Introduction

- What is forensic chemistry?
  - Analytical chemistry (Qual., Quant.) applied to the law
    - Criminal or civil
  - More than just analytical chemistry
    - Includes comparative analyses
    - Used to answer questions
- From the word forum
  - Place where Romans conducted business and legal proceedings

State of Forensic Science in USA

- In "normal" science, academically gifted students receive addition years of "socialization"
- ~96% of Forensic Scientists only hold Bachelor’s degrees (or less)
- ~3% Masters, ~1% Ph.D.
- Most Forensic Scientists not educated on methodological rigor, openness, cautious interpretation of data etc.
- "pressure" leads to data fudging and fabrication
- DNA analysis excluded

Paradigm shift

- Federal agencies providing more $$$ for statistical analysis and scientific validation of techniques
- Assisted by 911, war on terror, DHS etc.
- Examples of emerging fields
  - Isotope ratio analysis
  - Chemical sensors (esp. portable)
  - Raman, IR, MS, XFS, electrochemical etc.
  - Chromatography-MS methods for qualitative and quantitative analysis of body fluids (doping, pathology etc.)


Food for thought

"If the law has made you a witness, remain a man of science. You have no victim to avenge, no guilty or innocent person to convict or save — you must bear testimony within the limits of science."

— Dr. P.C.H. Brouardel

19th Century French Medico-legalist

CSI TV-show myths

- Most forensic chemists do not visit the crime scene
  - Costs, liability, contamination, time, expertise
- Most crime scene investigators do not analyze samples
  - Lack of expertise, time, money
- Analyses on TV are oversimplified
  - Need lab certification, personnel certification (& training), method validation, instrument calibration, verifiable standards, run blanks and standards, write reports etc. etc.
- But...Forensic Chemistry is still interesting and rewarding
Precedents

- Law, as science, follows that which has gone before: Precedent
  - Precedents are a guide for future decisions
- A forensic chemist uses the scientific method to determine the truth about a sample
- Courts use a “trier of fact” to determine “the truth”

Key concepts

- Criminal and civil cases
- Admission of evidence
- Who should question credibility: Judge or Jury?
  1) The Frye Rule (“General Acceptance”)
     - 1923, Frye v. United States
       - Evidence is admissible as long as the techniques are accepted as valid by the relevant scientific community
       - Gives a list of criteria for admissibility
       - Peer review process is proof of prior acceptance/validation
       - Need to prove general acceptance


Key concepts

- Admission of evidence:
  2) The Daubert Decision
     - Daubert v. Merrel Dow Pharmaceuticals (1993)
     - Re: Birth defects due to morning sickness drug Bendectin
     - US Supreme court ordered new standard for admissibility of forensic evidence in (federal) court: Gave Judges “gatekeeper role”
     - Requires scientific rigor more than “expertise” or historical use
     - E.g. US v. Starzecypzel (1995) found that handwriting analysis had no scientific foundation
     - However, evidence was not rejected because it wasn’t considered “scientific”
     - “nonscience” loophole

Key concepts

• Admission of evidence:
  3) Kumho extension
    - Kumho Tire Co., Ltd. v. Carmichael (1999)
    - Extended Daubert to all expert testimony, not just scientific
    - Requires different standards for different disciplines
    - Medical examiner devised new test to determine death by succinylcholine poisoning
    - Defendant’s lawyer claimed lack of corroborating support by other scientists
    - Evidence held up b/c of principles of the analysis

Direct and circumstantial evidence

• Direct
  - Establishes fact
  - E.g. eyewitness accounts, confessions etc.
  - Usually not very reliable

Forensic identification requires a more scientific approach including statistical as opposed to subjective analyses.

![Graph](image-url)
Skeletal Structures

- Assume there is a carbon atom at the junction of any two lines or at the end of any line.
- Assume there are enough hydrogens around each carbon to make it tetravalent.
- Draw in all heteroatoms and hydrogens directly bonded to them.
Convert to a Lewis structure:

\[
\text{H}_2\text{CO}_2\text{CH}_3 \quad \text{N} \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{CH}_3
\]

Convert to a condensed structure:

\[
\text{O} \quad \text{CH}_3\text{CH}_3\text{C} \quad \text{CH}_3\text{CH}_2\text{OH}
\]

Making a model of ethane illustrates one additional feature about its structure. Rotation occurs around the central C—C σ bond.

Bond rotation can occur here. Note where the colored H-atom is located in both structures.

Which of the indicated bonds is the shortest?

- a
- b
- c

B, the triple bond is the shortest.

Which C-H bond is the shortest?

- a
- b

A has 50% s character, due to it being made up of an sp hybridized bond, and is thus shorter.
Mass spectrometry: basics

• Whenever the word “mass” is used in mass spectrometry, it means mass/charge!
• Mass spectrometry only ever measures m/z
  – Biologists sometimes refer to Daltons (or kDa, MDa), but this really means Da/z
  – Acceptable terminology is the Thompson: 1 Th = 1 m/z
• Mass spectroscopes have not been used since 1940s: Therefore, we do not do mass spectroscopy
• Many types of mass spectrometers exist; they all require a source of ions, a vacuum, a method for m/z discrimination (magnetic or electric fields required) and a detection method

Ion sources: EI

• EI is most common for GC detection
  – Electron ionization (NOT electron impact ionization)
• Many events possible in an electron-neutral collision
  – excitation
  – electron capture
  – Ionization
  – ionization w/ excitation (w/ or w/out rearrangement)
  
  $e + A-B-C \rightarrow A-B-C^{-2e} \rightarrow A + (B-C)$
  
  $\rightarrow A + (B-C)$
  
  $\rightarrow A + (B^{-e})$
  
  $\rightarrow (A-C)^{-e} + B$ etc.
  – multiple ionization (w/ or w/out excitation, dissociation, rearrangement etc.)

**EI spectra of beta lactam at different e- energies**

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**Ion sources: EI**

Drugs and Pharmacology

- Drugs
  - Substances capable of a physiological change
    - Swallowing, injection, inhalation, absorption
  - “All substances are poisons...the right dose differentiates a poison from a remedy”
    - (Paracelsus 1493-1541)

- Medicines
  - Mixtures of drugs and inert ingredients used to prevent or treat symptoms or disease

- Forensic Toxicologists
  - detecting and identifying the presence of drugs and poisons in body fluids, tissues, and organs in relation to the law
Classification of drugs

- By origin, function, effect, chemistry, use or potential for abuse
  - Opiates, stimulants, analgesics, alkaloids, club drug, schedule II

- Controlled Substances Act (1970)
  - Five classes of drugs based on abuse, physical dependency and medical properties
  - The manufacture of Classes I and II are controlled by the government
  - The penalties for possession/dealing Classes I and II are the most severe – up to 20 years in jail

- How does a drug get scheduled?
  1) hazard to health or community
  2) used outside of medical subscription
  3) related to an already-listed substance

Drugs: by effect

- Analgesics
  - Pain relievers (at site (aspirin), or at CNS (morphine))
  - Opiates

- Depressants
  - Depress CNS (slowed heart beat, reduced anxiety, sleep)
  - Alcohol, benzodiazepines (huge class), barbiturates, inhalants

- Hallucinogens
  - Alter mental perception of time/space/feeling
  - LSD, MDMA (ecstasy), marijuana, cannabis, psilocybin (magic mushrooms), methamphetamine (high doses)

- Narcotics
  - Analgesic and depress CNS
  - Opiates, oxycodone, heroin

- Stimulants
  - Stimulate CNS (promotes alertness, reduces fatigue/sleep)
  - Cocaine, amphetamine, methamphetamine
  - Can be hallucinogenic in high doses

Drugs: by use

- Predator drugs
  - Date-rape drugs, drug-facilitated sexual assault (DFSA)
  - Alcohol, ketamine, rohypnol, GHB (gamma hydroxybutyrate)
  - Lack of memory often leads to delayed testing

- Club drugs
  - Used to create ‘highs’ and energy in parties and clubs
  - Ecstasy (MDMA, methylene dioxy methamphetamine), LSD (lysergic acid diethylamide), psilocybin, PCP (phencyclidine)

- Performance-enhancing drugs
  - Mostly humans and horses
  - Anabolic steroids, human growth hormones

- Inhalants
  - Not originally intended for drug use
  - Very nasty side-effects
  - Paint thinners, cleaners, solvents, butane, nail polish etc.
**Controlled substances**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Schedule</th>
<th>murderer</th>
<th>required possession</th>
<th>Punishment</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methamphetamine</td>
<td>3</td>
<td>Death</td>
<td>Yes in 90 days</td>
<td>Life</td>
<td>Methamphetamine meth lab</td>
</tr>
<tr>
<td>Heroin</td>
<td>1</td>
<td>Death</td>
<td>Yes in 90 days</td>
<td>Life</td>
<td>Heroin lab</td>
</tr>
<tr>
<td>Inhalants</td>
<td>2</td>
<td>Life</td>
<td>Yes</td>
<td>Life</td>
<td>Inhalant lab</td>
</tr>
<tr>
<td>Ecstasy</td>
<td>3</td>
<td>Life</td>
<td>Yes</td>
<td>Life</td>
<td>Ecstasy lab</td>
</tr>
</tbody>
</table>


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**World drug report: Amphetamines**

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**Abused drugs in the USA**

<table>
<thead>
<tr>
<th>Drug</th>
<th>% users</th>
<th># users</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caffeine</td>
<td>9%</td>
<td>9</td>
</tr>
<tr>
<td>Alcohol</td>
<td>53%</td>
<td>110M</td>
</tr>
<tr>
<td>Tobacco</td>
<td>26.00%</td>
<td>55M</td>
</tr>
<tr>
<td>Prescription drugs</td>
<td>0.80%</td>
<td>1.6M</td>
</tr>
<tr>
<td>Inhalants</td>
<td>1%</td>
<td>1.6M</td>
</tr>
<tr>
<td>Marijuana</td>
<td>5%</td>
<td>10M</td>
</tr>
<tr>
<td>Cocaine</td>
<td>0.80%</td>
<td>1.6M</td>
</tr>
<tr>
<td>Narcotics and analgesics</td>
<td>0.60%</td>
<td>1.3M</td>
</tr>
<tr>
<td>Hallucinogens</td>
<td>0.40%</td>
<td>0.8M</td>
</tr>
<tr>
<td>Depressants</td>
<td>0.30%</td>
<td>0.5M</td>
</tr>
<tr>
<td>Stimulants</td>
<td>0.10%</td>
<td>0.2M</td>
</tr>
</tbody>
</table>


I. Schedule I
- Have a high potential for abuse
- Have no current accepted medical use
- Examples include: heroin, marijuana, methaqualone, LSD

II. Schedule II
- Have potential for abuse
- Have restricted medical use
- Great physical and mental dependency
- Examples include: opium, cocaine, phenycyclidine, barbiturates, and amphetamines
III. Schedule III
- Have low potential of physical dependence but have the potential for mental dependency
- Have accepted medical use
- Examples include: codeine, certain barbiturates and anabolic steroids

IV. Schedule IV
- Have even lower physical and mental dependence
- Have current medical use
- Examples include: propoxyphene (Darvon), phenobarbital, and tranquilizers including meprobamate, diazepam, chlordiazepoxide (miltown, valium, and librium)

V. Schedule V
- Low abuse and dependency
- Have accepted medical use
- Examples include: opiate drug mixtures containing non-narcotic medicinal ingredients

Other drugs:
- Designer Drugs: non-listed drugs which are chemically related to controlled substances. Examples include Fentanyl
- Precursors to amphetamines and PCP are listed as schedule II.

Carryover refers to the contamination of a sample by the preceding sample. A laboratory should determine the concentration of drug that may result in carryover for each analyte. Drug standards with concentrations increasing over the range that the laboratory expects to encounter are injected and a solvent blank is injected on the next run. It is then determined how high the concentration must be in order for the drug standard to carryover and cause a positive response for the solvent blank.
Ergot and tryptamine alkaloids and hallucinogens

- LSD derived from ergot alkaloids
  - Ergot is a fungus found mostly on grains
  - Difficult synthesis = fewer, but more specialized labs
- Mescaline
  - From cactus plants (peyote)
  - Legal for native americans

www.mescaline.com/exp/
Ergot and tryptamine alkaloids and hallucinogens

- 5-MeO-DMT & bufotoxins
  - 5-methoxy-dimethyltryptamine
  - from Bufo alvarius (colarado river) toads
  - excreted in venum
  - semi synthetic versions enhance methylation
  - usually smoked, not licked!

Methamphetamine synthesis

Involves red phosphorous (from matches)
Can produce phosphine gas (PH3)
Requires Li (from batteries?) and ammonia (from fertilizers)

Marijuana and cannabis

- THC typically present at 1-5% w/w in cannabis sativa
- Some hybrids, such as sinsemilla, can have up to 13% w/w
- Hashish, hash oil, cannabis resin, draw, etc has elevated levels
- Analysis
  - Bear claws under microscope
  - Acid will create bubbles
Three Step Method for Comparing Analogs to Scheduled Substances

1. Synthesize

2-1 [tryptamine][total alkyl iodide] in water with SDS and NaHCO₃ for 1 hour at 80°C

2. Doped buffer solution

3. Measure BBB Permeability

4. Glycine

5. NHa

Gauge Permeability

Measure Receptor Activity

ESI-MS of Synthesis using 3 alkyl iodides

Parallel Artificial Membrane Permeability Assay (PAMPA)

Fingerprint Residue Lifts
Finger Cast

Fig. 8-Fingerprint lift of cocaine/red fluorescent powder

Fingerprint Lift with Cocaine/Red Fluorescent Powder

Fig. 9-Cocaine Extraction from fingerprint lift

Cocaine Extraction from Fingerprint Lift

Fig. 11-NSI-MS Cocaine Extraction Spectrum. Parent ion peak is at m/z 304.27
Forensic Chemistry

Electrostatic Lift

Left: Raman imaging of cocaine and soil mixture


Forensic Chemistry


Computer Chip with DNT/RTX
Nitroglycerine (NG) Extraction from Fingerprint Lift

**Fig. 11-** NG residue from fingerprint lift

**Fig. 12-** NG residue from fingerprint lift

**Fig. 13-** NSI-MS NG Extraction spectrum. The adduct peak is at m/z 287.13

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**Post Blast Analysis, Denton County Bomb Squad**

A KineStik (KinePak) is a binary explosive that consists of ammonium nitrate (solid) and nitroglycerin (liquid). The explosive is kept separate until just before detonation. In a test, a 1/3 stick of a premixed KineStik was placed in a glass vial. This was placed in the paint can and attached to a blasting cap with either RDX or PETN (Austin Star Detonator Company). A Scorpion HB-SBS Solid State Electronic Blasting Machine and Non-Electric Initiator was used in conjunction with a 7.3 m detonation cord to initiate the blast.
Forensic Chemistry

Extraction of particulate from paint can after detonation of KinePak (NH4NO3) with 1 mg/mL dextrose solvent in 50:50 MeOH/H2O


\[
\]

Nanomanipulation

Direct analyte probe nanoextraction (DAPNe)
Iron Gall Ink

- EDTA, a chelator, was added to the solvent to extract the metals from the ink.

Rhodamine-Red Sharpie

Identification of PEG peaks with protonated (+1) and sodiated (+23) adducts where n=number of monomers and M=parent ion.

Characterization of India ink, waterproof drawing.

Forensic Chemistry

Comparison of spectra after 4 hrs of applied heat.

Next slide: zoomed in from 900-1000 m/z

Next slide: zoomed in from 200-300 m/z

Waterproof drawing, India Ink

For this particular ink, the inner PEG distribution becomes more abundant over time.

Tracking the process of oxidation

- Relative peak area (RPA) is used to calculate the oxidation of PEG.

Waterproof Calligraphy, India Ink
The four was modified 2 days later. The extraction solvent used was MeOH:Water:1%Acetic acid. The extractions were done on 3 spots:

1. Top, only ink pen 2
2. Bottom, only ink pen 1
3. Intersect, both ink pens cross

**DAPNe-NSI-MS**

**Top**

<table>
<thead>
<tr>
<th>m/z</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>356.53333</td>
<td></td>
</tr>
<tr>
<td>372.46667</td>
<td></td>
</tr>
</tbody>
</table>

**Bottom**

<table>
<thead>
<tr>
<th>m/z</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>586.2</td>
<td></td>
</tr>
<tr>
<td>630.13333</td>
<td></td>
</tr>
<tr>
<td>674.13333</td>
<td></td>
</tr>
<tr>
<td>718.13333</td>
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<tr>
<td>762.13333</td>
<td></td>
</tr>
<tr>
<td>850</td>
<td></td>
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<tr>
<td>893.93333</td>
<td></td>
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<tr>
<td>1069.93333</td>
<td></td>
</tr>
<tr>
<td>1113.86667</td>
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</tr>
</tbody>
</table>

**PEG 800.136**
DAPNe-NSI-MS

Solvent Tip Chemistry

Uni-Ball Black waterproof pen has diversity when extracting with MeOH:H2O:1%Ac and Chloroform:MeOH:NH3OAc. The other pens show the same peaks for all three solvents.

DAPNe-Fluorescence Imaging

Red ink, two different pens, pre-extraction
Pilot and paper-1 pen

C-O-C stretching, Ethers (aromatic, olefinic or aliphatic) from glycol ethers.

O-H stretching (from cellulose of paper)

Ink 1

3223 cm\(^{-1}\)

O-H or N-H stretch

Raman Image of two different inks

Ink 1

600µmx300µm
Fingerprint Imaging

- Sample where material is available in limited quantities and integrity of sample must remain intact.
- Usable post analysis

- Fatty acids (FAs)
  - Unsaturated
  - Polyunsaturated
- Diacylglycerols (DAGs)
- Triacylglycerols (TAGs)
- Cholesterol
- Surfactant/detergent (cosmetics, fabric softeners, etc)
  - Dimethyldioctadecyl ammonium (DDA)
  - Dimethylbenzylammonium (DBA)
Overlapping prints

Doped Fingerprints

Forensic Chemistry

Tryptamine

m/z 144.07

Melatonin

m/z 232.12