

Technical Forensic Analysis

Rami Elias Kremesti B.Sc., M.Sc.,

CSci, CEnv, CWEM

rami@kremesti.com

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PASSION FOR CHEMISTRY

Table of Content

- Explosive Traces/Gunshot Residue/Bullet Ballistics/Accelerators
- Pyrogenic liquids/Unknown Chemicals
- DNA/Blood/Hair/Semen/Saliva
- Smart DNA
- Fingerprints/Digital Trail
- Fabrics
- Paints/Pigments/Dyes
- Fake Money/Fake Drugs
- Contaminated Spirits/Fake Spirits
- Poisons/Toxicology/Biocides
- Forensic Pathology/Autopsy
- Corpse Analysis/Time of Death
- Soil Forensics
- Art/Document Fraud
- Gem Fraud
- Precious Metal Fraud

Some Techniques Used

- Infra Red/FT-IR Spectroscopy
- NMR
- Raman Spectroscopy
- Mass Spectrometry
- LC-MS
- Confocal Microscopy
- XRF = X ray Fluorescence
- HPLC
- DNA/PCR

Gunshot Residue

- The most commonly used method for the chemical analysis of gunshot residue is scanning electron microscopy (**SEM**) with energy dispersive X-ray (**EDX**), which focuses on the inorganic elements present in ammunition propellants, particularly heavy metals.
- Gunshot residue (GSR) consists of unburned or partially burned gunpowder particles, soot, nitrate, and nitrites from the combustion of the powder, particles of primer (oxides of lead, antimony, and barium), and micro-pieces of the bullet or the bullet jacket that are vaporized when a firearm is discharged.

Raman Spectra of Explosive Residues

Pentaerythritol tetranitrate, also known as PENT, pentyl, PENTA, TEN, corpent, or penthrite, is an explosive material. It is the nitrate ester of pentaerythritol, and is structurally very similar to nitroglycerin.

TATP is a homemade **explosive** (HME) that has seen widespread illicit use over the last two decades. It stands for **TRIACETONE TRIPEROXIDE**.

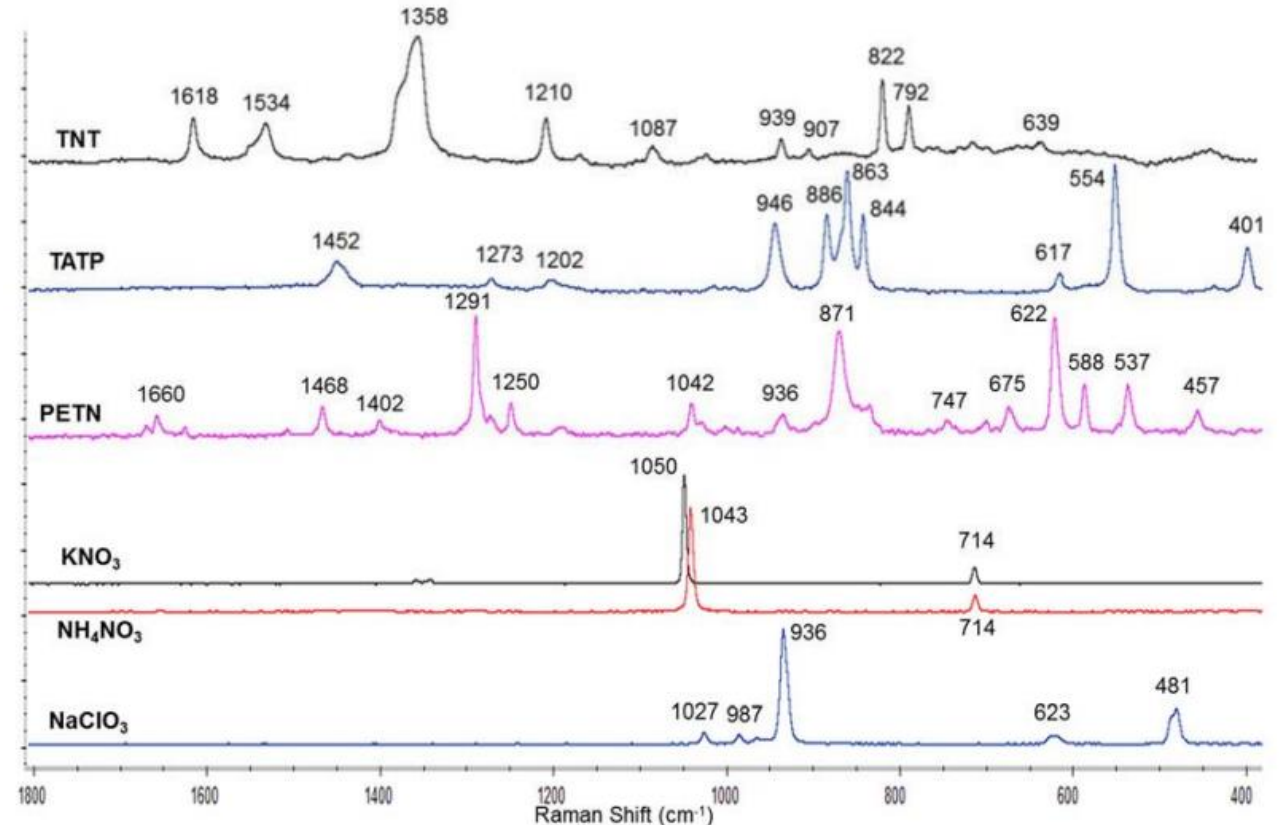


Figure 3. Raman spectra of several explosives and inorganic salts obtained using a 785 nm laser, 5 scans, 0.5 s acquisition time and 10% laser power. Baselines were corrected by software.

Deliberate Fire Investigations

Forensic tools

- Infrared cameras, gas chromatographs, and specially trained dogs can help analyse the physical elements of the fire.

Ignition devices

- Investigators look for obvious ignition devices like matches, electronic ignitors, or the glass of a Molotov cocktail.

Accelerant detection dogs

- These dogs can detect even the smallest hint of an accelerant, such as gasoline, acetone or lighter fluid.

Ethanol vs Methanol

Contaminated home brews
Can contain traces of methanol

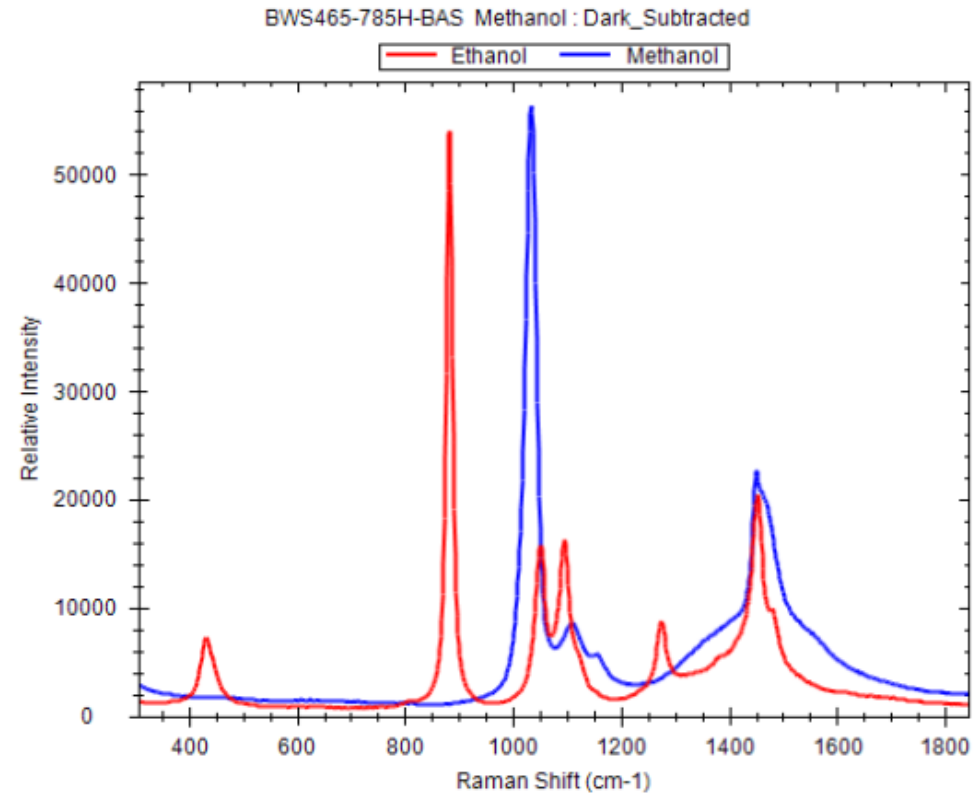


Figure 1 Raman spectra of reagent grade ethanol (red) and methanol (blue).

Poison Chemistry/Toxicology - I

POISON CHEMISTRY - WHITE ARSENIC

Arsenic is a notorious poison; colourless, odourless white arsenic was a popular choice for poisoners, and was commonly known as 'The King of Poisons'.

HISTORY



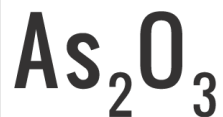
White arsenic has been known for centuries. In Ancient Rome, Nero's supposed use of it to poison his brother & become emperor is one of the first documented cases.



In the 17th & 18th centuries, white arsenic's use as a poison was widespread, and earned it the nickname 'inheritance powder'. However, its usage as a poison rapidly declined after the development of chemical tests.



Around 50,000 tonnes of arsenic trioxide are still produced annually, and used as a precursor to a range of compounds. It's also been used as a treatment for some leukaemias.

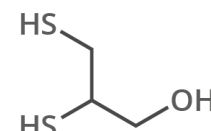


ARSENIC (III) OXIDE

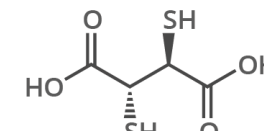


MEDIAN LETHAL DOSE: 15.1mg/kg

TREATMENT



DIMERCAPROL



DIMERCAPTOSUCCINIC ACID

Chelating agents, such as the above compounds, bind the arsenic ions and prevent them from inhibiting enzymes. However, chelation therapy itself can have side effects. Dimercaprol has been largely superseded by 2,3-dimercapto-1-propanesulfonic acid.

EFFECTS



HEADACHE



DISCOLOURATION OF NAILS



VOMITING & METALLIC TASTE



BREATH SMELLS OF GARLIC



STOMACH PAIN & DIARRHOEA



HAIR LOSS



CONVULSIONS

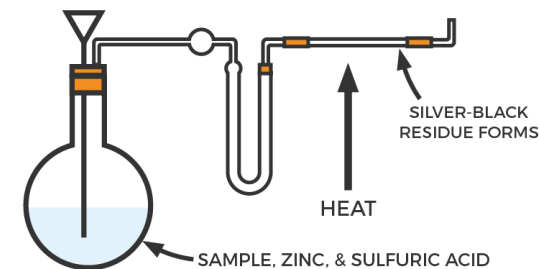


CONVULSIONS, COMA & DEATH

Symptoms usually appear around 30 minutes after ingestion. Arsenic interferes with cell enzymes, respiration and mitosis. The skin, lungs, kidneys and liver are the major organs affected, with death occurring either from circulatory inefficiency, or liver or kidney failure.



DETECTION



The Marsh Test involves reaction of a sample with zinc and acid. If arsenic is present, it is converted to arsine gas. Heating arsine decomposes it; a silver-black deposit of arsenic is formed on cooling. Modern spectroscopic methods are now used instead of this test.



Poison Chemistry/Toxicology - II

POISON CHEMISTRY - CYANIDE COMPOUNDS

Cyanide is a fast-acting, bitter-tasting poison, and one of the deadliest known. Its compounds have famously been utilised in suicide pills over the years.

HISTORY



Cyanide has been used for centuries as a poison, but was first identified in 1782 by the Swedish chemist Scheele; in fact, it's thought Scheele's death may have been contributed to by cyanide exposure.



During WWI, the French attempted to use hydrocyanic acid, then cyanogen chloride, in chemical warfare. In WWII, The Nazis used hydrogen cyanide in the form of Zyklon B to kill millions in their concentration camps.



Hydrogen cyanide gas has previously been used for pest control, which sometimes led to accidental deaths. Today, cyanides are still used in the mining of gold and silver, and in organic synthesis reactions.

HCN KCN NaCN

HYDROGEN CYANIDE POTASSIUM CYANIDE SODIUM CYANIDE

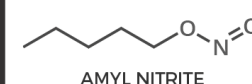
(Note: KCN and NaCN both get converted to HCN by stomach acid)



MEDIAN LETHAL DOSE: 3-8mg/kg

ORAL - VARIES DEPENDING ON FORM OF CYANIDE ADMINISTERED

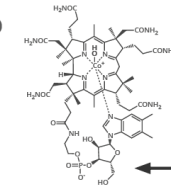
TREATMENT



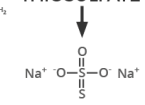
AMYL NITRITE



SODIUM NITRITE



SODIUM THIOSULFATE



VITAMIN B12a

The most prevalent antidotes are nitrites, which convert haemoglobin into methemoglobin, which then removes cyanide from cytochrome oxidase. Thiosulfate helps convert cyanide to thiocyanate so it can be excreted. Cobalt ions also form a stable complex with cyanide.

EFFECTS



DIZZINESS & HEADACHE



NAUSEA & VOMITING



RAPID BREATHING & HEART RATE



LOW BLOOD PRESSURE



LOSS OF CONSCIOUSNESS



RESPIRATORY FAILURE



CONVULSIONS & DEATH

Cyanide inhibits the cytochrome oxidase enzyme, preventing the body's cells from using oxygen. HCN smells of bitter almonds, but only ~40% of people have the genetic ability to smell it. Many fruit seeds also contain small amounts of cyanide-containing compounds.



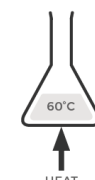
DETECTION

Sample added to 5% NaOH solution



1 MIN

Transferred to solution of 5% FeSO₄ & 1% FeCl₃



60°C

HEAT
10 MINS

Adding hydrochloric acid solution gives prussian blue.



1:6 HCl:H₂O
10-15 MINS

A common test for cyanide in the early 20th Century formed prussian blue, an iron-cyanide complex, in the presence of cyanide ions. There are several other chemical tests, including portable card-based tests, and instrumental methods can also be used.

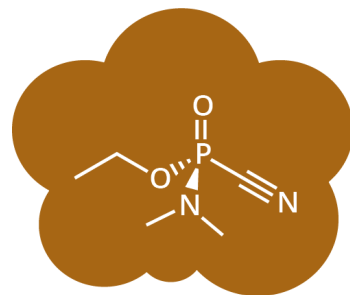


Nerve Agents

CHEMICAL WARFARE NERVE AGENTS

PART ONE: THE G SERIES

THE G SERIES NERVE AGENTS ARE SO NAMED BECAUSE THEY WERE ALL FIRST SYNTHESISED IN GERMANY. THEY ARE ALL EXTREMELY TOXIC VOLATILE LIQUIDS, CLASSIFIED AS WEAPONS OF MASS DESTRUCTION BY THE U.N., AND THEIR PRODUCTION & STOCKPILING IS OUTLAWED.



TABUN (GA)

(ethyl dimethylphosphoramidocyanidate)

SMELL & APPEARANCE

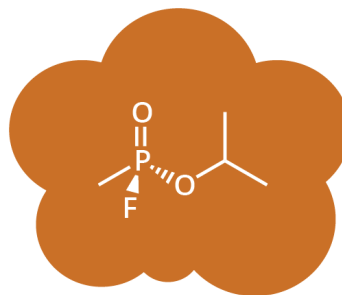
Clear, colourless liquid, though impure tabun can have a brown appearance. Pure tabun is odourless, but it often has a faint 'fruity' odour due to impurities.

SYNTHESISED

1936 Discovered accidentally by Gebhardt Schraeder, a German chemist who was investigating organophosphates as pesticides.

LETHALITY

median lethal concentration	median lethal dose
400	1000
milligram-minutes per cubic metre	milligrams per kilogram of body weight



SARIN (GB)

(isopropyl methylphosphonofluoridate)

SMELL & APPEARANCE

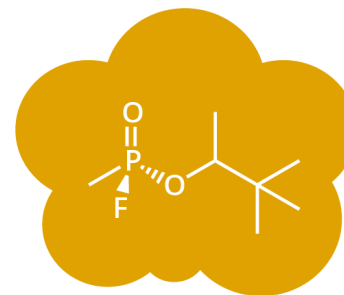
A clear, colourless liquid, tasteless and odourless in its pure form. It's a volatile liquid; like other nerve gases the vapour generated is heavier than air.

SYNTHESISED

1938 Named after the team of scientists behind its initial discovery: Schrader, Ambros, Ritter & Van der Linde

LETHALITY

median lethal concentration	median lethal dose
100	1700
milligram-minutes per cubic metre	milligrams per kilogram of body weight



SOMAN (GD)

(3,3-dimethylbutan-2-yl methylphosphonofluoridate)

SMELL & APPEARANCE

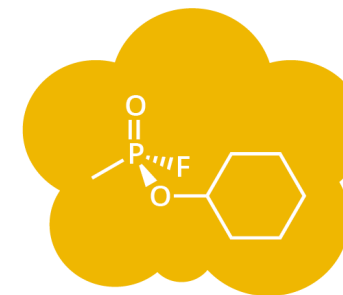
Soman is a clear, colourless, tasteless liquid. Its odour is faint when pure, but when impure it has a yellow-brown colour and has a strong, camphorous odour.

SYNTHESISED

1944 Discovered during research into the pharmacology of tabun & sarin funded by the German army.

LETHALITY

median lethal concentration	median lethal dose
70	50
milligram-minutes per cubic metre	milligrams per kilogram of body weight



CYCLOSARIN (GF)

(cyclohexyl methylphosphonofluoridate)

SMELL & APPEARANCE

Clear, colourless liquid with a sweet, musty smell, sometimes likened to peaches. It evaporates around 70 times slower than sarin, and is also flammable.

SYNTHESISED

1949 Also a result of German research, Iraq is the only country known to have manufactured significant quantities.

LETHALITY

median lethal concentration	median lethal dose
50	30
milligram-minutes per cubic metre	milligrams per kilogram of body weight

EFFECTS OF NERVE AGENTS



Inhibit breakdown of acetylcholine



Cause contraction of the pupils



Excessive mucus, tears, saliva & sweat



Nausea, gastrointestinal pain & vomiting



Bronchoconstriction & chest tightness



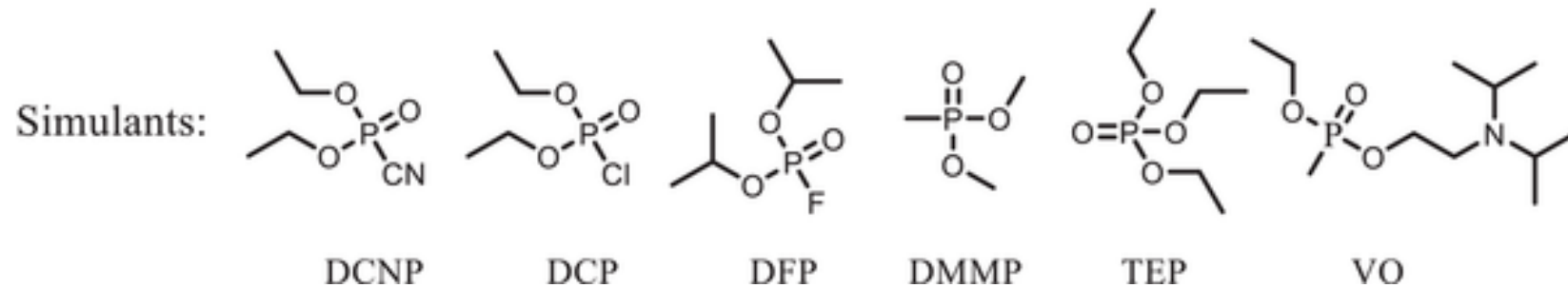
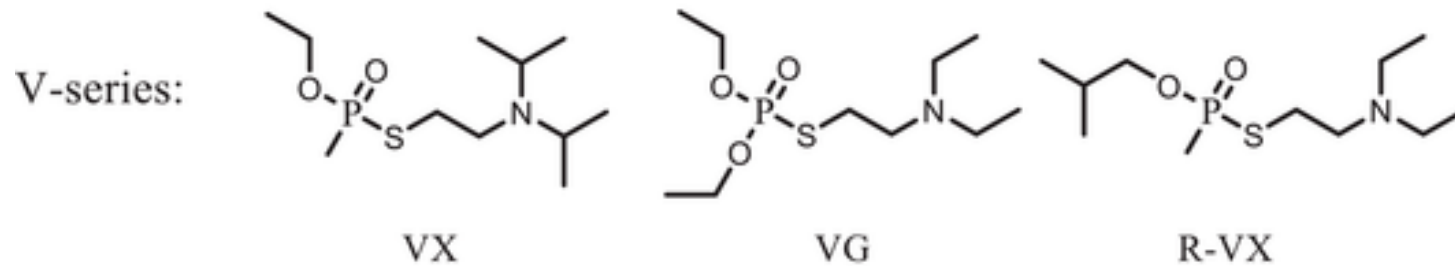
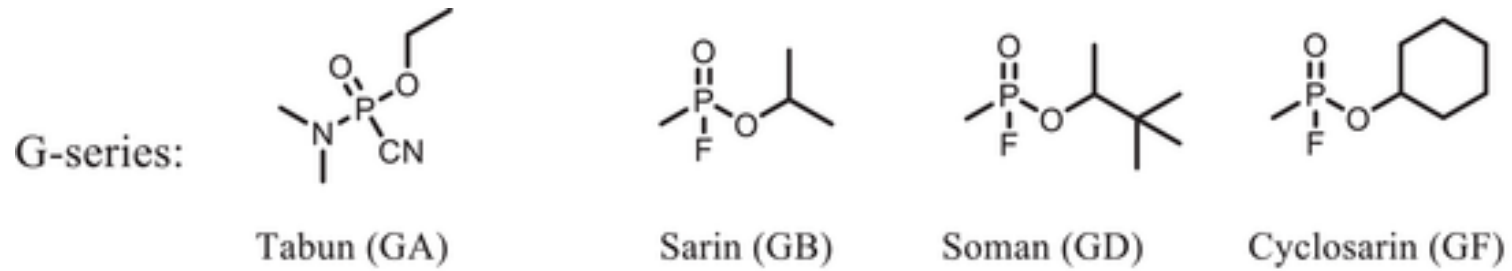
Spasms, convulsions & loss of bowel control



Coma & eventual death



Nerve Agents



Illegal Drugs

- Guidelines have been set up by various governing bodies regarding the standards that are followed by practicing forensic scientists. For forensic chemists, the international Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) presents recommendations for the quality assurance and quality control of tested materials. In the identification of unknown samples, protocols have been grouped into three categories based on the probability for false positives.

Illicit Drug Chemical Analysis

Categories/Techniques

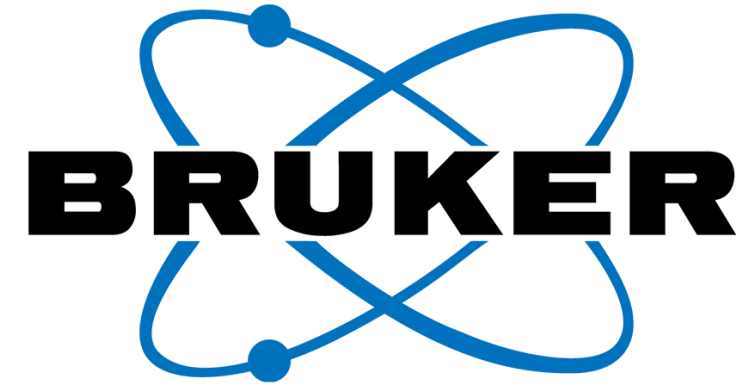
SWGDRUG analysis categories		
Category A	Category B	Category C
<ul style="list-style-type: none">• Infrared spectroscopy• Mass spectrometry• Nuclear magnetic resonance NMR spectroscopy• Raman spectroscopy• X-ray diffractometry	<ul style="list-style-type: none">• Capillary electrophoresis• Gas chromatography• Ion-mobility spectrometry• Liquid chromatography• Microcrystalline tests• Pharmaceutical identifiers• Thin-layer chromatography• Cannabis only: Macroscopic and microscopic examination	<ul style="list-style-type: none">• Colour tests• Fluorescence spectroscopy• Immunoassay• Melting point analysis• Ultraviolet spectroscopy

QA/QC: ISO 9001 and ISO 17025

- Quality assurance (QA) prevents and assesses quality problems through a system of processes and procedures including training, documentation, monitoring and audits. Quality control (QC) detects errors in the product/measurement.
- Quality control encompasses all activities that bring an analysis into statistical control. The most important facet of quality control is a set of written **directives** describing the relevant laboratory-specific, technique-specific, sample-specific, method-specific, and protocol-specific operations.

Instrument Suppliers

- Bruker
- Drager
- 908 Devices
- JEOL
- Thermo Scientific
- Oxford Instruments
- Renishaw
- HORIBA
- Shimadzu
- Agilent
- Perkin Elmer



SMART Water/Selecta DNA

- Each SelectaDNA property marker and spray contains a unique DNA code. These codes allow police to identify property/valuables and link criminals to the crime. Synthetic DNA is tested to PAS 820.
- SmartWater is a traceable liquid and forensic asset marking system (taggant), that is applied to items of value to identify thieves and deter theft. The liquid leaves a unique identifier.



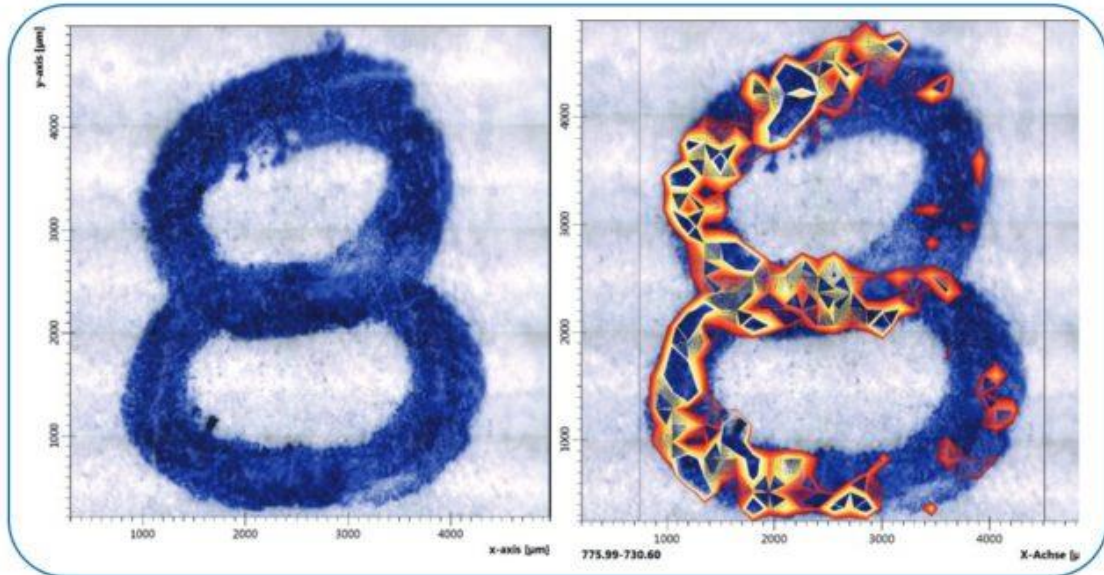
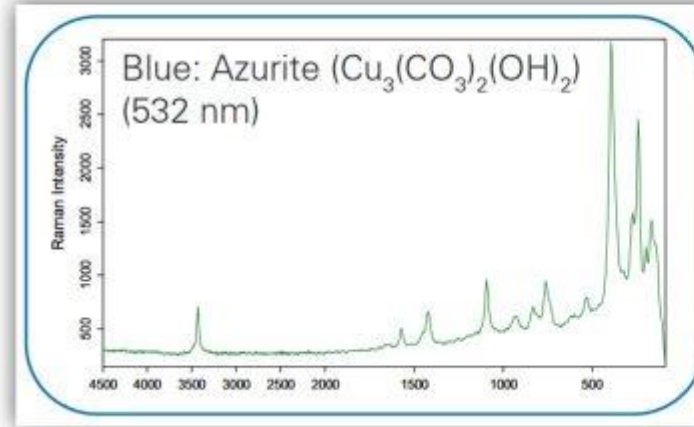
Art/Document Fraud

Analysing Ancient
Pigments using Raman



Art Forgery and Forensics

Pigments Analysis in an Ancient Nepalese Painting



Forged 8 made from a 3:
Different kind of Blue Ink
Analyzed by FT-IR

Fake Money

- If you shine an ultraviolet light on a bill, the **security thread** will glow. Each denomination glows a different colour.
- Magnetic & Colour Shifting Inks: Some counterfeit detectors can detect the **magnetic properties** of inks to tell if bills are real.
- Raman Microscopy can detect the chemical signature of real vs fake pigments on bank notes

Fake Medicine

- Fake medicines cause a lot of pain and suffering
- Sick people either get the wrong medication or a placebo
- There are many technologies to fight fake medicines such as difficult to reproduce packaging (holograms, etc)
- Hand held Raman spectrophotometers are one way to detect active ingredients
- IR also works for organic molecules

Forensic Pathology

- The forensic pathologist is a subspecialist in pathology whose area of special competence is the examination of persons who die **suddenly**, unexpectedly or violently. The forensic pathologist is an expert in determining cause and manner of death.
- Medical Pathology is the study and understanding of how illness and diseases work and their impact on people.
 - Chemical pathology (cross between toxicology and pharmacology)
 - Haematology (blood)
 - Histopathology (tissues)
 - Microbiology and virology (viruses and bacteria)

BF/VH Analysis

- BF = Bodily Fluids
- VH = Vitreous Humor
- Stomach content
- Urine
- Blood

Forensic Anthropology

- Forensic anthropology is a branch of physical anthropology that applies the science of anatomy to forensics. These scientists help law enforcement agents during criminal investigations to identify human remains, interpret the trauma, cause and estimated time of death.
- Forensic anthropologists concentrate mainly on **bone** anatomy, whereas, forensic pathologists concentrate on soft tissue anatomy, internal organs, bodily fluids, etc.
- Forensic anthropologists determine the ancestry of a skeleton by examining the morphology, or shape, of the skull and by taking measurements of the skull vault (cavity) and face.

Forensic Anthropology - II

- The skull is considered to be the most important bone for race determination because without it, the origin of race cannot accurately be determined. Forensic anthropologists use lengths, widths, and shapes of skull features along with population-specific dental traits to aid them in determining race/ancestry.

Forensic Taphonomy (Human Decay)

- “Decomposition is incredibly dependent upon local conditions: the surrounding temperature, rainfall, humidity, soil type, ecology, insects, scavengers... it’s all dependent on these variables. So, the information coming out of the existing facilities is very useful but it’s not directly applicable to forensic cases in the UK.”

Professor Anna Williams - University of Central Lancashire

Standards

- ASTM Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography:
<https://www.astm.org/e1387-95.html>
- ANSI Forensics Standards <https://webstore.ansi.org>
- <https://www.gov.uk/government/organisations/forensic-science-regulator/org/industry/forensics>

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