CHEMICAL FINGERPRINTING IN FORENSIC SCIENCE

By

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ABSTRACT

The evolving field of forensic science continues to incorporate new technologies and new procedures with the passing of time. As our scientific knowledge expands, we seek to apply this knowledge for the general improvement of society, in whatever ways that we can. The criminal justice system greatly benefits from scientific progress, primarily because science can assist in the justice system's search for truth in the courts. However, merely developing the method is not enough; new forensic methods must be carefully tested and evaluated before they can be introduced into the courts. Law enforcement and attorneys must become familiar with the theory and limitations of the new practice, and the technology to perform the analyses must be distributed and operated in forensic laboratories.

This paper attempts to review and examine one potential aid to forensic science, the ability to use mass spectrometry methods to obtain a chemical fingerprint of collected evidence. Following an overview of the aims of chemical fingerprinting and trace evidence, the MS methods in question are explained in detail. Afterwards, their capacity to analyze forensic evidence will be reviewed briefly, and some potential shortcomings of the science are explored. Third, the technique's ability to be applied to forensic issues will be examined from the perspective of law enforcement and forensic laboratories. Finally, some concerns about the courtroom presentation and reception of the results will be discussed.

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1.1 Introduction to Trace Evidence

Trace evidence is a category of physical evidence found at virtually any crime scene. Specifically, it is an especially small or fragmented piece of physical evidence that originates from a much larger article, the source, which is somehow connected to the crime scene.[1] The actual substance itself can be many things, including dust, dirt, fibers, residual moisture or residue, or chips and pieces of larger items like plastic, glass, paint, and wood.[2] Trace evidence can originate from virtually anything, but is of greatest interest to investigators when the source either originates from the offender and is found at the scene, or originates from the scene or victim and is found with the offender.

It is almost impossible to fully cover up or avoid leaving some form of trace evidence during the commission of a crime. Locard's Exchange Principle postulates that any interaction between two objects causes an exchange of small particulates. Therefore, in any crime, there is a three-way exchange of trace particulates between the offender, the victim (or whatever the object of the crime is), and the scene itself.[3] Likewise, any object that the offender interacts with prior to the crime may deposit trace materials on the offender that can later be left at the scene. If this evidence can be positively identified as originating from a known source, it provides a strong implication that the offender was present at the scene of the crime, or at least the source of the trace particulates. Often, this evidence will remain even when other evidence at the scene has been removed, covered up, or damaged, particularly because this exchange occurs automatically and any unconscious action may pick up or deposit trace evidence. If it can be collected, trace evidence can be very effective in linking the offender to the crime.[3]

Most of the time, trace evidence is, by its nature, very small and any chemical examination will usually lead to destruction of the evidence.[1] This limits the degree to which the

evidence can be subjected to chemical analysis. More often, physical analysis of its characteristics is used to attempt to identify a potential source. That being said, most of the characteristics – density, color, appearance, and refractive index – are only class characteristics, meaning that they are shared by a larger subgroup of items and are not unique to that specific source. Taking the size of the subgroup into consideration, an investigative group can state that the evidence *may* have come from that specific source, and give the estimated probability that the suspected origin is the actual origin.[2] Criminal cases, however, require the standard of proof beyond a reasonable doubt. The probability of the trace evidence originating from any given source is almost always too low to draw a legal conclusion, and trace evidence is most useful when used to exclude a source or suspect. The value of trace evidence comes in a situation where several trace substances can be used to tie the offender to the crime scene, since the *individual* probabilities multiply to significantly decrease the chances of there being an alternative explanation for the presence of the *total* evidence.

If trace evidence could be found to have sufficient class characteristics to make it as good as evidence with individual characteristics, unique traits that are found only in that source, then that single trace could be conclusively used to place an offender at the location of the source.[2] This is especially critical since trace evidence is usually the hardest to eliminate and destroy at the scene of a crime. At the moment, the most effective way to provide individual characteristics is for the trace evidence to be a fragment with clearly defined edges. These edges can then be fit into the source, as if the trace particle was a piece of a puzzle. In many situations, trace particles like fibers, dust, and residues cannot be fit into a larger source, while glass particles are sometimes too small to be fit back into the original source with certainty. Larger fragments that

can be utilized like a puzzle piece are likely too sizeable to fall into the category of "trace evidence" and should be called regular "physical evidence."[2]

1.2 Principles of Chemical Fingerprinting

One of the more interesting concepts surrounding trace evidence is the notion of chemically analyzing a substance to obtain a "chemical fingerprint." The idea behind chemical fingerprinting, at its roots, is that the molecular composition of a given object or substance can be used to identify that object as different from another.[2] The likelihood of another object being exactly chemically identical, when examined with a high degree of precision, is so small that it approaches the probability that any two individuals will have a matching fingerprint; hence, chemical fingerprinting. Of course, at some level almost every object will be chemically different from every other object, and current technology is not capable of exactly measuring the chemical makeup of any given object.[2] However, chemical analysis can be used to draw comparisons between two different samples in the sense that, if they derived from the same source, they should be chemically similar enough to draw the conclusion that they are identical.

There are several aspects in which two samples can be chemically identical or chemically different. If one sample contains a chemical, element, or compound not found in the other, then it can be assumed that the two are not identical unless the presence of the anomaly can be sufficiently explained. For example, if two glass samples are analyzed, and one contains a metal for coloring not found in the other glass, then the two samples are chemically different and most likely came from different sources. Even if the two samples contain the same substances, if the ratios of the substances are significantly different, the two sources can be distinguished from one another. Two soil samples could be found different if one has a much higher level of nitrates than

another. Two other markers for chemical uniqueness could include the presence of trace elements and the ratio of isotopes. Trace elements are essentially impurities that were not removed from the sample, but are not characteristic of that particular substance. They are randomly and unintentionally introduced to samples, and therefore, provide a level of individuality to that sample.[2] Soil again can contain trace levels of minerals or industrial waste products depending on the situation. These trace substances can often be used to determine uniqueness either by the presence or absence of those elements or the amount of the materials present. Isotope ratios of two samples can also indicate uniqueness. An isotope is an atom of a given element that has a varying number of neutrons.[2] Carbon, for example, has 6 protons, but can have 6, 7, or 8 neutrons; each combination is an atom of carbon, but is a different isotope. The ratio of isotopes is based on the source and its conditions of formation, and as a result is unique to that sample source.[4]

The chemical composition of a sample can be affected in many ways. Contaminants can be introduced to a sample source, such as a liquid or soil, and incorporated into a mixture. Organic compounds and substances are especially vulnerable to absorption of contaminants. Some samples are manufactured, such as glass, rubber, fibers, and so forth. The chemical composition of manufactured products is varied by the manufacturer, and rarely do two manufacturers use the same exact recipe when making their products (a practice supported by patent laws regarding a specific manufacturing process). Even when this is the case, the location and conditions that these ingredients come from can affect the final overall chemical composition; a contaminant that was absorbed by a tree during its growth may appear in future wood-based products. Finally, the ratio of isotopes in a substance varies depending on the conditions that the original materials were exposed to during formation and processing. When all

of these variables are taken together, it stands to reason that every finished product will be chemically unique, and that we can differentiate samples that come from different sources.

There are some assumptions and shortcomings of chemical fingerprinting. Since the chances of two samples being entirely identical is extremely low, we must distinguish when two samples become significantly different from each other. Samples that are on some level unique may still fall within the range of "different but statistically insignificant," and therefore we may still be unable to distinguish two different samples from each other. However, because our instruments are not infinitely precise, we must make the range wide enough that error cannot accidentally determine two samples from the same source are different. There is also the sticky issue of sampling. Ideally, the two samples should be of about the same size and come from the same section of the source material. Sampling variations could produce unwanted error that has nothing to do with either the content of the sample or the nature of the objects. Sources that are not homogenous, or uniform throughout, may have "pockets" of an element or compound that could distort analysis of relatively small samples. Samples that are particularly non-homogenous, or heterogeneous, can be especially hard to analyze unless a large enough sample size can exist that any local variation can be eliminated. In other words, the sample should either be homogenous, or should be large enough that any natural variation is eliminated.

Finally, chemical analyses generally destroy the sample, prohibiting further analysis with that same sample material.[1] This is especially a problem when evidence is expected to be preserved until the trial; the weight of analytical evidence decreases when the tests that show innocence or guilt cannot be performed again by the opposing counsel.[1] Allegations of lab error could entirely eliminate evidence from a trial, particularly when the analyses cannot be performed again. Also, since trace evidence by its nature is of extremely small quantity, it is

sometimes impossible to perform a sufficient number of analyses, and analysis error can seriously impact the chances of properly utilizing the evidence. There is also the possibility that one of the analyses may have failed due to a technical issue or instrument failure, which invalidates that test and requires another analysis of the sample. If there is no more sample to analyze, no conclusions can be drawn from the analyses. These shortcomings could prove especially damaging to analysis of trace evidence, particularly with destructive chemical examinations.

1.3 The Impact of Chemical Fingerprinting

If chemical analysis could be performed on trace evidence regularly and successfully, then it would provide the effect of making trace evidence potentially individual evidence. A chemical "fingerprint," much like a real fingerprint or a DNA fingerprint, could effectively set a single source (or at least a very narrow source range) to particulates found at a crime scene or on an offender's person or belongings. Such evidence could greatly improve the capacity for law enforcement to identify and detain criminals, and also reduce the chances of convicting the innocent. This could potentially be the next major milestone in forensic examination.

As of right now, trace evidence's weight in a courtroom is somewhat limited. Chemical analysis can potentially expand its use and value, and developing analytical methods and technology have made regular analysis of trace materials more practical. Because trace evidence is deposited and carried without conscious effort, it will be present at most crimes, and could allow law enforcement to obtain valuable information even when little other evidence remains. Also, the evolution of microanalysis, or the analysis of samples with mass in the microgram range, has allowed for chemical analysis of extremely small samples.[2] This could be especially

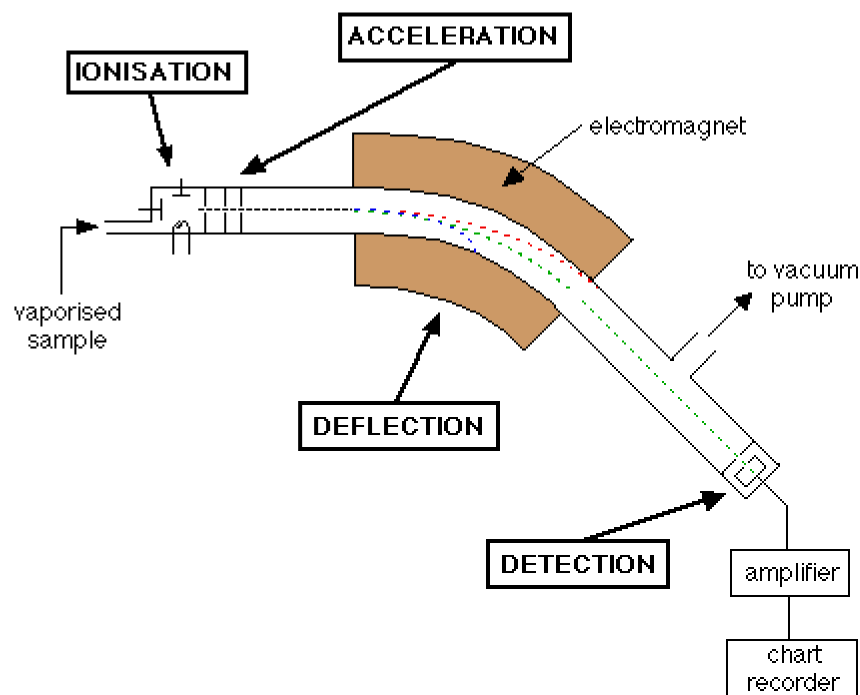
useful in preserving some part of the trace evidence for display in the courtroom and future analysis, and is valuable considering how trace evidence can sometimes be exceedingly limited to start with. However, this all rides on the assumption that these experimental principles can be properly applied to trace analysis.

The purpose of this paper is to explore the concept of chemical fingerprinting and its applicability to the field of forensic science. In the first half of the paper, we will examine current methods of chemical analysis and how they may be applied to the fingerprinting of trace evidence. Primarily, we would like to examine two increasingly prominent forms of mass spectrometry analysis, isotope ratio mass spectrometry and laser-ablation inductively-coupled plasma mass spectrometry. In addition to examination of the theory and methods of these techniques, we will also consider potential concerns or areas where such analytical methods may not be applicable. In the second half of the paper, we will convert to a legal point of view, and discuss what would be needed to incorporate such techniques into common procedure in criminal investigations. This will cover both potential issues in collecting and analyzing the evidence for use in a trial, as well as its possible introduction into the courtroom itself. Particularly, we will attempt to focus on any conditions whereby an improper use of the analysis may actually serve to further a miscarriage of justice, especially as relates to an incorrect understanding of the theory's principles and limitations. The purpose, therefore, is to consider the practical applications of this scientific principle and its potential effect on society if it is successful.

2.1 Principles of Mass Spectrometry

Mass Spectrometry (hereafter referred to as MS) is a common chemical analytical method, especially in the field of forensic science.[2] The principles of MS analysis form the basis for the two developing techniques explored later, and therefore it is important to briefly discuss what MS actually is. In a sentence, mass spectrometry measures the mass of the molecules in a sample and reports relatively how many times that particular mass appeared in the sample. Put differently, it can be said to sort molecules according to their mass.[5] The results of this counting allow the analyst to learn several bits of information about the sample, including its composition and structure.[2] Depending on the type of spectrometer, the device can analyze the sample composition across the full range of particle sizes, or it can select for only particles of a certain mass-charge ratio. The instrument can also be modified to analyze the sample molecules as they are presented, or fragment the molecules into smaller particles. Often, the MS instrument is junctioned onto other analytical instruments, such as gas chromatographs (GC-MS), in order to provide another layer of chemical differentiation. Below is a diagram showing the general process and components of a mass spectrometer.[6]

Figure 1: General Structure of a Mass Spectrometer



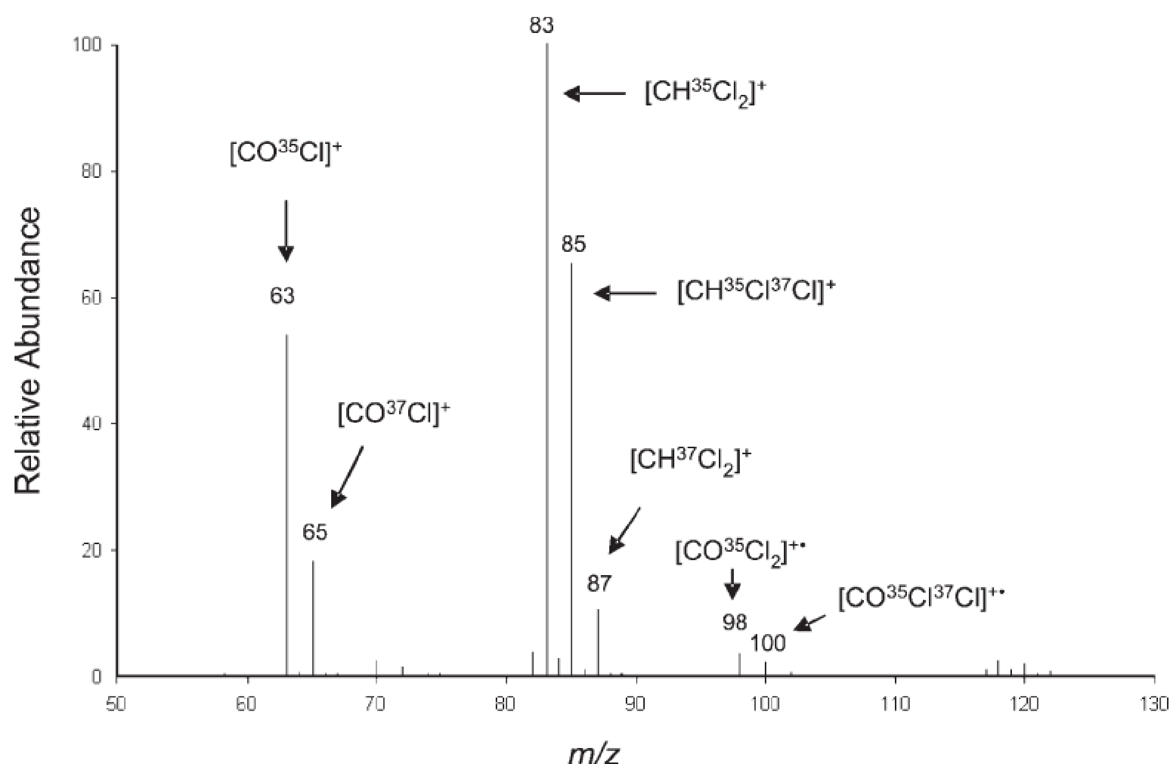
A diagram detailing the general structure and major components of the mass spectrometer. Note that the diagram is borrowed from a British chemistry website and therefore has some spelling variations.

The internal chambers of the instrument are kept under vacuum, as otherwise the particles may potentially collide with air molecules and be diverted from their pathway. The sample itself cannot be analyzed until the molecules are ionized. Ionization can occur in a number of different ways, whether through exposing the vaporized sample to a stream of electrons or exposing the vaporized particles to charged droplets. In the process, the molecule will lose an electron (or gain one, depending on the technique) and become a charged ion. This ion can then be subjected to magnetic and electrical fields, and is accelerated out of the ionization chamber. Once the ion is pushed into the deflection region, a magnetic force acting on it causes it to veer from its straight trajectory. The amount of deflection depends on two key factors, the ion's mass and its charge. Generally speaking, most of the ions are at the +1 level, but ions with a greater charge are prone to being deflected more by the magnetic field. The ion's mass inversely affects its deflection, so

that heavier ions are deflected less than lighter ions. Another form of MS uses an electric field to accelerate the ions, and the mass of the ions determines the time it takes them to reach the detector. This is called Time-Of-Flight Mass Spectrometry.[6]

In the above diagram, only specific ions are able to reach the detector at the end of the channel. Ions with too large a mass are not deflected enough and collide with the tunnel walls; ions with too small a mass are overdeflected into the near wall. Only ions with the correct mass-to-charge ratio are able to deflect enough to reach the detector. Alternatively, the detector can be much wider, and the ions can be deflected enough so that they travel to different points on the detector. The detector then determines the correct mass-to-charge ratio depending on where on the detector range the ion had hit. In either case, the amount of deflection, and consequently the ion range being selected for, can be altered by varying the magnetic field in the deflection zone. The instrument can therefore rapidly analyze the entire spectrum by altering the magnetic field inside the channel. Once the ions collide with the detector, they induce a current that is monitored and recorded for that particular mass-to-charge ratio. After the analysis is complete, the total induced current for that mass-to-charge ratio is converted into a mass-charge peak, with its height relative to the amount of current induced. In this manner, the relative abundance of each molecular mass in the sample is calculated; the chemical composition of the sample is determined. Below is one example of a mass spectrograph. Note how each displayed peak has a corresponding mass-to-charge number, which can be paired up with a molecule that would have that mass. Also, observe that the peaks are scaled by "relative abundance;" while the MS does "count and sort" particles, it does not directly count them, but instead reports relatively how frequently particles of that mass were detected compared with other particle masses.

Figure 2: Example of a Mass Spectrograph



This is an example of an actual mass spectrograph. Each vertical line represents a particle of a different mass-to-charge ratio. Several of the lines have been marked with expected sample products that have matching mass numbers.

The reason that mass spectrometry is such a prominent method of analysis is because it is generally quite simple to perform and interpret. Since most ions have a charge of +1, the mass-to-charge ratio can usually be read as the molecular mass. If the sample is comprised of simple, stable molecules, one can easily calculate the chemical composition of the substance based on the relative amount of molecules of that given mass. This is most effective when scanning for trace components such as rare-earth metals. However, there are some limits to MS analyses. The most obvious is that the instrument can only report the mass of the molecule, not the identity of the atoms comprising it. This means that there could potentially be two different molecules with the same molecular mass being recorded in the same mass-to-charge peak. This difficulty can often be sidestepped by combining MS with another analytical method, such as GC-MS, which

also sorts the molecules based on their structure. Complex molecules may also fragment inside the instrument, producing smaller particles derived from the parent molecule. However, this is again not an issue if the analysis in question is of a sample comprised of simple molecules that are unlikely to fragment, or if the analysis is to detect heavier metal contaminants. There are many forms of mass spectrometers, each designed to perform a specific function. Two types of spectrometers make use of the high sensitivity of these instruments in detecting elemental composition and isotopic composition of a sample.

2.2 Isotope Ratio Mass Spectrometry

While a mass spectrometer can normally detect elemental isotopes, some high-sensitivity instruments are designed to specifically measure the isotopes of the lighter organic elements. They usually have a specially-designed detector array comprised of Faraday cups, which are positioned to receive ions of a specific molecular mass.[4] By comparing the ratios of a given element's (or molecule's) isotopes, important information can be obtained about the sample being analyzed. This analysis is consequently called Isotope Ratio Mass Spectrometry, or IRMS. Although some information about the elemental composition of the sample is neglected, the greatest advantage to IRMS is that, by examining the isotopic ratios of elements, the source of the sample can be readily determined.

One of the main pitfalls of chemical forensics is that, in many situations, the object being examined is not unique; a mass-produced object may have the same chemical composition as every other object in its group. For example, accelerants may be composed of the same structural hydrocarbons, or synthetic fibers may be comprised of the same long-chain molecules. A simple analysis of what elements or molecules are present may not be enough to distinguish the two

samples. However, even though the two objects have the same elemental makeup, they differ in their isotopic composition. As mentioned before, isotopes are atoms of a given element that have a different atomic weight, owing to the varying number of neutrons in the nucleus.[2] Some of these isotopes are unstable, and experience gradual decay; carbon-14 is an example of an unstable isotope. Stable isotopes, however, remain unchanged and have a specific mass. As a result, the isotopes will show up as different masses on a mass spectrograph, and IRMS can possibly differentiate two otherwise chemically identical substances based on their molecular masses alone.

What forensic analysts can rely on is the natural variation in isotope ratios. Globally speaking, the large-scale ratios of isotopes throughout different regions of the world were fixed during the formation of the Earth. Since then, the ratios have not changed significantly, and there are some regions that have a greater abundance of heavy isotopes than others.[7] This provides scientists with a sort of isotopic origins map, as substances that are mined or grown in a particular region will have isotopic ratios similar to that region. On a smaller scale, isotope ratios can be altered during a physical mixing process or a chemical reaction. This causes a variation in the "natural" isotope abundance level that individualizes that product.[7] These varying effects are generally referred to as fractionation.[4] Heavier isotopes are less likely to participate in chemical reactions, but also have a lower energy reserve and are more resistant to thermodynamic influence. As a result, chemical processes tend to shift the product isotope ratio more towards the lighter isotope, whereas heavier isotopes have a higher boiling point and are more likely to evaporate last when heat is applied, again leaving behind heavier elements.[4] Because stable isotopes do not decay, these mixing effects remain permanent until further chemical or physical interaction affects the ratio.

It is highly unlikely that two substances will have exactly the same isotopic ratio when originating from two different sources, or when undergoing two different processes. Manufacturing processes and storage conditions will cause specific variations in the isotopic ratios naturally, whereas two substances coming from different locations will have drastically different "natural" abundance levels to start with.[4] Therefore, it is possible to trace a substance back to its point of origin, or establish that two different objects had a similar origin. Even if both substances have the same chemical identity, they can still be isotopically different. Due to the precision and sensitivity of the IRMS, it is often possible to conclude with a great level of certainty that two objects are identical (i.e. came from the same source, thereby linking suspect and evidence). However, IRMS has to be extremely sensitive, because the isotopes they are examining are already highly uncommon. The elements scanned for most frequently in IRMS are carbon and nitrogen, followed shortly by oxygen and hydrogen, and sometimes sulfur. Listed in the table below are the relative abundances of the isotopes of these elements.[4] The "heavy" isotopes occur far more infrequently in nature than their "lighter" isotopes, and as a consequence, detecting them, and detecting them accurately, requires an exceptional level of detection capacity.

Figure 3: Relative Abundances of Organic Elements

Element	Isotope	Relative abundance (%)
Hydrogen (H)	^{1}H	99.984
	^{2}H	0.0156
Carbon (C)	^{12}C	98.892
	^{13}C	1.108
Nitrogen (N)	^{14}N	99.635
	^{15}N	0.365
Oxygen (O)	^{16}O	99.759
	^{17}O	0.037
	^{18}O	0.204
Sulphur (S)	^{32}S	95.02
	^{33}S	0.76
	^{34}S	4.22
	^{36}S	0.014

The above table explains the relative abundance of the isotopes of five organic elements. These elements are commonly found in the majority of substances, both natural and manufactured, and can be studied through IRMS analysis.

In order to perform IRMS analysis, the sample compound to be examined must be broken down chemically to release the target elements being quantified (C, N, O, H). Carbon and nitrogen are analyzed for by converting the sample into CO_2, NO_x, and H_2O, and then extracting the CO_2 (to determine the ratio for carbon isotopes) and nitrates (as N_2) for ionization as per normal operation of the MS. When analyzing hydrogen and oxygen, the materials are converted into H_2, N_2, and CO, with CO and H_2 being sent through the remainder of the MS.[7] The sample can then be compared with a "standard" to assess the difference in the two isotopic ratios, which is given as delta δ. This measurement of delta is what is used to mark the individuality of the sample in question.[7] If delta can be acquired for all four elements, then there are four very precise ratios of elements that can be used to categorize the sample. To make a chemical match, an unknown sample's delta value is compared with that of a known reference sample. When the delta values of the unknown sample and the reference sample are statistically identical, then the two can be assumed to have the same origins. This is most helpful when analyzing similar

organic materials, since more often than not they are highly complex and are the most prone to isotopic fractionation, but are otherwise indistinguishable chemically. Shown on the next page are the results of an isotopic analysis of several plastic bags. Chemically, the bags are comprised of the same substances and molecules, but their isotopic ratios can in most cases clearly tell them apart. This is done by comparing the carbon and hydrogen isotopic ratios; note that the hydrogen isotope ratios tend to vary far more than the carbon isotope ratios.

There are furthermore two different primary methods of IRMS. One method is the continuous flow method, which gradually introduces the sample with a stable, nonreactive carrier gas. After a standard is used to "calibrate" the instrument, the sample is introduced and analyzed. The second method is the dual-inlet method, which alternates introducing the standard and the sample in a single, repetitive process. By alternating the sample and the standard, the analysis can self-stabilize its operation, and reduce the amount of variability in signal strength, or how much gas is being sent through to the detector. As a consequence, dual-inlet analyses are somewhat more precise than continuous-flow. However, the dual-inlet method requires a much larger sample size, on the order of 10 μmol, whereas the continuous flow method can operate with a sample size on the order of 100 nmol, or 10 nmol when used in tandem with GC. This allows for the use of a sample 100 or even 1000 times smaller than in the dual-inlet method, which makes it of particular interest to forensic analysts.[7]

Figure 4: Isotopic Analysis of Plastic Bags

Table 1
Physical and isotopic characteristics of sixteen assorted grip-seal bags

Bag #	1	2	3	4	5	6	7	8	9	10	11	12[a]	13[a]	14	15	16
Approximate width (mm)	88	200	113	115	100	154	134	100	120	200	112	73	73	100	323	227
Approximate length (mm)	130	280	127	127	195	248	200	175	190	305	168	100	100	170	342	340
Grammage ($g\ m^{-2}$)[b]	41	51	51	52	50	58	83	48	57	49	55	60	62	116	55	50
$\delta^{13}C$ data																
Top	−29.5	−27.3	−27.8	−27.8	−28.8	−28.4	−30.0	−27.2	−27.4	−32.1	−29.2	−29.3	−29.3	−28.7	−27.7	−27.7
Middle	−29.6	−27.3	−27.9	−27.8	−28.9	−28.5	−30.0	−27.2	−27.4	−32.1	−29.3	−29.3	−29.4	−28.8	−27.7	−27.7
Seam	−29.6	−27.2	−27.9	−27.8	−29.1	−28.4	−29.9	−27.2	−27.4	−32.1	−29.3	−29.4	−29.4	−28.7	−27.7	−27.7
Grip-seal	−29.6	−27.2	−27.8	−27.9	−29.2	−28.4	−28.3[c]	−27.2	−27.4	−32.1	−29.2	−29.4	−29.4	−28.8	−27.7	−27.7
Average	−29.6	−27.3	−27.9	−27.8	−29.0	−28.4	−30.0	−27.2	−27.4	−32.1	−29.3	−29.4	−29.4	−28.7	−27.7	−27.7
S.D. (n = 8)	0.04	0.07	0.07	0.08	0.14	0.03	0.04	0.03	0.03	0.05	0.07	0.04	0.06	0.03	0.06	0.06
$\delta^{2}H$ data																
Top	−101	−66	−66	−61	−75	−62	−84	−79	−66	−46	−74	−62	−61	−93	−54	−47
Middle	−102	−62	−65	−64	−75	−59	−80	−70	−63	−46	−70	−56	−61	−97	−52	−54
Seam	−107	−63	−67	−64	−76	−59	−84	−80	−60	−49	−70	−59	−58	−103	−59	−59
Grip-seal	−107	−69	−69	−66	−77	−62	−82[c]	−85	−61	−52	−74	−62	−60	−104	−54	−55
Average	−105	−65	−67	−64	−76	−60	−83	−79	−62	−48	−72	−60	−60	−99	−55	−53
S.D. (n = 8)	3	3	2	2	1	2	2	6	3	3	2	3	2	5	3	5

$\delta^{13}C$ value reported as permil versus VPDB (Vienna PeeDee Belemnite). $\delta^{2}H$ value reported as permil versus VSMOW (Vienna Standard Mean Ocean Water).
[a] Believed to originate from the same source.
[b] Calculated from the size and weight of the bag, making no allowance for the zip.
[c] The value for the zip was not included in the average.

Above are the results of an isotopic analysis of several plastic bags. The carbon isotope ratios, shown in the second row of results, tend to have very little within-sample variation and minor between-sample variations. The hydrogen isotope ratios vary much more widely. Note that some bags do not differ in carbon isotope ratios, but still differ in hydrogen isotope ratios.

2.3 Laser-Ablation Inductively-Coupled Plasma Mass Spectrometry

Whereas Isotope Ratio Mass Spectrometry is useful in determining the isotopic ratios of organic elements, there are sometimes complications in performing a chemical analysis. One issue might be that the sample being tested is exceedingly small, and that there is not much to test in the first place. If the evidence has to be preserved until the trial, this could be a hurdle to obtaining a scientific analysis.[1] In some cases, the evidence cannot afford to be physically modified at all, such as when the item is a work of art or artifact suspected of being forged. Sometimes, the sample is layered and not homogenous straight through, and dissolving it or otherwise fragmenting it may provide a much less clear analysis. One possible solution to these problems is another form of mass spectrometry, Inductively-Coupled Plasma Mass Spectrometry, or ICP-MS. The specific form that we will be looking at is the Laser-Ablation ICP-MS, which is capable of extracting an analytical sample so small it often leaves little to no visible mark on the object.

LA-ICP-MS, like IRMS, is highly sensitive, so while its precision may sometimes be lacking in comparison to other analytical methods, it is able to detect elements at far smaller concentrations.[8] As the name implies, the instrument uses a laser to fragment particles off the sample for the usual MS analysis, a process called ablation. Once the particles are ablated, they are moved into the ICP chamber of the instrument, where they are exposed to a high-temperature noble gas such as argon or helium. When a gas is superheated, it becomes a plasma, an ionized cloud of gaseous particles. By using an inert gas, chemical interactions are minimized, and the plasma is able to atomize and ionize the sample particles ablated by the laser in the first stage.[9] At this point, the carrier gas moves the particles into the deflection chamber and towards the detector. Generally, the most accurate analysis is achieved using a quadrupole rather than a time-

of-flight setup or other elemental analyzer, again because these instruments sacrifice detection sensitivity for precision.[8] Quadrupoles are often used in precision-based mass spectrometers because of their ability to filter ions based on their mass-charge ratio. Four metal poles are arranged parallel to each other, in a box formation, so that the ions are focused down the center of the four poles. Alternating electrical currents and radio frequencies cause an oscillation of the magnetic and electrical fields, literally throwing out ions that have too large or too small a mass-charge ratio.[10] Shown below is a diagram showing what LA-ICP-MS generally looks like; note that three of the four quadrupole rods can be seen in the "mass spectrometer" section.

Figure 5: Laser-Ablation Inductively-Coupled Plasma Mass Spectrometer

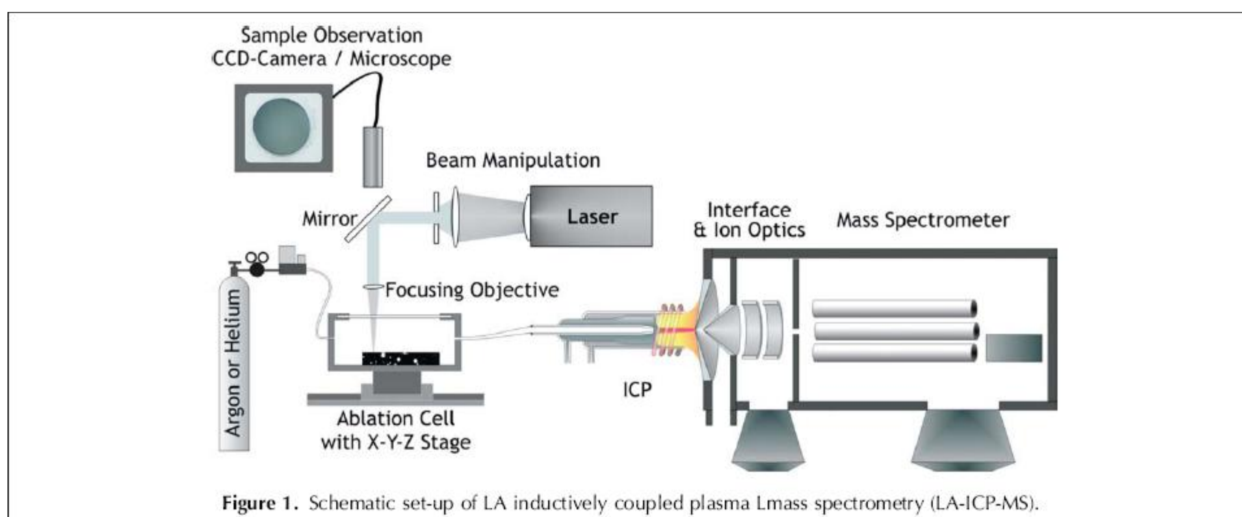


Figure 1. Schematic set-up of LA inductively coupled plasma Lmass spectrometry (LA-ICP-MS).

This is a diagram of the general construction of an LA-ICP-MS instrument. A laser source is focused and used to ablate particles from the sample, and can be controlled with optical systems. After the particles are released, they are carried into the plasma torch where they are ionized. They are then passed into the mass-spectrometer quadrupole for analysis.

One of the more helpful characteristics of LA-ICP-MS is that control can be exercised over the instrument parameters at virtually every step of the analysis. The microscope in the above diagram is used to verify where the laser is focusing and how wide the diameter of the laser spot is. This allows analysts to guide and monitor the bore of the laser, if needed. The laser

itself can be modified to ensure that the sample is being evenly analyzed. Problems with elemental fractionation occur when the laser ablates the sample unevenly or generates too much excess heat. This leads to irregular sampling both due to how the laser ablated the substance (the center would ablate faster than the outer part, leading to uneven sampling) and due to the effect of heat on certain elements (by varying the heat, different elements may vaporize faster than others). As a consequence, the results of the analysis will show an inaccurate elemental composition for that sample.[8] However, these errors have been corrected by limiting the fractionating effects of the laser. By using a higher-frequency laser, the thermal effects of the laser are mitigated, and fractionation is reduced. Furthermore, optical systems can be used to ensure that the laser maintains an even energy distribution across the impact surface. If the laser impacts the surface evenly, then sampling will be more even and regular, rather than cone- or drill-shaped. Errors due to laser sampling can therefore be controlled, and the precision of the analysis can be increased.[8]

The plasma chamber ionizes the particles that are sent in. However, there is one uncontrollable element in this phase of the analysis that may interfere with the results. Since the ablation laser breaks off particles of varying sizes, sometimes relatively larger particles are sent into the plasma chamber. These larger particles do not always fully ionize or break apart, and may cause interference or fractionation. Because of this, some systems have tried to develop mechanisms to ensure a slightly more uniform particle size. While traps can be used to filter out larger particles, this may affect the composition results of the sample. Some of the instruments have a nebulizer before the ionization chamber, which attempts to keep the size of the molecules somewhat more uniform. Using helium gas and a low-penetration laser have helped reduce overall particle size.[8] The only other variable that has to be monitored is the size of the ablation

chamber. Obviously, a larger chamber size leads to an increase in molecular dispersion, causing the vaporized particles to spread out and weakening the detector signal. Generally, signal strength is the only parameter affected by excess chamber space, and fortunately chamber size does not significantly affect the intensity of the detector signal.[8] However, depending on the object to be sampled, it may not always be possible to limit the size of the chamber.

LA-ICP-MS can have several forensics applications. One of the most obvious is that, due to its sensitivity, it can be effective in detecting trace elements and contaminants in a given sample. Its detection range is in the parts-per-billion or even parts-per-trillion range, depending on the element being analyzed for.[9] Because of this, it only requires very small samples in order to perform an analysis. These samples can be easily and selectively vaporized using the ablation laser. The actual ablation process leaves a highly indistinguishable mark on the evidence, a hole that is often micrometers thick and could be of a depth as little as a micrometer.[8] Although technically destructive, this low-level ablation generally leaves the original object untouched, allowing relatively harmless analysis of large objects such as suspected counterfeit artifacts or paintings. For trace evidence, this would be of even greater benefit since the actual mass of trace evidence is not high to start with. By controlling the amount of sample consumed, a (relatively) large amount of the evidence can be left for courtroom display or in the incidence of an opposing attorney challenging the test results.

Furthermore, the laser can be used for depth analysis as well. By ablating only a thin tunnel into the material, analysts can develop an elemental fingerprint by sample depth. Layered samples, such as paint chips or plated metal, can be characterized by composition at given depths. This adds physical qualifiers to the already-existing chemical analysis, and the thickness of layers may be just as helpful as a class characteristic in narrowing down possible origins or

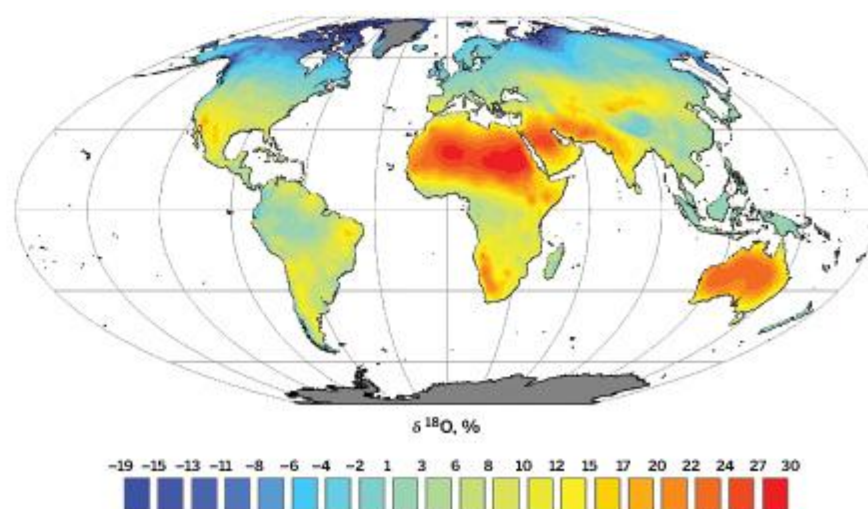
excluding suspect sources. Meanwhile, each individual layer of the sample can be analyzed as a separate substance as the laser passes through the material. The ability to construct a 3-D fingerprint map of sorts, combined with the sensitivity of the instrument, makes it likely to become a new primary tool for forensic analysis.[8]

3.1 The Theory in Practice

The above-described mass spectrometry techniques are not, by any means, entirely new or untested. However, it is only recently that they have begun to achieve widespread use and acceptance in various fields, particularly the field of forensic science. As our technology has matured, and continued research on the components of the instruments showed how to control error and improve accuracy, scientists began to consider how important a precise chemical fingerprint could be. An increased understanding of chemical reactions and processes, both in nature and manufacturing, has also led us to examine the concept of an elemental fingerprint more seriously. It is important to take a moment to explain how IRMS and LA-ICP-MS are being applied in fields outside of forensics, to lay the foundation of the instruments' reliability.

IRMS has become especially useful with the advent of isoscapes. The term first came about in 2005, used to describe maps that track changes in isotope ratios.[11] Visually similar to temperature or elevation maps, these aids chart the relative delta-value for a given element, showing geographically which areas have higher or lower levels of heavy isotopes. Below is an example of an isoscape map, developed for oxygen ratios in 2011. It is interesting to note that denser ratios of oxygen tend to occur more frequently in desert regions, such as in northern Africa and Australia, whereas the arctic regions of North America have much lighter oxygen isotope mixtures.

Figure 6: Oxygen Isoscape for 2011



This is a 2011 isoscape of oxygen isotope ratios. Redder colors signify a higher concentration of "heavy" oxygen-18 atoms, whereas bluer shades are indicative of higher concentrations of "light" oxygen-16. The delta values expressed are relative to oxygen isotopes in standard ocean water.

Though frequently such maps are used to help trace the origins of plants and drugs, a forensics team in 2005 successfully traced an unknown illegal immigrant, found dead in Ireland, back through Germany, Ukraine, and eventually to Vietnam based on the isotope ratios at different positions in his hair.[11] Since isotope ratios remain fairly constant at a given geographical location, any natural or organic object grown in that region will have similar isotopic ratios as a result of everyday metabolic intake of resources from the environment. As a consequence, IRMS has been employed in a host of different fields, particularly wherever it might be necessary to determine the origins of a substance. Applications have so far included pharmaceutical and drug analyses, counterfeit and contraband detection, environmental analyses such as identifying pollutant sources, food quality control, archaeological analyses of the origins of artifacts or fossils, ecological studies on food webs and nutrient pathways, metabolic studies, and toxicology.[4,7] With several food and environmental industries taking a particular interest in IRMS, it is safe to say that the method has largely become mainstream.

As mentioned previously, there are two main forms of IRMS. Dual-inlet IRMS is generally considered more precise, but requires a larger sample size. Continuous flow IRMS is simpler to operate and can utilize much smaller sample sizes. In particular, the continuous-flow IRMS can be connected to a gas chromatograph to provide for complete analysis of a given sample, a method called Compound Specific Isotope Analysis. The GC component of the instrument separates out the numerous compounds inside the sample and allows for all of them to be analyzed simultaneously, rather than checking for each element individually. The separated compounds are then sent to the IRMS component for isotopic analysis, which provides an isotope ratio not only for the overall sample, but for the individual components as well.[4] In other words, a hypothetical mixture of hydrocarbons A and B would be separated into two sample groups by the GC, and then IRMS would provide a ratio for both groups individually. The sensitivity of this method, combined with its ability to perform a full analysis of the sample, make it the most likely candidate for forensic research.[4] Already, it has been beneficial to biological and archaeological studies that deal with analysis of complex organic samples. However, one must keep in mind that isoscapes are rarely held on open databases, but rather are compiled when needed for a particular purpose.[11] Therefore, while there are databases for pollutant levels or imported plants, there is not yet a database available for forensic studies, something that may initially hinder attempts at making this a mainstream forensic technique.

LA-ICP-MS is also widely used, especially because of its high sensitivity. Not only is it able to detect extremely small amounts of trace elements, but it requires very little sample to perform an analysis and can leave larger objects virtually untouched. Another benefit to this method is that, since the samples are directly ablated and not dissolved, there is no solvent peak present, either in the actual instrument or in the spectrograph. This simplifies the analysis

significantly. So far, LA-ICP-MS has been used for identifying soil and ore composition, differentiating real and fake gemstones, detection of trace elements or contaminants in other materials, biomedical analyses for examining human tissue, and identification of counterfeit art or artifacts.[8,12] Like IRMS, LA-ICP-MS has applications in biology, archaeology, geology, and detecting counterfeits, although the main focus of ICP-MS is on identifying trace elements and contaminants rather than isotope ratios. Below is a chart showing the detection limits of each element that can be detected by LA-ICP-MS.

Figure 7: Elements Detected by ICP-MS

This is a chart detailing the detection limits of an ICP-MS instrument. The detection limits detail the relative range of the smallest samples of that particular element that the instrument can detect. Most of the transition metals are detectable in parts-per-trillion, which means the instrument can detect nanograms of that element within grams of the total sample. Light blue is the most acute detection limit, at less than 1 ppt; yellow is one order of magnitude larger; orange is one order of magnitude larger still. The elements in purple and green cells have detection limits in the parts-per-billion range, a detection level 1000 times larger, and weaker, than the parts-per-trillion range.

As seen above, the vast majority of transition metals, and for that matter, most elements in general, can be detected in the microgram or even the nanogram range. This allows researchers to identify the presence or ratio of trace elements in a given sample, identifying it as unique from other samples. Many contaminants come in the form of heavy metals or minerals, especially when soil is considered. These contaminants can potentially link two objects that have somehow obtained trace amounts of contamination. Whether the trace elements are there as a consequence of production equipment, or are unique to the location of origin or specific materials used, their presence has allowed multiple other fields to successfully identify their own unknown samples. Similar to isoscapes, analysts can also determine the origin of a sample by checking for trace elements that are regularly supposed to be in samples from that region. In particular, scientists were able to identify whether Australian aboriginal paintings were authentic based on the trace metals and compounds found in the paints.[13] As a consequence, LA-ICP-MS provides the other half of chemical fingerprinting, giving a strong analysis for trace elements and metals, while IRMS analyzes isotope ratios. Both have been frequently and regularly used in fields other than forensic science, and are only now being investigated as possible forensic tools. Both hold extreme promise as standard methods of analysis for trace evidence, especially with regards to identifying the origins of the sample.

3.2 Samples Applicable to Elemental Analysis

Evidence in a criminal case is rarely limited to a few specific compounds or substances. Virtually anything can become evidence. However, what evidence can be fingerprinted chemically? What tests have already been successfully performed? Fortunately, numerous investigations into the applicability of chemical fingerprinting to forensics have already been

undertaken, thanks in large part to the already frequent use of MS techniques in other fields. Some types of materials have already been tested for other purposes, such as for biological or geological studies, and these results can be directly applied to forensic uses. Other materials have been examined specifically for the aim of providing forensic identifications in the event that trace amounts of the materials are found at the scene of a crime. As a result, forensic analysts already have a wide array of materials that they can successfully examine should trace evidence come into play. The list of testable and tested materials is ever expanding, and scientists are also beginning to determine what the barriers to further analysis may be, as well as how they may be overcome.

IRMS shows significant promise in identifying the origins of trace evidence, particularly manufactured or grown organic materials. Even over a decade ago, IRMS proved effective in determining the major geographic sources of drugs such as heroin and cocaine with a high degree of certainty.[14] The general region or continent can be clearly determined by analyzing only carbon and nitrogen ratios (which are fixed through the soil and atmospheric quality), whereas a more specific location may be determined by examining hydrogen and oxygen ratios. Manufactured objects, such as plastic bags, have also been studied for isotope fingerprinting. While it is more difficult to tell apart two bags that originate from the same batch, bags produced by different manufacturers can be easily differentiated.[15] Where IRMS fails, physical examination techniques may be capable of differentiating the two samples, and since physical examinations are non-destructive, this is barely a setback. Similar results were obtained with respect to identifying packing tape, tire rubber, gasoline and fleece.[4] In other words, many objects that share the same chemical composition can be identified as isotopically unique thanks to IRMS. This is largely due to manufacturing and storage conditions. Isotopic differences

between manufacturers arise due to fractionation, a consequence of the physical qualities of isotopes. If these fractionating processes can be understood better, they may also allow us to trace a connection between products and starting materials. Already, researchers have been able to quantify a consistent isotopic change when hexamine is converted to cyclotrimethylene-nitramine, otherwise known as the explosive compound RDX.[16] By examining the isotopic ratios of the sample product, we may be able to identify the starting materials and even match that sample to a specific producer.

Homogeneity is critical in IRMS analysis. Materials such as glass, wool, bullets, steel, or stone can be fingerprinted accurately as long as they have a consistent distribution of components. However, when the material itself is too varied, pockets of particular elements may skew the results. For that reason, soil is one material that may prove difficult to accurately analyze. One study of soils in England found that the natural variations within soil may allow analysts to differentiate soil from two distant locations. However, in order to ensure that the exclusion is as certain as possible, at least five samples must be collected to identify the ranges of variation.[17] As long as the suspected sample falls within the range of the soil samples, a match may be inferred. Both ICP-MS and IRMS are useful in this approach, one for trace elements and the other for carbon and nitrogen isotopes. A similar approach can be taken with other heterogenous materials, such as wood fragments or composite stone; as long as an adequate sample size can be collected, isotopic ratios may provide origins. However, it is still far easier to exclude a suspect or evidence than it is to provide a certain match. One final field of interest is in using isoscapes to track the movement of suspects around the world. As shown in the 2005 Dublin case, human beings can be tracked based on the isotope ratios in their bones and teeth, the patterns in their hair, and water in human blood.[4,11] This may allow police to track suspects

who have traveled long distances, or verify that a suspect was living in a given area, based on the isotopic ratios in their bodies.

LA-ICP-MS also has been applied to several common forensics objects. One analysis of rare-earth metals suggested that ICP-MS could be especially useful in identifying ballpoint pen inks, provided that the inks had traces of the metals incorporated into them.[18] If banking or government institutions accepted this as a security measure, then tagged inks could be distinguished and identified by ICP-MS and only lightly sampled through laser ablation. This could then allow analysts to identify the origins of a given ink to establish document or property identity. LA-ICP-MS has also been recommended for the analysis of heavy metals in drugs, particularly due to the speed and simplicity of the analysis.[9] If any unknown or suspected poisonous substances are found at a scene, they can be easily analyzed using this technique. Glass fragments were also analyzed, and like soil, have been found to vary depending on the type of glass formed. Flat sheets of glass, such as those used for architectural windows, are generally homogenous, while molded glass, like that of bottles, tends to vary significantly throughout the bottle. As with soil, it is advised that analysts take at least five samples from variable glass to determine the overall characteristics and chemical range of the potential source, but otherwise one can distinguish two different sources of glass by analysis of trace metals inside the compound.[20] Windshields, as well as other two-layered glass surfaces, may have two unique sheets of glass on either side, and should be sampled from both sides. LA-ICP-MS also successfully identified the origins of slag created by oxy-acetylene torches and determined the authenticity of Valencian ceramics.[20,21] In all of these scenarios, trace contaminants and elemental composition helped establish common sources between a given sample and its origin,

and with minimal destruction of the evidence. The ability to identify a source for metal fragments, glass fragments, pottery fragments, and more, fits well with everyday forensic efforts.

Already, several items seem to be viable targets for chemical fingerprinting. Organic materials, metals and inorganic products, fragments, shavings, plastics, and more can be properly analyzed with either of the above techniques. It could be particularly helpful if biological fluids, such as blood, can also be used to provide not only a genetic fingerprint but a chemical roadmap that allows police to track their location or movements. However, there are several important considerations. First, not every type of evidence is fully homogenous. If it is not, like glass or soil, a significant sample must be obtained from the suspected source for comparison.[17,19] This may later produce sampling or backlog problems, but at face value means that it is critical not to come to a false conclusion based on a single point of comparison. Second, chemical identities are not wholly unique. The analysis of plastic bags could not differentiate between two bags of the same batch, and the same may apply to glass, soil, accelerants, and other samples that are mass-produced. Care must be exercised that a match is not concluded when two samples merely happen to have similar or identical compositions.[15] Third, chemical fingerprinting has not been perfected for forensic purposes yet. Although several forensic-specific tests have been run, forensics has not yet received the same level of rigorous examination as other fields have.[4] More tests need to be run in order to fully understand the best methods and procedure for chemically fingerprinting evidence, particularly trace evidence. For this reason, analysts should always be careful to consider potential analytical pitfalls, both in sampling the evidence and in collecting it.

3.3 Procedural Issues

As much as the technology may work, there is an underlying assumption that the tests will be carried out optimally and according to the correct procedure. If the analysis is not properly performed, the test is completely invalid and inaccurate, especially from a forensics standpoint. In the world of forensics, imperfect analyses could potentially lead to the acquittal of a guilty suspect, or the conviction of an innocent one. While these tests are powerful, there are several pitfalls that analysts must watch for, both in the preparation of the samples and in the actual analysis.

The most obvious procedural error, and the most important, would be sampling error. As mentioned before, the sample being analyzed should ideally be homogenous. If there is an uneven distribution of materials, it may be possible to conclude that two samples are entirely different from each other, even though they may be taken from the exact same sample. For example, while scientists were able to differentiate soil samples from two distant sites, they also found that, within either of the given sites, enough variation in the soil occurred to make some of the samples "clearly distinguishable" from others taken from the same site.[17] Glass fragments from molded objects, such as glass bottles, also seemed to show similar variability.[19] It is also cautioned, in the case of ICP-MS, that while this method is more sensitive than others, it has a tendency to be less precise, and there is a significant risk of a single analysis being off-the-mark enough to produce a faulty conclusion.[22] In these situations, it was advised that at least five samples be collected to use as source references when attempting to establish a match,[7,17,19] and preferentially running sample analyses in triplicate where applicable.[22]

Of course, trace evidence rarely comes in large, properly-sampled quantities. Whereas it may be easy to sample a known reference, such as the larger window a fragment came from or

the ground that a footprint was found on, care must be taken that the source references are extracted from a representative portion of the greater object. If the references are not representative of the overall object, then the estimated qualities of the source will be misstated, and the trace evidence itself may appear to fall outside the "range" of the source material. As for analysis of the trace evidence itself, there may not be enough evidence to allow for multiple runs, and in this case investigators must be content with running only one or two analyses and estimating the precision and error of the analysis. Fortunately, LA-ICP-MS can effectively limit the sample size needed to perform an analysis, but at the same time, it is still a quasi-destructive technique, and there are only so many holes that can be bored out of a single fragment of glass without seriously compromising it. Furthermore, caution must be exercised when sampling the evidence itself. If the evidence is a layered chip, such as paint or glass, sampling it at an angle, or perhaps from the reverse side, could produce drastically different results that could cause confusion in a trial presentation. Approximately the same part of the evidence should be sampled, and in the same manner, if there is any chance that the evidence is not homogenous, or the experimental results may become less precise.

Care must also be taken in drawing conclusions based on elemental analysis. While it is generally easy to distinguish two substances as having different fingerprints, it is still slightly harder to conclude a positive match. An examination of several plastic bags found that, while bags made by different manufacturers or made in different batches could normally be distinguished from each other, some bags could not even though they did in fact come from different sources. Physical examination, namely of the birefringence pattern of the plastic, was able to differentiate the two bags where isotope analysis failed.[15] Though highly unlikely, it is possible that two entirely different samples may end up with the same isotopic ratios or even

elemental composition. The "fingerprint" is not always unique to that one object alone. Analysts must always consider the possibility that the two samples perhaps match by chance rather than as a consequence of having the same origins.[15] In a way, the chemical fingerprint is still looking at class characteristics. However, it is possible to make the object itself more individual by examining more elements. It is far less likely that two objects will have the exact same elemental and isotopic ratios for forty elements than for four. That being said, IRMS is most effective on only four main elements, and LA-ICP-MS is not always precise for heavier elements. Some elements, such as lead, tungsten, zinc, and cobalt, have already given some soil analysts precision issues in ICP-MS analyses.[22] Forensic scientists must be cautious not to overanalyze a compound and come to an erroneous conclusion based on imprecise trace-element measurements, either when trying to force a possible match or find some difference in the two samples. Matches should be concluded preferably after physical analysis is shown to correlate to chemical analysis. As noted in the ICP-MS precision analysis, positive identification "can rarely be done on the basis of elemental analysis alone" for the above-stated reasons.[22]

While addressing possible precision errors, it is also wise to bring up the need for inter-laboratory uniformity of procedure. IRMS instruments have to be regularly calibrated and examined for potential leaks, particularly since atmospheric gases have a high capacity for throwing off the accurate measurements of the system. Current procedure also warns of potential "memory effects," where residual material from a previous sample can affect the next analysis. Further uncertainty arises from differences in normalization algorithms and standardization materials.[7] Similar concerns can be expressed for LA-ICP-MS, on top of the already-present issues with controlling variation introduced by the ablation laser, particle size, and chamber size.[8] As expressed earlier, these techniques have only begun to emerge prominently in the field

of forensics, and as a consequence many different procedures have been developed while databases for sharing and comparing results have not yet been set up. Some groups, such as the NITECRIME EU Thematic Network, have attempted to catalogue isotopic ratios and patterns in a variety of materials, particularly those that could have significance in a criminal investigation.[4] This is less simple, though, when different facilities use their own procedures and direct comparisons are impossible due to uncertainties in measurements. Just as DNA comparisons are made easier thanks to the Combined DNA Index System, or CODIS database, chemical fingerprinting will not be especially useful or easy to perform until a running database is available for analysts to check and compare evidence "fingerprints" to known standards.[2] This may also cut down on the need for additional analyses to establish the parameters of a suspected evidentiary source. For that reason, there needs to be a single developed forensic analysis procedure for all materials, as well as a national (or even global) database available to simplify and facilitate identifications. Without these, the benefit of the forensic analysis may be outweighed by the time and resources needed to properly perform it.

3.4 Issues Regarding Contamination

There is one last procedural issue that must be dealt with separately: the issue of contamination of samples. When using precision instruments, it is obvious that any minor addition to the sample might be detected and become visible on the spectrum. When nanogram-level samples are polluted even by microgram-level contaminants, there is a serious risk of skewing the results drastically. Contamination could very well prohibit the effective analysis of any evidence submitted. However, trace evidence, by its nature, is not delivered sterile and free of interference, but rather is found at the scene of a crime, and more often than not buried under

other materials. It is crucial for analysts to consider how to sidestep the issues of both contamination by police and potential analysts as well as contamination by the suspects and environment before the evidence is collected or even placed at the scene.

There are numerous ways for evidence to become contaminated. Most of the time, the evidence is large enough that general interference and chain-of-custody violations are larger concerns than getting the evidence dirty. In many situations, dirtied evidence can be of greater use than clean evidence, particularly when the contaminants allow forensic analysts to link the suspect to the object more clearly. That being said, chemical fingerprinting is an attempt to determine the exact elemental composition of an object. Any additional materials that have come into contact with the item can interfere with an accurate analysis, and if not removed, possibly even cover up the chemical fingerprint entirely. Comparatively speaking, additional contaminants do to chemical fingerprints what friction does to normal fingerprints; the prints are smeared and cannot be properly identified due to the introduced uncertainty. The instruments being used are precise enough that even small traces of materials can impact the analyses; as noted above, the instruments have sensitivities in the micro- to nano- range, which is sufficient to pick up trace contaminants.[7,9]

The key weakness of IRMS is that there can be no interference from organic elements, especially oxygen and carbon. Any traces of organic materials, such as water or palm grease, could alter the "composition" of the evidence. A wet isotopic analysis would be several times different from a dry analysis of the same object. If the object undergoes any biological decomposition, this could also seriously affect results; microorganisms will be providing their own chemical and physical changes on the material, which could affect isotopic ratios. The ability of scientists to track bacteria based on their water isotopes may be turned against them if

these same bacteria can alter the composition of potential evidence.[4] LA-ICP-MS, on the other hand, directly addresses the material surface. When the surface is contaminated, the contaminants will probably be removed along with the rest of the material. If the contaminants are just organic, there may be less of a concern, as ICP-MS focuses on trace elements. However, if dirt, dust, or other particulates make their way onto the surface, or trace particulates of a scraped metal are left behind by a tool, they could easily alter the elemental fingerprint observed. Also, any surface materials could make the ablation surface uneven, leading to an improper sampling by the ablation laser.[8]

Police and analysts themselves must be careful not to touch or in any other way contaminate the evidence. Any direct contact could deposit body oils and other contaminants that could interfere with analyses. They must also take care to prevent the evidence from being "dirtied" or damaged by environmental sources. Organic materials, such as wood or plants, could undergo decay over time, making it necessary for these objects to be chemically evaluated quickly. Environmental conditions, such as rust or acid rain, could also break down or alter the evidence being analyzed. During preparation for analysis, the type of evidence being examined may need to be treated in a specific manner as to minimize bias due to contamination. Porous samples, such as wood, fibers, or paper, should be allowed to dry, or at least left to dry in the same manner as the source reference when IRMS is being considered. This will eliminate any H- or O-isotope errors associated with the presence of outside water, whose isotopic ratios may be randomized by absorption. (On a side note, extracting and analyzing the liquid might prove useful as well.) If the object is seriously encrusted with contaminants, such as a muddy shirt, considerations should be made as to whether or not the material would have to be cleaned in order for a proper analysis to ensue.

LA-ICP-MS analyses should be particularly cautious about surface contaminants, and should consider whether the surface should be cleaned. If the contaminants are to be analyzed (say, soil deposits on a buried weapon), this could either be done first by direct laser ablation, or performed separately if the material can be carefully removed. What is critical is that the scientist does not accidentally combine both substances into the same analysis; that is, the contaminant is ablated and analyzed at the same time as the underlying object, because then it may be more complicated separating the two results. If the only necessary aim is to reach the material below the contaminant, then analysts can either clean the sample, or burn through the surface contaminants and disregard the "contaminated" part of the analysis.

There is contamination that the police and analysts cannot prevent, however, which must be addressed when the evidence is brought in for analysis. Before the evidence even reaches the crime scene, it undergoes interference from outside factors; it is held and covered with dirt and oils; it may be soaked or baked dry depending on temperatures and weather conditions; it could become mixed in with other materials. Depending on whether the evidence was recently purchased for its purpose in the crime or an item of opportunity spontaneously picked up, it may have contaminants reflecting its storage and usage conditions before the crime. Soil analysis can be extremely compromised by the presence of garbage or liquids introduced by bypassers, or by the rain and decomposition of leaves and branches. Wood, whether in a plank or in shavings, also tends to absorb outside materials, and may soak up hand oils or liquids. If the evidence itself has been contaminated in such a manner, it may be difficult to match the object to the source, since the source lacks the unique markings of the evidence. Burned evidence may severely limit the amount of IRMS analysis that can be done, though it may not affect heavier trace elements. Animals can also interfere with the evidence, and may introduce foreign traces that were not at

the original scene, further confusing the chemical fingerprint. All these factors have to be considered when examining the elemental composition of the evidence.

If the contaminant can be identified and separated out, then perhaps researchers can separate the fingerprints of the evidence and the contaminant, obtaining the "evidence-only" print. They may even learn something useful from the fingerprint of the contaminant itself, such as where the evidence may have been prior to being collected. Also, if the entire sample is large enough, the interference of small levels of contaminants may be irrelevant. However, the smaller the amount of trace evidence, the more detrimental the contamination is. When only a sliver or fragment is available for analysis, the contaminants may increasingly have a larger effect on the object's own print. One also cannot overlook the possibility of purposeful contamination in an attempt to mask the identity of the object being used. LA-ICP-MS, and its analysis of trace elements, may be less vulnerable to these effects, but its precision is still somewhat wanting, and it may be unable to identify which elements are from the evidence and which come from contamination.[8] Also, when the evidence must be preserved for trial or in case of a challenge by the opposing attorney, repeated analysis or swamping of the contaminants may not be feasible. So far, analyses with the actual components, the sterile objects, have been the focus of forensic analysis. The potential impact of contaminants on these precision instruments should also be considered in future studies. Care should also be given that evidence undergoes the same treatment before being analyzed to control for variations.[7] Source references should be as decomposed as the evidence, or as wet as the evidence, to minimize sampling error. If procedures can be drawn up addressing these potential snags, there is a better chance of accurate, precise analyses and a lower chance that the evidence is challenged and dismissed in an actual trial.

4.1 The Admissibility of Forensic Evidence

Even though chemical fingerprinting currently shows much promise for the forensic community, merely performing analyses is not enough. The results of these analyses must be brought into the courtroom at trial, and presented before the jury in order to make them better informed for rendering a verdict. The first challenge to the application of chemical fingerprinting is literally getting in the door. Depending on the setting, the rules for introducing evidence are slightly different, whether in a state or federal court. In order for chemical fingerprinting to be of any use to forensic analysts, it must meet the qualifications of competent evidence and be permitted in by the presiding judge.[23] To that end, it is important to briefly explain the two leading legal standards for the admissibility of scientific evidence.

The first standard of admissibility was developed in 1923 by the criminal case of *Frye v. United States*. James Alphonzo Frye was convicted of second-degree murder and appealed his case to the Washington, D.C. District Court of Appeals, claiming that the trial court improperly excluded the results of a systolic blood pressure deception test.[24] A form of lie detector test, the blood pressure test operated on the scientific principle that lying required a conscious effort to deceive and therefore would notably raise the speaker's blood pressure significantly during the course of interrogation. If the speaker's blood pressure remained unchanged, then he was not exerting an effort to lie and therefore was telling the truth. Although such theories were later largely dismissed as scientifically unreliable, during the trial the judge excluded the evidence with the following now-famous rationale:

> "Just when a scientific principle or discovery crosses the line between the experimental and demonstrable stages is difficult to define. Somewhere in this twilight zone the evidential force of the principle must be recognized, and while courts will go a long way

> in admitting expert testimony deduced from a well-recognized scientific principle or discovery, the thing from which the deduction is made must be sufficiently established to have gained general acceptance in the particular field in which it belongs."[24]

The evidence was excluded according to what would eventually be called the "general acceptance rule," or the *Frye* Standard. Put simply, no technique could be introduced as scientific testimony unless it was accepted as the established and normal analytical technique of that particular field. The benefits of this evidentiary rule are that it managed to help exclude many pseudoscientific theories and tests from the courts, and established a clear line as to what was or was not a valid scientific analysis. The downside, however, was that it excluded any novel or specific analyses that, although valid, were not generally accepted in that field. This issue came to light in the 1993 case of *Daubert v. Merrill Dow Pharmaceuticals*.

In *Daubert*, the plaintiffs brought a lawsuit against Merrill Dow Pharmaceuticals, alleging that one of the company's prescription drugs, Bendectin, had caused serious birth defects in their children. As proof of this allegation, they brought forward eight other credentialed scientists who reported that Bendectin has been shown to cause birth defects in "animal studies, chemical structure analyses, and the unpublished “reanalysis” of previously published human statistical studies."[25] However, not only were some of these studies unpublished, they were not the generally accepted epidemiological studies that the defense's expert analysts had run. Even though the eight plaintiff experts had valid findings, they were not capable of challenging the mainstream conclusions reached by the generally accepted technique, and therefore their testimony was unable to even be considered. On appeal, the case eventually reached the US Supreme Court, which overturned the decisions of the trial court. The explanation that they provided would eventually replace the Frye Standard, and became known as the *Daubert* Rule.

The *Daubert* Rule laid down four distinct qualifiers that a judge must evaluate in deciding whether or not to admit scientific evidence.[25] First, the judge has to consider whether the theory or technique in question has or can be tested. If the technique has not yet been evaluated or applied by the scientific community, then it is unlikely to be admitted to the court. The second qualifier is whether or not the theory has been subjected to peer review and publication. When a scientific finding is published, other scientists can evaluate and possibly challenge the findings; therefore, techniques that have been published and subjected to peer review are more likely to be accurate and may even have wider support in the scientific community. The third consideration is regarding the technique's rate of error, which is expected to be presented in the courts. Techniques that have high rates of error will likely not be admitted. Finally, *Frye's* criteria of "general acceptance" is incorporated as a fourth qualifier. Based on the total consideration of all four of these aspects, not necessarily the presence of all four as prerequisites, the judge will make a decision whether or not the evidence will be admitted.[25] The belief was that the judges would play the role of "gatekeeper" in the courts, throwing out unreliable studies while letting in valid but novel scientific techniques. The *Daubert* Rule became the standard for Federal Courts, as it was meant to adhere to the newly-published Federal Rules of Evidence. However, State Courts are not required to adopt every practice of the Supreme Court, and as a consequence some states use *Daubert* while others still rely on *Frye*. Some states have crafted their own rules, combining different aspects of *Daubert* and *Frye*.[26]

Chemical fingerprinting will have to be capable of meeting the requirements of both *Daubert* and *Frye* if it is to become a mainstream forensic technique for analyzing trace evidence, considering most cases will be at the state level. The only factor present from *Frye* is the "general acceptance" standard, which requires the technique to be the common method of

that particular field.[24] Although IRMS and LA-ICP-MS are being studied more closely in recent years, there are still concerns that the techniques have not been analyzed closely enough to meet general acceptance as forensics instruments, particularly where concerns of quality assurance lie.[4] The techniques have, however, received significant acceptance in corollary fields, such as geology and biology, so perhaps this will lend credence to their techniques. Issues of error rates are less of a concern, as the majority of analyses were able to confidently trace the origin or common source of a given sample. That being said, the precision of the analyses have still not been fully investigated for all samples, and there are still questions about what a chemical "match" suggests. The technique has also been tested and evaluated outside of litigation, and the techniques have in fact been published, making it of satisfactory quality according to the remaining *Daubert* conditions.

The greatest hurdles to admitting IRMS and LA-ICP-MS evidence, therefore, seem to be full general acceptance in the field of forensic science and a better understanding of the error associated with the tests. *Frye*-based exclusions will likely arise if these techniques are not considered to be prominent forensic analytical techniques. The most damaging claims against the methods are from the analysts themselves, who recommend that these techniques be used in tandem with other existing techniques.[4,15,17] If these techniques are considered supplementary, they may be excluded in favor of a more traditional analysis; the analysis of plastic bags showed that birefringence analysis was actually just as good as IRMS analysis.[15] *Daubert*-based exclusions are the consequence of the judge not concluding that the evidence is sound or helpful enough to be properly used. This is less likely, given the fact that both IRMS and ICP-MS have successfully cleared at least two of the *Daubert* requirements. However, the judge is still considered the gatekeeper, and one particular survey in 2001 found that almost half of the

surveyed judges felt unprepared to analyze scientific techniques and 96% were unfamiliar with the concepts of scientific error rates. There is also evidence that some judges consider the *Daubert* criteria to be an itemized requirement list, and have excluded evidence that cannot adequately meet all four requirements.[26] If the judge does not understand the theory well, there is the possibility that the judge will exclude it in favor of more tried-and-true evidence, especially if the analysis is only supplemental to other techniques. The responsibility of the judge to keep the trial direct and prevent excessive evidence may override the decision to bring in this evidence. As a consequence, efforts should be made by the scientific community to complete analysis of possible error and contamination, and establish databases in order to make the technique as mainstream as possible. If crime labs can begin to use the technique as supplementary now, then data can be compiled to show the general success or usefulness of the technique in actual criminal cases, and better lay the groundwork to its introduction as an analytical tool in and of itself.

4.2 Distribution and Operation of Equipment

With respect to the actual use of IRMS and LA-ICP-MS instruments, it is also necessary to consider the logistics of state and federal labs obtaining and operating the instruments themselves. The most obvious of these constraints are money and space, as well as the additional procedures, standards, and personnel needed to operate the instruments. The truth of the matter is that these limitations make it more likely that the equipment will need to be operated by a select group of analysts, and is unlikely to be a mainstay in most local laboratories.

Both IRMS and LA-ICP-MS are highly refined and elaborate instruments that require a great deal of understanding to operate well. LA-ICP-MS in particular must be monitored

carefully in order to control for possible error and deviation along any part of the analysis, whether during ablation, sampling, or detection.[8] IRMS, on the other hand, requires specific sample preparation protocols and a precise calibration sequence, the specifics of which are still being developed.[7] In both cases, a highly qualified analyst will likely need to be the one operating the instrument to ensure that all the parameters are within proper ranges, and if there is any deviation, troubleshoot the device on the spot. There is also the issue in both analyses of possible contamination of the samples and a need for precision and care. When presenting the evidence in the courtroom, specialized analysts will likely be needed in order to adequately explain the procedure and its results, especially when the judge is evaluating evidence according to the *Daubert* standard and is looking for error and accuracy assessments. All these considerations point to the need for a professional analyst in the lab in order to properly run the equipment. One cost-analysis of IRMS instruments evaluated for 2009 suggests that having a Ph.D. analyst on hand to perform the analyses would cost upwards of $100,000.[27] This alone is a critical consideration for state and local labs, which may not already have a qualified analyst to operate the equipment or the budget to hire another.

The instruments themselves are also not simple to set up or take care of, either. The majority of the instruments are full-size stationary laboratory instruments, desk-height at minimum and capable of requiring large amounts of floor space. LA-ICP-MS instruments require both the laser-ablation device as well as the ICP-MS analyzer, which means that both instruments will have to be properly stored and set up. Although IRMS is a controlled instrument in and of itself, the more precise GC-IRMS requires the purchase and storage of two separate devices. Because the instruments are measuring such precise quantities, it is advised that they be kept in a climate-controlled room with minimal heat fluctuations and low humidity.[7] This is

because temperature fluctuations can affect the isotopic composition of the samples inside the instruments, and humidity can lead to either chemical interaction with the sample itself or, in the case of IRMS, interference with the instrument readings. Already, this necessitates additional expenses to account for the storage of the units and climate control. There are also concerns for state labs that generally have extreme climate conditions, such as the Southwest US for heat and humidity issues near coastal or swampland regions.

Finally, there is the cost of the actual machines themselves. It was difficult to obtain prices for the instruments themselves, as prices are discussed primarily with purchasing institutions. However, the cost-analysis evaluation of IRMS estimates the flat price of the instrument itself to be approximately $300,000.[27] An ICP-MS instrument purchased by the University of Notre Dame for research also cost about $390,000, although this unit was purchased twenty years ago.[28] The IRMS unit was also estimated to have an annual operating cost of about $24,000, and a service contract would be an additional $30,000. All told, compared to a similar portable instrument that the reporting institution is developing, IRMS instruments cost $75,000 more on average, not counting the budget of the operator.[27] This also precludes the addition of a GC instrument for the most precise analyses. The University of Michigan also has an LA-ICP-MS instrument, which attempts to cover its costs of operation by charging a minimum fee of $600 for commercial analyses and an additional $300 per hour.[29] Analyses for regular ICP-MS from Notre Dame were priced per-sample, and depending on the sample being analyzed, ranged from $50 to $120. One year's analyses brought in approximately $44,000 income.[28] Though income was not listed for the University of Michigan, their prices are based on the costs of operating the instruments. Overall, it can be gathered that the instruments are not cheap to purchase or run, and as a consequence, it may be unrealistic for smaller forensic

laboratories to obtain and operate them, particularly depending on how many trace evidence samples they would be looking at. Wisconsin's Department of Justice was only able to budget $235,000 and $367,000 for DNA analyses alone in 2008 and 2009, and still was lacking the necessary funds for operation.[30] The US Department of Justice also reports that the estimated annual operating budget for publicly-funded labs is approximately $680 million at the federal level but only $314 million at the county level and $219 million at the municipal level.[31] By considering how Wisconsin is still unable to operate its forensics labs and falls above the estimated budgets of county and municipal levels, it is easy to see how the costs of a chemical fingerprinting system may be a massive hurdle for smaller labs.

That being said, it must be considered that there would be a great call for analysis of trace evidence in forensics labs, since the evidence could be found at virtually any and every crime scene. State or federal institutions may be able to effectively set up a system of analysis whereby smaller crime labs can send their samples in for analysis. They may be able to disperse some of the costs on a per-hour or per-sample basis to the smaller institutions while retaining responsibility for maintenance and purchasing the equipment, as the above universities have done. A similar concept is currently in place for DNA fingerprinting, which has a federally-backed network in place for analyzing DNA evidence. Also, research is currently underway to develop smaller, cheaper, and more portable elemental and isotopic analysis units, research that could possibly increase the feasibility of smaller laboratories affording the technology. Again, though, forensic labs must have standards available for comparison, materials for daily operation of the equipment, a qualified analyst to operate the machine, and the means to control the environment to ensure the best operation of the equipment. These costs will increase if analysts require or would like more complex devices, such as a GC instrument to couple to IRMS.

Lacking the means to meet these costs, it will be impossible to perform elemental fingerprinting analysis on any samples effectively in smaller local or even state crime labs.

4.3 Timeliness of Analysis

Since there is concern over whether or not chemical fingerprinting can be performed in virtually any laboratory setting, it is crucial to examine another "cost" of proper analysis: time. Even if chemical fingerprinting is done by select or concentrated labs and institutions, with all nearby jurisdictions sending in evidence, this does not consider the speed at which the analyses will be performed. If the analyses cannot be performed rapidly enough, and the results not returned quickly, then there is a serious risk of system backlog, which could prove disastrous to proper analysis. It is wise to make a direct comparison to another form of fingerprint evidence, the DNA fingerprint, to better understand the significance of timely analysis of materials.

When it became known that DNA fingerprinting could be used to positively identify suspects, the amount of DNA samples submitted to laboratories skyrocketed. DNA began to be tested to provide critical evidence in murder and rape cases, as well as in property crimes. Laboratories were unable to increase their processing capacity quickly enough to respond to the increased demand, and cases began to be backlogged. From 2005 to 2009, the number of DNA samples to be processed tripled from about 100,000 cases to 300,000 cases; the backlog also increased each year, from about 40,000 cases to 110,000 cases.[32] This is also not counting untested evidence, or evidence from cases that has not been submitted for analysis yet. In order to assist with the backlog, the US federal government has offered almost $400 million in grants from 2004 to 2010, about $50-$60 million annually. Even with this assistance, crime labs have still been unable to reduce the backlog. Instead, the National Institute of Justice finds that case

backlogs are primarily an issue of supply and demand; the case backlog is proportional to the total amount of samples submitted, the capacity of operating facilities, and the presence of qualified DNA analysts to perform the tests. As for the current backlog facilities are facing, a 2007 survey of crime labs found that 90% of the labs would not have sufficient funding to operate without federal grants, which cover approximately a quarter of their overall costs and 85% of their equipment budget.[32]

Applying these same concerns to chemical fingerprinting, there already seem to be large hurdles in place for forensic institutions. The fact that instrumental costs are largely covered by grants confirms what was discussed in the previous section, that the costs of the instruments and of operation are large hurdles. However, DNA backlogs were largely the consequence of factors such as an increased awareness of the potential for DNA evidence, the high number of property crimes requiring DNA evidence to be processed, and scientific advancements that reduced the sensitivity of the equipment. Post-conviction and cold-case analysis also contributed to the new samples to be analyzed.[32] Trace evidence faces the same exact problem if its worth as conclusive evidence can be realized. Property crimes will probably rely heavily on trace evidence analysis, even more than DNA analysis, simply because of the amount of substances that can provide identification and draw connections to the suspect. The scientific advancements and sensitivity of the technology have already made it the new focus of forensic analysts, and once its worth is demonstrated on a regular basis in the courts, its popularity may develop among law enforcement and criminal justice systems as well, leading to more trace evidence submitted for chemical analysis. Investigators may also look for chemical fingerprints to bring closure to previously unsolved cases, where only minimal amounts of trace evidence were found at the scene, or to vindicate convicted felons in the same manner as the Innocence Project uses DNA analysis to

overturn previously decided cases.[1] These are all concerns about the trace evidence backlog that, despite its similarity to the DNA backlog issue, have not yet been examined.

However, merely developing a backlog of cases is not the end of the troubles. DNA evidence can be backlogged and preserved for long lengths of time, although some degradation may occur as the space of time between collection and analysis lengthens.[32] The same cannot be said of evidence awaiting chemical fingerprinting. As mentioned above, physical processes and state changes, such as melting or freezing, may severely hamper isotopic analysis due to fractionation.[4] High or low temperatures may distort the true nature of the elemental composition even in storage, making it useless to investigators or potentially misleading unaware analysts. There is an even larger issue when dealing with samples that tend to degrade or alter over time, such as biological or organic materials. If these materials degrade between the time of collection and the time of analysis, the chemical fingerprint may not be accurate. This is less of an issue with ICP-MS, since it is looking for trace elements, but the fractionating effects of freezing the evidence (a preferred technique with DNA) make it impractical for IRMS. Since any alterations in the evidence makes it harder to obtain a proper chemical fingerprint, especially for the isotope-sensitive IRMS, it is important to know how long-term storage affects experimental results, in anticipation of a backlog. It is also important to develop storage protocols to ensure that, if there is a backlog, the evidence is not thrown out in court for unreliability by a cautious analytical expert for the opposing counsel.

The amount of federal funding already invested into DNA casts a heavy shadow over developing a system for trace evidence analysis. However, there is some positive news for chemical fingerprinting. One of the major sources of delay for DNA analysis results from the need for scientists to first confirm whether the material submitted is biological in nature, and if it

is, where the DNA is.[32] They may also need to deal with degraded DNA samples or separate out multiple donors. Trace evidence will likely not have to worry about confirming whether or not the evidence is trace material, or what kind of evidence it is; the elemental analysis should prove sufficient, when combined with physical examination. Although contamination and degradation are still a large problem for effective chemical analysis, trace samples will not have to be subject to the same multitude of confirmation tests as is DNA. The federal funding for DNA research also tries to assist in developing long-term efficiency strategies, whether by obtaining high-throughput equipment, setting up information management systems, and training and hiring qualified personnel.[32] In the same manner, before the backlog emerges, institutions can prepare the necessary framework for efficient analysis of the samples. This can also include the development of testing procedures and protocol,[7,8] the establishment of chemical databases for trace substances,[4,11] and the examination of the effects of storage and contamination on the evidence itself.

Furthermore, whereas DNA analysis often take approximately 50 to 60 hours to fully process a sample,[33] IRMS takes only about 20 minutes to analyze a sample,[34] with LA-ICP-MS also returning fast analysis times of minutes per sample.[35] This means that the issues of backlogging may be significantly reduced if forensic samples can be analyzed and processed quickly enough. That being said, there is often only one or two DNA samples from a single scene, while there may also be several trace samples from different sources that need analysis. This also does not consider how many other forms of evidence may be submitted for chemical fingerprinting, particularly controlled substances.[14] It is hard to say how many samples will need to be analyzed per day if chemical fingerprinting suddenly becomes mainstream, but if similar numbers of trace samples are submitted for analysis, it may be possible to fully process and

return results without concern of a backlog – provided the necessary personnel and equipment are already in place.

4.4 Evidentiary Protocol

The main concerns facing the incorporation of chemical fingerprinting into current criminal investigation practices so far have been focused on admissibility of the evidence, the costs associated with the technology, and the time it will take to properly perform an analysis. One further area that is critical to address is the protocol associated with the collection and processing of trace evidence. As mentioned earlier, chemical analysis of trace evidence can be affected by contaminants on or in the sample. Depending on the material in question, different collection and storage protocols may be necessary to ensure accurate analyses in the lab. If the evidence is not properly collected or stored, it may not be valid at the conclusion of the testing.

When investigators process a scene, they first need to search the scene for anything that could be considered evidence. It is often good procedure to start at one space in the outer perimeter and gradually cover all the ground in the scene to ensure that any dropped evidence is found.[2] Trace evidence, though, is an even greater concern, largely because it is extremely small and hard to see in the first place. If investigators are not aware of what they are looking for, they may accidentally overlook some trace particulates, or worse, contaminate them by stepping on them. Depending on the method of collection, there may also be unintended contamination, such as the contamination of fibers and dust with the adhesive on the tape used to lift the evidence. Trace evidence vacuums may effectively pick up the evidence without contaminating it, though care must be exercised that the evidence is not also exposed to isotopic fractionation in the process.[1] They must also avoid the other extreme, of collecting trace evidence that is not related

to the crime scene that instead clogs up the analytical network. In particular, investigators may need to wear protective suits more often so as not to track outside materials into the scene, which may be confused with material already present.[2] It would be problematic if, in the investigation of a robbery, it is discovered that most of the trace fibers and dirt particles were traced back to the officers or victim rather than the suspect, since this would imply a massive waste of time to analysts. In addition to cautioning investigators about where trace evidence may be, and how to find it, the investigators should be warned about the dangers of depositing their own particulates at the scene.

After evidence is found, it must be properly catalogued, photographed, and collected.[2] However, notation of trace evidence may be slightly more complex than notation of other evidence. Depending on the material in question, various sized particles may behave differently at a crime scene, with smaller particulates in dirt and lightweight fiber fragments being more prone to being moved due to wind or even air currents by close motion. If the sample in question is heterogenous, and different particles have varying sizes and compositions, then wind may potentially skew the results of the analysis by moving the evidence around and altering its physical composition. Again, it is important to remember fractionation effects.[4] These effects can occur during any physical process, including extreme temperature changes. If trace evidence undergoes phase changes due to temperature variations, then this too could affect the evidence. Traces of semisolids like wax might melt and reform depending on whether it was in a heated room or near a hot object; in cold weather, other samples may freeze and unfreeze, and even separate if wet. Accelerants may also evaporate and undergo slight fractionation effects. Outdoor crime scenes must be watchful of rain or dew that could alter the sample or carry away smaller particles, or possibly dissolve away some trace materials in a deposited soil sample. It is critical

that investigators make note of any potential environmental conditions that could affect isotopic analysis in particular, including temperature, heat sources, sources of air movement, and how long the evidence may have been there. This information may be useful in determining the error involved in the chemical analysis.

Once the evidence is collected, storage is the new concern. The evidence must be stored in such a way that it is least likely to undergo any chemical changes and is in the best possible condition for isotopic or trace element analysis. Organic materials, fibers, plastics, and accelerants should be assumed to be eligible for IRMS isotopic fingerprinting, and as a result should be stored in an environment that minimizes humidity, biodegradation, and temperature change. Evidence that appears likely to decompose should be analyzed almost immediately to ensure the most accurate and characteristic isotopic ratios, since extended storage and decomposition may chemically affect the organic isotopes. The practice of using paper bags to store evidence, especially wet evidence, may be helpful in preventing mold growth, but likewise exposes the evidence to environmental humidity conditions.[2] It may be helpful to establish a procedure for analyzing the water content of the evidence and ensuring that different samples do not enter the instruments at different moisture levels, since this may impact oxygen-isotope and hydrogen-isotope readings. Transportation is likewise a concern, as evidence that is transported in a particularly cold or hot compartment (say, the back of a police car in the summertime), or is sufficiently mixed or shaken during transportation, may be subject to isotopic fractionation. All evidence that is submitted for LA-ICP-MS analysis should preferably be sealed to ensure no other contaminants enter the container. Care must be taken to ensure that the evidence is not physically altered in any way, since a lack of uniformity may be an important feature in that evidence. Physically mangling a layered chip may impact the elements ablated during sampling.

Also, if there are to be reference samples, such as samples of a broken car windshield that suspect shards are believed to have come from, the investigators must make sure to take sufficient reference samples in order to allow for accurate comparisons.[19]

Finally, during the collection process, investigators should be conscious of potential sources of chemical contamination of the samples. If the response to the crime scene is relatively quick, then there is less of a chance that the evidence has been compromised. When the evidence has been collected days after the presumed incident, such as at a secondary scene or when the crime does not immediately come to the attention of the police, identification of any potential contaminants may assist in interpreting the results of chemical analysis. Proximity to other substances may explain a possible trace contaminant that would otherwise have led to a conclusion of the sample being significantly different, for example, traces of a cleaning fluid leaking into the mud on a shoe hidden in the suspect's house. If the evidence appears to be contaminated by another material, investigators should consider whether the contaminant or the underlying evidence could be more useful in chemical analysis. A sauce or oil smear on a fiber may be even more informative than merely establishing that the fiber came from a shirt the suspect was wearing, as it can identify a secondary element of what the suspect was eating or working with shortly before the crime. However, it could introduce a secondary sample background; the analytical results will be of the fiber plus the contaminant for IRMS and possibly LA-ICP-MS. It may be difficult to separate the two unless the original fiber and the contamination source can also be sampled.

It is necessary for law enforcement agencies and analytical forensic chemists to discuss potential impacts on evidence collection procedures in the event that chemical fingerprinting becomes the next major type of evidence. If trace evidence suddenly becomes as vital to

processing a scene as DNA evidence, procedures must be established in advance to avoid a clumsy adaptation by investigators in the field. If DNA evidence can be dismissed over concerns of potential contamination, then elemental or isotopic evidence is even more sensitive. Whereas DNA can be separated out and analyzed when identified on a surface, chemical fingerprinting cannot readily separate out contaminants from evidence, and is equally vulnerable to elemental fractionation during long-term storage and transportation. As long as these concerns are met, trace evidence should continue to be collected and analyzed with regularity and precision.

5.1 Explaining the Science

Once the trace or other evidence has been properly collected and analyzed, it must be presented in the actual courtroom. Part of the responsibility of the forensic analyst is to explain to the judge and to the jury the principles behind the science, how the analysis was conducted, and what the results are. Scientists are unable to simply conclude the likelihood of a match and send the results to the court, but must instead lay a proper foundation for the evidence so that the jury can properly weigh the evidence.[23] Of course, most jury members are not familiar with scientific procedures, and neither are judges.[26] If the analyst cannot explain the process clearly enough in lay terms, the resulting confusion may make it hard for jurors to understand or properly consider the evidence, and may even cause judges to throw it out entirely.

In order for scientific results to be accepted as evidence, they must first be admitted by the presiding judge in accordance with that court's rules of evidence.[23] This usually relies on some variation of the *Frye* or *Daubert* standards, which have already been discussed. For courts still using *Frye* to validate evidence, the analyst must explain to the judge how the evidence is generally accepted in the field of forensic science, particularly if opposing counsel challenges the technique as being too novel.[24] The analyst should also be able to show how the technique has long been used in other fields beneficially, and is not a new technique as much as it is a technique being applied from other fields into forensics as a consequence of its high sensitivity. Courts relying more on the *Daubert* standard present a more rounded challenge. Though an analyst may not have much difficulty explaining how the method has been previously tested and peer-reviewed, they must also be able to adequately explain what the experimental error is and where it comes from.[25] Recall that only 4% of judges have a strong understanding of scientific rates of error.[26] Because of this, analysts should develop a routine explanation that conveys the

uncertainty in the experiment, perhaps using error bars on result charts and visually showing how exact the results are. The American Society for Mass Spectrometry (ASMS) advises that multimedia approaches be used to help explain the science, and results should be framed in terms of everyday examples to keep the information as direct and understandable as possible.[5] As long as the judge has a clear understanding of error, the chances of the evidence being dismissed under *Daubert* are reduced. Obviously, an uninformed judge may simply give the technology a pass without fully understanding error, but this also makes it easier for opposing counsel to confuse the issue of error. It should also be noted that many of the lower-level courts applying *Daubert* tend to apply all parts of *Daubert* as more of a "checklist" than as factors, so a poor explanation of error rates may lead to dismissal of the evidence.[26]

Once the evidence is admitted into the courtroom, it must still be explained to jurors. Before the results can be introduced, the witness must explain his or her credentials and lay a foundation for the reliability of the evidence.[23] The normal procedure for questioning a witness is to use non-leading questions on direct examination; therefore, the attorney presenting the evidence and the scientist who performed the study must have sufficiently gone over the details of the testimony beforehand. If an objection arises from the opposing counsel, the attorney must know how to bypass the question and continue the presentation without stumbling along or skipping important information. Although expert witnesses may have more leeway in explaining evidence, they must also be cautious of being interrupted for narrating.[23] Since statements will have to be short, succinct, and successive, it would be doubly beneficial for scientific witnesses to respond with direct, simple statements that convey the theory in lay terms. Shorter statements will also be more likely to keep the attention of the audience, and make it less likely that opposing counsel can confuse the issue on cross-examination.

In laying a foundation for IRMS and LA-ICP-MS, it will be important for the witness, preferably someone with a reasonable background in operating mass spectrometers or analytical equipment, to explain what mass spectrometry is. It has been recommended that scientists explain MS as a method for "weighing molecules," and the principle of mass analysis is the mechanism for "sorting and counting" molecules of a given mass.[5] These explanations are short and to the point, and if opposing counsel asks for further explanation, then the scientific principle can be expounded on and clarified. The main foundation will have already been laid, though. One of the main sources of confusion, however, comes about when discussing the process of ionization and how molecules must be ionized before being analyzed. It is suggested that scientists emphasize the use of magnets and their ability to attract and repel different charges, and frame ionization as the ability to make the sample particles able to move in the machine.[5] The fact that IRMS often uses specially-aligned Faraday cups should make it easier for scientists to explain IRMS detection, as long as they explain how isotopes have different masses. The most challenging explanation for LA-ICP-MS will be explaining the concept of plasma. Following the thought patterns of the ASMS, it might be wise to describe the plasma as what it basically is; a very hot gas capable of imparting an electric charge to entering molecules. The concept of laser ablation, on the other hand, should be well-enough understood; the laser breaks off molecules of the sample for analysis.

After the foundation for the evidence is laid, the analyst must then explain the results. This is where the explanation could get complicated, particularly when the results are questioned under cross-examination. Unlike DNA fingerprints, which provide a very high likelihood of the given evidence coming from a specific person, such as the victim or suspect, chemical fingerprints cannot always establish the absolute identity of a single object. Although the

investigator or another witness may be responsible for drawing the link between this object and the suspect, the testifying scientist must still work to facilitate this matter. If the analysis is trying to establish an elemental or isotopic match between the evidence and an object that the suspect has, the analyst must explain that this is a high likelihood of chemical similarity, not necessarily chemical identity. While doing this, it may help if they explain that the suspect's object and the evidence appear to share a common origin; they are at least related, but certain characteristics suggest that they are identical. For objects that are somewhat unique, such as soil or accelerants, and particularly drugs, scientists may be more capable of making a positive conclusion due to the presence of signature trace elements of isotopic ratios. They should establish how these differences came about, whether due to isotopes (characteristics of their growth and beginnings) or trace elements (additives found in that specific object that only that object would have). However, when identifying the source of a fragment of glass or plastic, and sometimes soil, the analyst must be careful in drawing conclusions. The scientist must make it clear that it is likely that the evidence came from the same batch or sample size as the suspect's object, and not conclude that it most assuredly IS from that object.

The reason for this caution is because there are some items that chemical fingerprinting may not be able to tell apart. One IRMS analysis of soils showed that two particular sites could be differentiated, but the two sites had completely different environments; one was natural and developed on gravelly sand, and the other was heavy in leaves and other nearby materials.[17] Two soils coming from similar regions may have less variation and be hard to tell apart. The analysis of plastic bags also warns of the inability to differentiate two samples that happen to have the same chemical fingerprint.[15] When dealing with generic or manufactured materials, chemical fingerprinting may not be able to determine absolute identity. A knowledgeable opposing

counsel would catch this mistake, and suggest that the analysis cannot establish chemical identity at all, an intimation that could severely bias an unknowing jury. It may also make it appear that the expert witness was caught in a lie or is not really knowledgeable. Therefore, it is important for the analyst to explain, clearly and on direct examination, how similar the items are. If the item in question may be part of a batch of mass-produced objects like a plastic bag, then the scientist should conclude this and state how likely it is that other people may have access to a similar batch. The witness presenting the original evidence, such as the investigator, would be responsible for linking the evidence to the suspect. That individual would state, for example, the plastic bag had to come from Brand X, which the suspect was found with, and no other suspects with motive or opportunity have used Brand X. On cross examination, the analyst must be careful not to let the opposing counsel lead him or her into concluding identity. If counsel asks whether the scientist can prove identity, they should try to explain why all items in a batch are chemically identical, and how this is merely proof of a matching brand or type. They should also be ready to explain, if questioned, how they controlled for natural variation and that their analyses are not biased due to the reference samples used.

If databases for particular types of evidence are developed, the testifying analyst may even go as far as to introduce other possible sources, and one by one cross them off if they can be excluded. This would be a visual way to minimize the criticism from the opposing counsel, provided most of the other alternatives can be eliminated. This can be especially helpful in soil analyses or isotopic origin scenarios, where one has to establish where a sample originated based on its isotopic fingerprint. However, if the analyst's testimony is twisted in any way, it may be used to discredit the evidence. This makes it even more important to have a plain, simple way of explaining the likelihood of the match and its significance to the jury.

5.2 The Weight of a Fingerprint

When evidence is finally presented in the courts, jurors will have to evaluate the evidence and come to a verdict of guilt or innocence. Most criminal courts carry the burden of proof of guilt beyond a reasonable doubt, which falls short of the absolute certainty of guilt but still rests beyond the likelihood of significant error.[23] In order to be of any use to the criminal justice system, the evidence must be sufficient enough to assist in producing a conclusion of guilt. Chemical fingerprinting has the potential to, like DNA fingerprinting, enact a large sway over the jury and strongly contribute to a verdict. However, the weight of the chemical fingerprint depends largely on exactly what the analytical results are proving.

Obviously, it is impossible in every situation to determine a positive identity. There are some substances that will have the same chemical fingerprint even though they are entirely different samples. It is critical for forensic institutions to develop a database for these substances, and determine when the analysis is likely to have shown identity or similarity. DNA evidence itself does not claim to establish a perfect match, but rather states that there is a match and then gives the probability that this match may have arisen from chance.[36] As a consequence, the jurors are left to weigh the evidence and determine whether the DNA likely originated from the defendant – though, in most cases, the probability of random match is small enough to allow jurors to conclude a positive match. However, the possibility of two matching DNA samples is going to be far smaller than the possibility of two matching manufactured samples. When the same manufacturer produces multiple products from the same resources, under the same conditions, the chance of two of the products having the same chemical makeup is going to be larger since there is no difference in the processes that would produce random fractionation. When different processes and resources are considered, fractionation will produce the telltale

"unique" attributes of that product.[4] This, of course, means that it is easier to prove that two sources do not match and exclude a suspect or source. Where a match is made, analysts must then determine the probability that this match is the result of chance.

There are several catches to this type of determination. First, the chance standard in DNA analysis is the chance that any other person chosen at random would have an identical DNA fingerprint.[36] However, the same cannot necessarily be said of chemical fingerprints because, unlike DNA, isotopic and elemental ratios are not entirely random. If we again consider plastics, then the chance of any randomly chosen bag having the same chemical fingerprint would be equivalent to the proportion of people who use that brand bag in the population of interest. This means that chemical fingerprints will rarely get the astronomically high figures of 1/20,000,000, a factor that may lead to jury misinterpretation of the evidence. However, if in such a case, the analyst concludes that the sample definitely came from a Brand X plastic bag, produced in a particular batch, then depending on the manufacturer's processes and between-batch isotopic variations, the analyst may be able to give the possibility that a randomly-chosen Brand X bag would have the same chemical fingerprint. It may be possible to differentiate between different batches of the same product, providing an extra level of depth.[15] If not, then at least the only uncertainty in the analysis is due to lab error, and a specific type of object was identified.

Furthermore, some heterogeneous materials, such as glass fragments and soil, may show significant variation even within the same pane of glass, bottle, or patch of dirt.[17,19] To determine the chance that any randomly taken sample would produce a statistical match would necessitate an understanding of the total variation across specific sample sizes. It may also be far too confusing to explain clearly and directly to jurors, primarily because two samples even within the same source may be found to be chemically "different." For these samples, the random-match

comparison may be a major hurdle to the analyst. In the worst-case scenario, the evidence would be good only to show that there cannot be an exclusion of the suspect source, and perhaps also exclude sources that the sample could definitely not have come from. If the vast majority of glass or soil profiles cannot include the sample in question, then the chance of random matching will be reduced, and the evidence will carry more weight in court. Physical characteristics should also be used in tandem with these analyses in order to give the evidence the greatest level of individuality.[15] Furthermore, if there is a trace element found using LA-ICP-MS, then accounting for the presence of this substance could prove highly useful in establishing the uniqueness of the given sample. If a particular metal or a complex molecule has drifted into the soil, and can be traced back to a particular type of contaminant that the suspect had interacted with, then the evidence will have an additional degree of connection to the suspect, although this one is more circumstantial than statistical.

If there are unique isotopic ratios in the substance, or if certain trace contaminants are present, then the case may be made that the chemical fingerprint may be as unique as a DNA fingerprint. However, more often than not, it would be better to introduce the evidence as definitively coming from a particular type of object, especially if this object can then be tied to the suspect. Whereas a unique positive identity will carry more weight than a class-characteristic identity, the uncertainty attached to the unique identity may make the weight of the evidence plummet in the eyes of jurors. Due to the burden of proof in criminal cases, reasonable doubt in the certainty of evidence may result in the evidence being thrown out entirely from consideration by the jurors. In such cases, a more certain link is likely to survive and carry influence with the jurors, even if it is a circumstantial one. As with other forms of evidence, the individual probabilities of circumstantial evidence multiply to produce an overall probability of the same

exact sequence of events occurring. There are often many different types of trace evidence left at a given scene, including soil, fibers, wood and glass fragments, metal shavings, and more. By combining chemical analyses for several different types of trace evidence left at a single scene, it may be possible to prove the identity of the suspect just as well as if they had left an actual fingerprint. Again, however, when it comes to manufactured objects, though chemical fingerprints may help to differentiate unrelated samples, it is harder to differentiate samples from the same source, and the commonality of the brand in question may play a significant part in the weight of that particular analysis.

5.3 Potential Influential Effects on a Jury

It is clear that, depending on the conclusions reached by the analysis, a chemical fingerprint may carry significant weight in a trial or only contribute partially to the burden of proof. However, the weight assigned to evidence depends wholly on the jury's evaluation of it. Jurors alone are responsible for evaluating the evidence and determining how much weight it is to carry.[23] As a result, the jury's perceptions of the evidence and their expectations about scientific evidence in general may significantly affect how the evidence is used in coming to a verdict. It is important for analysts to know about jury biases and how a juror will reach a verdict so that they may better adapt and explain their results in a way that would most benefit the courts.

One of the more well-known and often-blamed potential sources of jury bias is what is called the "CSI Effect." It is widely believed that, as a direct consequence of criminal-investigation shows and movies, the public, and consequently jurors, are misinformed about the reality of forensic capabilities. As a result, they are more prone to acquittal if they do not believe

that sufficient forensic evidence has been used, or if the evidence is not considered "precise" enough to conclude with scientific certainty.[37] Another suggested juror bias is the somewhat-related "technical effect," which, like the CSI Effect, favors an acquittal by jurors because they expected more from forensic evidence. However, it instead explains that this effect is not the direct consequence of CSI-media, but rather a misunderstanding of modern technology itself. Jurors have greater access to scientific information and hear about the precision and capabilities of the technology, and consequently see lower certainty rates or partial results as lacking in conclusiveness.[38] In both situations, jurors form predisposed notions about what scientific evidence they expect to see, and then measure the presented evidence against their expectations. The fear is that jurors, expecting to see more than what they did, will dismiss the evidence entirely rather than weighing it fully.

There have been several studies on the so-called CSI Effect, in an effort to determine whether or not it does exist. The results, however, have been far from clear. Generally speaking, there is a noticeable effect present in the courts; namely, that jurors who view CSI-related media tend to have higher expectations of forensic evidence. Jurors generally expect more types of forensic evidence to be presented, are more demanding when it comes to certainty rates, and are usually dissatisfied with the evidence that is presented in court.[38] In rape cases in particular, DNA analysis seemed to be a prerequisite for finding guilt for at least a quarter of those surveyed. However, it is unclear whether or not viewing of CSI media tends to produce this effect. Mere viewership of shows has alternatively been correlated and not been correlated with dispositions towards scientific evidence, whereas some studies assert that other factors, such as a need to analyze the information presented, are the true source of the biases.[37] This may also have its grounding in the public concept that science is wholly objective and can come to a precise

solution in all circumstances. On the contrary, science generally prefers to work with hypotheses and probabilities rather than complete yes-or-no answers, which is what courts are designed to work towards. Furthermore, science prefers an experiment to end in a false negative rather than a false positive, and while this works in favor of the accused innocent, it results in skeptical analyses from other experts and enough reasonable doubt to lead to dismissal of the evidence as insufficiently certain for legal standards.[26] Furthermore, it appears that, even though these studies show that there is a bias in the jurors, there seems to be no difference in the conviction rates of either the CSI-heavy or CSI-light juror pools.[37]

The way that the evidence is understood may also lead to variations in whether or not chemical fingerprinting is accepted or dismissed outright by jurors. As mentioned above, it is slightly harder to determine probability-of-match rates because, unlike DNA, the chemical ratios of a given object are not always unique. If DNA is considered as a point of analogy, though, we can consider how error and likelihood of a positive match may be treated by jurors. It has been found in some instances that DNA evidence is actually undervalued by jurors. No one particular cause has been held responsible, although possible theories include the chance that jurors automatically dismiss the evidence because they cannot properly incorporate the probability of a random DNA match with the chance of error.[39] There may be some confusion in how jurors compare the laboratory rate of error in DNA analyses with the probability of a random match occurring, which prompts them to either dismiss the evidence as too confusing or to combine them improperly and acquire an improper likelihood that the test results are false.[39] In particular, DNA evidence was found to be far less influential on juries when there was a clear sense of how many other samples could theoretically match the evidence sample. High probabilities of a

positive, unique match also fell off after a certain point, suggesting that jurors recognized that the laboratory error eclipsed the match probability.[40]

It has also been shown in other analyses that, when expert scientific testimony is presented by both sides of a case, the defense expert is often more influential on the jury than the prosecution expert.[41] Jurors are also prone to developing a story to explain their verdict. In doing so, they tend to incorporate clear, favorable evidence and personal knowledge and intuition into their "view" of events, and evidence that does not support their own theories is somewhat disregarded. At the same time, juries are more likely to favor the side that presented its evidence in a manner amenable to story construction.[42] Considering all this, it is clear that jurors will carry their own biases into the case, and expert witnesses presenting chemical fingerprints must be at least conscious of these effects. If they present the information as too technical or too separate from the rest of the case evidence, they run the risk of losing the jurors. They may also be challenged by an expert brought forward by the opposing counsel, who could convince the jury that there is significant doubt about the certainty of the original analysis.

Because of a slight bias towards skepticism, there is less of a chance that jurors will choose to blankly believe an expert scientific witness, even if the technology is purported to be a "fingerprint." Although there is the possibility that a juror, if not properly informed, could conclude that a chemical fingerprint proves guilt, this is not as common as the possibility that a juror could dismiss the evidence entirely. Jurors are more demanding of modern science, and expect any forensic evidence presented to be as direct as possible. They also are not scientifically objective, and may disregard the evidence if they feel that they do not understand it or if it is not sufficiently "trustworthy." While it is not the job of forensic scientists to work towards either acquittal or conviction, efforts must be made to ensure that the evidence presented is accepted

and weighed properly by jurors. Making the process behind the evidence more accessible to lay jurors may improve their ability to comprehend the evidence and incorporate it into their understanding of the case at hand. It is also important to present clear error issues, and to explain what the analysis is suggesting. In particular, expert witnesses must be careful not to provide too many different error rates or match probabilities, but rather make the evidence as precise as possible. This is another reason why it may be beneficial to describe chemical analyses in terms of what brand or characteristics the evidence has rather than the blank chance that it has been positively matched with the suspect. The jury may be more likely to incorporate the knowledge that the evidence *definitely* originated from a brand or region the suspect has access to rather than knowledge that the evidence *probably* came from the suspect. For the chemical fingerprint to be used properly, it must be as accessible and objective as possible when presented in court.

5.4 Downfalls to Improper Analysis or Sampling

The presentation and interpretation of chemical fingerprinting has been examined for potential downfalls and issues. The final consideration remaining to be made is, of course, its actual impact in the outcome of a trial. Depending on how the evidence is analyzed, what results come out, and how the evidence is perceived in court, the chemical fingerprint has the potential to link a particular suspect to the scene just as conclusively as a DNA or regular fingerprint. Because of this potential, it is important to examine possible ways in which an improper analysis will impact a trial, both in presenting truthful evidence that is dismissed and in presenting faulty evidence that is accepted as true. Due to the general intent of the criminal justice system to prefer a guilty suspect's acquittal to the conviction of an innocent, the latter circumstance will be considered first.

It is worth repeating that IRMS and LA-ICP-MS have their shortcomings. In an ideal situation, opposing counsel would bring up these shortcomings and identify where improper conclusions have been drawn. Preferably, the results would be confirmed or rebutted by multiple analysts or other analyses before being forwarded to the courts. However, the criminal justice system does not always allow for such a slow and methodical examination, and not every court has a full understanding of the scientific principles underlying the analyses. Both judges and jurors have the capacity to misunderstand evidence; although jurors tend to expect more from scientific analyses, they do not always acquit on the basis of these expectations alone.[26,37] Therefore, it is not only possible that jurors may misapply the evidence when it is correctly presented, but they have no way of knowing that the evidence has been accurately analyzed. Most courts and even some attorneys have a tendency to accept the scientific evidence as accurate, and will not challenge the admissibility of the evidence but instead insist that the evidence interferes with other facts in question or cannot alone lead to a conviction. Such tactics do not always work, particularly when the evidence is accepted as scientifically objective by the audience.[26,36] It is especially important that analysts in the lab take all necessary precautions to avoid having tainted analyses, on the offchance that the evidence is not properly dismissed but, instead, is improperly brought forward to the jury.

Analysts must take care when concluding the likelihood of similarity or identity. When the object in question is glass or plastic, or any other type of mass-produced object, they should strongly consider finding the actual sample group that the evidence belongs to, such as a brand or particular type of product.[15,19] If they conclude that the evidence definitively came from the suspect, they exclude the chance that the evidence may have come from another source. An attempt to determine the likelihood of a random match to the suspect's property or person should

ideally only occur if such a determination can provide reasonable assurance of individuality. Positive identification should also not be done only on the basis of chemical analyses, and physical matches should also be incorporated into the results. When determining the origin of an organic compound or suspect through isoscapes, the analysts should make sure to test several isotopic ratios and attempt to draw a conclusion based on multiple elements. They should also note any other locations that the evidence may have potentially come from; alternative origins should be dismissed logically from circumstances of the case, and not solely on the basis of a match to one location. In all these circumstances, the analysts must not improperly exclude the possibility of alternative origins or identical samples, since such results, if accepted by the court, may lead to a false conviction.

Furthermore, analysts should take care not to allow any form of contamination to slip into analyses. IRMS and LA-ICP-MS are sensitive enough that they might be able to read any contaminants as part of the sample itself. If scientists are sloppy in transferring materials, or do not have an adequately clean working area, there is a possibility that the results will be altered slightly. This is especially devastating for IRMS, as any organic contaminants can cause variation in the isotope ratios of the sample. Although it is far more likely for the lab to conclude a false negative, there is still the possibility that a false positive can arise when two different samples are "read" as identical due to contamination on one sample. The false positive may lead to a strong bias against an innocent or non-matching suspect, while the false negative may stand as strong scientific proof that the suspect was not the source of the data. In the latter case, this will cause almost assuredly lead to an irreversible acquittal, as further evidence can only suggest innocence or conflicting evidence, while refutation of the scientific evidence to affirm guilt will only cast more doubt on the validity of the science itself. Care should also be exercised when the

evidence collected is contaminated by pre-crime-scene materials. No trace evidence will enter the lab "sterile," so it is important for labs to develop protocol addressing this added material. If the debris on the "actual" evidence is cleaned off, it must be done in a way that the evidence is then dried and left unaffected. "Wet" samples that still have residual moisture, or samples that are not wholly cleaned, may provide a random element of variation that may escape detection or observation, producing false results again. Furthermore, it may be wise to also match a "contaminated" evidence sample with a "contaminated" source sample; for example, a fiber with dirt or liquid should be compared whole with dirty fibers from the soiled rug it is believed to come from. This may help to eliminate any error resulting from an improper cleaning. Both of these results should be explained neutrally to the jury, with whatever caution regarding the presumed accuracy or error of the analysis.

Error rates and chances of random matches should be reported as clearly but also as accurately as possible, and should be reasonably beyond reproach in case an opposing expert challenges the findings. All anomalies should have a prepared explanation or response to prevent the appearance of surprise or fumbling when on the witness stand. If any part of the analysis cannot be clearly explained, or the opposing counsel has the potential to introduce doubt, even a proper analysis will be struck from consideration in the jury's mind. Analysts must both be aware of how the evidence was analyzed and how it was collected and stored at the scene. If there are any questions about the integrity of the evidence, the analyst should be prepared to address them and whether or not the analysis could be significantly flawed as a result. If possible, such issues should be incorporated into potential error rates when presented to the jury, again to keep the number of variables and probabilities they must combine to a minimum. If the presenting analyst is able to account for all parts of the analysis clearly, there is less chance that the opposing

counsel will be able to convince the jury that the analysis was faulty. It will also be beneficial if the presenting analyst can show that they are aware of what the investigators did with the evidence, as it will show a level of continuity between the law enforcement end of the justice system and the scientific end.

The last concern is over the sampling of the evidence. Some collected evidence may not be entirely homogenous, and depending on how it is sampled, different results may be obtained. This is especially crucial in instances where the opposing counsel performs their own analysis and acquires different results. If the evidence in question is from a material that is regularly known to have variability within the object, several reference samples should be used to set up the outer limits that the evidence would be expected to fall between. Analyzing each of these samples may take time, but is necessary to provide a complete analysis to the court. It should also be noted that, if the reference sampling was performed improperly, it may be possible to conclude that the evidence falls outside of the expected range and did not originate from that source, which would offer a false negative to the court. The results should be with the intention of showing that the evidence may have originated from the suspect source, and again avoid concluding that the evidence certainly originated from that source in the absence of specific chemical peculiarities such as trace contaminants. The evidence, where possible, should be sampled in such a manner that minimizes the chance of variation, and this should be included in the presentation of the evidence. For LA-ICP-MS, the path of the laser should also be noted, as it may provide a visual aid assisting with court understanding. In the absence of documented sampling procedure, the opposing counsel may obtain an expert witness whose analysis returns different results, which would completely destroy any credibility of the presenting analyst and raise reasonable doubt. Likewise, analysts should be careful of letting faulty results get by, such

as when the source is sampled differently from the evidence and different results are obtained, leading to a conclusion that the evidence did not originate from the suspect source. It is unlikely that such data will be challenged by opposing counsel as a matter of course, and the requesting counsel may simply abandon the case.

While chemical fingerprinting could be extremely beneficial to the interests of justice, it is a powerful tool that has the potential to be horribly misused. Any errors in analysis could make the difference between a return of "no match" and "positive match," which in turn may, like DNA, make the difference between a verdict of "guilty" and "not guilty." It is far more likely that a wrong analysis will shift the results towards a false negative, which will likely lead to either acquittal or dismissal of the evidence. However, this may lead to several botched analysts that get guilty suspects let free. There is also the possibility that improper analysis will provide a false positive, but it is far more likely for analysts to wrongfully conclude a false positive based on data that may be interpreted as such. In light of the certainty attributed so often to scientific analyses, and the fact that even growing expectations of forensic science have been unable to induce acquittals,[37] analysts must take care not to provide a jury with incorrect results. Otherwise, chemical fingerprinting will do even greater harm to the justice system than it will help.

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