PEARSON NEW INTERNATIONAL EDITION

Forensic Chemistry

Suzanne Bell
Second Edition

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Introduction

OVERVIEW AND ORIENTATION

Forensic chemistry exists where science and the law overlap. You might expect the marriage of science and the law to be an easy and natural one, but frequently it is not. The widespread perception is that science and the judicial system both exist to seek the truth, but that is an incomplete description. Although tackling the definitions of scientific and legal truth is beyond the scope of this book, their intersection is at the heart of it, even when hidden behind chemical equations and reaction mechanisms. The term *forensic* refers to law enforcement, the judicial system, and the courts, and without *forensic*, there is no forensic chemistry. Accordingly, this brief chapter will provide you with the minimum legal context needed to explore forensic chemistry and the larger world of forensic science.

1 WHAT IS FORENSIC CHEMISTRY?

Forensic chemistry is applied analytical chemistry. If that were the extent of it, however, there would be no need for a separate course or textbook on the subject. What then makes forensic chemistry unique? Arguably, it is the same consideration that defines forensic science as a distinct discipline: the skill, art, and science of comparison. Analytical chemistry encompasses qualitative and quantitative analysis, but forensic chemistry adds comparative analysis to the task list. For example, spectroscopic analysis can quickly determine whether a fiber is made of nylon or whether a piece of plastic is polyethylene. These are analytical descriptors that answer analytical questions such as, What is it? and How much of it is there? Analytical chemistry provides qualitative and quantitative data that are required to answer **forensic questions** such as the following:

- Where could this fiber have come from?
- Could this piece of plastic have come from this plastic trash bag?
- Was weathered gasoline used to start this fire?
- Did this paint chip come from that car?

From Chapter 1 of *Forensic Chemistry*, Second Edition. Suzanne Bell. Copyright © 2013 by Pearson Education, Inc. All rights reserved.

- Does this white powder contain a controlled substance?
- Do the quantities of drugs and metabolites found in these postmortem samples allow for determination of a cause of death?

The forensic question is often not the same as the **legal question**. For example, if a drug analysis section receives a white powder as evidence, the forensic question is probably, Does this white powder contain a controlled substance? If so, what and how much? The chemist performs the analysis and provides data such as "The sample was found to contain cocaine as the hydrochloride salt. The net weight of the powder was 6.234 g ± 0.012 g." This statement provides a concise answer to the forensic question but not the legal question, which is probably, Is the defendant guilty of felony possession of a controlled substance? The forensic chemist has supplied data that can contribute to answering this question, but only a piece of the total answer. It is good practice to keep this distinction in mind.

EXHIBIT A

The Origins of Science and Chemistry

Ancient chemistry was likely related to medicines and materials. Knowledge was based on experiment and experience and was passed on to a select few. Early humans used plant and animal products as treatments and learned from experience what worked and what did not, but there was no understanding of natural laws (i.e., science) to guide them. The Greeks were the first to set forth the idea of science as a system or method of looking at the world, and this system began to take shape 2500 years ago. By that time, chemistry was already well established in certain areas, including natural dyes, simple metallurgy, soapmaking, cosmetics, fermented beverages, and ceramics. The Greeks created a philosophy that allowed knowledge derived from experiment to be studied systematically and then extended logically to new situations.

Source: Salzberg, H. W. "Ancient Technology: The Roots of Chemistry," in *From Caveman to Chemist: Circumstances and Achievements.* Washington, DC: American Chemical Society, 1991, 1–15.

When a forensic scientist works with an exhibit of evidence, generally there are three tasks to be accomplished. First is **identification**. In drug analysis, this task incorporates qualitative identification and, sometimes, quantitative analysis. In other cases,

EXHIBIT B

Live by the poison, die by the poison

The Greeks may have formulated the idea of science, but it was the practical Romans who formulated the first essential elements of forensic science. One of the most common, most feared, and most difficult crimes to detect in the ancient world was poisoning. A very early law outlawing this crime was set forth by Rome in 82 B.C. Nearly 250 years prior to that, the Romans had executed a number of women convicted of poisoning husbands, fathers, other relatives, and significant others. The women were executed by being forced to drink their own concoctions, leading to various versions of the title quotation. The word *forensic* is tied to the Latin word *forum,* a place where the Romans conducted business and legal proceedings. To speak in the forum was to speak the truth (or so it was hoped or assumed), leading to the link between forensic and modern debate teams. However, the word also refers to speaking the truth in public, a good job description for forensic chemists.

such as fiber analysis, identification is the easy part. The next step is **classification** of the evidence. Is the fiber nylon 6 or nylon 66? Is it red, yellow, or blue? Has it aged? What is its cross section? The answers to these questions reduce the size of the class to which the fiber belongs. The smaller the class membership, the more meaningful is the evidence. Taken to its logical conclusion, classification results in placing the fiber in a class with only one member. This process is referred to as **individualization** or establishing a **common source**, although this terminology seems to be losing favor in the forensic community. Regardless, the concept is a useful one, even if reducing the number of possible sources to a single entity is rarely possible.

Continuing with this example, assume that a fiber is found at a crime scene. The forensic analyst determines that it is a red nylon fiber with a circular cross section. A suspect wearing a red nylon windbreaker is arrested. Nylon fibers from the windbreaker (often labeled *K* for "known") are subjected to the same tests as was the fiber in question (*Q*) from the scene, with similar results. The analysis demonstrates that *Q* and *K* belong to the same class, but this is not proof of a common source. Rather, this is an example of inclusive evidence (described below). In other words, the test fibers from the jacket and the fiber from the crime scene have not been individualized, and the analyst cannot assign a common source (the jacket) to *Q* and *K*. This does not mean that the evidence is useless, but it does limit what can be said with confidence. The jacket is not excluded as a possible source.

Drug analysis, both of physical and biological evidence, falls outside the traditional forensic framework of identification–classification–individualization. Analytical instrumentation, properly applied, nearly always allows for the unambiguous identification of a chemical compound, be it a drug or metabolite. Classification involves presumptive testing and screening tests, but identification follows classification rather than preceding it, as in the case of our hypothetical fiber. Identification, classification, and individualization are all involved in forensic chemistry, even if the order varies.

2 PRECEDENT IN CHEMISTRY AND THE LAW

Science exists to uncover a deeper understanding of the universe, guided by the principles of the scientific method. The tools used are experimentation and observation. Courts exist to settle disputes between individuals and the state (**criminal law**) or among individuals or entities (**civil law**). Courts are guided by the law, precedent, and function using an **adversarial system**. It would be a mistake to assume that the courts use a model similar to the scientific method or that science works on the basis of argument. There are elements of each in both systems, but to the forensic chemist, the differences are as important as the similarities (Figure 1).

Both science and the courts are tasked with deriving information from evidence pertinent to the issue at hand. Science employs the scientific method to do so, whereas the courts employ the adversarial system, in which two opposing parties present arguments before the **trier of fact**. Scientific evidence and testimony may support or refute either argument. The relative strengths of the arguments guide the court in settling the issue. Scientific knowledge and findings are part of that process, but only part. All scientists can and should do is produce the best science possible, followed by making the clearest presentation possible. How the data are used is for the courts to decide. Many such decisions are based on **precedent**, or that which has gone before. When a precedent is created, new rules or new applications of rules to decide a case or issue are developed and used.[1] Precedent is a guide for decisions and is based on past lessons. In that sense, precedent is knowledge gained previously in similar settings. Science also invokes the concept of precedent, since new ideas are derived from previous observations and experiments.

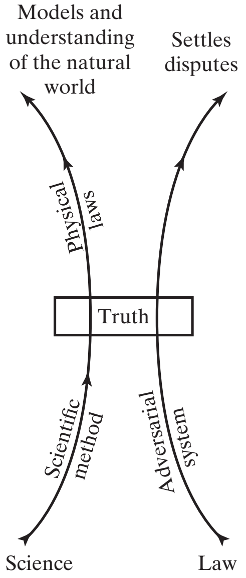

FIGURE 1 Different paths toward similar, but not identical, destinations.

EXHIBIT C

The Origin of Law

The Greeks and the Romans could not have made their contributions to forensic science had it not been for a much earlier invention: the law. The first-known codified laws were put forth by the peoples who occupied the Tigris and Euphrates River valley areas in what were the earliest-known cities and civilization. The earliest-known laws and legal systems appeared around 2000 B.C. Arguably, the most famous was Hammurabi's code, named for the Babylonian king in power around 1700 B.C.

3 KEY FORENSIC AND LEGAL CONCEPTS

This is a chemistry text first and foremost, but because it is a *forensic* chemistry text, brief mention of the discipline's legal foundation is in order. The central precepts applicable to forensic chemistry are summarized in the paragraphs that follow, and the "Further Reading" and "References" sections at the end of the chapter list additional resources.

3.1 Criminal and Civil Cases

Forensic chemists working in local, state, and federal laboratories are usually involved in criminal cases. Criminal law deals with crimes by a person or persons against the state, which can be any level of government, including cities, counties, states, and the federal government.[1] Civil cases arise from disputes that involve private rights or from disputes such as those between two individuals or two corporations. Cases referred to informally as lawsuits, wherein the complainant is said to be "filing suit," involve civil law.

3.2 Admission of Evidence

The history of the admissibility of scientific evidence in the United States is surprisingly short, less than a century old.[2] To date, standards of admissibility are founded on four court rulings, and their application varies with the jurisdiction.

The Frye Rule (**general acceptance**): This standard of admission was established in a 1923 case heard in the District of Columbia Circuit Court: *Frye v. United States*, 293 F. 1013, 1014 (D.C. Cir. 1923). Distilled to its essence, the court's ruling held that evidence produced by scientific analysis is admissible as long as the techniques are accepted as valid by the relevant scientific community.[3] In effect, the court said that if the test has survived the rigor of the scientific method and peer review to reach the status of general acceptance, then it has already been tested and validated. For example, if a new technique was developed for the chemical characterization of dyes in ink, the results of tests performed in accordance with that technique would not be admitted under the ***Frye* rule** unless the court determined that analytical and forensic chemists generally recognized the technique as useful and reliable. The *Frye* standard was predominant into the early 1990s and is still used in some jurisdictions.

*The **Daubert** Decision:* This ruling, handed down by the U.S. Supreme Court (*Daubert v. Merrell Dow Pharmaceuticals* (113 S.Ct. 2786 (1993)), was based on the Federal Rules of Evidence enacted in 1975. The case focused particularly on Federal Rule 702. The decision in *Daubert* gave judges what is referred to as a **gatekeeper** in determining admissibility.

Although this decision applied only to federal cases, several states have adopted the same approach to admissibility.

Daubert has had a significant impact on forensic science in the past decade, particularly in the realm of DNA evidence, which came of age under this decision. The *Daubert* decision provided judges with a list of tools and tests that could be used to determine the admissibility of evidence. General acceptance by the relevant scientific community is one of these, but a host of others were put forward including testability of the method, peer review (e.g., publication in peer-reviewed journals), existence of standards that can be used to test the method, and the existence of known error rates. In cases where admissibility is an issue, judges can convene **admissibility hearings** (also called ***Daubert* hearings**) to determine the merit of the method. The rigor required for acceptance under *Daubert* and the role of *Daubert* in hearings that determine admissibility are forcing a reexamination of forensic mainstays such as fingerprint evidence. No doubt forensic chemistry will be affected as this situation evolves.

General Electric v. Joiner (522 U.S. 136 (1997)): This case was the second of what is now called the ***Daubert* trilogy**. In this case, the issue was related to workplace exposure to hazardous chemicals (PCBs) and the outcome was clearly going to depend heavily on which scientific studies were admitted. In terms of admissibility, the ruling in the case stressed the need to weigh the **relevancy** of the data to the question at hand. For a method or technique to be considered admissible, it must be clearly and unambiguously pertinent to the question at hand.

Kumho: *Daubert* was extended by the 1999 decision in *Kumho Tire Co., Ltd. v. Carmichael* (119 S. Ct. 1167 (1999)). This ruling, which completes the trilogy, extended the scope of *Daubert* and the judge's gatekeeper role to *all* expert testimony, not just scientific. The decision also acknowledged that standards for determining admissibility would differ, depending on the discipline in question.[3]

3.3 Inclusive versus Exclusive Evidence

Often, forensic chemists produce scientific evidence that can be described as either **inclusive** or **exclusive**. Recall the red fiber example mentioned earlier in the chapter. In that example, successive classification based on analytical data demonstrated that the red fiber from a crime scene belonged to the same class as fibers from a suspect's red nylon jacket. This is an example of inclusive evidence: the jacket is included in the population of items that could have been the source of the fiber in question. Had the fibers from the jacket been found to have a cross section different from that of the fiber found at the scene, they would have been exclusionary evidence: The jacket could *not* have been the source.

3.4 Direct and Circumstantial Evidence

Direct evidence is that which is known to a person by personal knowledge, such as eyewitness testimony. Such evidence, if found to be true, would prove a point in contention without requiring any additional analysis or inference.[3] Forensic scientists, by contrast, produce **circumstantial evidence**, or evidence that requires inference to move logically from the information provided to the answer to a question. For example, if blood is found on a knife, and DNA typing showed that the blood matched that of a suspect, with a probability of 1 in 6 trillion, the trier of fact must still infer that the blood came from the suspect, since the deposition of the blood was not directly witnessed. Contrary to popular belief, circumstantial evidence is not, by definition, weak evidence.

3.5 Chain of Custody

The "chain" as it is called, is a paper form that tracks evidence from its creation or collection to its final disposal. A "cradle-to-grave" document that completely describes the history of a sample or an exhibit constituting evidence, the chain is initiated when the sample is collected or created and is updated each time the sample is transferred from one person to another. The chain ensures that the sample's history has no gaps and that the sample was in the direct control of one person at all times, though not always the same person. When a sample is in the laboratory, it either is stored in a secure, locked storage area or is being analyzed. Any break in the chain, no matter how innocent or inadvertent, raises the possibility that the sample could have been tampered with. Accordingly, painstaking steps are taken to ensure the integrity of all evidence. Among these steps are establishing security measures, guaranteeing controlled access to storage areas, and implementing specific protocols for opening, marking, sealing, and transporting evidence. Maintenance of the chain is a fundamental responsibility of any forensic analyst.

3.6 Destructive Testing

If an exhibit of evidence is consumed in testing, the tests performed on it can never be repeated or verified. Although this is not a limitation when the case consists of several milliliters of blood or a large bindle of white powder, other cases are not so simple. If the exhibit is a single fiber or one tiny paint chip, analytical options are limited. Solubility tests would be a poor choice for a single paint chip, but microspectrophotometry (nondestructive) would be ideal.

Applying the Science 1 The Power of a Common Source and Circumstantial Evidence

The Wayne Williams case was made without eyewitnesses, without DNA, and without fingerprints. In 1982, Wayne Williams was convicted of murdering 2 young boys in Atlanta, but he was likely responsible for the killings of at least 10 others. The key evidence in the case was fibers and dog hair that represented an accumulation of circumstantial evidence the jury could not ignore. In 11 of 12 fiber correlations, fibers found on the victims and in Williams's home or car were determined to be members of the same small class. Any one of these 11 correlations was inclusive evidence, but when they were considered together, the chances that 11 different fiber or hair types would be found both on the victims and in Williams's environment were too small for the jury to consider as coincidence.

Source: Deadman, H. A. "Case Reading: Fiber Evidence and the Wayne Williams Trial." In *Criminalistics: An Introduction to Forensic Science,* ed. R. Saferstein. Upper Saddle River, NJ: Prentice Hall, 2004.

4 THE FLOW OF A FORENSIC ANALYSIS

It is important to understand that forensic chemists work on the basis of a finite universe of substances that are of interest. The method selected must answer the forensic question, such as, Does this fire debris sample contain an accelerant? The forensic question dictates the method, which must be fit for the purpose of detecting accelerants. The chemist (and the legal system) is not interested in determining what kind of wood was in the fire or what other materials are present—only whether there was an accelerant. Similarly, in forensic toxicology, the universe of analytes consists of drugs, poisons, and their biotransformation products. If a postmortem blood sample arrives at the laboratory, the toxicologist will not apply a method to determine the cholesterol level in the blood, because that information is not relevant to the case at hand (as per the *Joiner* decision). Such a method would not be fit for the purpose of detecting drugs, poisons, and metabolites. You should keep this in mind as we begin to delve deeper into the specifics of different analyses. A forensic analysis is usually a narrowing-down process, as shown in Figure 2. Although the sample matrix may be known (blood, urine, fire debris, etc.), many samples are complex mixtures that require a systematic approach to characterize them. Generically, a forensic chemist relies on three groups of techniques: visual examination and inspection (both macroscopic and microscopic), organic chemical analysis, and inorganic chemical analysis. The sample or exhibit of evidence is often referred to as a **general unknown**, even though the analyst usually has some idea of what is or might be present in the sample.

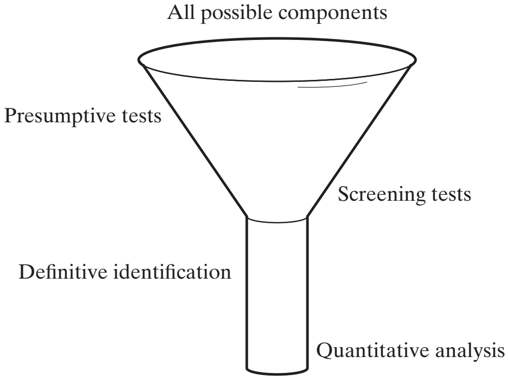

FIGURE 2 The flow of a forensic analysis.

Analysis starts with qualitative presumptive tests that narrow down the list of potential analytes and direct subsequent analysis. In some cases, visual or microscopic examination suffices as a first step. Presumptive tests utilizing chemical reagents belong to a family of analytical techniques referred to as **wet chemical methods**. Most are based on observing results when specific reagents are added to small portions of the samples. Color and crystal tests, as they are commonly called, are used in analyzing drugs, gunshot residues, and explosives. These tests will be discussed in detail in subsequent chapters. It is worth noting that as instrumentation improves and becomes more affordable, there is decreasing reliance on wet chemical methods; however they will continue to play a role for the forseeable future.

Once presumptive tests have focused the analysis on a small set of potential components, the next step usually involves the separation and isolation of target components, either for screening tests or for definitive identification. Typically, such steps involve extraction and chromatography. Forensic chemists often employ thin-layer chromatography (TLC) in the analysis of inks and drugs as a follow-up to presumptive tests, whereas toxicologists may use immunoassay to narrow the field of potential analytes. Chromatography can also be employed for sample cleanup and analyte isolation, as can solvent extractions, headspace methods, and solid-phase extractions. Confirmation of tentative identification follows, using instrumental techniques such as infrared spectrophotometry and gas chromatography–mass spectrometry (GC-MS). The latter is particularly valued because of its capabilities in separating, identifying, and quantitating analytes, although the degree of quantitative analysis required varies. In seized drug analyses, GC-MS is often the primary analytical instrument used, whereas for other purposes, such as analyzing fibers, it may be less important or even inapplicable.

As we discussed previously, the majority of forensic chemical analyses do not require the complete characterization of a sample. For example, a small resinous cube of brown material may be found to contain heroin along with many other materials; however, analytical interest usually ends with the identification of the illegal drug or substances. Occasionally, the materials used as cutting agents (diluents) are identified, but that is usually the extent of the testing. Although a complete characterization could be invaluable for linking the resin to others and for determining origins, testing for such purposes is not routinely performed, given the time and expense required. Like all analytical chemists, forensic chemists balance the need for accuracy, precision, and completeness against the reality of limited time, money, and resources. The overriding consideration is always how well the method answers the forensic questions. The next chapter describes the acceptable compromises that yield useful, reliable, and legally defensible data.

5 THE FORENSIC MIND-SET

There is a core set of skills that any forensic scientist should cultivate as part of a forensic mind-set. The importance of comparison in forensic analyses imposes conditions on methods selected, how they are applied, and how the results are interpreted. Consider a case in which the forensic chemist is provided a tiny fragment of a thick, fibrous, silvery material with one adhesive surface. The evidence is the only remaining trace of the material that was used to bind a homicide victim. A suspect has been identified and a search of his house reveals three different rolls of duct tape. The forensic question is, From which roll, if any, could the fragment of tape have come? The identification part of analysis is simple: A quick look through a stereomicroscope shows the material to be duct tape. The challenge is how to proceed, given that the evidence cannot be destroyed.

If the analyst is lucky, it may be possible to physically match the fragment to one of the rolls (identifying a common source, or individualization). If not, the tape can be examined microscopically and with microspectrophotometry. Careful study of the fiber pattern in the tape, combined with some database searching and phone calls, may narrow the possible manufacturers of the tape (classification). A trip to the library (a building or an electronic repository) may uncover an article in a forensic, analytical, or industrial journal (e.g., *Journal of Forensic Sciences*, *Forensic Science International, Canadian Journal of Forensic Science*, *Adhesives Age*, or *Adhesives and Sealants Industry*) that describes how others have approached similar problems. Experimentation with tapes unrelated to the case can further refine the approach.

Although this kind of case is not routine, it highlights the skills that constitute the forensic mind-set. Forensic scientists and forensic chemists should

- assume nothing.
- be resourceful. Finding at least two journals devoted to adhesives would be of significant help in the case and would take only minutes via an electronic search. Browsing articles could produce names of experts in adhesives to contact for assistance.
- think outside the discipline. Forensic science integrates many areas, chemistry being only one, but the core skills and principals of science are always the same. The analyst in this case would probably find reading adhesives journals easier than expected.
- be creative. Often, creativity is attributed to the arts (painting, music, etc.), but successful scientists and researchers must be creative as well. Creativity involves applying a novel approach to a problem or finding a novel application of existing tools and skills. All painters use paint, but there are an infinite number of ways to assemble the colors on a canvas. Similarly, all analytical chemists have access to the same set of tools; it is how they are applied that makes an approach creative. Challenging cases require creativity.
- build a big toolbox that never stops growing.
- know their limitations and never speak beyond what their data and expertise support.
- be flexible. Just because something works in this case does not necessarily mean that it will work in the next one. The more knowledgeable and resourceful a scientist is, the more flexible he or she is.
- be persistent. The case described in this section might at first glance have seemed hopeless to the analyst, but it was not. *Difficult* is not the same as *impossible*; a good forensic scientist recognizes the difference.

6 FORENSIC CHEMISTRY TODAY

Analytical chemistry in the forensic field is generally divided into two areas: forensic toxicology and forensic chemistry. The divisions are somewhat artificial, but an understanding of them is important. Forensic toxicologists work with biological evidence and follow the trail of drugs and poisons ingested by humans or other organisms. Forensic toxicology is often associated with death investigation and the medical examiner's or coroner's office, depending on the jurisdiction. Certainly, forensic toxicologists are also forensic chemists; the division between forensic toxicology and forensic chemistry and the use of those job descriptors are rooted in history and tradition.

Forensic chemists work with physical evidence and are often employed in what are often called "crime labs," although this term seems to be falling out of favor. In general, qualifications for employment in either type of laboratory (crime lab or toxicology lab) are a B.S. in a natural science (preferably chemistry) with an emphasis on analytical and instrumental methods. Entry-level toxicology positions may require additional training or experience in toxicology or pharmacology. The moniker "drug chemist" is sometimes used if the person works exclusively in that area; some forensic chemists work in trace evidence and other forensic specialties. Forensic chemists also work with materials such as inks, dyes, fire debris, gunshot residues, dusts, explosives, polymers, paints, and glass. If there is physical evidence and it is amenable to, and benefits from, chemical analysis, a forensic chemist or someone trained in that area can be involved in analyzing that evidence.

EXHIBIT D

The First Forensic Testimony

In truth, the first instance may never be known. It has been reported that a surgeon who examined Julius Caesar's body was asked to testify as to which wound was fatal to the emperor. However, one of the first instances of modern forensic testimony was given by a chemist, M. J. B. Orfila (1787–1853), in a poisoning case. Orfila, held by many to be the father of forensic toxicology, was a prominent toxicologist and skilled chemist when the case of Marie LaFarge crossed his path in 1840. Marie LaFarge was a young French widow who, at 24, remarried. Her second marriage, to Charles LaFarge (age 30), was reportedly not a happy one. In 1839, Charles died after eating cake made by his wife; the symptoms were consistent with arsenic poisoning. Marie was charged and chemical tests were performed on the body, but the results were inconclusive. The court was unsatisfied and commissioned Orfila to journey from Italy to France to conduct a review of the scientific work in the investigation. Orfila eventually had Charles's body exhumed. A skilled analytical chemist, Orfila was able to detect arsenic in the tissues. He also showed an appreciation for the need for control samples, testing the soil in which Charles had been buried and demonstrating that the arsenic did not originate from it. Marie was convicted and sentenced to involuntary servitude, during which time she wrote a book.


National Library of Medicine

M. J. B. Orfila


Mary Evans Picture Library/Alamy

Marie Lafarge