbent SPE approach enabled detection at the low picogram-on-column level. Additionally, the on-site sample preparation potential of miniaturised SPE is highly advantageous, minimising the chance of losing explosive analytes through evaporation or degradation and enhancing the likelihood of forensic detection.
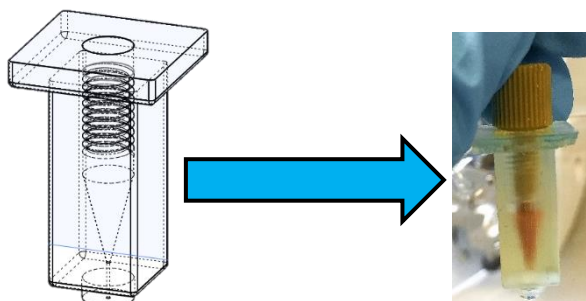
Figure 1: *CAD drawing of optimised sorbent block design (left) and the final 3D-printed part packed with selective extraction sorbent (right).*

Phthalate detection by APCI ion mobility spectrometry

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Abstract

In this work we have studied three phthalate molecules, concretely dimethyl phthalate (DMP), diethyl phthalate (DEP) and dipropyl phthalate (DPP), using Ion Mobility Spectrometry (IMS) with ion source based on Atmospheric Pressure Chemical Ionisation (APCI). We determined IMS spectra for mentioned phthalates. This study also shows ability of APCI-IMS technique for separation of DMP and DEP phthalates from prepared mixture. Phthalates are esters of phthalate acid and are widely used in many products of daily use, for instance building materials, furnishing, personal care products, cosmetics, food wrapping, coating of pharmaceuticals, medical devices or children's toys. [1] These chemical substances are adding into plastic products for increasing their life time, durability, transparency and flexibility. The main use for phthalates is softening of polyvinyl chloride (PVC), which is commonly used as flooring material. In recent studies are shown that some phthalates are toxic for animal's reproductive systems [2].
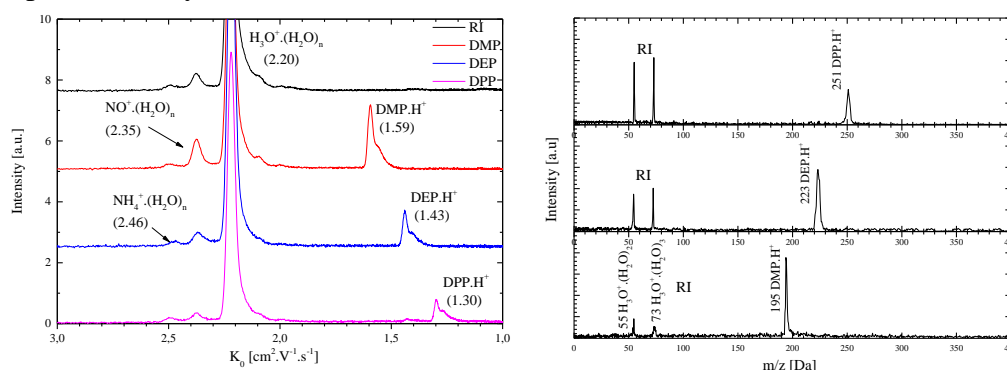
Figure 6: IMS and MS spectra of investigated phthalates

We have observed unique reduced ion mobility peaks for each molecule. For DMP is reduced ion mobility peak $1.59 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, for DEP $1.43 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and for DPP $1.30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (Figure 1). After separation of molecules we have tried detection of analysed phthalates from mixture. We were able to separate DMP and DEP from the mixture. DPP peak was not occurs in the final IMS spectrum. We assume that ion-molecule reactions between RI and molecules DMP or DEP are faster than reaction between RI and DPP.

Acknowledgements

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Rapid quantitative analysis of volatiles in oak wood by Ion Mobility Spectrometry

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Abstract

Corona Discharge used in Ion Mobility Spectrometry (CD-IMS) as an APCI source allows to detect compound (whisky lactone) present in oak wood which is one of the main factors responsible for unique flavour of whisky. In this study we present results for whisky lactone using CD-IMS coupled with mass spectrometer.
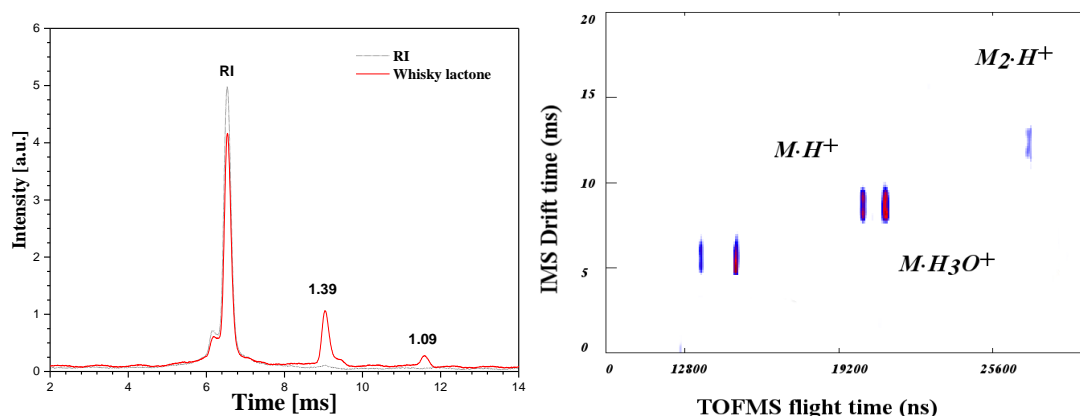
Figure 7 IMS (left) and 2-dimensional map (right) spectra of whisky lactone

Whisky lactone which has aroma of celery, coconut or fresh wood is not only present in whisky but also in other alcoholic beverages that have been matured in oak barrels. Barrel staves are classified in ten categories depending on the concentration of whisky lactone (first category: 0-7 µg/g while tenth category: 63-70 µg/g) of course more of lactone in wood is desirable. In case of whisky lactone IMS spectrum reveals two peaks with reduced mobilities 1,39 and 1,09 $cmV^{-1}s^{-1}$. Mass spectrum of whisky lactone shows three major peaks with m/z= 157, 175 and 313 which correspond to $M \cdot H+$, $M \cdot H_3O^+$ and dimer $M_2 \cdot H^+$ respectively. Finally, 2D map shows that monomer ions are related to peak with 1,39 $cmV^{-1}s^{-1}$ and dimer ion with 1,09 $cmV^{-1}s^{-1}$ in IMS spectrum. [1-2]

Acknowledge

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Headspace characterisation of firearms and ammunition

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Abstract

To enable optimal vapour detection of materials, it is necessary to understand the volatile and semi-volatile compounds they release into their headspace.

In the work presented, bespoke methods for the sampling of the volatile headspace emitted from firearms and ammunition will be discussed. Thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) is employed to analyse and identify the sampled headspace components, generating a data-rich profile of samples.

A range of firearm types and component parts have been sampled at different usage points (before / after firing and after cleaning) to improve understanding of the effects of routine operation on headspace profiles. These therefore contain components from many sources including gunshot residue, maintenance procedures and handling. The headspace is affected by external factors such the storage environment and time since firing or handling.

This poster will demonstrate how the headspace profile of a firearm can change in different situations and conclusions drawn from this data. Future work will investigate how more complex methods for data interpretation would enable further insights to be made.
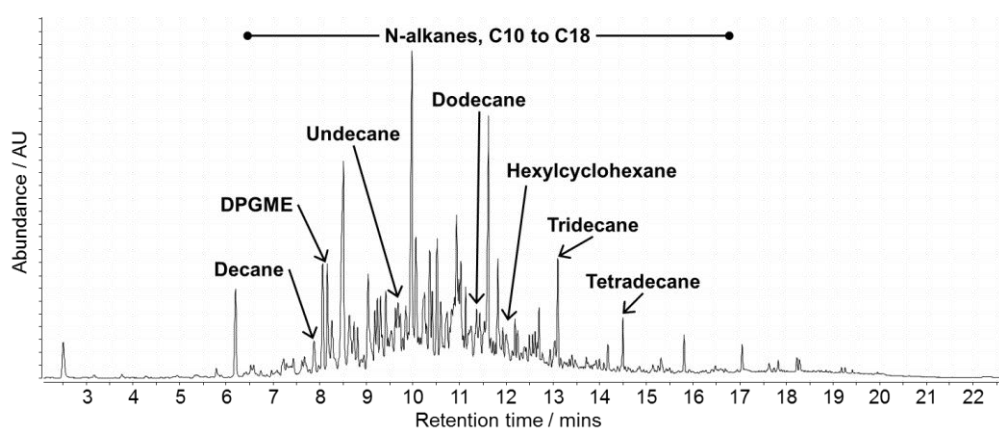
Figure 8 Vapour headspace of an assault rifle. NIST library (v1.4) assignments of dominant hydrocarbon components are shown. N-alkane structural isomers are indicated by the range bars.

Evolution and Developments of Proton Transfer Reaction-Mass Spectrometry for Security Applications

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Abstract

Proton Transfer Reaction-Mass Spectrometry (PTR-MS) is a broad-based technique that has proved its analytical use for fast trace explosives detection.[1,2] It has been almost a decade since the first publication for explosives detection came to light.[1] From that moment on, the PTR-MS technique has developed into a more multidimensional technique, overcoming the challenges for achieving fast, selective and sensitive detection of threat agents for security applications. For such a journey to be sucessful, hardware developments had been necessary. Among these, this talk will revise the developments of a)- new inlet unit based on commercial swabs allowing no (or minimun) memory effects; and new methodologies for improving selectivity, based in enhancing collisional induced dissociation in a controlled way by manipulating the ion-molecule chemistry within the drift tube of a PTR-MS, through b)- the use of a radio frequency ion-funnel (RFIF) DT,[3] and c)-rapid switching (less than a microsecond at a frequency of 0.1-10 Hz) of the reduced electric field.[4] All these improvements translate into allowing identification of a compound of interest with higher specificity in complex chemical environments.

Finally, all these recent developments have been combined and recently applied to the detection of organic additives used in smokelss powders,[5] expanding thus the range of compounds and applications where PTR-MS can be used as the detection tool.

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