Pointing to Poison

Modern forensic toxicology was established by Mathieu Orfila and the Marsh test in the 19th century.

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When the general public is exposed to forensic science, it is usually through popular novels, television programs, or news coverage of famous court cases. But the origins of forensic science are ancient. For example, in the 6th century A.D., the Emperor Justinian recognized physicians as expert witnesses in the Roman courts. In 8th-century China, fingerprints were used for the first time to establish the identity of documents. Sometime near the beginning of the first millennium, the Roman orator Quintilian described a case of bloody palm prints used to frame a blind man of his father's murder.

For chemists, the most important branch of forensic science is toxicology—the study of substances that can have a toxic effect in the body. It is forensic toxicology that made the chemist an essential player in modern investigative police work.

The word "toxicology" derives from the Greek term *toxon*, which meant a bow for shooting arrows. In the ancient world, poisons were occasionally placed on the tips of arrows to make them more lethal; thus the word *toxicos* came to refer to such a poison. As an aside, it also led to the term "intoxicated," which initially meant that one was made sick by poisoned arrows.

The formal history of poison is itself ancient. The oldest written document concerning toxic substances is an Egyptian scroll dating to 1500 B.C. Later, the Greeks did not simply study poisons disinterestedly but used them as a means of execution, as when Socrates was forced to drink hemlock for corrupting the youth of Athens.

Toxins were also extremely popular as secret weapons in ancient Rome. The emperor Nero employed a personal poisoner named Locusta, who murdered several of Nero's wives and killed his brother with cyanide. The Roman Empire passed the first law against poisoning in 82 B.C. in an attempt to stem the tide of murder by poison. Roman emperors and noble families hired food testers to protect themselves from poisoners. Arsenic, derived primarily from lead or tin ore, was the poison of choice for Roman assassins and became known as the "king of poisons."

Mathieu Joseph Bonaventure Orfila

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A Poisoner's Renaissance

Poisoning as a criminal art form increased in popularity in the centuries following the demise of the Roman Empire, and according to many historians, it reached its height during the Renaissance. Murder by poison was a stealthy endeavor, and the poisoner was viewed as crafty, unemotional, and sinister. Poison was considered the weapon of choice for female murderers, as it did not require a direct frontal assault and it fit the prevailing prejudiced view of deceitful feminine nature.

Some of the most notorious criminal poisoners during and after the Renaissance were women. In the 16th century, Catherine de Medici of Florence, who would later become queen of France, tested the effects of various poisons on the poor and the ill. Indeed, the illustrious Medici family became renowned for their use of poisons to deal with enemies. Another famous Renaissance clan, the Borgias of 15th- and 16th-century Italy, was also widely known for its skill in dispatching adversaries with poison.

The brother–sister team of Cesare and Lucrezia Borgia are supposed to have killed several of their foes with a secret family poison called La Cantarella. This odd mixture was purportedly a combination of arsenic, phosphorus, and copper, prepared in the abdomen of a hog's decaying corpse. Other Renaissance Italians were also remarkably efficient as poisoners, so much so that there existed in 15th-century Venice a "Council of Ten" that poisoned people for a fee. The records of their contracts are still preserved. There were also schools in Rome and Venice to teach people how to become adept at murdering with poison.

The greatest poisoner in history is also reputed to have been an Italian woman. Madame Giulia Toffana (1635–1719) invented a poisonous liquid containing arsenic called *agua Toffana*, or "water of Toffana." She sold her concoction to interested buyers and trained them in its use. Toffana was reputedly responsible for 600 deaths, either directly or indirectly, and was allegedly involved in the murder of two popes.

Although Toffana was captured and executed for her crimes, many poisoners throughout history escaped prosecution, as it was very difficult to prove the use of poison in a murder. Most convictions relied on circumstantial evidence or intent, as there was no scientific basis to chemically identify a poison in the body. But from the middle of the 18th century to the dawn of the 19th, things began to change.

The first person to suggest a chemical method for the detection of poisons was Hermann Boerhaave, although his tech-

nique was rather unsophisticated. He placed suspicious substances on hot coals and made distinctions between the odors. An even more important event in the history of modern toxicology was the invention of the "arsenic mirror" in 1787. Johann Daniel Metzger developed a method of detecting arsenic in solutions, although not in the human body. He learned that when arsenic oxide was heated with charcoal, it formed a black, mirror-like deposit on a cold plate held over the coals. This dark substance was arsenic.

Murderous Mary

The first murder trial to feature toxicological testimony from medical experts took place in 1752 in England. Mary Blandy was accused of poisoning her father, a prominent attorney, with white arsenic (arsenous oxide). She had obtained the poison from Capt. William Cranstoun, a Scotsman who wished to marry her. Blandy initially placed the arsenic in her father's tea, but this failed to work. Ultimately, she mixed it with gruel, and this was more successful, making her father and two servants ill. Although the servants were suspicious of Mary, her father continued to allow her to prepare his food, and within a short time he died.

The Marsh Test

A new test for arsenic, designed by James Marsh, a chemist at the British Royal Military Academy in the 1830s, greatly increased the contribution of the toxicologist to forensic science. Marsh treated a flask of suspected arsenic solution with pure zinc and either sulfuric or hydrochloric acid. Gas was then released through a narrow glass tube and heated in a flame. If the solution contained arsenic, the heated gas would leave a deposit of metallic arsenic on a white porcelain dish held in the flame, or white arsenic oxide if the dish was held above the flame. This test, hereafter known as the Marsh test, was precise enough to test for minute amounts of arsenic.

British medical examiners tested a white powder found in Mary's cooking pan. They noted that it gave off an odor of garlic if heated, and that if placed in water it turned milky, with some sinking to the bottom and part of it floating on top in a thin film. Its behavior was identical to a white arsenic sample tested in the same way.

In her trial, Mary claimed that the chemical mixture she added to the food was meant to improve her father's temperament. This was not an utterly ludicrous assertion, as physicians of the time often prescribed arsenic compounds as tonics and antiseptics. But the evidence that seemed to be strongest against Mary was the testimony of the servants that she tried to destroy the arsenic residue in the pan by throwing it in a fire. She was convicted of murder and executed by hanging.

Enter Orfila

These early tests for poisons like arsenic were important but primitive. A strong theoretical apparatus was lacking. The critical historical moment in the development of toxicology as a science was the emergence of Mathieu Joseph Bonaventure Orfila.

A Spaniard by birth, Orfila was professor of legal medicine and chemistry at the University of Paris when he published a groundbreaking text on toxicology in 1814. His book, *A Treatise of General Toxicology* (loosely translated from the longer French title), was the first successful attempt to classify poisons as corrosives, astringents, acrids, stupefying or narcotics, narcotico-acrids, or putrefacients. An impressive achievement for a young man of 26, the book established Orfila's international reputation as the preeminent authority on toxicology; indeed, it essentially founded the discipline.

Much of Orfila's laboratory work dealt with arsenic. His experiments on animals demonstrated that arsenic was distributed throughout the body after ingestion, negating the previously dominant theory that poisons act on only one type of body tissue. Orfila was also the first scientist to extract arsenic from organs rather than just the contents of the stomach. But it was his testimony at an infamous murder trial that established Orfila's reputation among the general public.

The Marsh test (see box, "The Marsh Test") gained recognition for its creator and for Mathieu Orfila in the 1840 trial of Marie Lafarge. Madame Lafarge was accused of murdering her husband with arsenic a year after they were married. Initial tests of the deceased husband's stomach contents did not locate arsenic. The prosecution had the body exhumed to test organ tissues but still found no arsenic. At the same time, however, the food given to the victim before his death contained large amounts of arsenic. Orfila, engaged as an expert witness by the prosecution, reexamined the evidence and determined that arsenic was present in every tissue sample. He concluded that the previous testers had achieved false negative results because of their improper use of the Marsh test. He also asserted that the presence of poison alone did not determine guilt, but must be considered in light of all the additional evidence. Orfila's testimony helped create a professional forensic science by emphasizing the importance of professional toxicological training and endorsing the use of toxicology in concert with all available evidence to give a more complete picture of a crime.

Modified versions of the Stas method and the Marsh test are still used by forensic toxicologists today.

A Poison Arms Race

The success of the Marsh Test reduced, but by no means obliterated, the popularity of metallic poisons such as arsenic. Many killers turned instead to vegetable alkaloids, for which there was no analytical procedure for isolation. Morphine, strychnine, and atropine were some of the toxins available in the mid-19th century. But even these poisons became susceptible to discovery by toxicologists after 1850. In that year, Belgian chemist Jean Servais Stas discovered a method for the extraction of nicotine from the organs of a murder victim. The Stas method became the primary isolation technique for analysis of nonvolatile organic substances.

Modified versions of the Stas method and the Marsh test are still used by forensic toxicologists today. There have been significant advances in the field, however. GC and MS are used to confirm the presence of the smallest chemical traces. The development of modern instrumentation has made contemporary forensic toxicology more complex, yet many of the basic principles remain the same as in the early years. Thus, the achievements of Orfila, Marsh, and Stas live on as much more than mere historical footnotes.

Suggested Reading

Forensic Science, 2nd ed.; Davies, G., Ed.; American Chemical Society: Washington, DC, 1986.

More Chemistry and Crime: From Marsh Arsenic Test to DNA Profile; Gerber S. M.; Saferstein, R., Eds.; American Chemical Society: Washington, DC, 1997.

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