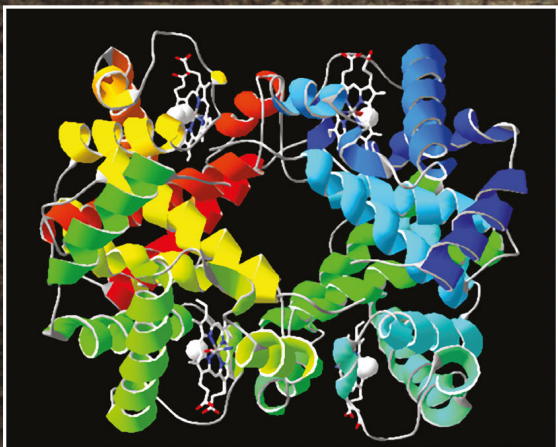
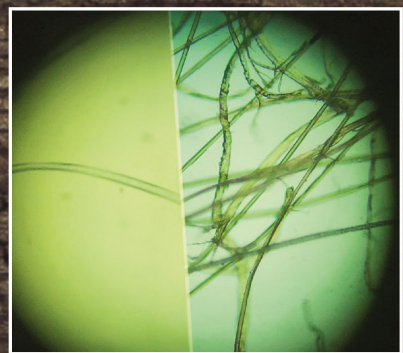


Introduction to **FORENSIC CHEMISTRY**



Introduction to Forensic Chemistry



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Introduction to Forensic Chemistry

Kelly M. Elkins



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To my husband, Tim, and our children, Madeleine, Katie, and Sara



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List of abbreviations

AA	atomic absorption
AAFS	American Academy of Forensic Sciences
ABC	American Board of Criminalistics
ABFT	American Board of Forensic Toxicology
ACS	American Chemical Society
ADH	alcohol dehydrogenase
ALDH	acetaldehyde dehydrogenase
ALS	alternate light source
amu	atomic mass units
ANFO	ammonium nitrate fuel oil
ANZFSS	Australian and New Zealand Forensic Science Society
ASCLD	American Society of Crime Lab Directors
ASCLD-Lab	American Society of Crime Laboratory Directors-Laboratory Accreditation Board
ASTM	American Society of the International Association for Testing and Materials
ATCC	American Type Culture Collection
ATF	Bureau of Alcohol, Tobacco, Firearms and Explosives
ATR FT-IR	attenuated total reflectance Fourier transform-infrared spectroscopy
BAC	blood alcohol concentration
Bq	becquerel
BWC	biological weapons convention
BZP	N-benzylpiperazine
CBRNE	chemical, biological, radiological, nuclear, and explosives
CDC	Centers for Disease Control
CE	capillary electrophoresis
CI	chemical ionization
CMYB	cyan-magenta-yellow-black
COSY	correlation spectroscopy
CSA	Controlled Substances Act
CSFS	Chartered Society of Forensic Sciences
DART	direct analysis in real-time
DDT	dichlorodiphenyltrichloroethane
DEAE	diethyl amino ethyl cellulose
DEA	Drug Enforcement Agency
DHS	Department of Homeland Security
DMT	dimethyltryptamine
DNA	deoxyribonucleic acid
DRIFTS	diffuse reflectance infrared Fourier transform spectroscopy
DURC	dual use research of concern
E	energy
ECD	electron capture detector
EDS	energy dispersive spectroscopy
EDTA	ethylene diamine tetra acetic acid
EI	electron impact ionization
ELISA	enzyme-linked immunosorbent assay
EM	electron multiplier
EPA	Environmental Protection Agency

ESI	electrospray ionization
FBI	Federal Bureau of Investigation
FI	field desorption ionization
FID	flame ionization detector
FPLC	fast performance liquid chromatography
FSS	Forensic Sciences Society
GC	gas chromatography
GC-MS	gas chromatography–mass spectrometry
GHB	gamma-hydroxybutyrate
GPCR	G protein-coupled receptor
GSR	gunshot primer residue
HDPE	high-density polyethylene
HGH	human growth hormone
HPLC	high-pressure liquid chromatography (also known as high-performance liquid chromatography)
HMBC	heteronuclear multiple bond correlation
HOMO	highest occupied molecular orbital
HSQC	heteronuclear single quantum coherence
IAFIS	Integrated Automated Fingerprint Identification System
IAI	International Association for Identification
IBIS	Integrated Ballistic Identification System
ICP-MS	inductively coupled plasma emission spectroscopy–mass spectrometry
IDDA	instrumental data for drug analysis
IED	improvised explosive device
IR	infrared spectroscopy
ISO	International Organization for Standardization accreditation
LA	laser ablation
LC	liquid chromatography
LDPE	low-density polyethylene
LUMO	lowest unoccupied molecular orbital
LSD	lysergic acid diethylamide
MALDI	matrix-assisted laser desorption/ionization
MDA	3,4-methylenedioxymphetamine
MDMA	3,4-methylenedioxymphetamine
MMDA	5-methoxy-3,4-methylenedioxymphetamine
MP	melting point
MRSA	methicillin-resistant <i>Staphylococcus aureus</i>
MSDS	material safety data sheet
NAA	neutron activation analysis
NCI	negative chemical ionization
NIBIN	National Integrated Ballistics Information Network
NIH	National Institutes of Health
NIST	National Institutes of Standards and Technology
NFPA	National Fire Protection Association
NHTSA	National Highway Traffic Safety Administration
NMR	nuclear magnetic resonance spectroscopy
NOESY	nuclear overhauser effect spectroscopy and experiments
NPS	new psychoactive substances
OSAC	Organization of Scientific Area Committee
PBI	polybenzimidazole
PCC	1-piperidinocyclohexanecarbonitrile
PCI	positive chemical ionization
PCP	phencyclidine
PCR	polymerase chain reaction

PD	plasma desorption
PDQ	paint data query
PEEK	polyether ether ketone
PEN	polyethylene naphthalate
PETE	polyethylene terephthalate
PETN	pentaerythritol tetranitrate
PFTBA	perfluorotributylamine
PI	photoionization
PID	photoionization detector
PLA	polylactic acid
PP	polypropylene
PPE	personal protective equipment
ppm	parts per million
PS	polystyrene
PSA	polysulfone
PTT	polytrimethylene terephthalate
PVA	polyvinylalcohol
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
QNB	3-quinuclidinyl benzilate
RDX	Research Department eXplosive
RNA	ribonucleic acid
RFLP	restriction fragment length polymorphism
RFU	relative fluorescence units
RGB	red-green-blue
ROESY	rotating frame nuclear overhauser effect spectroscopy
RUVIS	reflected ultraviolet imaging system
SCAN	scan mode
SERS	signal-enhanced Raman spectroscopy
SEM	scanning electron microscope
SIM	single ion monitoring mode
SOFT	Society of Forensic Toxicologists
SOP	standard operating procedure
SPME	solid phase microextraction
SRM	standard reference material
Sv	sievert
SWGDRUG	Scientific Working Group for the Analysis of Seized Drugs
TATP	triacetone triperoxide
TEM	transmission electron microscope
TEPP	tetraethyl pyrophosphate
THC	tetrahydrocannabinol
TIC	toxic industrial chemicals
TLC	thin-layer chromatography
TMS	tetramethylsilane
TNB	trinitrobenzene
TNT	trinitrotoluene
TOF	time-of-flight
TOCSY	total correlation spectroscopy
TS	thermospray ionization
TTI	transmitting terminal identifier
TWGFEX	Technical Working Group for Fire and Explosions
UMHW	ultra-high-molecular-weight polyethylene

UPLC	ultra-performance liquid chromatography
USDA	United States Department of Agriculture
UV	ultraviolet spectroscopy
UN Manual	United Nations Rapid Testing Method of Drugs of Abuse Manual
UNDOC	United Nations Office of Drugs and Crime
Vis	visible spectroscopy
WADA	World Anti-Doping Agency
WHO	World Health Organization
WMD	weapons of mass destruction
XRF	x-ray fluorescence spectroscopy

CHAPTER 1

An introduction to forensic chemistry and physical evidence

KEY WORDS: forensic science, forensic chemistry, criminalistics, physical evidence, crime scene investigator, chain of custody, class characteristics, individual characteristics, presumptive test, reference samples, comparison standards, safety data sheets, control samples, background controls, positive control, negative control, accuracy, precision, replicates, standard operating procedures, quality control, quality assurance, expert witness

LEARNING OBJECTIVES

- To explain the difference between forensic science, criminalistics, and forensic chemistry
- To understand the historical development of forensic science
- To know the locations and identities of several forensic laboratories
- To list the units of forensic laboratories that use forensic chemistry
- To identify physical evidence in a forensic case
- To differentiate between class and individual characteristics for physical evidence types
- To identify the Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) categories of analytical techniques by category
- To understand the role of the forensic chemist in the laboratory, in the forensic community, and in court

ALCOHOL POISONING: METHANOL AND OTHER DENATURANTS

A man arrived at the hospital hallucinating. Although not readily apparent, the hallucinations turned out to be a symptom of methanol present in the alcohol he had consumed.

Alcohol, also known as ethanol or ethyl alcohol, is the most widely used legal drug. It is a depressant and affects the central nervous system. At low doses, it can lead to the loss of inhibitions and increased talkativeness. At higher doses, it affects reasoning, behavior, memory, speech, emotion, and abstract thinking. At very high doses, it can lead to a loss of consciousness and death.

Passed in 1919, the 18th Amendment to the US Constitution banned the manufacture, sale, and transportation of alcoholic beverages into the country. Enforcement began with the passage of the Volstead Act on January 1, 1920. Thus began prohibition. As a result, drinkers resorted to drinking wood alcohol and industrial alcohol with severe effects. Although alcohol was illegal to consume as a beverage, it was still used in industry and manufacturing in paint thinners, fuels, and medical supplies, and was also used as a solvent.

On September 7, 1919, the *New York Times* reported an increase in the numbers of deaths from people drinking wood alcohol as a substitute for grain alcohol. Methanol (methyl alcohol) is found in alcohol produced by distilling wood. The National Committee for the Prevention of Blindness recorded over 1000 reported cases of blindness (across the country) resulting from the consumption of wood alcohol. Dr. Alexander Gettler, a toxicologist with

ALCOHOL POISONING: METHANOL AND OTHER DENATURANTS (continued)

the New York Office of the Chief Medical Examiner and Chemical Laboratory of the Pathological Department, Bellevue and Allied Hospitals, also reported an increase in deaths due to wood alcohol. He reported examining over 700 human organs for alcohol in 1918–1919. As a result, states began to pass laws to regulate and control the sale of wood alcohol.

Beginning in 1906, industrial users could purchase ethanol without paying the tax levied on drinking alcohol. The US government devised a method of making the ethanol deadly to drink—by adding methanol—while leaving the bulk chemical properties unchanged. (Methanol is used today in windshield washer fluid and is poisonous and extremely toxic.) The resultant alcohol was labeled as “denatured” alcohol. Several other denaturing methods followed. Some involved the addition of poisonous metals such as mercury, cadmium, and zinc to the ethanol. Others involved the addition of less lethal but extremely bitter compounds to the ethanol, rendering it undrinkable. Bootleggers hired chemists to distill the alcohol to remove the contaminants and return the ethanol to a composition that was safe to consume. In response, by mid-1927, new denaturants were added to the alcohol including common chemicals such as gasoline, kerosene, chloroform, camphor, ether, formaldehyde, acetone, iodine, and quinine.

Eventually, prohibition was overturned with the ratification of the 21st Amendment and consumption of alcohol was again legalized on December 5, 1933.

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Forensic science is the application of the scientific method to legal questions. The laws themselves are enforced and upheld by the criminal justice system including federal, state, and local law enforcement agencies and the courts. The goal of the criminal justice system is the establishment of the guilt or innocence of a suspect or suspects accused of a crime.

Forensic chemistry is a subdiscipline of forensic science. Its principles guide the analyses performed in modern forensic laboratories. Forensic chemistry’s roots lie in medicolegal investigation, toxicology, and microscopy. Deaths due to tainted food products, new applications of materials in the home, drug use and abuse, and industrial pollution sped up the development of modern forensic science investigations and practices.

Forensic chemistry emerged in Europe in the 1830s with advances by scientists including James Marsh. Marsh was a British chemist who developed a method for testing the presence of arsenic in human tissue that was the first use of toxicology in a jury trial. The Marsh Test (1836), as it is now widely known, employs testing using zinc and sulfuric acid. Arsine gas is formed in the presence of even small amounts of arsenic; the method was used to detect the ingestion of rat poison containing arsenic in cases of suspected poisonings.

Approximately 50 years later, University of Pennsylvania professor Theodore Wormley authored the first American book, *Micro-chemistry of Poisons* (1885), dedicated in the preface to “the study of the chemical properties of poisons as revealed by the aid of the microscope.” The United States Pure Food and Drugs Act (1906), which was signed into law by then President Theodore Roosevelt, regulated food and medicines and ultimately paved the way for the modern Food and Drug Administration. The Pure Food and Drugs Act prevented the production and trafficking of poisonous, mislabeled, or adulterated foods as well as pharmaceutical drugs and alcoholic beverages. The American toxicologist Dr. Alexander Gettler was instrumental in advancing forensic chemistry in his work as chief chemist at the New York Medical Examiner’s office; he significantly advanced the science through his several publications including his paper “The Toxicology of Cyanide” published with his student J. Ogden Baine in 1938 in the *American Journal of the Medical Sciences*. It documents the case study of Fremont and Annie Jackson who died in 1922 by the inhalation of fumigation products in their Manhattan apartment.

As forensic chemistry is focused on materials analysis, innovations that have advanced the field have been many and varied as shown in Table 1.1. The innovations include the development of new discernible chemical reactions,

Table 1.1 Brief history of some notable advances in forensic chemistry

Year	Advance
1590s	Zacharias Janssen develops first compound light microscope
1784	First use of fracture edge matching/pattern matching in John Toms' case
1810	Konigin Hanschritt document dye analyzed by chemical test
1828	William Nichol invents polarized light microscope
1835	Charles Wheatstone invents emission spectroscopy
1836	James Marsh develops test for arsenic and it is used in a jury trial
1858	Johann Peter Griess develops test for nitrites
1867	Alfred Nobel receives US patent for his invention of dynamite
1880	Henry Faulds suggests using fingerprints on clay and glass to solve crimes
1883	K. Mandelin develops test for strychnine later applied to alkaloids
1885	Theodore Wormley publishes book <i>Micro-chemistry of Poisons</i>
1889	Alexandre Lacassagne matches bullets using lands and grooves to a gun barrel
1891	Hans Gross describes the use of physical evidence in solving crimes in his book <i>Handbuch für Untersuchungsrichter</i> and coins the term Kriminalistik (Criminalistics)
1892	Francis Galton publishes first book on fingerprints
1894	Alphonse Bertillon's handwriting analysis is used to convict Alfred Dreyfus (falsely)
1898	J. J. Thomson measures mass-to-charge ratio of the electron
1898	Paul Jeserich uses minutiae to individualize bullets
1903	Will West prison case solved using latent fingerprints
1903	M. S. Tswett separates plant pigments using paper chromatography
1906	President T. Roosevelt signs US Pure Food and Drugs Act signed into law
1910	Albert Sherman Osborn publishes <i>Questioned Documents</i>
1915	First use of chemical weapons
1919	Francis Aston builds the first fully functional mass spectrometer and later uses it to discover 212 naturally occurring isotopes
1928	Geneva Protocol signed that prohibits use of chemical and biological weapons in war
1928	C. V. Raman develops Raman spectroscopy
1930	Edmond Locard's Principe de l'échange "Exchange Principle" coined
1930s	Pierre Duquenois develops color test for THC
1940	Glenn Seaborg, Joseph Kennedy, Edwin McMillan, Emilio Segre, and Arthur Wahl discover plutonium-239
1945	First nuclear magnetic resonance spectroscopy (NMR) spectra of liquids and solids by Felix Bloch and Edward Mills Purcell, independently
1948	Founding of the American Academy of Forensic Sciences
1951	Archer John Porter Martin and Richard Laurence Millington Synge invent modern gas chromatography
1955	Modern flame atomic absorption spectrometer developed by Sir Alan Walsh
1962	Rachel Carson publishes book <i>Silent Spring</i>
1970	First meeting of the Society of Toxicology on Long Island
1973	GC-MS applications to analysis of drugs and metabolites
1974	Richard Ernst pioneers two-dimensional NMR COSY experiment
1974	SEM-EDX is applied to gunshot residue analysis
1977	Application of FT-IR in forensic science
1988	Franz Hillenkamp and Michael Karas pioneer the matrix-assisted laser desorption ionization-MS technique
1988	Introduction of enzyme-multiplied immunoassay technique (EMIT) in forensic toxicology
1991	Richard Ernst develops high-resolution nuclear magnetic resonance spectroscopy
1992	GC-IR is applied to forensic drug analysis
1996	Raman spectroscopy is introduced to forensic use
1997	Scientific Working Group for the Analysis of Seized Drugs is created by the US National Institute of Standards and Technology
2001	US Federal Bureau of Investigation investigates Amerithrax case of deaths due to mailed letters containing anthrax spores

instrumental tools, books, laws, methods, index cases, and even the development of dual-use materials so often misused by criminals.

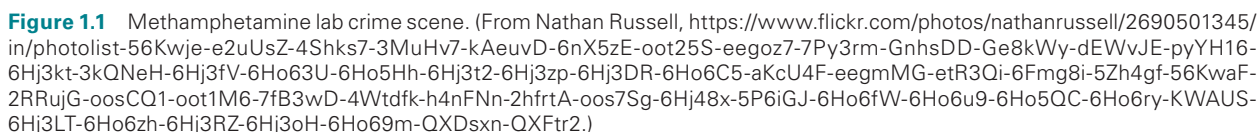
While federal, state, and local law enforcement agencies are the primary providers of forensic chemistry services to the criminal justice system, private and university laboratories are also available for this purpose. In the United States, major federal agencies including the Federal Bureau of Investigation (FBI), Drug Enforcement Agency (DEA), Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF), Environmental Protection Agency (EPA), Department of Homeland Security (DHS), and the Postal Service (USPS) have their own labs or contract with outside laboratories to perform forensic testing and research. In addition to the federal labs, states, cities, and counties may have their own forensic labs focused on criminal investigations. University forensic labs are common in Europe and other parts of the world. Forensic chemistry analyses are performed in sections including controlled substances analysis, toxicology, explosives and fire debris, trace evidence, latent prints, firearms, tool marks and impression evidence, and questioned documents. The units of the crime laboratory that utilize forensic chemistry, which will be covered in this book, are listed in Table 1.2. Forensic laboratories also examine environmental samples that may contain pesticides, herbicides, and chemicals used as weapons, and the improper use or disposal of these and other chemicals by individuals and industry. Crime scene investigation and forensic biology are also important sections of forensic laboratories, and while both utilize chemical principles and tests in their evaluation of evidence, they will not be covered in this book.

Criminalistics describes the branch of forensic science focused on evaluating physical evidence collected at crime scenes. Scientists working in the field of criminalistics are termed criminalists and may conduct crime scene investigations, perform analyses in the laboratory, write reports, and testify as expert witnesses in court. Criminalists focus on recognizing, documenting, collecting, preserving, analyzing, and reporting on physical evidence. A methamphetamine drug synthesis crime scene is shown in Figure 1.1. Several evidence items are visible including glassware, drug material or chemical intermediates, containers, and tubing. Notably, discarded matchboxes are visible in the photo; the red phosphorous from the strike pads is used in the synthesis of methamphetamine.

Physical evidence may include any type of physical material found at a crime scene. This type of evidence can include everyday items such as household chemicals, fabrics and fibers, hairs, glass, fingerprints, soil, plant material, hand-written or typed documents, checks, polymers and plastics, inks and dyes, serial numbers, and tools and tool marks.

Table 1.2 Units of forensic laboratories that use forensic chemistry

Unit	Evidence	Methods
Controlled substance analysis	White powders, colored chemicals, botanical material, and other suspected controlled substances or their starting materials or intermediates	Color spot tests, macroscopic tests, stereomicroscopy, microcrystalline tests, FTIR, GC-MS
Toxicology	Blood-alcohol samples Body fluid-drug samples including blood, urine, saliva, stomach contents, and vitreous humor	GC-MS, LC-MS, ELISA
Latent print examination	Latent and visible prints, impression evidence	ALS, photography, fingerprint powder, superglue fuming, chemical latent print development methods, lifts
Questioned documents	Handwritten and typewritten documents including checks, suicide notes, and ransom notes, among others	ALS, stereomicroscopy, TLC, Raman spectroscopy, IR imaging, SEM
Trace evidence	Polymers, paint, glass, hair, fiber, plastic, paper, soil	Stereomicroscopy Compound light microscopy Polarizing light microscopy Microspectrometer (UV-Vis, FTIR) Scanning electron microscope (SEM) Phase contrast microscopy Fluorescence microscopy Solubility testing Hot stage microscopy
Firearm and tool mark examination	Firearms, tools, serial numbers	Stereomicroscopy comparisons
Explosive and fire debris examination	Burned materials, explosives remnants, accelerants	GC, GC-MS, SEM



Physical evidence is collected and labeled by a *crime scene investigator* or technician who is trained in forensic science. These specialists are responsible for identifying, photographing, logging, collecting, tagging, and transporting evidence from the crime scene that can be used to gain knowledge of the events, persons, and circumstances surrounding the crime. Each evidence item is logged on an evidence submission form. Care must be taken not to introduce outside contaminants such as DNA, fingerprints, hairs, and clothing fibers to the physical evidence as well as

