Network Developing Forensic Applications of Stable Isotope Ratio Mass Spectrometry Conference 2005

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Executive summary

On the 9th and 10th March 2005 a Forensic Isotope Ratio Mass Spectrometry (FIRMS) Network conference was hosted by the Forensic Explosives Laboratory at the Thistle Hotel, Brands Hatch, Kent. The conference was attended by approximately sixty delegates from forensic establishments, police forces, instrument manufacturers, service providers and academia.

Presentations were made together with key note addresses in four sessions. The conference also had the following objectives; to exchange information between the researchers and end users, to expand the network, to review the requirement, to assess the strategy for development and to chart progress since the last FIRMS conference.

This document summarises each presentation and the main points arising from discussions regarding the presentations as well as summarising the proposed "Next Steps" of the FIRMS Network.

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1 Introduction

1.1 Prof. Max Coleman of Reading University and Sean Doyle of the Forensic Explosives Laboratory (FEL), Dstl, formed the Forensic Isotope Ratio Mass Spectrometry (FIRMS) Network in 2002. The network was funded for three years by the United Kingdom (UK) Engineering and Physical Sciences Research Council (EPSRC) following a call for forensic network proposals under the UK Government Foresight programme. The EPRSC support period ended in July 2005 and a report issued.

1.2 As part of the continuing network development the second FIRMS conference, FIRMS 2005, was held at the Thistle Hotel, Brands Hatch, Kent on the 9th and 10th March 2005. Additional corporate sponsorship for the conference was provided by Dstl, Thermo Electron Corporation, GV Instruments, Pelican Scientific and Iso-Analytical Ltd.

1.3 A one day practical and theoretical workshop on Forensic isotope ratio mass spectrometry (IRMS) applications was held at the Forensic Explosives Laboratory, Dstl prior to the conference on the 8th March 2005 provided by Charles Belanger of Iso Analytical Ltd , Dr Wolfram Meier-Augenstein of Queens University Belfast and Dr James Carter of Mass Spec Analytical Ltd.

1.4 The conference was attended by over 60 delegates from forensic establishments, police forces, instrument manufacturers, relevant service providers and academia both within the UK and internationally. The conference aimed to bring together IRMS researchers, end users and instrument manufacturers. The objectives of the conference were to:

- Exchange information between the researchers and end users.
- Expand the network.
- Review the requirement.
- Assess the strategy for development.
- Chart progress since the first FIRMS conference.

1.5 The conference was a mix of presentations and discussion sessions. A summary of each presentation and the discussions are given below.

1.6 Sean Doyle welcomed everyone to the second FIRMS conference and thanked participants for their continued support of the network. Dr Robin Hiley, Chief Technologist, Energetics Department, Dstl was then introduced as the chairperson for the first day.

2 Summary of Presentations – Session 1

2.1 The FIRMS Network – from the Early Years to Now – but what of the future?

Prof. Max Coleman, Postgraduate Research Institute for Sedimentology, University of Reading, Whiteknights, Reading, RG6 6AB, UK (and National Aeronautic and Space Administration, Jet Propulsion Laboratory, USA).

2.1.1 The first presentation aimed to review progress since the first FIRMS conference, suggest ways forward for the network and to introduce relevant topics for discussion in the final session of the conference.

2.1.2 The network, now known as FIRMS, was founded just over three years ago by ten members with a grant won from the EPSRC. Its scientific objectives included definition of characteristic ranges of isotope values for relevant manufactured chemicals, their heterogeneity, controls on these compositions, what could change the values, and thus identification of the limitations of this approach. The other aims were to identify analytical barriers to application of the technique, raise awareness of its potential and stimulate research. The network now has over 100 members, has held one previous general meeting in 2002, established a web-site, issued newsletters, produced a technical strategy document and formed three groups focusing on drugs, explosives and general forensics. The network has already had a positive impact which will be detailed in the final report to EPSRC. However, the aim of this paper is to act as an introduction to a discussion session. The purpose of the discussion is to harvest the opinions of those who really count; those who are attending this meeting. Frank input is required to effectively review the network and its work to date, and to capture future requirements.

2.1.3 Sean Doyle thanked Professor Coleman for his talk and led the discussion following his opening remarks. Mr Doyle mentioned that a challenging agenda had been set and that progress had been made in some areas but unfortunately not in all.

2.1.4 A question from the floor was asked about how IRMS had been challenged in court.

2.1.5 IRMS data has been presented in court on a number of occasions and in a number of jurisdictions but, to date, no challenge of this evidence type has been made. Where the data has been included and taken with other evidence suspects have pleaded guilty. The IRMS community eagerly awaits the challenge of this evidence type recognising this as an important part of the validation process. Forensic validation is a key stage in the forensic application of this technique.

2.1.6 A discussion arose on the topic of forensic intelligence with regards to the quality of information. The general opinion is that if forensic intelligence is to be presented as evidence in court, then it must be of the same high standard as that required for forensic evidence. There is the risk of a miscarriage of justice if an investigation is misdirected as a result of flawed intelligence. A debate arose regarding the ‘end user’ of forensic intelligence/evidence. It is not always clear who the ‘end user’ is, e.g. the investigator or a court of law, and what the requirements are. It may be that we need to take

responsibility for quality in our own areas and robustly advise end users so as to avoid misdirected investigations and potential miscarriages of justice. This is an important topic that needs to be debated by investigators and forensic practitioners.

2.1.7 The point was then made that IRMS will not reach its full potential until databases are established. There is a need to understand and reach a consensus on what controls are required for database population and management.

2.1.8 This led to a discussion regarding databases and the cost of development which will be large (certainly many £100k). The cost of establishing a database will depend on a number of factors including the development of the techniques and what the likely range is going to be. It would be useful to use orthogonal techniques in building databases and not just IRMS alone. This would require additional dimensions to the database. The use of orthogonal techniques will of course increase the cost of building and maintaining databases. Such databases will need to be continuously updated, with new products being constantly added. It was considered that these tasks are too burdensome for one country/institute to complete alone. The cost and burden will need to be shared, possibly using higher education institutes to help populate the database. It was generally felt that we need a high profile event in order to raise the public profile of the technique to ensure funding is forthcoming.

2.1.9 Views on the next steps included ensuring that the methods employed are giving accurate results so that there is confidence that databases are populated with valid data. It was pointed out that if IRMS data is being presented in court then that data must be valid, if so then this data is fit to be used to populate databases. It was also pointed out that some small databases already exist and a mechanism for further population and the sharing data should be explored. The discussion ended with consideration being given to how a government owned database can be shared by the wider scientific community and how to promote collaboration between governments regarding ownership of databases.

2.2 Analysis of Explosives by Isotope Ratio Mass Spectrometry – An Australian Perspective

Sarah Benson, Australian Federal Police, GPO Box 401, Canberra, ACT, Australia 2601

2.2.1 *"In Forensic Science it is generally not possible to distinguish one source of the same substance from another. As a result, in the case of explosives, if the explosive residues identified at a scene cannot be differentiated from a known source of explosives (e.g. in the possession of a suspect) the strongest conclusion reported is that they are chemically the same substances. However, the question often arises: could they have originated from different sources? Stable isotope ratio mass spectrometry (IRMS) shows the potential to be able to differentiate between different sources of the same substance. The Australian Federal Police (AFP) is in the process of developing, optimising and validating methods for the analysis of explosives using IRMS. Once methods are validated, a range of different explosives will be analysed from manufacturers in the region to determine if it is possible to differentiate substances from different manufacturers and different batches. Field experiments will be conducted and post-blast samples analysed by IRMS for comparison with the pre-blast samples. The aim is to create an explosives database incorporating products manufactured in Australia and the South-East Asian region. An Australian aspect will be presented, highlighting the types of explosives commonly encountered in Australia and the South-East Asian region. Some preliminary IRMS results and the development of a suitable database will be discussed."* (From presenter's supplied abstract).

2.2.2 This presentation gave a background of the AFP in Canberra, federal crimes and also an overview of the AFP IRMS project including their method of calibration, problems encountered with setting up their laboratory for IRMS analysis, the range of evidence types, trace analysis, accelerants and explosives. The presentation also described how they were trying to establish a database of different explosives received from different manufacturers including the military plastic explosive PE4.

2.2.3 In discussion, Miss Benson mentioned that co-operation with Australian manufacturers had been relatively easy as they were happy to assist providing they knew what the samples were for. In reference to the challenge of setting up an IRMS instrument and incorporating it into a current laboratory, it was thought that perhaps the AFP and FEL could write a list of problems encountered and solutions found which could be distributed to FIRMS members.

2.3 Preliminary studies of smokeless powders using molecular and stable isotopic analysis

Ryan Brogden, Curtin University of Technology, Australia

2.3.1 *"Smokeless powders and their residues may be found at crime scenes where a firearm has been discharged or an improvised explosive device (IED) such as a pipe bomb detonated. The unambiguous matching of the original powder or residues found at the scene, with original material and residues found on a possible suspect, will facilitate forensic investigations into provenance establishment of this material and confident prosecution of offenders. While traditional analytical methods such as SEM-EDX, GCMS, HPLC and more recently CE have been variously applied to the identification of both organic and inorganic constituents of powders, all these techniques still lack definitive specificity and the ability to provide unambiguous data with which to ensure prosecution. This preliminary study combines the techniques of pyrolysis (Py)-GCMS and EA-irMS to discriminate between a set of smokeless powders. (Py)-GCMS is used to identify differences between relative ratios of the combustion products of the smokeless powder, while bulk stable isotopes of carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) in the residues are compared using EA-irMS. The data is interpreted using a combination of statistical techniques to ensure positive identification and discrimination between all smokeless powder samples investigated in the study. The study involved the analysis of 7 different smokeless powers containing a variety of constituents including nitrocellulose, nitroglycerine and stabilisers. Pyrolysis (Py)-MS indicated the presence of up to 22 different compounds from the pyrolysis of these 7 powders. Analysis of the detected species in each sample re-run against the set of 7 reference samples gave a good correlation match (e.g. 'A' compared with 'A' = 98.4%). However, samples with a similar composition also gave a good correlation with each other (e.g. 'A' compared with 'F' = 95.2%)."* (From presenter's supplied abstract).

2.3.2 EA-IRMS was used to attempt to differentiate samples. Using the carbon isotope ratio alone was not sufficient, but carbon and nitrogen isotope ratios combined gave distinguishable results.

2.3.3 The presentation concluded that by using a combination of techniques the detection, identification and provenance establishment of smokeless powders was possible.

2.3.4 Discussions centred on linking unfired powder with fired residue and whether isotope signatures would be conserved. This was thought to be a significant challenge, as the isotope ratio would be expected to change, but the degree of change would be uncertain. In addition, there could well be un-reacted powder present. This area of work is planned to be the next step.

2.3.5 Mr Brogden mentioned that they did not need to break propellant grains in order to introduce them into the quartz tube for (Py)-GCMS. On the issue of mixed grains, he stated that heterogeneity was not observed within the sample.

2.4 Cl and O isotopic characterisation of perchlorate: lessons learnt mutually between Explosives and Environmental applications.

Prof. Max Coleman, Postgraduate Research Institute for Sedimentology, University of Reading, Whiteknights, Reading, RG6 6AB, UK (and NASA, Jet Propulsion Laboratory).

2.4.1 *"The impetus to develop a method for isotopic analysis of Cl in perchlorate came from the need to characterise explosives. This led to the environmental application of the method to the problem of small amounts of perchlorate in groundwater. Environmental applications drove further developments: ability to analyse trace amounts, oxygen isotope characterisation ($\delta^{18}O$ and $\delta^{17}O$) and quantification of the isotopic effect of microbial reduction. For explosive forensic use, solid perchlorate now can be characterised by its chlorine and oxygen isotope compositions and heterogeneity within and between crystals. There is now the possibility to apply the method to trace perchlorate. If there is sufficient total material for analysis it can be concentrated using a specially developed bifunctional anion exchange resin. Especially for trace perchlorate, there is the possibility of microbial change of the initial isotope signature by bacteria, which are almost ubiquitous. We have now measured this large isotope fractionation effect for oxygen ($\simeq$ -30‰) as well as for chlorine. This could provide a forensic challenge to isotopic evidence of source of material, but there is a counter, an easily applied test for expression of the functional gene used in microbial perchlorate reduction. Thus the two applications have proved to be mutually supportive."* (From presenter's supplied abstract).

2.5 Panel Discussion – Session One Speakers

Panel members: Prof. Max Coleman, Sarah Benson, Ryan Brogden and Dr Robin Hiley

2.5.1 Questions were put to the panel regarding the following: guidelines for setting up an instrument; the issue of residues being compared with bulk material, and whether this was valid; microbial degradation and whether this affects the forensic work and concerns raised by Miss Benson with regards to method validation.

2.5.2 With respect to microbial degradation and whether it was worth trying to stop it, some panel members were not convinced that this actually happens but it is mentioned in the literature and will have to be addressed as part of the development strategy. The argument may be raised that microbial degradation has occurred and therefore the results are not representative of the original sample. However, microbial degradation could be turned around and used to our advantage – bugs are very particular about what they eat and how they eat it. Thus, this phenomenon could be used to monitor reactions, contaminants in soil, and used, for example, in breath tests.

2.5.3 The question as to whether anyone had done any comparison work on post-explosion residues and bulk material was put to the floor. Professor Ehleringer announced that he would be covering some work they have done in this area in his talk the following day. It was also suggested that some explosives, for example nitro-glycerine, also suffer microbial degradation.

2.5.4 Miss Benson had some concerns with regards to method validation and told the audience that she intended to produce a plan for this and would distribute it to the FIRMS network for peer review. This led onto a discussion regarding international standards and it was suggested that sucrose should not be used as a standard for explosives, rather it would be preferable to use 'like for like', for example, an RDX standard for analysis of RDX. Obtaining standards for more basic materials is difficult and obtaining explosives standards may be more problematic. The opinion amongst some of the delegates was that there should be an international standard method for IRMS analysis and that the principles laid down in ISO17025 were not entirely sufficient to satisfy our purposes and would need to be adapted.

2.5.5 A number of delegates highlighted problems setting up their own instrumentation and the question was put to the panel and all those present as to whether there could be some guidelines issued for setting up an instrument in addition to the manufacturer's pre-instalment manual. This is an area where networking between laboratories would be of benefit.

2.5.6 The issues of staffing and skill levels were also raised; the technical challenges of the technique are considerable and these issues need to be addressed. It was suggested that there is a correlation between staff turn over and the quality of the results. The promotion by the FIRMS network of inter-laboratory visits for training and a review of facilities was proposed.

2.5.7 The panel was asked about using a combination of techniques and whether this is beneficial. The selection of techniques depends on requirements. IRMS will be added to the techniques available to the forensic scientist.

3 Summary of Presentations – Session 2

3.1 Evaluation of preliminary isotopic analysis (^{13}C and ^{15}N) of explosives. A likelihood ratio approach to assess the links between semtex samples through a Bayesian framework

Georges Pierrini, Insitut de Recherche de la Gendarmerie Nationale, France

3.1.1 *"Currently the use of isotopic ratio as corroborative evidence in criminal trials is explored. Beyond the analytical challenges that have been reported elsewhere, the crucial issue of the interpretation of analytical results in a fair and balanced way remains poorly documented. The aim of this presentation is to propose a likelihood ratio approach for the evaluation of stable isotope data acquired from semtex samples which takes place in a Bayesian framework. It is proposed that these data are evaluated using a likelihood ratio framework that has received increasing attention in the past 15 years in all areas of forensic science. The main advantage of the approach is that it forces the scientist to assess the respective likelihood of the data under a competing set of propositions. That mechanism allows a balanced assessment of the contribution of the findings in the criminal proceeding. It is proposed to explore data with common statistical tests before introducing three continuous models."* (From presenter's supplied abstract).

3.1.2 This presentation introduced the network to the issue of statistical analysis of IRMS data, in particular outlining a likelihood ratio approach using a Bayesian framework. Six replicate analyses (n=6) of 26 semtex samples (m=26), assumed to have come from different sources, were described. Two isotopes ratios (C,N) were considered (p = 2).

3.1.3 Hotelling's significance test conducted on p variables can determine whether there is a significance difference between two set of measurements, semtex A and semtex B (with respectively n_a and n_b replicates).

3.1.4 The T^2-statistic has a scaled F-distribution such that:

$$T^2 \sim \frac{(n_a + n_b - 2)\cdot p}{n_a + n_b - p - 1} \cdot F_{p, n_a + n_b - p - 1}$$

3.1.5 Where in this case, $n_a = n_b = 6$ and $p = 2$.

3.1.6 Thus $(n_a + n_b - 2)\, p / (n_a + n_b - p - 1) = 20/9$ and the F-distribution has (2,9) degrees of freedom. The significance test can then be determined by evaluating T^2, multiplying the value obtained by 9/20 and referring the result to the F-distribution with (2,9) degrees of freedom at the $\alpha = 5\%$ point using statistical tables or software. Using Hotelling's T^2-test, proposition Hp : "semtex A and semtex B samples come from the same bulk source" is not rejected if the outcomes of the tests are not significant at the $\alpha = 5\%$ level.

3.1.7 The testing procedure, based on Hotelling's T^2 for the 26 semtex samples was found to have 17 false positive results over 325 tests. The presentation explained however, that

while Hotelling's-T^2 tests are suitable for statistical comparison between two sets of measurements, their use in the forensic context suffers some problems. One is that the hypothesis failed to incorporate relevant information, such as the relative frequency of the isotopic ratios. In addition, hypothesis testing does not answer the questions in which the court is interested.

3.1.8 The use of Likelihood ratios was described. The likelihood ratio approach calculates the probability of the outcome of a comparison between the control and the recovered samples based on a given set of isotopic measurements (E) given two competitive propositions, for example:

Hp , The control (A) and recovered (B) semtex samples come from the same bulk source

Hd , The control (A) and recovered (B) semtex samples come from different bulk sources

3.1.9 There are three inter-related factors that determine the nature of the inference: the number of replicate measurements; within-source variation; and between source variation.

$$LR = \frac{Pr(E|Hp)}{Pr(E|Hd)}$$

3.1.10 The numerator addresses the probability of the observed degree of correspondence between recovered and control, taking into account within-bulk source variations (the variation that is observed between isotopic values obtained within replicate measurements from the same bulk sample). The denominator addresses the probability of the observed degree of correspondence taking into account between-bulk source variations (the variation of the isotopic ratio among semtex from different origins).

3.1.11 The data was analysed using three alternative multivariate methods described as MVN, MVH and MVK. In each method, the proposition Hp is supported if the likelihood ratio is greater than 1. In all cases shown, when the semtex came from the same source, there was no misleading evidence in favour of the proposition that the semtex samples were from different sources when Hp was true.

3.1.12 In the converse case, when the proposition that the semtex samples came from different sources was true (Hd was true) the three methods produced cases of misleading evidence in favour of the proposition that the semtex samples came from the same source (LR > 1). We have a rate of misleading evidence of 37/325, 36/325 and 18/325 respectively for MVN, MVK and MVH.

3.1.13 In an evaluative approach, the LR directs the scientist to express conclusions in terms of degree of support for Hp versus Hd.

3.1.14 In this study of semtex samples, the misleading evidence rate of 5.5% is high and caution would be necessary in the scientist's statement. However the subpopulation of semtex used in this study could have come from the same sources or from the same batches. For these reasons it is very important to disclose the history of the origin of explosive matter.

3.1.15 George Pierrini considered that a continuous likelihood approach for multivariate (isotopic ratios) data evidence is considered to have a great potential in evaluative approaches in assessment of links between semtex samples.

3.2 Interpretation of 1st FIRMS Inter-laboratory IRMS analytical exercise 2004

Mr Sean Doyle, Forensic Explosives Laboratory, Defence Science Technology Laboratory (Dstl), Fort Halstead, Sevenoaks, Kent, TN14 7BP

3.2.1 *"The FIRMS Network agreed at the May 2003 workshop that an inter-laboratory collaborative exercise to evaluate repeatability and reproducibility of results obtained using different IRMS methods in different global laboratories should be undertaken. The collaborative exercise took place during May – July 2004. Two samples, 'Flour A' and 'Sugar A' were prepared by Iso-Analytical Ltd and were distributed to the 16 participating laboratories by the Forensic Explosives Laboratory. 'Flour A' required analysis for carbon-13 and nitrogen-15 with each isotope being measured separately i.e. no dual carbon/nitrogen, and 'Sugar A' required analysis for carbon-13. Each laboratory was required to measure each sample 10 times for the relevant isotopes against their own in-house standards, and was also advised to measure traceable international references as controls. When reporting the data, participants were asked to provide the carbon-13 and nitrogen-15 values in terms of δ13C vs V-PDB (‰) and δ15N vs air (‰) respectively. They were also asked to provide details and values of the control samples measured, details of the in-house reference materials used, their assigned delta values and brief details of the instrumentation used."* (From presenter's supplied abstract).

3.2.2 An interpretation of the resulting data from this 1st inter-laboratory exercise was presented for discussion.

3.2.3 The raw data sets of results were compared to the set obtained by Iso-Analytical Ltd. and described graphically indicating outlying laboratories where applicable. A Youden test for outlying laboratories was described with the results indicating that of the 14 laboratories used for this analysis, 8 laboratories were accurate at less than 0.15‰, 11 laboratories were precise at less than 0.11‰. These results are very encouraging; the carbon results being particularly impressive, given that the participating laboratories are using different instruments, methods, standards and working conditions. This is still work in progress.

3.3 Panel Discussion – Session Two Speakers

Panel members: George Pierrini, Sean Doyle and Dr. Robin Hiley

3.3.1 Questions were put to the panel regarding whether or not the methods used for carbon and nitrogen analysis were valid and whether the observed uncertainty could be attributed to the laboratory or to the raw data.

3.3.2 It was pointed out that means alone are insufficient; the uncertainties associated with the measurement made by each laboratory are required in order to correctly assess the data and, in particular, to determine whether or not laboratory means are from the same population. This will be the subject of further statistical analysis.

3.3.3 A question was put to the panel regarding the weight that could be attached to a particular result. Basically, if two samples match and the population variance is quite narrow, then it was thought that the evidence is very weak. However, if the population variance is wide, then matching results would provide very strong evidence. Nevertheless, the uncertainties would still need to be known as values from different sources are being compared.

3.3.4 This led to a discussion regarding presenting results and statistics to a jury and Mr Todd from the Forensic Explosives Laboratory proposed describing the information from a recent case to test views on what he would have said to the jury. This was accepted and after a break Mr Todd gave his 'explanation to the court'.

3.3.5 The issue of the precision of the nitrogen analysis from the inter laboratory collaborative exercise was raised and suggestions on how to improve this was discussed. Possible differences may arise from the way the samples have been prepared, the instrument, furnace, temperature and conditions may also all have an effect. It was thought that this should be looked into in more detail with the second inter laboratory exercise and if similar variation is seen with the nitrogen values then more information regarding the instrument conditions and methods will be required from the participating laboratories. If the nitrogen is variable, this raises other issues as to the usefulness of this data and how we interpret results.

3.3.6 The issue of outliers being rejected by software was raised. Outliers may be members of the population which we would ordinarily accept. It was thought that laboratory memory and experience would be important in making decisions regarding outliers. Not all present agreed with this scenario and preferred a statistical approach. In forensic investigations, outliers would quite likely be investigated further by other methods.

3.3.7 The discussion turned to the Bayesian interpretation of IRMS data. In terms of particular evidence types, such as DNA and fibres, the likelihood ratio approach is well established in the UK. The judiciary accepts that the issues of posterior and prior odds are not matters for forensic scientists but for the triers of fact.

3.4 A new Concept for isotope ratio monitoring LC/MS

Andreas Hilkert, Thermo Electron (Bremen) GmbH, Barkhausenstr. 2, 28197 Bremen, Germany

3.4.1 *"A new interface for the on-line connection of a liquid chromatograph to a stable isotope ratio mass spectrometer has been developed and tested. The interface enables the $^{13}C/^{12}C$ determination of organic compounds. The carbon content of the analytes is converted into CO_2 while the compounds are still dissolved in the liquid phase. This is accomplished by an oxidizing agent, such as ammonium peroxodisulfate. The CO_2 is separated from the liquid phase and transferred to the mass spectrometer. It is shown that the whole process does not introduce an isotopic fractionation. The measured carbon isotope ratios are accurate and reproducible. The Finnigan™ LC IsoLink is a completely new concept for isotope ratio monitoring LC/MS. First approaches for irm-LC/MS systems used a desolvating nebulizer or a moving wire system to separate the liquid phase from the sample before combustion. In the Finnigan LC IsoLink, the liquid phase is not removed from the sample prior to oxidation. The sample is oxidized still in the mobile phase followed by on-line separation of the CO2 from the liquid phase and transfer into the isotope ratio MS. In marked contrast to former approaches the processes in the LC IsoLink are quantitative and fractionation-free. The principle of the measurement and first results for two different injection modes (direct injection and HPLC injection) on reproducibility, linearity and accuracy were presented. Furthermore, first applications in the field of authenticity control of food and ingredients, investigation of the drugs and measurements of important compounds for biochemical studies were also presented."* (From presenter's supplied abstract).

3.4.2 Session 2 concluded with this presentation in which a new concept for isotope ratio monitoring (Irm) LC/MS was introduced and compared to that of Irm-GC/MS. Applications of the technique in foodstuffs, drugs and molecular biology were described and results of paracetamol and aspirin analysis given.

3.4.3 A question relating to the problem of sample solubility was raised. The problem is being investigated by methods such as wet oxidation, column-column measurements, stop flow principals, ramped measurements, transference of samples onto a pre-column, washing and then eluting onto an analytical column.

3.4.4 Liquid chromatographic separation of organic compounds may be possible using a water mobile phase at 150 – 180°C. At this temperature it was reported that the water can act like an (ambient temperature) 60% acetonitrile/water mobile phase.

3.4.5 In answer to a question on whether non-carbon containing solvents had been considered, the answer was yes, such solvents have been considered.

3.4.6 Dr Hilkert made a request for the FIRMS network to consider and recommend applications. Finnigan have a dedicated analyst and desire to widen their application field.

3.4.7 Mr Doyle gave his thanks to Dr Hiley for chairing the day's sessions and thanked all presenters for their contributions before closing the day with details of the conference dinner, kindly sponsored by GV Instruments and Dstl.

4 Summary of Presentations – Session 3

4.1 Dr Stroud of the Police Scientific Development Branch was introduced as the chairperson for the day and after his own welcome and introduction, he handed the floor over to the second keynote speaker, Prof. Ehleringer.

4.2 Forensic applications of stable isotope analyses

James Ehleringer, SIRFER, Department of Biology, University of Utah, 257 South 1400 East, Salt Lake City, UT 84112 USA

4.2.1 *"Stable isotope concentrations at natural abundance levels may prove useful in several areas related to forensics and to domestic and international terrorism. Today stable isotopes of carbon ($^{13}C/^{12}C$), nitrogen ($^{15}N/^{14}N$), oxygen ($^{18}O/^{16}O$), sulfur ($^{34}S/^{32}S$), and hydrogen ($^{2}H/^{1}H$) in both organic and inorganic compounds can be determined routinely using an isotope ratio mass spectrometer. These analyses can be performed on both bulk materials (organic and inorganic) and materials that have been purified from a mixture. Of particular interest in forensic science are applications of stable isotope ratio analyses where the information can be used to determine region-of-origin, authenticity, or relatedness of two or more materials of identical chemical composition. Stable isotope analyses have a rich history of application in the geochemical and biological sciences; they are just now being more extensively applied to forensic science. This talk explored the utilisation of stable isotopes to determine the region-of-origin in three key areas of forensic interest: (a) the geographic origins and movements of humans, (b) the manufacturing location of pathogenic microbes, and (c) origins of explosives recovered either as undetonated or detonated materials. Each of these cases highlight situations in which key information is recorded permanently in the stable isotopic composition of organic molecules that are of forensic interest."* (From presenter's supplied abstract).

4.2.2 Specific Isotope Analysis (SIA) can help detect adulteration e.g. food-stuffs, processing e.g. transformation of material (evaporation) and sourcing e.g. is it 'consistent with' or can we 'exclude'.

4.2.3 A number of cases were then outlined involving food adulteration, anthrax analysis, human remains together with geographical information and explosives analysis – pre and post-explosion comparison.

4.2.4 The relationship between the isotope ratio of bulk explosive and explosive residues was discussed in relation to trials with TNT, RDX, and PETN. Good correlation was observed when there was sufficient residue recovered although statistically the values differed by approximately 1‰. The explosive residue was, on average, slightly heavier isotopically than the bulk.

4.3 Forensic Stable Isotope Signatures from Biological and Non-Biological Materials

Wolfram Meier-Augenstein, Environmental Engineering Research Centre, Queen's University Belfast, Belfast, BT9 5AG, United Kingdom.

4.3.1 *"Stable isotope ratio analysis is well established in fields such as environmental science, geology, biology and oceanography but has limited forensic applications to date. It has become more established in forensic fields such as food adulteration and the arts but recent advances in stable isotope technology have opened up a wide range of forensic applications. Though the potential of using isotope signatures for forensic applications has been demonstrated by several research groups across the globe, applications using this tool as part of ongoing criminal investigations or forensically driven studies are still far and few between. Here, we present isotope data, interest in which was triggered by two ongoing criminal investigations, a murder enquiry and a case of perverting the course of justice, conducted by the Police Service Northern Ireland (PSNI) as well as a forensically motivated study of household and car paints carried out by the Forensic Service Northern Ireland (FSNI)."* (From presenter's supplied abstract).

4.3.2 In discussion, a question was raised about the paint examples and whether the different components were contributing to the different carbon signatures. Dr Meier-Augenstein commented that the resins and binders were probably man made based on linseed oil and that most of the paints appeared the same with the exception of acrylic paint but he mentioned that it had been difficult to get the exact composition from the paint manufacturer. He also mentioned that he would be looking into weathering effects and hydrogen isotope ratios, which might provide greater discrimination.

4.4 Bulk and compound specific isotopic characterisation of illicit drugs and drug packaging.

Dr James Carter, Mass Spec Analytical Ltd., Building 20F, Golf Course Lane, PO Box 77, Filton, Bristol BS99 7AR

4.4.1 *"A number of seized heroin samples and their cling film packagings were studied. The heroin was visually similar, the colour suggesting an origin in southwest Asia (Afghanistan). The samples were found to comprise mixtures of natural opium alkaloids (codeine, acetylcodeine, morphine, mono- and diacetylmorphine, noscopine and papaverine). The purity of the DAM was found to range from approximately zero to seventy percent. The most common cutting agents were caffeine, detected in all but one of the samples, phenobarbital, diazepam and acetaminophen. δ2H, δ13C, δ15N and δ18O analysis of the bulk heroin was able to distinguish between all but two of the seizures. However, bulk isotope ratios are readily affected by the addition of other components which may not be detectable by gas chromatography, e.g. proteins and sugars. Therefore, although bulk isotope analysis can establish links between seized samples it is not suitable for tracing a line of distribution from production to sale. δ2H and δ13C GC-IRMS data did not distinguish these two samples, suggesting that they originated from the same importation. Applying data reduction techniques, δ2H of caffeine and DAM was found to provide greater discrimination than the δ13C of the other components. Combining δ2H and δ13C data for DAM and caffeine enabled the majority of samples to be distinguished. The use of Solid Phase Extraction to recover trace heroin samples was found to produce degradation of the DAM to 0-6-MAM, 0-3-MAM and morphine. SPE was also found to cause isotopic fractionation of both the opiate molecules and the cutting agents, with respect to both δ2H and δ13C. Liquid-liquid extraction (from a phosphate solution pH 6.0) was less destructive and no degradation of DAM or MAM was observed. Storage time of solutions was found to affect the carbon but not the hydrogen isotopic composition. A range of commercially available cling films were analysed and found to divide into two broad groups, poly(vinyl chloride) and polyethylene. The majority of these samples were distinguishable by δ13C. All the case studies were correctly grouped according to the heroin seizure from which they were obtained by δ13C. However, it was necessary to employ multivariate analysis, incorporating δ2H, δ13C and δ18O to fully distinguish the samples from each other. Although GCMS data suggested that material leached between the heroin and the cling film no effect on the bulk isotopic properties of heroin was observed following a period of storage."* (From presenter's supplied abstract).

4.4.2 In discussion, Dr Carter mentioned that it was difficult to do work on the changes within a bulk sample as the samples they receive have already been homogenised by the Forensic Science Service (FSS). The MSA are planning a research project with the aim of developing a policing tool for court. Currently it is possible to determine that samples come from different sources but it is not so easy to say they are from the same source.

4.5 Comparison of Cocaine and MDMA Samples by Stable Isotope Ratio Mass Spectrometry (IRMS)

Helmut Neumann, Bundeskriminalamt, Forensic Science Institute, Central Chemistry Laboratory (KT12), D-65173 Wiesbaden, Germany

4.5.1 *"The presentation starts by explaining the mission of the Federal Criminal Police Office (Bundes¬kriminalamt) and its Central Chemistry Laboratory in the police system of Germany. In 1996 an isotope ratio mass spectrometer with an elemental analyzer was installed at the BKA Central Chemistry Laboratory. The isotope ratio measurements have been focused on the determination of carbon and nitrogen values. Tracing back of the determined delta (δ) - values to international standards and the multiple analysis of a quality control check sample in each sequence ensure accurate and reproducible data. After initial tests for the comparison of explosives (e.g. TNT samples of different origin) and of polymers (polyurethane foams) we concentrated on the comparison of cocaine and MDMA samples. Besides cocaine samples from big seizures in Germany we were fortunate to get samples from South America with documented origin for isotopic analysis. Concerning the major origin countries Bolivia, Colombia and Peru we observed an interesting shift of the δ15N values to higher numerical values for the Colombian samples of 2000 in comparison with the samples from 1985. Also for MDMA samples the δ15N isotopic values proved to be very valuable for sample comparison because of the large range we and others found for this parameter. A maximum of samples was detected around a δ15N value of +1. Finally the application of the developed method for comparison of MDMA samples in a proceeding of a Regional Superior Court is presented. In this case a judgement about the operation of a big clandestine laboratory for the production of MDMA had to be made. The result from sample comparison by IRMS was the crucial evidence to prove that at least two batches of MDMA had been produced. Future work will be directed to the exploration of gas and liquid chromatographic devices coupled to the IRMS instrument and the use of hydrogen and oxygen isotopic ratios from sample comparison in different forensic areas."* (From presenter's supplied abstract).

4.5.2 When asked about the possible source of the nitrogen variation, Dr Neumann said he thought it could have been a result of fractionation occurring at different stages of the reaction process. Different samples were taken from different stages in the process. The BKA get about 100 MDMA samples a year and are getting asked to do more and more each year. They are keen to get another analyst as the potential is there, but not the time to do the full research.

4.6 Panel Discussion – Session Three Speakers

Panel members: Prof. Jim Ehleringer, Dr. Wolfram Meier-Augenstein, Dr. Jim Carter, Dr. Helmut Neumann and Dr. Mark Stroud

4.6.1 Dr Stroud commented that at the last FIRMS conference the focus was on particular techniques and instrumentation whereas this time the focus seems to be on the variety of applications. It was discussed and this was noted as the current trend. Questions for the panel included whether IRMS could be used for hair analysis in combination with drug analysis to profile drugs, whether or not isotopic signatures were conserved post blast and whether there was scope for fine tuning the specificity of geographic location.

4.6.2 Addressing the drugs in hair question, Jim Carter mentioned that the MSA had had little success with this to date as solid phase extraction techniques affect the IRMS. He mentioned that using liquid-liquid extraction can give a very similar isotope ratio to the starting product but that samples left in buffer solution produced unusable results. Wolfram Meier-Augenstein mentioned he would like to try thin layer chromatography as a way of separating such components for IRMS analysis.

4.6.3 With regards to a question posed on geographical locations and fine-tuning the specificity, it was explained that it is possible to do this by combining IRMS with other techniques; the more discriminators you can get the better.

4.6.4 Prof. Ehleringer commented that it is not possible to place great confidence on the shift in isotope ratios between explosive residues from his study and the original sample at this time as it was questionable whether enough residue had been collected. The precision of measurements between residue and bulk were not observed to have changed, although standard deviations were much higher on individual measurements for the residue samples. No information was given with regard to degradation products as these were purposefully avoided.

4.6.5 Dr Stroud thanked the panel for their presentations.

5 Summary of Presentations – Session 4

5.1 Isotopic and trace element analysis of human tissues for provenance purposes

Kenneth Pye, Kenneth Pye Associates Ltd., Crowthorne Enterprise Centre, Crowthorne Business Estate, Old Wokingham Road, Crowthorne, Berkshire, RG45 6AW, UK.

5.1.1 "Isotopic and trace element data have been used for many years in geology and environmental science to facilitate stratigraphic correlation, determine sediment provenance, to elucidate a wide range of environmental processes, and forensic comparison of geo-materials. They have also been used extensively in life sciences, archaeology and anthropology, primarily to assist in studies of animal and human migration. Their potential for forensic science investigations of human tissue material has also been recognized for a number of years, but application to casework has been limited. Trace element and isotopic analysis of hair, skin and nail tissue can provide information about short-term diet and environmental exposure (days to months), while bone records dietary and environmental signatures over longer time periods, (a few months to a few years). Teeth provide a record of conditions mainly during the early years of life. On the case of buried remains, post-mortem alteration due to chemical exchange and diagenetic processes may be an issue and care needs to be taken in the selection and handling of material for analysis. In general, femoral cortical bone and tooth enamel are the materials of choice owing to their lower susceptibility to environmental exchange and diagenesis. However, other bones, such as clavicle, rib and ulna, have also yielded useful results, and analysis of several different bones can provide time series information. There are a considerable number of chemical characteristics which may provide useful forensic information. These include stable light isotopes, heavier radiogenic isotopes, radioactive isotopes, and elemental concentrations. H, O, C, N & S isotopes have been widely used in archaeological and anthropological research as indicators of climate and diet. Sr, Pb & Nd also provide useful indicators of environmental exposure, diet and geographical origin. Sr isotopes have been most widely used in this regard since strontium concentrations are relatively high and the main source of Sr in the body is food and drinking water. Radioactive isotopes can also provide useful information about geographical origin, for example in relation to geological terrains which contain uranium-rich rocks such as granites and shales, or proximity to nuclear weapons testing facilities, nuclear power stations and nuclear re-processing plants. Radiometric dating of individual minerals within human tissues may also be helpful in determining geographic provenance and environmental exposure. Elemental concentrations in bones and teeth have also been used as environmental indicators. Ba and Sr have been used as marine indicators, and Pb, Cu, Zn, Ni and Cd as indicators of local geology, diet and anthropogenic contamination, High levels of Pb, Cu, Zn, Ni and Cr may indicate exposure to natural mineralized geological terrain or source of industrial pollution. Elemental ratios (e.g. Pb/Zn, Zn/Na, Mg/Nz and Cr/Na) have proved useful in correlating body parts in multiple grave sites. Fluoride concentrations in teeth can also be used to differentiate areas where drinking water is high in fluoride, due either to geological reasons or to artificial fluoridation, and those where concentrations are low. Several analytical methods are available for isotopic and

trace element analysis of human tissue. While most are capable of providing high precision instrumental measurements, the data obtained are only as useful as the sample material provided. However, the major issue is one of data interpretation. Existing database information is patchy and of variable quality. However, this approach has been employed with some success in quite a number of serious crime investigations. Further research is required to better understand the degree and causes of variation within and between regional populations, to develop better databases. At present the information which can be obtained is generally suitable for intelligence rather than evidential purposes." (From presenter's supplied abstract).

5.2 LA-ICP-MS and IRMS investigations on packaging and duct tapes

Gerard J.Q. van der Peijl, Netherlands Forensic Institute (NFI), PO Box 24044, 2490 AA The Hague, The Netherlands

5.2.1 *"Results are presented for packaging and duct tape comparison experiments using the forensic IRMS (Isotope Ratio Mass Spectrometry) technique. Results will be discussed and compared with results using other new forensic techniques such as solution nebulisation ICPMS and LA-ICPMS. Time permitting some other forensic applications (polypropylene rope, paper, burnt polymers, isolation material from electricity wire) from our NFI forensic practice will be discussed. Brown packaging tape until recently was encountered in 60% of the violent crimes (murder, rape) committed in The Netherlands where tape is found at the crime scene. Nowadays grey duct tape is encroaching on the crime scene. Normally, the forensic scientist is requested to compare the tape retrieved from the crime scene with tape found with a suspect. At the NFI a combination of visual investigation (physical fit, tape dimensions, colour, morphology), FT-IR and XRF is used routinely to compare tapes. FT-IR can be used to identify the type of glue and backing polymer. A combination of visual comparison and XRF analysis generally suffices to discriminate between different tape products but cannot be used for further discrimination between different batches of one brand of tape product.*

Solution ICPMS *In earlier studies, the more varying adhesive layers of packaging tapes were investigated using both solution nebulisation ICPMS (Inductively Coupled Plasma Mass Spectrometry) and LA-ICPMS. With these techniques trace levels of elements are detected and identified. Solution nebulisation ICPMS experiments, especially, produced very discriminatory results. An Element (ThermoFinnigan) HR-ICPMS was used. For solution nebulization measurements, the glue (ca 50 mg) was first separated from the backing material through mobilisation in a solvent (methanol, hexane) and then digested in a microwave oven (75 bar, 290ºC) in a nitric acid/H2O2/H2O mixture. For the three investigated different packaging tape brands, commercial samples from the same tape product acquired at different times from one commercial outlet and at one time from different outlets could be discriminated on the basis of the solution nebulisation ICPMS results whereas visual comparison and XRF (macro elements) were not sufficient for discrimination between these tapes.*

LA ICPMS *Laser ablation measurements on intact packaging tape samples of the above rolls were made directly on the glue layer using a 266 nm Nd:YAG laser. Packaging tape samples were placed in the sample chamber and the glue layer was laser ablated. Volatiles and aerosols produced in this way were swept into the ICPMS system (low mass resolution mode). As optimal values a laser pulse energy of 2 mJ, a pulse repetition rate of 10 Hz, a spot size of 80 µm and an ablation distance (lateral shift of laser spot) of 30 µm were chosen. Laser spots were therefore partially (50 µm) overlapping. Signals were integrated for 60 seconds over a grid area of 1 mm2. Similar conditions were used for duct tape investigations where both the glue and the backing layers can be investigated independently.*

LA ICPMS *results for the different rolls of one brand of packaging tape demonstrate for each brand that discrimination power is sufficient to discriminate the rolls but is*

somewhat lower relative to solution nebulization results. In these experiments all tapes could be discriminated. Upon repetition of the LA ICPMS experiments for the three different rolls of one brand on another day the same distribution pattern is observed. The exact location of the distribution pattern is not exactly the same however, reflecting in our opinion variations in laser pulse energy observed during these specific experiments.

5.2.2 ***IRMS*** *(Isotope Ratio Mass Spectrometry) focuses on stable isotope ratios of abundant elements in the samples such as H, C and O (O only in the oxygen containing materials). Isotope ratios used were 2H/1H, 13C/12C and 18O/16O. Tape samples were analysed for us at Iso-Analytical Ltd (Sandbach, Cheshire CW11 3HT, UK). The IRMS used was a Europa Scientific Geo 20-20 instrument. All samples were measured in triplicate. Tape samples were prepared for analysis by separating the glue and backing layers which were analysed separately. Also complete tape samples, without further sample preparation, were analysed. IRMS conditions Hydrogen isotope analysis (ca. 6 mm2 tape sample) was conducted by total conversion at 1080 °C in a quartz reactor lined with a glassy carbon film, filled to a height of 180 mm with glassy carbon chips. Hydrogen was separated from other gaseous products on a GC column packed with molecular sieve 5A at a temperature of 30 °C. A Faraday cup collector array was used to monitor the masses 2 and 3. Carbon isotope analysis (ca. 5 mm2 tape sample) was conducted by EA-IRMS using a combustion furnace, reduction furnace and GC oven temperature of 1000, 600 and 90 °C, respectively. Oxygen isotope analysis (ca. 22 mm2 tape sample) was conducted by total conversion at 1080 °C in a quartz reactor tube lined with a glassy carbon film, filled to a height of 170 mm with glassy carbon chips and topped with a layer (10 mm deep) of 50 % nickelised carbon. Carbon monoxide and nitrogen were separated on a GC column packed with molecular sieve 5A at a temperature of 50 °C. Excellent IRMS results were obtained. For the three different packaging tape brands investigated, commercial samples from the same packaging tape product acquired at different times from one commercial outlet and at one time from different outlets could be discriminated on the basis of a combination of the δ13C and δ2H results. Alternatively, for the two oxygen containing packaging tape brands, samples could easily be discriminated using a combination of the δ13C and δ18O results. This could be done using either results for the full tape, the glue or for the backing material. Especially the latter is of great value since this means that, together with the glue, all other debris (blood, hairs, fibers) can easily be removed. The results even indicate potential for within production batch discrimination. For duct tape materials also good discrimination is obtained although we did not yet investigate intra production batch materials. Comparing IRMS with ICPMS an interesting characteristic is that whereas ICPMS focuses mostly on trace elements and is therefore inherently more sensitive to contamination, IRMS focuses on the abundant elements (H, C and O) in organic chemical samples and therefore is less sensitive to contamination problems. The above results demonstrate the strong potential of novel forensic techniques such as (LA-) ICPMS and IRMS for forensic investigation of packaging and duct tapes. We have found this is only one example of a wider forensic application of these techniques for forensic material comparisons."* (From presenter's supplied abstract).

5.3 Panel Discussion – Session Four Speakers

Panel members: Prof. Ken Pye, Dr. Gerard van der Peijl and Dr. Mark Stroud

5.3.1 The Panel discussion centred on questions relating to information that could be obtained from bones, the organic components of tape and whether someone's origin can determined with any certainty.

5.3.2 With regards to bones, one bone (generally a bulk sample), can give the history of a person. As far as identifying bone morphology and strigraphy, it is easier for children than for adults. Imaging and laser applications have been tried with varying success. Fragments of bone and work on density and micro-drilling can also be examined. Interpretation is the most important factor.

5.3.3 In terms of looking at organic components of brown packaging tapes, infra-red spectrometry is used for classification of the tape backing (mostly polypropylene) and the adhesive fraction (both acrylate and hydrocarbon resins). Recent NFI tape method development was initiated by a Dutch murder case in which a brown packaging tape was used that appeared to be a special roll of tape from South East Asia. The use of pyrolysis GCMS, Size Exclusion Chromatography and Nuclear Magnetic Resonance methods widened the approach but still provided limited discrimination. The combination of IRMS analysis of both adhesive and backing materials as well as LA ICPMS inorganic fingerprinting of the adhesive fraction proved to be a very discriminating method combination.

5.3.4 As far as determining a person's origin, a question was posed with particular regards to immigration. It was explained that some immigrants may purposefully destroy their documents in order to make it difficult for the authorities to identify their country of origin. To what degree of certainty can IRMS identify one's country of origin to assist with the process of deportation and repatriation? IRMS can be used to exclude a number of places but there would need to be additional evidence to base such a hypothesis. There could be a legitimate problem in obtaining samples, for example, hair sampling of certain religious groups. This again highlights the need for databases. It is preferable to be able to use a real database with human data rather than a proxy database and database construction is currently occurring around the world.

6 Discussion Session – Next steps

Chair: Sean Doyle, Forensic Explosives Laboratory, Dstl, Fort Halstead, Sevenoaks, Kent TN14 7BP UK.

6.1.1 The conference has provided an update as to the progress within the FIRMS network. This discussion needs to address the next stage in the development of the network and to seek a host for the next FIRMS conference.

6.1.2 At the start of the conference, Max Coleman mentioned the Technical Strategy document setting out objectives for the next five years. The working group produced a task list and a tasking document detailing requirements and how those requirements were to be met. Names and dates were allocated to the tasks but unfortunately there has been some slippage. FEL has had staffing problems and particularly the loss of key members of staff has had a significant negative impact.

6.1.3 Tasks identified:

- Task 1: Primary and working standards used by FIRMS members for the analysis of listed target materials will be collated by the FEL, to be completed by the end of August 2004.

- Task 2: A list of recommended primary and working standards suitable for the target materials will be circulated to FIRMS members, to be completed by the end of September 2004.

A question was posed as to the value of having a working standard for the different types of material and is it worth having two different working standards of similar material covering as wide a range as possible? It was agreed that this would be a good idea for all types of material. FEL and FBI have reference systems they currently use which are to be shared with others. It was recognised that Dstl could acquire and characterise the bulk of explosives but someone else would need to provide working standards for other disciplines. FEL will explore this issue.

- Task 3: Preparation of guidelines for the validation of IRMS methods, to be drafted and circulated to FIRMS members by the end of October 2004.

- Task 4: Collation of standard methods for the bulk analyses of target materials, to be completed by the end September 2004.

- Task 5: 2nd Inter-laboratory collaborative exercise, to be completed by the end December 2004.

The delivery of the 2nd inter-laboratory collaborative exercise has slipped. The samples are available at the conference and the analysis is due to be completed by June 2005.

- Task 6: Development and validation of methods for the remaining target materials, to be completed by the end of March 2005.

- Task 7: 3rd Inter-laboratory collaborative exercise, to be completed by end September 2005.

- Task 8: Investigation of optimum packaging and storage conditions for the preservation of isotopic signatures, to be completed by September 2005.

- Task 9: Identification of and establishment of liaison with commercial manufacturers of target materials, to be completed by the end of December 2004.

- Task 10: Details of the manufacturing process for selected target materials, to be completed by September 2005.

- Task 11: Collection and analysis of samples from selected manufacturing sites, to commence October 2005.

The comment was made that Sarah Benson had made some progress here with getting samples in Australia. All FIRMS members need to liaise with manufacturers and to acquire details of process and samples for analysis including starting materials, intermediates and products.

- Task 12: Collation of recipes for the improvised manufacture of target materials, to be completed by end December 2004.

- Task 13: Investigation of the inter batch variation of products produced from the same precursors, to be completed August 2005.

- Task 14: Study into the effect of inter-batch variation to be completed by the end of August 2006.

- Task 15: Study of the prediction of product stable isotope ratio values from the precursor values.

Look at starting materials and predict what the product would be and reverse the method.

- Task 16: Draft a proposal for the structure and population of FIRMS databases, to be completed by March 2005.

6.1.4 The task list was discussed at a meeting in July 2004 and a number of actions were allocated. Revisions to the tasking document are still waiting to be made. Crack cocaine was added to the list of target materials for the drugs focus group and human remains was added to the list for the general forensics focus group.

6.1.5 A number of other points which arose from the meeting in July 2004 were discussed and actions updated. Points raised over the two days of this conference were then discussed.

6.1.6 UKAP (UK Analytical Partnership of the Royal Society of Chemistry) The FIRMS network would appreciate any advice and/or guidance on including them at meetings and conferences such as this. Max Coleman and Sean Doyle are to invite them to act as observers.

6.1.7 Research priorities – It was decided this could be discussed in detail at the next focus group meeting but it was thought it would be useful to speak to the main forensic providers and find out which areas would be most beneficial. It was mentioned that IRMS may be featured in the presentations at the European Academy of Forensic Sciences conference next year. There is real progress being made and the profile of IRMS is increasing. The real issue is the funds for academia.

6.1.8 EPSRC – Max Coleman and Sean Doyle will prepare a final report on the network.

6.1.9 Limiting factors – When should IRMS be used and when can't it be used? These are considered to be difficult questions.

6.1.10 Who are the end users? – The end user is the justice system. Other stakeholders include forensic science providers and investigative bodies such as the police service. There is a need to know who is being served their requirements.

6.1.11 Database – Jim Ehleringer and Kelly Mount both use Filemaker software and it was mentioned that relational databases are transferable. There needs to be some reflection on this issue with advice and guidance given. Issues to consider include who is going to control the database. In the UK the DNA database is owned by the Association of Chief Police Officers (ACPO) but a Forensic Science Service (FSS) representative acts as the custodian with the FSS and other forensic science providers populating and using the database. It was decided that as much information as possible should be put into the database in terms of results, including raw data, background information and history and this information should be updated regularly. An international database is probably a long way off, but smaller databases can be created and combined at a later date. A position in which information cannot be exchanged should be avoided. It is also worth involving police services to seek to define their requirements. Ann Franc of Forensic Alliance mentioned that she would be happy to provide Mr Doyle with the details of their database. Mr Doyle also mentioned that NITECRIME had offered to host the database on their server.

6.1.12 The question was posed as to whether you can justify adding all databases together if there are no agreed international standard methods in place. There was no definitive response to this.

6.1.13 A list of the work currently being carried out is required and what has previously been analysed so that the knowledge is not lost. Is it possible to have a file on a web site in which people can input information – areas of interest could be put in rather than actual figures as some of this information may not be able to be given for one reason or another. It would be useful to know who has done what especially if you have problems as this could help direct you to others who have tried similar work.

6.1.14 Another area of discussion was references and literature and the question was asked whether it was possible to have a database of this information available on the website as sometimes literature is difficult to find. Jim Ehleringer mentioned that he had one using "Endnote" which he would be willing to share and place on the web site. Sarah Benson also mentioned that she had written a review with Forensic Science International with literature references.

6.1.15 Quality of data – How much information is needed and are additional techniques required to support the IRMS data? Forensic science provides information 'fit for purpose' and there could be differences in acceptable data in different countries – may not be a consensus so this issue needs to be explored further.

6.1.16 Lessons learnt – The issue of new people coming into the field and having a document of 'lessons learnt' was discussed again. It was decided that this is a good idea and should be freely available. Sarah Benson is do this and to circulate it to other members for any additions. It will then be placed on the FIRMS Network web site.

6.1.17 Characterisation and supply of working standards – This issue was raised with the idea of the FIRMS network being able to take some responsibility for this so that institutional memory is not lost. There was some thought that perhaps reference material would be preferable to 'working standards' with a database available consisting of information regarding the material and the range of values. One possibly problem could be with regards to explosives and the transportation of materials, although if only transporting small amounts this may not be a problem.

6.1.18 Training – It was thought that the FIRMS network should take an active part in training and information exchange, could help with institutional memory. The question was asked as to whether universities would be interested in an exchange programme and did people think this was a good idea. Sean Doyle said that FEL would be prepared to take on a post Doc.

6.1.19 Inter-laboratory Collaborative Exercises – FEL is to inform laboratories of the results of the round robin. The results should be in the IAEA format. If people don't get the 'correct' answer we can't expect an explanation but individuals could carry out their own investigation voluntarily and FIRMS could offer help to find out where the differences occurred. It was suggested that for the next exercise we try to look into the yield obtained for each of the isotopes which may give us some idea. We should also request more information regarding the method used which may help pinpoint areas of discrepancy.

6.1.20 There was no comment from delegates as a whole with regards to whether they were happy with the direction FIRMS was going in and the way things are being done.

6.1.21 Newsletter/Web site – It was decided that the newsletter would now be done every six months and this would continue to be e-mailed to FIRMS members as well as being placed on the FIRMS website. The website should also have a 'What's New' link. Wolfram Meier-Augenstein is to look into the availability of free LIST servers.

6.1.22 Next FIRMS conference – It was decided that the next conference should be held in three years time. Sean Doyle mentioned that FEL had organised it twice and would be looking to someone else to host it next time.

6.1.23 In the closing statements, Sean Doyle said that the proceedings would be published in Science & Justice again and gave his thanks to all those involved with the conference, network organisation and to all the delegates for giving their support.

7 Acknowledgements

7.1 The authors would like to thank all of the attendees of the FIRMS conference and in particular those who presented papers and keynote speeches. Thanks also for the corporate sponsors and the UK Home Office for supporting FIRMS.

8 List of abbreviations

AFP	Australian Federal Police
CE	Capillary Electrophoresis
DAM	Diacetylmorphine
Dstl	Defence Science and Technology Laboratory
EA-irMS	Elemental Analyser – Isotope Ratio Mass Spectrometry
EPSRC	Engineering and Physical Sciences Research Council
FEL	Forensic Explosives Laboratory
FIRMS	Forensic Isotope Ratio Mass Spectrometry Network
FSNI	Forensic Science Northern Ireland
FSS	Forensic Science Service
FT-IR	Fourier Transform Infrared Spectroscopy
GC-IRMS	Gas Chromatography – Isotope Ratio Mass Spectrometry
GCMS	Gas Chromatography Mass Spectrometry
HPLC	High Performance Liquid Chromatography
IAEA	International Atomic Energy Authority
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IRMS	Isotope Ratio Mass Spectrometry
LA-ICP-MS	Laser Ablation - Inductively Coupled Plasma Mass Spectrometry
LC/MS	Liquid Chromatography – Mass Spectrometry
MAM	Mono-acetylmorphine
MDMA	3,4-methylenedioxymethamphetamine
MSA	Mass Spec Analytical Ltd.
NFI	Netherlands Forensic Institute
PE4	Plastic Explosive 4
PETN	Penta Erythritol Tetra Nitrate
PSNI	Police Service Northern Ireland
(Py)-GCMS	Pyrolysis Gas Chromatography Mass Spectrometry
RDX	Research Department Explosive
SEM-EDX	Scanning Electron Microscopy – Energy Dispersive X-Ray Microanalysis
SIA	Specific Isotope Analysis
SPE	Solid Phase Extraction
TNT	Trinitrotoluene
XRF	X-Ray Fluorescence

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13. Abstract (A brief (approximately 150 words) factual summary of the report) On the 9th and 10th March 2005 a Forensic Isotope Ratio Mass Spectrometry (FIRMS) Network conference was hosted by the Forensic Explosives Laboratory at the Thistle Hotel, Brands Hatch, Kent. The conference was attended by approximately sixty delegates from forensic establishments, police forces, instrument manufacturers, service providers and academia. Presentations were made together with key note addresses in four sessions. The conference also had the following objectives; to exchange information between the researchers and end users, to expand the network, to review the requirement, to assess the strategy for development and to chart progress since the last FIRMS conference. This document summarises each presentation and the main points arising from discussions regarding the presentations as well as summarising the proposed "Next Steps" of the FIRMS Network.		
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