

MFRC

Midwest Forensics Resource Center

**Research and Development
Program Summary**

December 2013

Acknowledgments

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Midwest Forensics Resource Center (MFRC)

Research and Development Program

Introduction

The mission of the MFRC Research and Development Program is to provide technological advances in forensic science for the benefit of our regional partners, as well as the forensic science community at large. Key areas of forensic science needs are identified through participation in national meetings in forensic science and guidance by national studies and reports. Under the sponsorship of the National Institute of Justice (NIJ), the MFRC solicits proposals for the development of practical and useful forensic science tools that require proof-of-concept experimentation and tools proven in other fields that require experimentation to demonstrate feasibility for addressing specific forensic science needs. The MFRC facilitates proposal development by working to establish partnerships between researchers and our regional partners. The MFRC administers a peer-review of the proposals and then funds the selected projects at the level of approximately \$75,000 each, with a 12-month period of performance.

The process for selection of these projects includes the following steps: 1) Drafting of a call for proposals by MFRC staff; 2) Review of the draft call by members of the R&D Advisory Committee; 3) Review and approval of the call by NIJ; 4) Issuance of the call to Iowa State University (ISU), Ames Laboratory, regional partners, and various academic and non-academic research organizations; 5) Receipt of proposals; 6) Review of proposals by the R&D Advisory Committee; 7) Ranking and selection by MFRC staff using Advisory Committee reviews; 8) Concurrence by NIJ of selected proposals; 9) Notification of proposers and awards; 10) Receipt and review of progress reports by MFRC; 11) Receipt and review of final reports by MFRC, R&D Advisory Committee, and NIJ; and 12) Posting of final reports on the MFRC website.

The decision to fund any specific project is based upon a peer-reviewed call-for-proposal system administered by the MFRC. The reviewers are crime laboratory specialists and scientists who are asked to rate the proposals on four criteria including: 1) Relevance to the mission of the MFRC; 2) Technical approach and procedures; 3) Capabilities, teaming, and leveraging; and 4) Dissemination and implementation of research findings. A successful proposal demonstrates knowledge of the background for the research and includes a research methodology with a well-defined plan to transfer research findings into the hands of stakeholders to pursue further research or into the hands of users to facilitate application of the developed tools.

Program Summary Technical Sheets

The following project summaries, while not a complete summary of all research areas, are meant to demonstrate the range of research funded by the MFRC. The project summaries describe the forensic need the projects serve as well as the benefits derived from the technology. The summaries provide a brief description of the technology and the accomplishments to date. In addition, the collaboration with regional partners and the status of the dissemination of project results and implementation of the product are highlighted. These technical summaries represent the development and implementation of practical and useful technology for crime laboratories that the MFRC hopes to accomplish.

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Abstracts of Funded Projects

CHEMISTRY

Chemical Characterization of Emerging Designer Drugs

Jeremiah Morris, Johnson County Sheriff's Office Laboratory, Olathe, KS

Analytical data for synthetic cannabinoids and substituted cathinones is rarely available. Without verified analytical data from known sources, structural elucidation of unknown compounds by mass spectral data alone is insufficient. This project elucidates the chemical structure of emerging designer drugs using four different analytical techniques and a presumptive color test. In doing so, it provides the forensic drug chemist with the analytical data to identify synthetic cannabinoids and substituted cathinones in emerging designer drugs.

Random Probability Match Procedure for Statistical Comparison of Mass Spectral Data

Ruth Waddell-Smith and Victoria McGuffin, School of Criminal Justice and Department of Chemistry, Michigan State University, East Lansing, MI

A method is developed for statistical comparison of mass spectral data obtained using gas chromatography mass spectrometry (GC-MS) to address the need for accessing the significance of associations in the comparison of evidence. The procedure is based on classic probability theory: determining the random probability that a match between the mass spectrum of a questioned sample and that of a reference standard occurs by chance. The mass spectra used are those of controlled substances.

PATTERN EVIDENCE

The Development of a New Model to Study Firearms Related Blood Spatter

Michael Taylor, Institute of Environmental Science and Research, Christchurch, NZ., Kevin Winer, Kansas City Police Crime Laboratory, Kansas City, MO, and Jules Kieser, Sir John Walsh Research Institute, University of Otago, Dunedin, NZ.

The study of firearm-related blood spatter is a common and often critical task for investigators. Simulating the formation of the spatter to answer case-related questions is difficult, partly because of the lack of suitability models. This project develops a physical model of the human head to study cranial gunshot wounding and associated blood spatter formation. Construction of the model is accomplished using anatomically accurate dimensions and best available simulant materials. Validation of the model is based on ballistic testing utilizing a high speed digital imaging system.

Chemical Characterization of Emerging Designer Drugs

FORENSIC TECHNOLOGY NEED

In 2009, products marketed as “herbal incense” started to appear on the market. Rather than legitimate incense materials, these products contained “synthetic cannabinoids”. By 2010, the number of synthetic cannabinoids detected in incense products increased to more than 20. Analytical data for these cannabinoids is rarely available. Substituted cathinones represent another rapidly evolving class of designer drugs. These compounds emerged as substitutes for cocaine and methamphetamine.

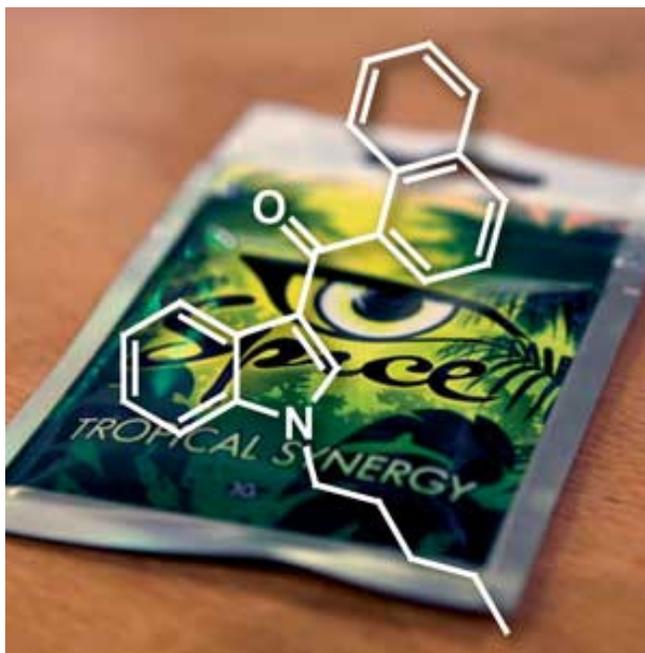


Figure 1. Spice: a herbal incense containing cannabinoids.

TECHNOLOGY DESCRIPTION

In forensic drug chemistry, identification of unknown substances is difficult. Without verified analytical data from known sources, structural elucidation of unknown compounds by mass spectral data alone is insufficient. In this project, analytical data for emerging designer drugs of abuse were obtained using gas chromatography-mass

spectrometry (GC/MS), liquid chromatography-tandem mass spectrometry (LC/MS/MS), Fourier Transform Infrared Spectroscopy (FTIR), and presumptive color tests.

METHODOLOGY

The specific goal of this project was to provide forensic drug chemists with an awareness of emerging drugs of abuse along with the analytical data to identify the various compounds.

Specific objectives of the project were to:

- Monitor known sources of “research chemicals” and emerging drugs of abuse
- Obtain samples of new compounds as they become available
- Verify the chemical structure of new compounds
- Obtain various types of analytical data (instrumental and presumptive color tests)
- Publish the analytical data and specific methodologies utilized to obtain the data for forensic drug chemists
- Categorize the compounds into chemical classes to assist legislative initiatives

ACCOMPLISHMENTS AND ONGOING WORK

Initially, the project focused on developing a new approach to obtain samples for characterization. Rather than purchasing samples from legitimate analytical standard supply vendors (e.g., Alltech or Sigma-Aldrich), the project focused on internet-based vendors selling “research chemicals.” These online vendors are the original source for manufacturers seeking new chemicals for their

“bath salt” or “herbal incense” products. As such, monitoring these websites allowed the project team to purchase samples of emerging drugs of abuse as soon as they were introduced to market.

Eighty six different samples were purchased from seventeen different online vendors. Countries of origin included the United States, Canada, the United Kingdom, the Netherlands, Russia, and China. In general, samples were received with little or no paperwork with international packages often having misleading information on the shipping forms (i.e., contains “Caffeine citrate”). Only two international shipments were held up at U.S. Customs. All other shipments were delivered without incident although towards the end of the project a number of shipments had been opened and sampled by the U.S. Department of Homeland Security.

Chemical class	# of samples
Synthetic cannabinoids	22
Substituted cathinones	14
Stimulant phenethylamines	7
Hallucinogenic phenethylamines	11
Hallucinogenic tryptamines	9
Arylcyclohexylamines	6
Benzodiazepines	2

Table 1. Partial list of classes of compounds, and the number of compounds in each class, analyzed in this project.

Samples were pre-screened using GC/MS to determine sample suitability for further analyses. It was found that almost 20% of the samples contained compounds other than what was ordered. Some were different chemicals of the same class (AM-2201 instead of JWH-424 – both synthetic cannabinoids), some were different classes but of the same CNS category (fluoromethamphetamine instead of dichloropane – both stimulants), and some were complex mixtures of multiple substances. In one instance, the ordered compound was 1-aminomethyl-5-methoxyindane (a stimulant with MDMA properties). However, the sample actually contained a mixture of methiopropamine (stimulant), 5-APB (MDMA-like hallucinogen), 4-methyl buphedrone (substituted cathinone) and

5-MeO-DALT (hallucinogenic tryptamine).

After pre-screening, a portion of the sample was shipped for NMR analysis to confirm the chemical structure, and to obtain the following analytical data: presumptive color test results, electron impact mass spectra including trimethyl silyl (TMS) derivatives, infrared spectra (including polymorph studies on select samples) and triple quadrupole (QQQ) mass spectra from a liquid chromatograph system. For the majority of compounds, obtaining the analytical data was straight-forward. However, a few issues of interest for forensic drug chemists were observed:

For indole-containing synthetic cannabinoids, the Liebermann reagent which contains sodium nitrite in concentrated sulphuric acid was not suitable for testing. The samples, which are primarily vegetation, char with the sulphuric acid thus masking any color changes. A new presumptive color test was developed to remedy the problem. The new test utilizes a solvent extraction to remove the synthetic cannabinoids from the vegetation matrix and then adds Liebermann’s reagent directly to the organic extraction solution. Validation of the new test method determined that it resulted in yellow to red-orange colors for all cannabinoids containing an indole nucleus. However, samples which contain an indazole nucleus (AKB48) rather than an indole nucleus (STS-135) do not change color with this test.

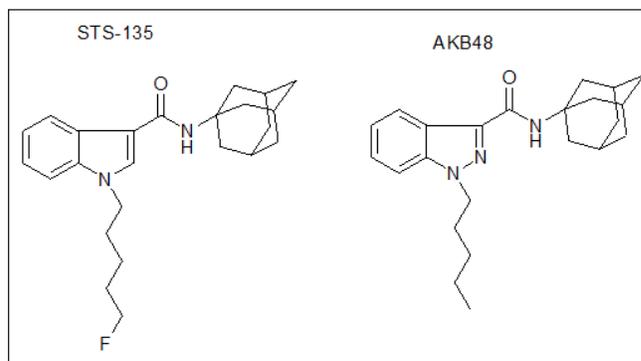


Figure 2. Chemical structures of STS-135 (an indole) with AKB48 (an indazole). With the new test, STS-135 changes color, whereas AKB48 does not.

During chemical data analysis, it was found that a number of substituted cathinones had different polymorphs, i.e., single compounds existing in multiple crystalline structures. The different infrared spectra resulting from these polymorphs are problematic for drug chemists and potentially may lead to the misidentification of compounds present. A series of polymorph studies were subsequently performed. Infrared spectra of the original material were obtained and then compared to the spectra of residues obtained from dissolving portions of the material in various solvents and evaporating them down to dryness.

One of the compounds obtained was 4-Acetoxydimethyltryptamine (4-AcO-DMT or acetylated psilocin). This compound was also detected in case submissions. 4-AcO-DMT is the active constituent of the psilocybe hallucinogenic mushrooms. While Psilocin is a Schedule I controlled substance federally and in most states, acetylated psilocin is not. Yet, it was discovered that over time 4-acetoxydimethyltryptamine can easily convert into psilocin, especially when stored at room temperature or during certain acid-base extractions.

Follow-up studies indicated that the acetoxy group is not stable and readily converts to a hydroxyl. Other acetoxy tryptamines, such as 4-acetoxydiethyltryptamine, are expected to have the same stability issues. A new substance called 5-(2-aminopropyl) indole (5-IT) was purchased to test the theory. 5-IT is a structural analog of N-methyltryptamine (NMT), a non-controlled substance, and alpha-methyltryptamine (aMT), a Schedule I controlled substance federally and also in many states.

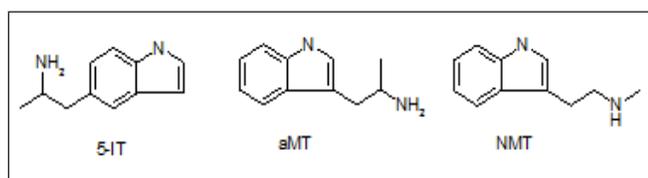


Figure 3. Chemical structures of three indoles

Initial GC/MS studies demonstrated that 5-IT, aMT, and NMT have indistinguishable retention times and mass spectra. Acetylation resulted in the ability to differentiate NMT from 5-IT and aMT but the acetylated derivatives of 5-IT and aMT were still indistinguishable. This presented a situation where a sample containing a non-controlled substance (5-IT) could easily be misidentified as containing a controlled substance (aMT). Although GC/MS analyses were not suitable for differentiation, infrared analyses, and certain color tests were able to differentiate 5-IT and aMT.

Color Test	5-IT	aMT	NMT
Marquis	Dark Red	Yellow-Green	Yellow-Green
Liebermann's	Brown	Black	Brown
Mecke's	Brown	Green to Black	Green
	Light Red	Yellow	Yellow
PDMB	Red	Purple	Purple
	No Color	No Color	Blue
Para-dimethylaminocinnamaldehyde	Green solution with purple streaks changing to pink	Orange changing to purple	Yellow changing to purple

Table 2. Presumptive Color Test results for 5-IT, aMT, and NMT.

TECHNOLOGY BENEFITS

By creating a mechanism to obtain and characterize emerging designer drugs of abuse, the reaction time for analytical chemists is dramatically decreased. Also, by providing analytical data on emerging drugs of abuse, forensic scientists can identify and confirm sample drugs as they appear in casework.

COLLABORATION

The project is collaborative effort between the Johnson County Sheriff's Office Criminalistics Laboratory in Olathe, KS; the Washington State Patrol Crime Laboratory (WSP-CL) in Spokane, WA; the Sioux Falls Crime Laboratory in Sioux Falls, SD ; and the Montgomery County Coroner's Office Laboratory (MCCOL) in Dayton, OH.

DISSEMINATION

Research findings and results were presented at the Midwestern Association of Forensic Scientists (MAFS), the NIST/DEA Emerging Drugs and Abuse Symposium, and at the Clandestine Laboratory Investigation Chemists Association annual meeting. Information on the new presumptive color test for synthetic cannabinoids was published in the *Journal of the Clandestine Laboratory Investigating Chemists Association*. A final technical report on the project has been posted on the MFRC website.

PUBLICATIONS AND PRESENTATIONS

- Stenzel, J. *Structural Characterization of Designer Drugs Using 1-Dimensional Nuclear Magnetic Resonance (NMR) Techniques*. Oral presentation at the Clandestine Laboratory Investigating Chemists Association Annual Meeting, Indianapolis, IN. September 2012.
- Stenzel, J. *Rapid Structural Elucidation of Designer Drugs*. Oral presentation at the Clandestine Laboratory Investigating Chemists Association Annual Meeting, Indianapolis, IN. September 2012.
- Poyner, B. and Morris, J. *Differentiation between Three Structurally Similar Indoles*. Poster presentation at the Midwestern Association of Forensic Scientists Fall Meeting, Milwaukee, WI. October 2012.
- Morris, J. *Review of a Research Project on Emerging Drugs of Abuse*. Oral presentation at the Midwestern Association of Forensic Scientist Fall Meeting. Milwaukee, WI. October 2012.
- Morris, J. *Color Tests and Analytical Difficulties with Emerging Drugs of Abuse*. Oral presentation at the NIST/DEA Emerging Trends in Synthetic Drugs Workshop, Gaithersburg, MD. May 2013.
- Poyner, B. and Morris, J. *Presumptive Color Test for Synthetic Cannabinoids Containing an Indole Substructure*. *Journal of the Clandestine Laboratory Investigating Chemists Association*. Volume 22, Issue 4, pages 27-31 (October 2012).
- Poyner, B., Spangler, M., Morris, J., Stenzel, J. *Analytical Profile of Three Cyclopropanoyl Indole Cannabinoids*. *Journal of the Clandestine Laboratory Investigating Chemists Association*. Volume 23, Issue 2-3, pages 6-13 (April-July 2013).

IMPLEMENTATION

The project intended to create and disseminate a mass spectral library containing spectra of all investigated compound and to also submit these spectra to the database on the Forendex website which is offered through SAFS. Only data from compounds whose chemical structure has been confirmed by NMR analyses are suitable for official dissemination. The DEA Special Testing Laboratory has provided an extensive amount of mass spectra data for a number of compounds studied in this project. The DEA data has been incorporated into the Forendex website at this time. The data for the majority of the compounds has recently been obtained and will be published in the near future.

CONTACTS

Principal Investigator

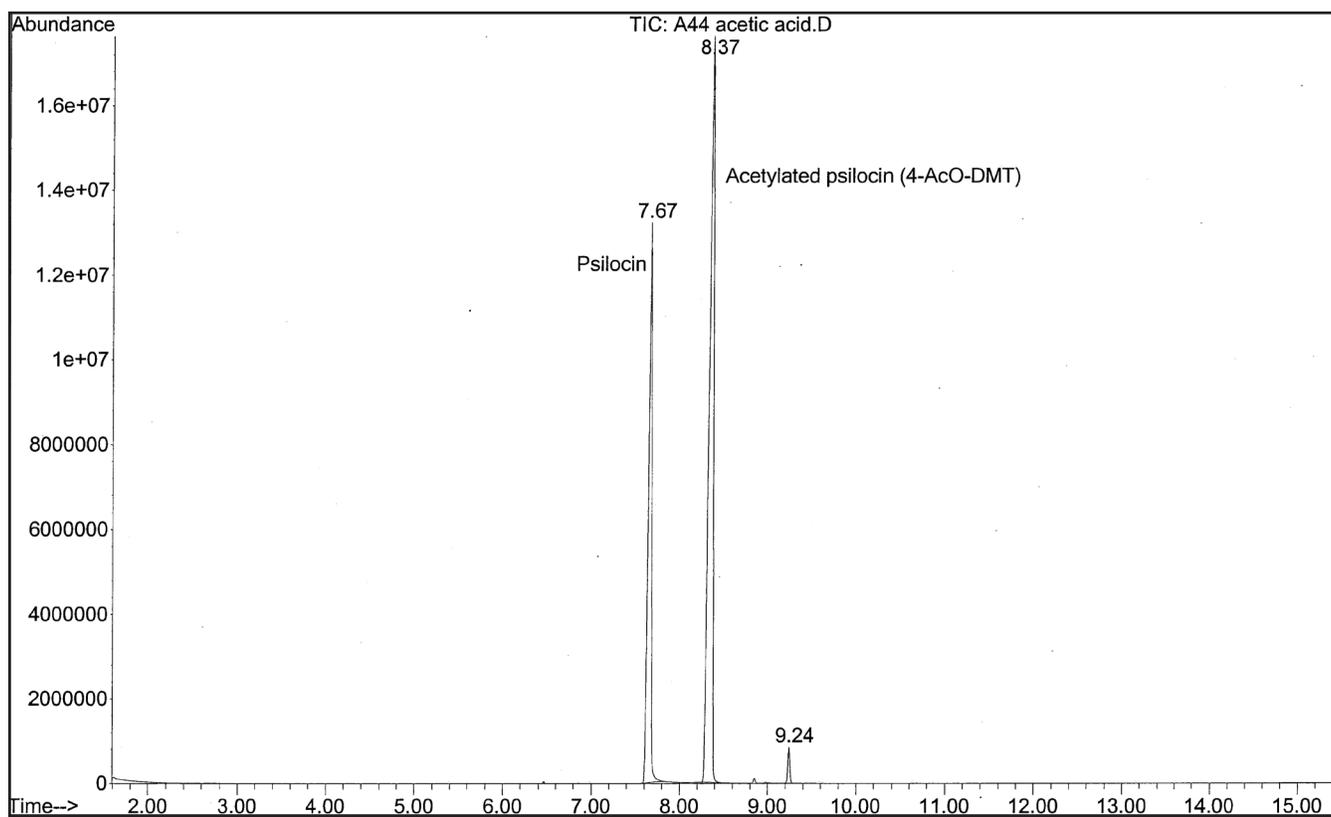
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Table 3. Partial list of 70 samples analyzed by WMR.

Project lot#	Sample name	Drug class	Supplier
MFRC-2012-A1	MDAI	Stimulant/hallucinogen	mdairesearch.com
MFRC-2012-A2	4-fluoroamphetamine	Stimulant	mdairesearch.com
MFRC-2012-A3	UR-144	Cannabinoid	RCS Chemicals
MFRC-2012-A4	JTE-907	Cannabinoid	RCS Chemicals
MFRC-2012-A5	CB-13	Cannabinoid	RCS Chemicals
MFRC-2012-A6	AB-001	Cannabinoid	RCS Chemicals
MFRC-2012-A7	AM-1248	Cannabinoid	RCS Chemicals
MFRC-2012-A8	A-834,735	Cannabinoid	RCS Chemicals
MFRC-2012-A9	A-796,260	Cannabinoid	RCS Chemicals
MFRC-2012-A10	AB-034	Cannabinoid	RCS Chemicals
MFRC-2012-A11	URB597	FAAH Inhibitor	RCS Chemicals
MFRC-2012-A12	URB602	FAAH Inhibitor	RCS Chemicals
MFRC-2012-A13	URB754	FAAH Inhibitor	RCS Chemicals
MFRC-2012-A14	5-MeO-DALT	Hallucinogen	RCS Chemicals
MFRC-2012-A15	1,3-DMAA	Stimulant	RCS Chemicals
MFRC-2012-A16	5-APB	Stimulant/hallucinogen	Buckledbonzi
MFRC-2012-A17	6-APB	Stimulant/hallucinogen	Buckledbonzi
MFRC-2012-A18	Camfetamine	Stimulant	Buckledbonzi
MFRC-2012-A19	4MemAPB (4-methylbuphedrone)	Stimulant	SenseAromatic
MFRC-2012-A20	Pentedrone	Stimulant	SenseAromatic
MFRC-2012-A21	4-fluoroamphetamine	Stimulant	SenseAromatic
MFRC-2012-A22	3-fluoroamphetamine	Stimulant	SenseAromatic
MFRC-2012-A23	Methoxetamine	Dissociative	SenseAromatic
MFRC-2012-A24	Methiopropamine	Stimulant	SenseAromatic
MFRC-2012-A25	Buphedrone	Stimulant	SenseAromatic
MFRC-2012-A26	Butylone	Stimulant	SenseAromatic
MFRC-2012-A27	Etizolam	Benzodiazepine	BulkRC.net
MFRC-2012-A28	Methoxetamine	Dissociative	BulkRC.net
MFRC-2012-A29	Pentedrone	Stimulant	buy-jwh.com
MFRC-2012-A30	JWH-307	Cannabinoid	buy-jwh.com
MFRC-2012-A31	alpha-PVP	Stimulant	buy-jwh.com
MFRC-2012-A32	2C-I-NBOME	Hallucinogen	Biochem Distribution
MFRC-2012-A33	AB-23	Unknown	bpblabs.com
MFRC-2012-A34	PB-2	Unknown	bpblabs.com
MFRC-2012-A35	Phenazepam	Benzodiazepine	bpblabs.com
MFRC-2012-A36	BZ-6378	Unknown	bpblabs.com

MFRC-2012-A43	2C-P	Hallucinogen	Biochem Distribution
MFRC-2012-A44	4-Aco-DMT	Hallucinogen	Biochem Distribution
MFRC-2012-A45	4-Met-aET	Hallucinogen	Biochem Distribution
MFRC-2012-A46	5-MeO-DALT	Hallucinogen	bpblabs.com
MFRC-2012-A47	Naphyrone	Stimulant	bpblabs.com
MFRC-2012-A48	5-IAI	Stimulant/hallucinogen	bpblabs.com
MFRC-2012-A49	FUR-144	Cannabinoid	buy-jwh.com
MFRC-2012-A50	AKB48	Cannabinoid	buy-jwh.com
MFRC-2012-A51	Demoxepam	Tranquilizer	Composynth chemicals
MFRC-2012-A52	beta-methoxy-2C-D HCl	Hallucinogen	Composynth chemicals
MFRC-2012-A53	Etaqualone	Tranquilizer	Composynth chemicals
MFRC-2012-A54	Phenprobamate	Depressant	Composynth chemicals
MFRC-2012-A55	MDAI	Stimulant/hallucinogen	Composynth chemicals
MFRC-2012-A56	Dichloropane	Stimulant	Organic Home and Garden Supply
MFRC-2012-A57	4-MeO-PCP	Dissociative	Benzo Fury
MFRC-2012-A58	3-beta-FBT	Stimulant	Benzo Fury
MFRC-2012-A59	5-MeO-BFE	Hallucinogen	Benzo Fury
MFRC-2012-A60	alpha-methyltryptamine	Hallucinogen	Benzo Fury
MFRC-2012-A61	1-Aminomethyl-5-methoxyindane	Stimulant	Benzo Fury
MFRC-2012-A62	methoxy-methyl-aminoindane	Stimulant	Benzo Fury
MFRC-2012-A63	5-fluoro-AB-001	Cannabinoid	chemicals-trade.com
MFRC-2012-A64	STS-135	Cannabinoid	chemicals-trade.com
MFRC-2012-A65	4-methyl-N-benzylcathinone	Stimulant	chemicals-trade.com
MFRC-2012-A66	K-Mex	Dissociative	Wide Mouth Frogs
MFRC-2012-A67	C1C	Stimulant	Wide Mouth Frogs
MFRC-2012-A68	A3A Methano	Stimulant	Wide Mouth Frogs
MFRC-2012-A69	Methoxetamine (replacement)	Dissociative	Organic Home and Garden Supply
MFRC-2012-A70	4-MePPP	Stimulant	bpblabs.com
MFRC-2012-A71	Brephedrone	Stimulant	buybestrc.com
MFRC-2012-A72	4-ACO-DALT	Hallucinogen	buybestrc.com
MFRC-2012-A73	4-HO-MET	Hallucinogen	buybestrc.com
MFRC-2012-A74	4-HO-MIPT	Hallucinogen	buybestrc.com
MFRC-2012-A75	2-DPMP	Stimulant	Composynth chemicals
MFRC-2012-A76	3-HO-PCE	Dissociative	Composynth chemicals

Figure 4. 4-AcO-DMT sample after acid/base extraction.



Random Probability Match Procedure for Statistical Comparison of Mass Spectral Data

FORENSIC TECHNOLOGY NEED

The National Academy of Science in its recent report “Strengthening Forensic Science in the United States: A Path Forward” draws attention to several limitations in the current state of forensic science. Among these is the need to statistically assess the significance of associations as currently there is no widely accepted method for comparison of evidence.

TECHNOLOGY DESCRIPTION

This project addresses that need through the development of a statistical method for the comparison of mass spectra. The method is based on classical probability theory and utilizes spectra of normal n-alkanes. These compounds were selected because they have relatively simple mass spectra with similar fragmentation patterns. To demonstrate the practical application in forensic laboratories, the developed method was applied to complex data sets containing mass spectral data of controlled substances.

METHODOLOGY

The objective of the project was to develop a probability-based method for the comparison of mass spectral data. To achieve this goal, the spectrum of a questioned sample was compared to the spectrum of a reference standard at each mass-to-charge (m/z) value in the mass scan range using an unequal variance t-test at a user-defined confidence level. If the two spectra were determined to be statistically indistinguishable (i.e., the calculated t-statistic is less than the critical t-value at all m/z values), the random-match probability of the mass spectral pattern occurring by chance was calculated. This probability indicates the statistical significance of the comparison.

Specific tasks to achieve the objective were:

- Define a threshold level to remove mass spectral noise present at low abundance
- Develop the random probability match method using alkane standards analyzed under a variety of different conditions
- Apply the developed method to more complex GC-MS mass spectral data obtained from the *Salvia* plant species
- Apply the developed method to case samples obtained from a controlled substances

ACCOMPLISHMENTS AND ONGOING WORK

Standards of the normal alkanes decane (C_{10}), undecane (C_{11}), dodecane (C_{12}), tridecane (C_{13}), tetradecane (C_{14}), and hexadecane (C_{16}) were prepared at concentrations of 0.05, 0.1, 0.5, 1, and 5 mM. The standards were analyzed in triplicate by gas chromatography-mass spectrometry (GC-MS) with the analysis repeated 10-15 hours later, using the same standard solutions. Two sets of standards were thus generated, with each standard containing all six alkanes in equal concentration.

Generated mass spectra were exported to an Excel file where the full mass range was tabulated with a zero value entered for all masses for which no abundance was recorded. The normalized abundance, relative to the base peak, was then calculated at all m/z . An unequal variance t-test was performed at every m/z value in the mass scan range to determine if the spectra were statistically associated at the specified confidence level. If so, the random-match probability was calculated based on the frequency of ion occurrence at each m/z value in a selected database.

Comparisons were made between the same compounds in Sets 1 and Set 2, as well as between each compound in Set 1 and the remaining compounds in Set 2. Spectra were compared at each m/z using an unequal variance student t-test.

For the alkane spectra, statistical association of corresponding alkanes and discrimination of different alkanes was possible at the 99.9% confidence level. For compounds that were statistically associated, the random match probabilities were on the order of 10^{-29} to 10^{-50} , indicating the low probability that the characteristic fragmentation patterns occur by random chance alone. Appropriate association and discrimination of the alkane spectra was possible at various different concentrations.

Spectra of the alkanes were successfully associated and discriminated from alkane spectra in the NIST database, even though these spectra were collected over different time periods and on different instruments under different experimental conditions.

Alkane (Set 1 vs, Set 2)	Confidence Level (%)	Random Match Probability
C ₁₀	99.9	5.2×10^{-37}
C ₁₁	99.9	1.9×10^{-44}
C ₁₂	98.0	5.8×10^{-49}
C ₁₃	99.9	1.1×10^{-50}
C ₁₄	99.0	1.5×10^{-55}
C ₁₆	98.0	1.1×10^{-60}

Table 1. Random-match probability for comparison of the same alkane in Set 1 and Set 2 using a t-test at the lowest confidence level for which association was maintained. Confidence levels of 98.0, 99.0, and 99.9% were investigated.

Mass spectra of salvinorum A were then compared in a similar manner using the developed method and predicted standard deviations. It was found that three extracts of salvinorum A from *Salvia divinorum* were statistically associated to salvinorum A standards at six different concentrations at the 99.9% confidence level. It was also found that mass

spectra of salvinorins B, C, and D in these extracts were statistically distinguishable from salvinorum A at the same confidence level.

Furthermore, it was found that mass spectra of salvinorum A extracted from *Salvia divinorum* from different geographical locations, using different methods, and using different instruments and conditions, were statistically associated at confidence levels of 90-99.9%. Finally, 441 *Salvia* species were discriminated from *Salvia divinorum* based on either retention time of salvinorum A or comparison to the salvinorum A mass spectra using this method.

For case samples of amphetamine-type stimulants obtained from an accredited forensic laboratory, association to the appropriate reference standard was possible at the 99.0% confidence level, despite the lack of instrument replicates for each case sample. Also, the case samples were statistically discriminated from the other reference standards at the 99.9% confidence level, which is the most rigorous confidence level for discrimination. The exceptions to this were some case samples containing methamphetamine and psilocin when compared to the MDMA reference standard, and one case sample of methamphetamine compared to the phentermine reference standard. For these exceptions, discrimination was possible at the 99.0% confidence level.

Case Sample	Reference Standard	RMP	Case Sample	Reference Standard	RMP
1	Amphetamine	1.7×10^{-39}	19	MDA	3.1×10^{-38}
2	Amphetamine	3.5×10^{-39}	20	MDA	1.6×10^{-38}
3	Amphetamine	1.7×10^{-39}	21	MDMA	9.1×10^{-38}
4	Amphetamine	1.7×10^{-39}	22	MDMA	2.6×10^{-37}
5	Amphetamine	7.7×10^{-38}	23	MDMA	7.7×10^{-38}
6	Amphetamine	7.7×10^{-38}	24	MDMA	1.5×10^{-37}
7	Amphetamine	3.3×10^{-39}	25	MDMA	2.5×10^{-37}
8	Methamphetamine	1.2×10^{-37}	26	MDMA	2.2×10^{-37}
9	Methamphetamine	1.5×10^{-37}	27	MDMA	2.0×10^{-38}
10	Methamphetamine	6.7×10^{-39}	28	MDMA	1.2×10^{-38}
11	Methamphetamine	1.5×10^{-37}	29	MDMA	7.9×10^{-38}
12	Methamphetamine	1.5×10^{-37}	30	MDMA	1.4×10^{-37}
13	Methamphetamine	1.0×10^{-38}	31	Phentermine	8.5×10^{-36}
14	MDA	3.1×10^{-38}	32	Psilocin	1.5×10^{-38}
15	MDA	3.7×10^{-39}	33	Psilocin	5.6×10^{-41}
16	MDA	1.6×10^{-38}	34	Psilocin	5.3×10^{-40}
17	MDA	2.3×10^{-38}	35	Psilocin	9.7×10^{-39}
18	MDA	1.7×10^{-38}	36	Psilocin	4.9×10^{-41}

Table 2. Random-match probability calculated for pairwise comparisons of mass spectra of case samples and corresponding reference standard (a two-tailed t-test at the 99.9% confidence level).

This is especially noteworthy in the comparison of methamphetamine and phentermine, which are elute at similar retention times. They also have similar fragmentation patterns to the point that the mass spectra are sometimes reported as indistinguishable. Mass spectra of the case samples were generally associated to relevant spectra in the NIST database at the 99.9% confidence level and discriminated from spectra of other standards in the database at confidence levels ranging from 98-99.9%.

TECHNOLOGY BENEFITS

Currently, there is no widely accepted method for the statistical comparison and evaluation of evidence. The method developed and validated in this project assigns statistical confidence in the comparison of two mass spectra. As such, it meets the requirements of a Daubert standard. While for method development mass spectra of controlled substances were used, the procedure is equally applicable to mass spectral data obtained for other types of forensic evidence.

COLLABORATION

This project is a collaborative effort between Michigan State University (MSU) in East Lansing, MI; the Alaska Scientific Crime Detection Laboratory (SCDL) in Anchorage, AK; and the Northeastern Illinois Regional Crime Laboratory (NIRCL) in Vernon Hills, IL. The SCDL and NIRCL provided access to data sets of regulated substances necessary for optimization, validation, and refinement of the procedure.

DISSEMINATION

The results of this project were presented at an annual meeting of the American Academy of Forensic Sciences (AAFS). Research results were also presented at Michigan State University as part of a thesis defense. Manuscripts were submitted for publication in Analytical and Bioanalytical

Chemistry, Rapid Communications in Mass Spectrometry, and the Journal of Forensic Sciences. A technical report on the project and its findings has been posted on the MFRC website.

PUBLICATIONS AND PRESENTATIONS

- Bodnar-Willard, M., McGuffin, V., and Waddell-Smith, R. *Statistical Comparison of Mass Spectral Data in the Identification of Amphetamine-Type Stimulants*. Oral presentation at the 65th Annual Meeting of the American Academy of Forensic Sciences, February 2013, Washington DC.
- Bodnar-Willard, M., Waddell-Smith, R., and McGuffin, V. *Statistical Approach to Establish Equivalence of Unabbreviated Mass Spectra*. Rapid Communications in Mass Spectrometry. Volume 28, Issue 1, pages 83-95 (2014).
- Bodnar-Willard, M., Hurd, J., McGuffin, V., and Waddell-Smith, R. *Statistical Approach to Establish Equivalence of Unabbreviated Mass Spectra: Application to Salvinorin A Extracted from Salvia divinorum and other Salvia species*. Manuscript currently being revised for publication in Analytical and Bioanalytical Chemistry.
- Bodnar-Willard, M., Glassburg, G., McGuffin, V., and Waddell-Smith, R. *Statistical Comparison of Mass Spectra for Forensic Identification of Amphetamine-Type Stimulants*. Manuscript submitted to the Journal of Forensic Sciences.
- Bodnar-Willard, M. *Development and Application of a Statistical Approach to Establish Equivalence of Unabbreviated Mass Spectra*. Dissertation submitted to the Department of Chemistry at Michigan State University.

IMPLEMENTATION

The method can readily be implemented as all calculations are performed in Microsoft Excel. An on-line seminar will be developed and made available through MSU's on-line learning center to demonstrate the procedure. In addition, a workshop on the statistical approach will be offered at the annual meeting of the Midwestern Association of Forensic Scientists, Dayton, OH. October 2013.

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	Random Match Probability Calculated for Pairwise Comparison						
	Extract 1	Extract 2	Extract 3	0.5 g/L standard	2.5 g/L standard	5.0 g/L standard	10.0 g/L standard
Extract 1							
Extract 2	9.5×10^{-126}						
Extract 3	6.8×10^{-126}	5.00×10^{-133}					
0.5 g/L standard	1.8×10^{-124}	3.3×10^{-128}	6.8×10^{-127}				
2.5 g/L standard	2.5×10^{-126}	1.2×10^{-132}	9.2×10^{-129}	7.9×10^{-131}			
5.0 g/L standard	6.9×10^{-126}	6.5×10^{-129}	1.5×10^{-127}	3.1×10^{-125}	3.0×10^{-131}		
10.0 g/L standard	2.6×10^{-126}	1.7×10^{-129}	4.4×10^{-127}	1.8×10^{-126}	3.3×10^{-129}	1.4×10^{-128}	
12.0 g/L standard	1.9×10^{-126}	2.7×10^{-131}	7.0×10^{-129}	1.9×10^{-127}	1.7×10^{-132}	1.0×10^{-128}	2.5×10^{-129}

Table 3. Random match probabilities calculated for pairwise comparisons of mass spectra of salvinorin A from three extracts and five standards analyzed using the same instrument.

The Development of a New Model to Study Firearms Related Blood Spatter

FORENSIC TECHNOLOGY NEED

The study of gunshot-related blood spatter is a common and often critical task for investigators. Relatively few studies have examined the dynamics of firearms-related blood spatter. In part this is due to the difficulty of mimicking bloodstain pattern formation, which in turn is a function of the availability of suitable models. These models need to be realistic in both their materials and their design in order to answer case-related questions

TECHNOLOGY DESCRIPTION

In this project, a physical model of the human head is designed and developed to study cranial gunshot wounding and associated blood spatter. Construction is accomplished by using anatomically accurate dimensions and best available simulant materials. Validation of the model is based on ballistic testing incorporating a high speed digital video imaging system.



Figure 1. Preliminary human head model as it collapses in on itself. Large bone fragments can be seen on the left of the image. Blood droplets, traveling in a backwards direction, can be seen in the middle of the image.

METHODOLOGY

The objective of the project is to design and develop a realistic model of the human head that provides forensic scientists with a tool to simulate the formation of blood spatter and to understand the mechanism of spatter projection resulting from a gunshot wound.

To achieve these objectives, the following tasks were performed:

- Sourced candidate materials for the simulation of the relevant anatomical features of the human head
- Assemble blood, skin, skull and brain components into a composite physical model of the human head
- Test the materials and compare ballistic test results with data from animal and human experiments and documented findings from homicide autopsy reports
- Conduct specific experiments to study critical cranial mechanistic components such as intra-cranial cavitation and external spatter formation
- Use high speed video imaging to compile of a set of video clips to illustrate gunshot-induced blood spatter mechanisms

ACCOMPLISHMENTS AND ONGOING WORK

Anatomical structures of relevance to cranial gunshot wounding were identified as brain, skull bone, skin tissue, and blood. A thorough review of the literature was conducted to determine which simulant materials have been researched and validated to date. It was found that common

simulant materials for soft tissue are ballistic soap and gelatin of various concentrations; for skin, different types of leather, polyurethane-coated polyamide fleece, and polyurethane sponges coated with silicone; for bone, polyurethane composites; and for brain, gelatin, silicone gel, and siloxane-based polymers.

Brain simulant

An experimental set-up was constructed to test and assess a range of brain simulants which were ultimately restricted to various concentrations of gelatin (3%, 4%, 5%, and 10%). Utilizing an air rifle and .22 long rifle (LR) ammunition, projectiles were fired into the brain simulant as well as into a sheep and a cow brain. The depth of penetration was measured, and the kinetic loss of energy of the ammunition as it passed through the simulant and the brain material was calculated, as was the expansion velocity of the material and its subsequent recoil.

It was found that gelatin underperforms as a brain simulant during ballistic impacts. Gelatin appears to have too high an elastic modulus to replicate the response of brain tissue and recoils elastically in a way which cow brain does not. Furthermore the brain was observed to deform like a highly viscous flowing fluid and gelatin did not. The recoil became more pronounced as the concentration of gelatin was increased. It was concluded that if gelatin is to be used, the concentration should not exceed 3% w/w.

Skull simulant

Ballistic tests were also used to evaluate the suitability of skull bone simulants. Properties evaluated included kinetic energy loss, material fracturing characteristics, particle distribution and “wound” size. Comparison of material behavior under ballistic conditions was made with animal bone (sheep skull, pig scapula, and cow scapula and rib) and two samples of human skull bone.

It was found that, because of the brittleness of the materials and the resulting fragmentation patterns, a number of materials were unsuitable for further testing. They included: cement/wood fiber composites, polyester/calcium carbonate composites, ceramic composites, epoxy resins, and Forton MG casting resin. On the other hand, a number of two component, fast-curing, rigid polyurethane resins performed well in ballistics tests. They included: Procast (65 Shore D), Supercast (70 Shore D), and TC-891 (80 Shore D).

Gypsum-based materials with epoxy or z-bond (cyanoacrylate) resin infiltrants also performed well in ballistic trials using both .22 caliber LR and 9 mm ammunition. However, a 3-D printed head shape, complete with gelatin brain and skin simulant in place proved to be too brittle, with major structural failure resulting. Given the current high cost of 3D printing, the gypsum-based material approach to modeling was not further investigated.



Figure 2. 9 mm bullet passing through a 5 mm layer of Procast resin bone simulant.

Skin simulant

Ballistic tests were further used to evaluate a range of materials for suitability as a skin simulant. Properties evaluated included material deformation and entry “wound” size. Animal skin (pig head) was used to compare material behavior under ballistic conditions. The following addition-cured two component silicone rubbers were evaluated: Platsil gel 10 (10 Shore A) with “deadener”; Platsil

gel 71-10 (10 Shore A); Pinkysil (20 Shore A); and Wacker M4601 (28 Shore A) and 4642 (37 Shore A).

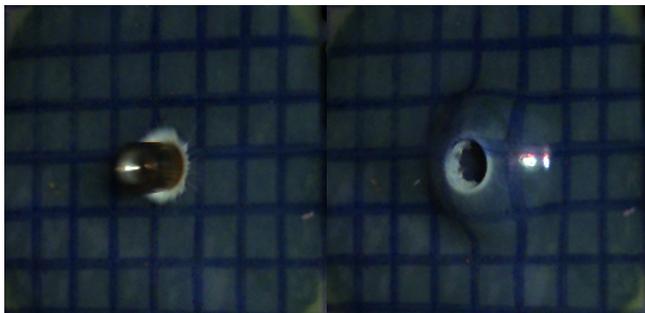


Figure 3. 9 mm bullet impacting a Platsil gel 10 skin simulant.

Videos

A number of videos were collected during the course of the simulant projects. Those collected in the brain tissue simulation experiments include videos of penetration shots using .22 air rifle pellets and LR ammunition through gelatin brain tissue simulant compared with bovine brain samples.

Tests to assess skull bone simulation include videos of penetrating shots using .22 LR and 9 mm ammunition through ceramic, plaster, polyester, epoxy, and poly-urethane resin materials compared with animal bone samples. The impact of 9 mm bullets on skin stimulants such as silicone rubber compared with pig skin formed the basis of tests to develop suitable simulants for the scalp.

Blood simulant

A number of blood simulants were tested in a separate study. It was concluded that, although the cranial was designed for the assessment of blood spatter utilizing both animal and human blood, synthetic blood simulants can be used in those cases where the use of biological fluids is unsuitable.

3D Model Construction

For the construction of the 3D model, moulds were

built to cast replicas of the top half of a human head, using an existing cast of a human cranium. Silicone rubber moulds were used to cast the skull bone while dental stone moulds have been used to cast the scalp.

On-going work focuses on building the composite 3D half skull models. The model, along with the brain, skull, and blood simulants will be used in ballistic testing. As a brain simulant, an alternative material to gelatin will be synthesized based on glycerol, water, starch and carbon fiber. As bone simulants Procast and TC-891 will be tested along with Platsil gel 10 and Platsil 71-10 as skin simulants. A household sponge cloth, selected for its absorbent properties, will be incorporated into the silicone rubber to act as a reservoir for blood or blood simulant.



Figure 4. Resin skull with skin simulant being prepared for ballistic testing.

Model validation

To assist with the validation of the model, a study of cranial gunshot wounds from criminal cases was performed. Head gunshot wound photographs from fifty-three US victims were compiled. Gunshot wounds from eight caliber classes and those from shotguns were represented.

Photographs were organized in presentation files by caliber class of the involved firearm, as determined or presumed by crime scene findings,

Medical Examiner reports, and Firearm Section reports. Medical Examiner reports were also used to label photographs as entrance or exit wounds. Each photograph contains case-specific notes.

TECHNOLOGY BENEFITS

This research project provides a new tool to assist forensic personnel investigating cases involving cranial gunshot deaths and instructors of forensic training courses. The model is suitable for the scientific simulation of cranial gunshot wounding and associated spatter formation. It gives investigators and researchers the opportunity to control the variables of interest to give reliable results from inflicted gunshot trauma.

COLLABORATION

This project is a collaborative effort between the Institute of Environmental Science and Research (ESR), Christchurch, NZ, the University of Otago (UO), Dunedin, NZ, and the Kansas City Police Crime Laboratory (KCPCL) in Missouri. In addition, project goals and experimental designs were shared with Drs. Carl Nelson of the University of Nebraska–Lincoln, Mark Jermy of the University of Canterbury, Christchurch, New Zealand, and Raj Das of the University of Auckland, Auckland, New Zealand. The project brings together forensic scientists from New Zealand and the United States.

DISSEMINATION

Project findings and results were presented at the International Association of Bloodstain Pattern Analysts (IABPA). A manuscript may be drafted for submittal to a peer-reviewed journal. A final technical report, along with a set of high speed videos have been posted on the MFRC website.

PUBLICATIONS AND PRESENTATIONS

- Taylor, M and Winer, L. *The Use of a Novel Physical Model for Gunshot-Related Blood*

Spatter Simulation. Oral presentation at the IABPA Training Conference, San Diego, CA. October, 2013.

IMPLEMENTATION

Materials from the project will be incorporated into a course titled “Fluid Dynamics: Advanced Bloodstain Pattern Analysis” offered worldwide by the ESR. Additionally, BPA instructors can take advantage of the model and the videos posted on the MFRC website for use in their courses. Also on the MFRC website, blueprints for the construction of a realistic physical human head model have been posted along with step-by-step instructions on how to construct and use the model. The model can be used to test theories relevant to specific case investigations.

CONTACTS

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Abstracts from Project Publications

List of Publications

One of the tools used to provide technological advances in forensic science to our regional partners, and the forensic community at large, is the diffusion of scientific and technical knowledge resulting from MFRC-funded research and development projects. The information obtained is used by our partners and other stakeholders to pursue further research in advancing the state of forensic science and to promote and facilitate the implementation and application of the developed new tools.

Over the past 10 years, the MFRC has funded 59 research and development projects targeting proof-of-concept experiments, feasibility tests, and product and process evaluation and validation studies. The findings of which have been shared with researchers, forensic scientists, crime laboratory managers, and other stakeholders the world over through presentations, seminars, workshops, and technical reports. Recently, webcasts and other digital media have been added to the toolbox.

Publication of research results in a peer-reviewed journal is another pursued knowledge dissemination strategy. This venue is particularly important to forensic practitioners as peer-reviewed published research is a Daubert factor for establishing the validity of scientific testimony and the admissibility of scientific evidence. As such, the ability of forensic practitioners to acquire and utilize the peer-reviewed, published scientific and technical information is of paramount importance to the practice of forensic science.

In this booklet, we have included a list of publications which resulted from the MFRC-funded projects and were published in peer-reviewed professional journals. Several more were published in peer-reviewed association newsletters and conference proceedings. Although important

to the forensic practitioner, they are not included in this list as the information presented is typically not court admissible.

Project Abstracts

For each funded project, a project title is given as well as the name(s) of the author(s) and of the journal where results were published. Also provided is a project abstract stating the reason(s) for conducting the research and listing the project's main findings and results as well as the project's main conclusions. Finally, contact information is presented on the lead author should the reader wish to communicate with the principal investigator(s) to obtain additional information.

Project abstracts were downloaded directly from the Journal in which the article was published. To avoid problems with copyright protection, Journal editors were contacted to obtain permission to reprint the journal abstract for distribution in this booklet to MFRC partners and stakeholders. In those cases where permission to reprint was not granted, or not received by the time the booklet went to press, we created our own abstract. By providing project abstracts, we hope to inspire the reader to read the full text article.

Continued Project Publications

Besides peer-reviewed publications resulting from direct MFRC funding, the list also includes peer-reviewed publications which resulted from projects funded by NIJ as continuations of the MFRC-funded projects. They are included because readers interested in proof-of-concept results most likely are also interested in project continuation findings. Collectively the publications provide the latest information on the state of forensic science on the topic investigated.

FORENSIC PROFESSIONAL JOURNALS

Journal of Forensic Sciences

Analysis of Forensic Soil Samples Via High-Performance Liquid Chromatography and Ion Chromatography

Volume 52, Issue 1, pages 24-30 (2007)

Christopher R. Bommarito; Amanda B. Sturdevant;
and David W. Szymanski

Abstract: Traditional forensic soil comparisons are performed via physical and/or chemical examinations of color, texture, and mineral content, leaving any organic- or water-soluble fractions unexamined. This study uses high-performance liquid chromatography (HPLC) and ion chromatography (IC) to assess the qualitative and quantitative variation in these fractions of soil. Soil samples (n=120) were collected over the course of 3 weeks from urban, suburban, and rural locations in and around Lansing, MI. Additional samples from six of these locations (two urban, two suburban, and two rural) were collected once a week for 10 weeks for temporal analysis. Nine additional samples, equally spaced over a 1 m(2) grid, from these same six locations were collected for spatial analyses. Qualitative and quantitative analysis of the resultant chromatograms separated the 120 samples into 10 groups by HPLC and 23 groups by IC. This study shows that using HPLC and IC to analyze the organic- and water-soluble fractions of soil can successfully discriminate samples. Quantitative analysis of the results eliminates some false inclusions by providing further differentiation of samples. The results of this study indicate that adding HPLC and IC analyses to traditional forensic soil analysis schemes can improve overall sample differentiation. The methods used in this study were also able to detect both qualitative and quantitative variations in soil over a relatively small geographic area. This demonstration of soil heterogeneity underscores the importance of the collection of a representative known sample population when assessing a forensic soil comparison. Significant

temporal variation was also demonstrated over the course of 10 weeks of sampling; however, samples were found to be consistent over shorter periods of time. Baseline levels of inorganic anions were determined via IC; these levels may be useful in assessing the significance of anions detected in soil from cases involving low explosives.

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Link: <http://onlinelibrary.wiley.com/doi/10.1111/j.1556-4029.2006.00301.x/abstract>

Testing for Potential Contextual Bias Effects during the Verification Stage of the ACE-V Methodology when Conducting Fingerprint Comparisons

Volume 54, Issue 3, pages 583-590 (2009)

Glenn Langenburg; Christophe Champod; Pat Wertheim

Abstract: This study was conducted to assess if fingerprint specialists could be influenced by extraneous contextual information during a verification process. Participants were separated into three groups: a control group (no contextual information was given), a low bias group (minimal contextual information was given in the form of a report prompting conclusions), and a high bias group (an internationally recognized fingerprint expert provided conclusions and case information to deceive this group into believing that it was his case and conclusions). A similar experiment was later conducted with laypersons. The results showed that fingerprint experts were influenced by contextual information during fingerprint comparisons, but not towards making errors. Instead, fingerprint experts under the biasing conditions provided significantly fewer definitive and erroneous conclusions than the control group. In contrast, the novice participants

were more influenced by the bias conditions and did tend to make incorrect judgments, especially when prompted towards an incorrect response by the bias prompt.

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Link: <http://onlinelibrary.wiley.com/doi/10.1111/j.1556-4029.2009.01025.x/abstract>

Validation of Tool Mark Comparisons Obtained Using a Quantitative, Comparative, Statistical Algorithm

Volume 55, Issue 4, pages 953–961 (2010)

L. Scott Chumbley; Max D. Morris; M. James Kreiser; Charles Fisher; Jeremy Craft; Lawrence J. Genalo; Stephen Davis; David Faden; Julie Kidd

Abstract: A statistical analysis and computational algorithm for comparing pairs of tool marks via profilometry data is described. Empirical validation of the method is established through experiments based on tool marks made at selected fixed angles from 50 sequentially manufactured screwdriver tips. Results obtained from three different comparison scenarios are presented and are in agreement with experiential knowledge possessed by practicing examiners. Further comparisons between scores produced by the algorithm and visual assessments of the same tool mark pairs by professional tool mark examiners in a blind study in general show good agreement between the algorithm and human experts. In specific instances where the algorithm had difficulty in assessing a particular comparison pair, results obtained during the collaborative study with professional examiners suggest ways in which algorithm performance may be improved. It is concluded that the addition of contextual

information when inputting data into the algorithm should result in better performance.

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Link: <http://onlinelibrary.wiley.com/doi/10.1111/j.1556-4029.2010.01424.x/abstract>

Association of Ignitable Liquid Residues to Neat Ignitable Liquids in the Presence of Matrix Interferences using Chemometric Procedures

Volume 56, Issue 1, pages 70-81 (2011)

Jamie M. Baerncopf; Victoria L. McGuffin; Ruth Waddell Smith

Abstract: In fire debris analysis, weathering of ignitable liquids and matrix interferences can make the identification of ignitable liquid residues (ILRs) difficult. An objective method was developed to associate ILRs with the corresponding neat liquid with discrimination from matrix interferences using principal components analysis (PCA) and Pearson product moment correlation (PPMC) coefficients. Six ignitable liquids (gasoline, diesel, ultra pure paraffin lamp oil, adhesive remover, torch fuel, paint thinner) were spiked onto carpet, which was burned, then extracted using passive headspace extraction, and analyzed by gas chromatography-mass spectrometry. Both light and heavy burn conditions were investigated. In the PCA scores plot, ignitable liquids were discriminated based on alkane and aromatic content. All ILRs were successfully associated with the corresponding neat liquid using both PCA and PPMC coefficients, regardless of the extent of burning. The method developed in this research may make the association of ILRs with corresponding neat liquids more objective.

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Link: <http://onlinelibrary.wiley.com/doi/10.1111/j.1556-4029.2010.001563.x/abstract>

The Temporal Fate of Drugs in Decomposing Porcine Tissue

Volume 56, Issue 3, pages 694-699 (2011)

John F. Wyman; Dorothy E. Dea; Rachel Yinger; Amber Simmons; David Brobst; Michael Bissell; Fernando Silveira; Nancy Kelly; Robert Shott; Joseph Ohr; Rick Howard; and Bradley Lewis

Abstract: Drug levels in decomposed individuals are difficult to interpret. Concentrations of 16 drugs were monitored in tissues (blood, brain, liver, kidney, muscle, and soil) from decomposing pigs for 1 week. Pigs were divided into groups (n = 5) with each group receiving four drugs. Drug cocktails were prepared from pharmaceutical formulations. Intracardiac pentobarbital sacrifice was 4 h after dosing, with tissue collection at 4, 24, 48, 96, and 168 h postdosing. Samples were frozen until assay. Detection and quantitation of drugs were through solid phase extraction followed by gas chromatograph/mass spectrometer analysis. Brain and kidneys were not available after 48 h; liver and muscle persisted for 1 week. Concentration of drugs increased during decomposition. During 1 week of decomposition, muscle showed average levels increasing but concentrations in liver were increased many fold, compared to muscle. Attempting to interpret drug levels in decomposed bodies may lead to incorrect conclusions about cause and manner of death.

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Link: <http://onlinelibrary.wiley.com/doi/10.1111/j.1556-4029.2011.01725x/abstract>

Effect of Substrate Interferences from High-Density Polyethylene on Association of Simulated Ignitable Liquid Residues to the Corresponding Liquid

Kaitlin R. Prather; Suzanne E. Towner; Victoria L. McGuffin; Ruth Waddell Smith.

Volume 59, Issue 1, pages 52-60 (2014)

Abstract: In this research, the application of statistical procedures for the association of simulated fire debris samples to the corresponding ignitable liquid standard is demonstrated. Simulated debris samples were prepared by spiking lighter fluid, gasoline, and kerosene onto a high-density polyethylene (HDPE) substrate and subsequently burning the sample. Debris samples and corresponding reference standards of the three liquids were extracted using a passive headspace procedure and then analyzed by gas chromatography-mass spectrometry. The total ion chromatograms were background corrected, smoothed retention time aligned, and normalized prior to statistical analysis. Two statistical procedures, Pearson product moment correlation (PPMC) coefficients and principal components analysis (PCA), were used to investigate association of the debris samples to the appropriate reference standard. Using this combination of procedures, association was possible, even in the presence of interference compounds from the HDPE substrate.

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Distortion in Fingerprints: A Statistical Investigation Using Shape Measurement Tools

*H. David Sheets; Anne Torres; Glenn Langenburg;
Peter Bush; Mary Bush*

Accepted for publication.

Abstract: Friction ridge impression appearance can be affected due to type of surface touched and pressure exerted during deposition. Understanding magnitude of alterations, regions affected, systematic/detectable changes occurring would provide useful information. Geometric Morphometric techniques were used to statistically characterize these changes. One hundred fourteen (114) prints were obtained from a single volunteer and impressed with heavy, normal and light pressure on computer paper, soft gloss paper, 10 print card stock and retabs. Six hundred (600) prints from 10 volunteers were rolled with heavy, normal, and light pressure on soft gloss paper and 10 print card stock. Results indicate that while different substrates/pressure levels produced small systematic changes in fingerprints, the changes were small in magnitude: roughly the width of one ridge. There were no detectable changes in degree of random variability of prints associated with either pressure or substrate. In conclusion, the prints transferred reliably regardless of pressure or substrate.

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Association of Firearm and Toolmark Examiners (AFTE) Journal

Statistical Confirmation of Empirical Observations

Volume 39, Issue 3, pages 211-220 (2007)

David. Faden, Julie A. Kidd, Jeremy Craft, L. Scott Chumbley, Max D. Morris, Lawrence J. Genalo, M. James Kreiser, Stephen Davis

Abstract: Toolmarks produced by 44 sequentially manufactured screwdriver tips have been characterized for surface roughness using a profilometer. Toolmarks were produced in lead at angles of 30+, 60+, and 85+. A computer program developed to compare and match the profilometer data has been used to show that marks from a single tip produced at similar angles yield much higher correlation values than marks produced from the same tip but at different angles. This analysis provides statistical support for the widely-accepted empirical observation that toolmark striae must be reproduced at similar angles in order to be unambiguously identified as being made by a particular tool.

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Clarity of Microstamped Identifiers as a Function of Primer Hardness and Type of Firearm Action

Volume 44, Issue 2, pages 145-155 (2012)

L. Scott Chumbley, M. James Kreiser, Todd Lizotte, Orest Ohar, Taylor Grieve, B. King, David Eisenmann

Abstract: The transfer of microstamped identifiers to the primers of fired cartridges was examined using a stereomicroscope and scanning electron microscope (SEM). The identifiers were placed on the firing pins of three different 9mm handguns, namely, a Sig Sauer, a Taurus, and a Hi-Point. Ten different brands of ammunition were fired from each handgun, 100 rounds being fired using each brand for a total of 1000 rounds fired per handgun. The quality of the markings was evaluated using a simple observation rubric. These results were compared to Vickers hardness values obtained from the ammunition primers and are discussed in light of the types of actions of firearms used.

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Gear Code Extraction from Microstamped Cartridges

Volume 45, Issue 1, pages 64-74 (2013)

Taylor N. Grieve; L. Scott Chumbley; M. James Kreiser; Todd Lizotte; Orest Ohar

Abstract: The firing pins of three different handguns were modified to stamp a six-digit alpha-numeric code and a circumferential digital code (gear code) into the primer of a cartridge when fired. In this paper the transfer of gear codes from firing pin to primers was evaluated using scanning electron microscopy (SEM). Only those cartridges that received poor clarity marks optically regarding the alpha-numeric code were chosen for evaluation in the SEM. Photo editing software was employed to clearly outline and decipher the gear code around the circumference of the microstamped primer. Results show that the better imaging of the SEM allows more of the alpha-numeric identifiers and more of the gear code structure to be distinguished. Yet complete recognition is not possible in all cases.

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Forensic Science International

Informing the Judgments of Fingerprint Analysts Using Quality Metric and Statistical Assessment Tools

Volume 219, Issue 1-3, pages 183-198 (2010)

Glenn Langenburg; Christophe Champod; T. Gennessay

Abstract: The aim of this research was to evaluate how fingerprint analysts would incorporate information from newly developed tools into their decision making processes. Specifically, we assessed effects using the following: (1) a quality tool to aid in the assessment of the clarity of the friction ridge details, (2) a statistical tool to provide likelihood ratios representing the strength of the corresponding features between compared fingerprints, and (3) consensus information from a group of trained fingerprint experts. The measured variables for the effect on examiner performance were the accuracy and reproducibility of the conclusions against the ground truth (including the impact on error rates) and the analyst accuracy and variation for feature selection and comparison. The results showed that participants using the consensus information from other fingerprint experts demonstrated more consistency and accuracy in minutiae selection. They also demonstrated higher accuracy, sensitivity, and specificity in the decisions reported. The quality tool also affected minutiae selection (which, in turn, had limited influence on the reported decisions); the statistical tool did not appear to influence the reported decisions.

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Effect of Evaporation and Matrix Interferences on the Association of Simulated Ignitable Liquid Residues to the Corresponding Liquid Standard

Volume 222, Issue 1-3, pages 242-251 (2012)

Kaitlin R. Prather; Victoria L. McGuffin; Ruth Waddell Smith

Abstract: Identification of an ignitable liquid in fire debris evidence can be complicated due to evaporation of the liquid, matrix interferences, and thermal degradation of both the liquid and

the matrix. In this research, liquids extracted from simulated fire debris were compared to the original liquid using multivariate statistical procedures. Neat and evaporated gasoline and kerosene standards were spiked onto nylon carpet, which was subsequently burned. The ignitable liquid residues were extracted using a passive headspace procedure and analyzed by gas chromatography–mass spectrometry. Pearson product moment correlation coefficients, hierarchical cluster analysis, and principal components analysis were used to compare the liquids extracted from the carpet to the corresponding neat liquid. For each procedure, association of the extracts according to liquid type was possible, albeit not necessarily to the specific evaporation level. Of the three procedures investigated, principal components analysis offered the most promise since contributions from matrix interferences were essentially eliminated.

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Shape Measurement Tools in Footwear Analysis: A Statistical Investigation of Accidental Characteristics over Time

H. David Sheets; Susan Gross; Glenn Langenburg; Peter Bush; Mary Bush

Volume 232, Issue 1-3, pages 84-91 (2013)

Abstract: Presence of accidental characteristics on footwear strengthens the linkage of a given piece of footwear to a footwear impression left at a crime-scene. Thus an understanding of rate of appearance and disappearance of these characteristics is of importance. Artificial cutmarks, 1–3 mm in depth, were cut into outsoles of 11 pairs of athletic shoes. Loss of these cutmarks and acquisition of new accidental characteristics/wear patterns were monitored over a seven-week time-span. Feature-

vector methods were used to acquire multivariate data on wear/acquisition rates. A repeatability study indicated the feature vector method could detect small differences among shoes relative to measurement uncertainty. The shoes displayed a strong retention of artificial cut-marks over the study interval. Net rate of wear was 0.1% of the textured area of the shoe per week, predominantly in the heel and ball area. Results indicate accidental characteristics can reasonably be expected to persist over time.

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International Journal of Legal Medicine

The Effect of Firearm Muzzle Gases on the Backspatter of Blood

Volume 125, Issue 5, pages 617-628 (2011)

Michael C. Taylor; Terry L. Laber; Barton P. Epstein; Dan S. Zamzow; David P. Baldwin

Abstract: Injuries caused by gunshots can produce what bloodstain pattern analysts know as “backspatter.” Observations about the presence or absence of backspatter on an individual may be used in court as evidence of guilt or innocence. The discharge of three firearms (.22 caliber revolver, .38 caliber revolver, and .308 caliber rifle) and the resulting impact of bullets on a blood source were recorded using high-speed digital video imaging. Blood droplets, firearm muzzle gases, and ballistic shock waves were visualized using standard reflected light and shadowgraphy imaging techniques. A significant interaction between air currents, muzzle gases, and particulate material emanating from the firearms upon discharge with backspattered blood was observed. Blood droplets,

initially spattered back toward the firearm and the shooter, were observed to change direction under the influence of firearm-induced air currents and were blown forward toward and beyond their original source location. Implications for experts testifying in court and for bloodstain pattern instructors are discussed.

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Journal of Forensic Identification

Quantification of the Individual Characteristics of the Human Dentition: Methodology

Volume 58, Issue 4, pages 409-418 (2008)

L. Thomas Johnson; Thomas Radmer; Peggy VanScotter-Asbach; Daniel Blinka

Abstract: This study provides a method for comparing six individual human dentition characteristics using the standard measuring tool in Adobe Photoshop CS2 as compared to measuring individual characteristics with an automated software program under development at Marquette University, which has been adapted for bitemark analysis. The algorithm identifies color-specific pixels and automatically calculates the measurements.

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Link: http://works.bepress.com/thomas_johnson/3

The Correlation of Dental Arch Width and Ethnicity

Volume 59, issue 3, pages 268-274 (2009)

Thomas W. Radmer, L. Thomas Johnson

Abstract: This study sought to demonstrate a correlation between arch width, ethnic background, individual height, weight, and whether orthodontic treatment had been rendered. Conclusions revealed that arch widths were significantly larger ($p=0.002$ for the mandible and $p=0.008$ for the maxilla) in non-Whites than in Whites. In addition, arch widths of the mandible were significantly larger in individuals who had orthodontic treatment compared to those who had not ($p=0.005$). This did not carry through to those arch widths in the maxilla of orthodontic versus nonorthodontic care ($p=0.258$).

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Quantification of the Individual Characteristics of the Human Dentition

Volume 59, issue 6, pages 609-625 (2009)

L. Thomas Johnson; Thomas W. Radmer; Thomas S. Wirtz; David Cadle; Nicholas Pajewski; James Brozek

Abstract: The considerations for admissibility suggested by the Daubert trilogy challenge forensic experts to provide scientific support for opinion testimony. The defense bar has questioned the reliability of bitemark analysis. Under an award from the U. S. Department of Justice, via the Midwest Forensic Resource Center, a two-year feasibility study was undertaken to quantify six dental characteristics. Using two computer programs, the exemplars of 419 volunteers were digitally scanned, characteristics were

measured, and frequency was calculated. The study demonstrates that there were outliers or rare dental characteristics in measurements. An analysis of the intra-observer and inter-observer consistency demonstrated a high degree of agreement. Expansion of the sample size through collaboration with other academic researchers will be necessary to be able to quantify the occurrence of these characteristics in the general population. The automated software application, Tom's Toolbox, developed specifically for this research project, could also provide a template for precisely quantifying other pattern evidence.

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Link: http://works.bepress.com/thomas_johnson/1

The Quantification of Tooth Displacement

Volume 60, issue 1, pages 4-18 (2010)

Thomas W. Radmer; L. Thomas Johnson; Mingan Yang; Thomas Wirtz

Abstract: By using reference points from a single pixel marker placed at the center point of the cuspid teeth and the center point on each of the incisor teeth, a polynomial curve was generated as a native curve for each dental arch studied. The polynomial curve generated from actual tooth position in each arch provides the forensic odontologist with another reference point that is quantifiable. The study represents that individual characteristics, such as tooth displacement, can be quantified in a simple, reliable, and repeatable format.

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Link: http://works.bepress.com/thomas_johnson/5

A Methodology for Three-dimensional Quantification of Anterior Tooth Width

Volume 61, issue 3, pages 296-311 (2011)

L. Thomas Johnson; Thomas W. Radmer; Alexis D. Visotcky; Kwang W. Ahn; Daniel D. Blinka; Thomas Wirtz

Abstract: The use of cone-beam computed tomography (CBCT) technology has been shown to be more accurate in measuring individual incisor tooth widths than the use of wax exemplars. There were fewer differences by investigators using CBCT than others using an F-test in a mixed model of the measurement differences of investigators, wax type, and which tooth was measured. In addition, the frequency of outliers was less in the CBCT method (a total of 5) as compared to the two-dimensional measurements in ether Aluwax (a total of 8) or Coprwax (a total of 12). Both results indicate that CBCT measurements accounted more precisely for tooth width and level of eruption.

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Link: http://works.bepress.com/thomas_johnson/4

A Fluorogenic Method for Lifting, Enhancing, and Preserving Bloody Impression Evidence

Volume 61, Issue 3, pages 260-280 (2011)

Jessica L. Zarate; Charles B. Morden

Abstract: This paper describes the use of Zar-Pro fluorogenic lifting strips that can be used on bloody impression evidence. These easy-to-use strips successfully lift and enhance bloody impressions

from a variety of substrates, regardless of porosity or background color. The lifting strips are highly sensitive and fluoresce when coupled with proteins and excited with an alternate light source.

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NON-FORENSIC PROFESSIONAL JOURNALS

Analytical & Bioanalytical Chemistry

Forensic Analysis of Salvia divinorum using Multivariate Statistical Procedures. Part I: Discrimination from Related Salvia Species

Volume 402, Issue 2, pages 833-842 (2012)

Melissa Bodnar Willard; Victoria McGuffin; Ruth Waddell Smith

Abstract: *Salvia divinorum* is a hallucinogenic herb that is internationally regulated. In this study, salvinorin A, the active compound in *S. divinorum*, was extracted from *S. divinorum* plant leaves using a 5-min extraction with dichloromethane. Four additional *Salvia* species (*Salvia officinalis*, *Salvia guaranitica*, *Salvia splendens*, and *Salvia nemorosa*) were extracted using this procedure, and all extracts were analyzed by gas chromatography–mass spectrometry. Differentiation of *S. divinorum* from other *Salvia* species was successful based on visual assessment of the resulting chromatograms. To provide a more objective comparison, the total ion chromatograms (TICs) were subjected to principal components analysis (PCA). Prior to PCA, the TICs were subjected to a series of data pretreatment procedures to minimize non-chemical sources of variance in the data set. Successful discrimination of *S. divinorum* from the other four *Salvia* species was possible based on visual assessment of the PCA scores plot. To provide a numerical assessment of the discrimination, a series of statistical procedures such as Euclidean distance measurement, hierarchical cluster analysis, Student *t* tests, Wilcoxon rank-sum tests, and Pearson product moment correlation were also applied to the PCA scores. The statistical procedures were then compared to determine the advantages and disadvantages for forensic applications.

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Forensic Analysis of Salvia divinorum using Multivariate Statistical Procedures. Part II: Association of Adulterated Samples to S. divinorum

Volume 402, Issue 2, pages 843-850 (2012)

Melissa Bodnar Willard; Victoria McGuffin; Ruth Waddell Smith.

Abstract: *Salvia divinorum* is a plant material that is of forensic interest due to the hallucinogenic nature of the active ingredient, salvinorin A. In this study, *S. divinorum* was extracted and spiked onto four different plant materials (*S. divinorum*, *Salvia officinalis*, *Cannabis sativa*, and *Nicotiana tabacum*) to simulate an adulterated sample that might be encountered in a forensic laboratory. The adulterated samples were extracted and analyzed by gas chromatography–mass spectrometry, and the resulting total ion chromatograms were subjected to a series of pretreatment procedures that were used to minimize non-chemical sources of variance in the data set. The data were then analyzed using principal components analysis (PCA) to investigate association of the adulterated extracts to unadulterated *S. divinorum*. While association was possible based on visual assessment of the PCA scores plot, additional procedures including Euclidean distance measurement, hierarchical cluster analysis, Student's *t* tests, Wilcoxon rank-sum tests, and Pearson Product Moment correlation were also applied to the PCA scores to provide a statistical evaluation of the association observed. The advantages and limitations of each statistical procedure in a forensic context were compared and are presented herein.

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Journal of Chromatography A

Fast Gradient Elution Reversed-phase High-Performance Liquid Chromatography with Diode-Array Detection as a High-throughput Screening Method for Drugs of Abuse: I. Chromatographic Conditions

Volume 1137, Issue 2, pages 153-162 (2006)

Dwight R. Stoll; Changyub Paek; Peter W. Carr

Abstract: A new approach for the high-throughput screening of biological samples to detect the presence of regulated intoxicants has been developed by modifying a conventional gradient elution HPLC. The goal of this work was to improve the speed of gradient elution screening methods over current approaches by optimizing the operational parameters of both the column and the instrument without compromising the reproducibility of the retention times, which is the basis for the identification of intoxicant compounds. Most importantly, the novel instrument configuration substantially reduces the time needed to re-equilibrate the column between consecutive gradient runs, thereby reducing the total time for each analysis. The total analysis time for each gradient elution run is only 2.80 min, including 0.30 min for column re-equilibration between analyses. Retention times of standard calibration solutes are reproducible to better than 0.002 min in consecutive runs. A corrected retention index was adopted to account for day-to-day and column-to-column variations in retention time. For a set of forty-seven target compounds, the discriminating power and mean list length were found to be 0.95 and 3.26, respectively. In comparison to previous work with similar numbers of target compounds, the current approach provides an order of magnitude improvement in analysis time, and a four-fold decrease in mean list length.

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Fast Gradient Elution Reversed-phase Liquid Chromatography with Diode-array Detection as a High-throughput Screening Method for Drugs of Abuse: II. Data Analysis

Volume 1137, Issue 2, pages 163–172 (2006)

Sarah E. Porter; Dwight R. Stoll; Changyub Paek; Sarah C. Rutan; Peter W. Carr

Abstract: In Part I of this work, we developed a method for the detection of drugs of abuse in biological samples based on fast gradient elution liquid-chromatography coupled with diode array spectroscopic detection (LC-DAD). In this part of the work, we apply the chemometric method of target factor analysis (TFA) to the chromatograms. This algorithm identifies the target compounds present in chromatograms based on a spectral library, resolves nearly co-eluting components, and differentiates between drugs with similar spectra. The ability to resolve highly overlapped peaks using the spectral data afforded by the DAD is what distinguishes the present method from conventional library searching methods. Our library has a mean list length (MLL) of 1.255 and a discriminating power of 0.997 when both retention index and spectral factors are considered. The algorithm compares a library of 47 different compounds of toxicological relevance to unknown samples and identifies which compounds are present based on spectral and retention index matching. The application of a corrected retention index for identification rather than raw retention times compensates for long-term and column-to-column retention time shifts and allows for the use of a single library of spectral and retention data. Training data sets were used to establish the search and identification parameters of the method. A validation data set of 70 chromatograms was used to calculate the sensitivity (correct identification of positives) and specificity (correct identification of negatives) of the method, which were found to be 92% and 94%, respectively.

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Application of Snyder–Dolan Classification Scheme to the Selection of “Orthogonal” Columns for Fast Screening of Illicit Drugs and Impurity Profiling of Pharmaceuticals – I. Isocratic Elution

Volume 1216, Issue 38, pages 6587–6599 (2009)

Wenzhe Fan, Yu Zhang, Peter W. Carr, Sarah C. Rutan, Melanie Dumarey, Adam P. Schellinger, Wayne Pritts

Abstract: Fourteen judiciously selected reversed phase columns were tested with 18 cationic drug solutes under the isocratic elution conditions advised in the Snyder–Dolan (S–D) hydrophobic subtraction method of column classification. The standard errors (S.E.) of the least squares regressions of $\log k'$ vs. $\log k'_{\text{REF}}$ were obtained for a given column against a reference column and used to compare and classify columns based on their selectivity. The results are consistent with those obtained with a study of the 16 test solutes recommended by Snyder and Dolan. To the extent these drugs are representative, these results show that the S–D classification scheme is also generally applicable to pharmaceuticals under isocratic conditions. That is, those columns judged to be similar based on the 16 S–D solutes were similar based on the 18 drugs; furthermore those columns judged to have significantly different selectivities based on the 16 S–D probes appeared to be quite different for the drugs as well. Given that the S–D method has been used to classify more than 400 different types of reversed phases the extension to cationic drugs is a significant finding.

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Analytical Chemistry

An RNA Aptamer-based Microcantilever Sensor to Detect the Inflammatory Marker, Mouse Lipocalin-2

Volume 84, Issue 20, pages 8763–8770 (2012)

Lijie Zhai; Tianjiao Wang; Kyungho Kang; Yue Zhao; Pranav Shrotriya; Marit Nilsen-Hamilton

Abstract: Lipocalin-2 (Lcn2) is a biomarker for many inflammatory-based diseases, including acute kidney injury, cardiovascular stress, diabetes, and various cancers. Inflammatory transitions occur rapidly in kidney and cardiovascular disease, for which an in-line monitor could be beneficial. Microcantilever devices with aptamers as recognition elements can be effective and rapidly responsive sensors. Here, we have selected and characterized an RNA aptamer that specifically binds mouse Lcn2 (mLcn2) with a dissociation constant of 340 ± 70 nM in solution and 38 ± 22 nM when immobilized on a surface. The higher apparent affinity of the immobilized aptamer may result from its effective multivalency that decreases the off-rate. The aptamer competes with a catechol iron-siderophore, the natural ligand of mLcn2. This and the results of studies with mLcn2 mutants demonstrate that the aptamer binds to the siderophore binding pocket of the protein. A differential interferometer-based microcantilever sensor was developed with the aptamer as the recognition element in which the differential response between two adjacent cantilevers (a sensing/reference pair) is utilized to detect the binding between mLcn2 and the aptamer, ensuring that sensor response is independent of environmental influences, distance between sensing surface and detector and nonspecific binding. The system showed a detection limit of 4 nM. This novel microcantilever aptasensor has potential for development as an in-line monitoring system for mLcn2 in studies of animal models of acute diseases such as kidney and cardiac failure.

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Applied Physics Letters

Differential Surface Stress Sensor for Detection of Chemical and Biological Species

Volume 93, pages 143107(1) – 143107(3) (2008)

Kyungho, Kang, Marit Nilsen-Hamilton, Pranav Shrotriya

Abstract: We report a sensor consisting of two micromachined cantilevers (a sensing/reference pair) that is suitable for detection of chemical and biological species. The sensing strategy involves coating the sensing cantilever with receptors that have high affinities for the analyte. The presence of analyte is detected by determining the differential surface stress associated with its adsorption/absorption to the sensing cantilever. An interferometric technique is utilized to measure the differential bending of the sensing cantilever with respect to reference. Surface stress associated with hybridization of single stranded DNA is measured to demonstrate the unique advantages of the sensor.

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Journal of Applied Physics

Cantilever Deflection Associated with Hybridization of Monomolecular DNA Film

Volume 111, Issue 7, pages 74310(1) – 74310(9) (2012)

Yue Zhao, Baskar Ganapathysubramanian, Pranav Shrotriya

Abstract: Recent experiments show that specific binding between a ligand and surface immobilized receptor, such as hybridization of single stranded DNA immobilized on a microcantilever surface, leads to cantilever deflection. The binding-induced deflection may be used as a method for detection of biomolecules, such as pathogens and biohazards. Mechanical deformation induced due to hybridization of surface-immobilized DNA strands is a commonly used system to demonstrate the efficacy of microcantilever sensors. To understand the mechanism underlying the cantilever deflections, a theoretical model that incorporates the influence of ligand/receptor complex surface distribution and empirical interchain potential is developed to predict the binding-induced deflections. The cantilever bending induced due to hybridization of DNA strands is predicted for different receptor immobilization densities, hybridization efficiencies, and spatial arrangements. Predicted deflections are compared with experimental reports to validate the modeling assumptions and identify the influence of various components on mechanical deformation. Comparison of numerical predictions and experimental results suggest that, at high immobilization densities, hybridization-induced mechanical deformation is determined, primarily by immobilization density and hybridization efficiency, whereas, at lower immobilization densities, spatial arrangement of hybridized chains need to be considered in determining the cantilever deflection.

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Langmuir

Aptamer Functionalized Microcantilever Sensors for Cocaine Detection

Volume 27, Issue 23, pages 14696-14702 (2011)

Kyungho Kang, Ashish Sachan, Marit Nilsen-Hamilton, Pranav Shrotriya

Abstract: A cocaine-specific aptamer was used as a receptor molecule in a microcantilever-based surface stress sensor for detection of cocaine molecules. An interferometric technique that relies on measuring differential displacement between two microcantilevers (a sensing/reference pair) was utilized to measure the cocaine/aptamer binding induced surface stress changes. Sensing experiments were performed for different concentrations of cocaine from 25 to 500 μM in order to determine the sensor response as a function of cocaine concentration. In the lower concentration range from 25 to 100 μM , surface stress values increased proportionally to coverage of aptamer/cocaine complexes from 11 to 26 mN/m. However, as the cocaine concentration was increased beyond 100 μM , the surface stress values demonstrated a weaker dependence on the affinity complex surface coverage. On the basis of a sensitivity of 3 mN/m for the surface stress measurement, the lowest detectable threshold for the cocaine concentration is estimated to be 5 μM . Sensing cantilevers could be regenerated and reused because of reversible thermal denaturation of aptamer.

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Ultramicroscopy

A statistical Analysis of the Variation in Measured Crystal Orientations Obtained through Electron Backscatter Diffraction

Volume 110, pages 1312-1319 (2010)

Melissa A. Bingham; Barbara K. Lograsso; Francis C. Laabs

Abstract: Electron backscatter diffraction (EBSD) techniques are used to determine the crystallography of individual metal grains. This paper examines the variability in the orientation of measurements obtained by EBSD. Although precision and statistics of orientation have been explored in the literature, little attention has been paid to formal statistical inference for quantifying variation in orientation measurements. Our intention is to study precision by developing statistical analyses for quantifying multiple sources of orientation variation, given repeat scans of a metal sample. Three sources of variability are simultaneously explored: variation in repeat measurements at a fixed location, variation among locations within a grain, and grain-to-grain variation. Bayes statistical methods will be applied to a hierarchical model with the uniform-axis-random-spin (UARS) components of Bingham et al. to quantify these sources of variation. Repeat scans of an Inconel 600 specimen will be used to provide an illustrating example of how the statistical methods can be used to arrive at precision estimates.

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Journal of the American Statistical Association

Modeling and Inference for Measured Crystal Orientations and a Tractable Class of Symmetric Distributions for Rotations in Three Dimensions

Volume 104, Issue 488, pages 1385-1397 (2009)

Melissa Bingham; Daniel Nordman; Stephen Vardeman

Abstract: Electron backscatter diffraction (EBSD) is a technique used in materials science to study the microtexture of metals, producing data that measure the orientations of crystals in a specimen. We examine the precision of such data based on a useful class of distributions on orientations in three dimensions (as represented by 3×3 orthogonal matrices with positive determinants). Although such modeling has received attention in the statistical literature, the approach taken typically has been based on general “special manifold” considerations, and the resulting methodology may not be easily accessible to nonspecialists. We take a more direct modeling approach, beginning from a simple, intuitively appealing mechanism for generating random orientations specifically in three-dimensional space. The resulting class of distributions has many desirable properties, including directly interpretable parameters and relatively simple theory. We investigate the basic properties of the entire class and one-sample quasi-likelihood-based inference for one member of the model class, producing a new statistical methodology that is practically useful in the analysis of EBSD data. This article has supplementary material online.

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Bayesian Analysis

Bayes One-sample and One-way Random Effects Analyses for 3-D Orientations with Application to Materials Science

Volume 4, Issue 3, pages 607-629 (2009)

Melissa A. Bingham; Daniel J. Nordman; Stephen B. Vardeman

Abstract: We consider Bayes inference for a class of distributions on orientations in 3 dimensions described by 3×3 rotation matrices. Non-informative priors are identified and Metropolis-Hastings within Gibbs algorithms are used to generate samples from posterior distributions in one-sample and one-way random effects models. A simulation study investigates the performance of Bayes analyses based on non-informative priors in the one-sample case, making comparisons to quasi-likelihood inference. A second simulation study investigates the behavior of posteriors for some informative priors. Bayes one-way random effect analyses of orientation matrix data are then developed and the Bayes methods are illustrated in a materials science application.

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Rapid Communications in Mass Spectrometry

Statistical Approach to Establish Equivalence of Unabbreviated Mass Spectra

Volume 28, Issue 1, pages 83-95 (2014)

Bodnar-Willard, M., Waddell Smith, R., McGuffin, V.

Abstract: In many legal and regulatory applications, mass spectral comparisons of an unknown or questioned sample to a reference standard or database are used for identification. Yet, statistical confidence levels or error rates are typically not determined thus making a method needed to establish the statistical equivalence of mass spectra.

This project describes the development and validation of a method to assign statistical

significance to the comparison of mass spectra. The standard deviation of the abundance at each m/z ratio was determined from replicate measurements and from a statistical model. These standard deviations were used in an unequal variance t-test to compare two spectra at every m/z ratio over the entire scan range. If determined to be statistically indistinguishable at every m/z ratio, the random match probability (RMP) that the specific mass spectral fragmentation pattern occurred by chance was calculated.

n-Alkane and alkylbenzene standards of varying concentrations were analyzed on the same instrument at different ionization voltages. Using the proposed method, replicate spectra were successfully associated at the 99.9% confidence level with RMP values less than 10^{-29} . Despite the similarity in fragmentation patterns, spectra were distinguished from others in the homologous series. Moreover, the n-alkane spectra were appropriately associated to and discriminated from those in a standard reference database at the 99.9% confidence level thus suggesting that the method may be useful for legal and regulatory application like the identification of controlled substances.

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