ANALYTICAL METHODS FOR MONITORING OF STABILISERS

SUPERVISORS

**Flinders University**  Dr Claire Lenehan  (claire.lenehan@flinders.edu.au)

**DSTO**  Dr Chad Prior  (chad.prior@dsto.defence.gov.au)

**Thales**  Dr Stephen Njuguna  (stephen.njuguna@thalesgroup.com.au)

It has been well documented that propellants made from nitrocellulose and nitroglycerine type materials are not stable, and that during storage they start to degrade, releasing nitrogen oxides. This process accelerates over time as a result of auto catalysis. As a consequence stabilizers such as diphenylamine (DPA), 2-nitrodiphenylamine, car bamite are akardite added to the propellant in order to prevent or retard the degradation. These stabilisers act by readily reacting with nitrogen oxides and thus preventing autocatalytic decomposition from occurring. Due to this consumption of the stabilisers by nitrous oxides, there is increased risk of degradation as the propellant formulation ages. Consequently analytical methods for the determination of stabiliser content are important and can be used to give an indicator of propellant ‘health’.

Monitoring of propellant formulations and the degradation of propellants is often achieved with HPLC with a variety of detection methods. Recently HPLC has undergone a movement towards rapid separations with the use of either monolithic columns or ultra high pressure systems in conjunction with reduced particle size stationary phases. The determination of diphenylamine from a mixture of amines has been achieved with a monolithic column in under 4 minutes.

This initial study proposes an investigation into the use of FTIR in conjunction with chemometric analysis along with square wave voltammetry for the determination of stabilizers in propellants. Results will be compared with those obtained using HPLC with standard and monolithic columns. The use of Stable Isotope-Ratio Mass Spectrometry (SIR-MS) for the analysis of military and home-made explosives. The aim of this work is to determine the possibility of matching an explosive, military or home-made, to the precursor used in the manufacturing/synthetic process and point of origin.
THE USE OF STABLE ISOTOPE-RATIO MASS SPECTROMETRY (SIR-MS) FOR THE ANALYSIS OF MILITARY AND HOME-MADE EXPLOSIVES

SUPERVISORS

Flinders University  Prof Stewart Walker  (stewart.walker@flinders.edu.au)

DSTO  Dr Simon Ellis-Steinborner  (simon.ellis-steinborner@dsto.defence.gov.au)

Isotope Ratio Mass Spectrometry (IRMS) will be used to probe the exact composition of energetic materials. This project will continue on from work that has been undertaken in the application of IRMS to explosive and drug analysis to determine starting material, synthetic routes and confirm place of origin. If the initial stages are completed successfully, IRMS will be combined with analysis by LA-HR-MC-ICPMS as the combined techniques will extend the range of isotopes that can be investigated beyond the C, N, O, H and S that are available from light IRMS to include other stable isotopes of Lithium, Zinc, Lead etc.
2,4-dinitroimidazole is an explosive compound with good thermal stability, impact sensitivity and performance. This material is most conveniently prepared by a thermal re-arrangement of 1,4-dinitroimidazole, a material which is considered insensitive. According to the scientific literature, this re-arrangement is thought to occur via a 1,5-sigmatropic re-arrangement (Grimmett, 1989).

A project is proposed to examine the effects of various catalysts on this 1,5-sigmatropic re-arrangement, in particular Lewis acids and light, both of which are known to influence such reactions. In addition investigations into substituted imidazoles would be of interest with a view to decreasing the activation barrier between the 1,4- and 2,4- dinitro materials. Such a decrease would be observed in the lowering of the temperature required for reaction and would increase the suitability of these materials to in situ generation of energetic materials.
This project will involve plasma polymer coatings of explosive materials such as RDX. These nanometric coatings could improve mechanical properties and afford desensitisation. In the first instance, allylamine, hexylamine and acrylic acid will be used as monomers. We will use our RF plasma reactor to prepare the coatings and will use atomic force microscopy to study coating morphology. Mechanical properties and explosive sensitivity to discharge and friction will be studied at DSTO.
THE COLLECTION AND PRESERVATION OF AIR SAMPLES FOR THE DETECTION OF PATHOGENS

SUPERVISORS

*Flinders University*
- Prof Andy Ball (andy.ball@flinders.edu.au)
- Dr Claire Bird (claire.bird@flinders.edu.au)

*DSTO*
- Dr Arthur Provatas (arthur.provatas@dsto.defence.gov.au)

FTA paper, as developed by Leigh Burgoyne, School of Biological Sciences, Flinders University, is used worldwide for transportation of nucleic acids for forensic applications. Additionally, it is offers a suitable storage system for nucleic acids by preventing their degradation under standard temperature and pressure. The application of FTA paper as a collection surface for airborne viral and bacterial pathogens has been successfully trialled at Flinders, using tobacco mosaic virus as a surrogate pathogen, and this project is intended to take this proof of concept into a field situation.

The MS2 virion is a laboratory non-pathogenic coliphage used to simulate enteric human pathogens and will be cultured, aerosolised and used as a positive control for human pathogen detection. Air will then be sampled following explosion and spraying of a culture of MS2 in the field, with the assistance of DSTO. The sample will then be analysed by real-time qPCR to examine the dispersal of virulence factors. This will be carried out either by applying qPCR with specific primers, or by microarray analysis subsequent to multiplex PCR, using a platform containing probes for virulence factors from *Aeromonas hydrophila* and *A. caviae* with aerosolised MS2 as a positive control.
THE USE OF LASER IONISATION BREAKDOWN SPECTROSCOPY (LIBS) FOR THE ANALYSIS OF MILITARY AND HOME-MADE EXPLOSIVES

SUPERVISORS

*Flinders University*  Prof Stewart Walker  ([stewart.walker@flinders.edu.au](mailto:stewart.walker@flinders.edu.au))
*DSTO*  Dr Ben Hall  ([Benjamin.hall@dsto.defence.gov.au](mailto:Benjamin.hall@dsto.defence.gov.au))

The use of Laser Ionisation Breakdown Spectroscopy (LIBS) for the analysis of military and home-made explosives. The aim of this work is to determine the possibility of detecting and identifying trace amounts of military and home-made explosives from surfaces for forensic purposes. LIBS shows great potential (because of its relative size, simplicity of operation, cheapness and mobility) but it can suffer from problems of reproducibility, fluorescence and swamping of spectra from compounds with a high organic content. This project will therefore attempt to optimise the LIBS by changing intensity of the laser, atmospheric gas, and time delay between laser shot and data recording to optimise the signal integrity of the LIBS. Other techniques will also need to be used to ground-truth the results from the LIBS.
Propellants used in small arms ammunition are typically coated with a deterrent that modifies its ballistic performance. Although this type of processing has been performed for over 65 years, little is known about the penetration characteristics of the deterrent in the propellant grain. To improve the ballistic performance of propellant requires an understanding of the location and concentration of the different chemical components in the propellant grain. It is important not only to determine the type and thickness of the coating but the concentration profile is also critical to the propellants ballistic performance.

Fourier Transform Infrared (FTIR) and Raman microspectroscopy are the most powerful methods for the determination of concentration profiles of inhomogeniously distributed compounds in gun propellants. This technique has been shown in the literature to be extremely useful in determining the location and concentration profile of deterrents in propellants. Raman mapping of these samples will be the starting point for this project to determine and then perhaps change the diffusion profiles leading to testing of energetic properties.