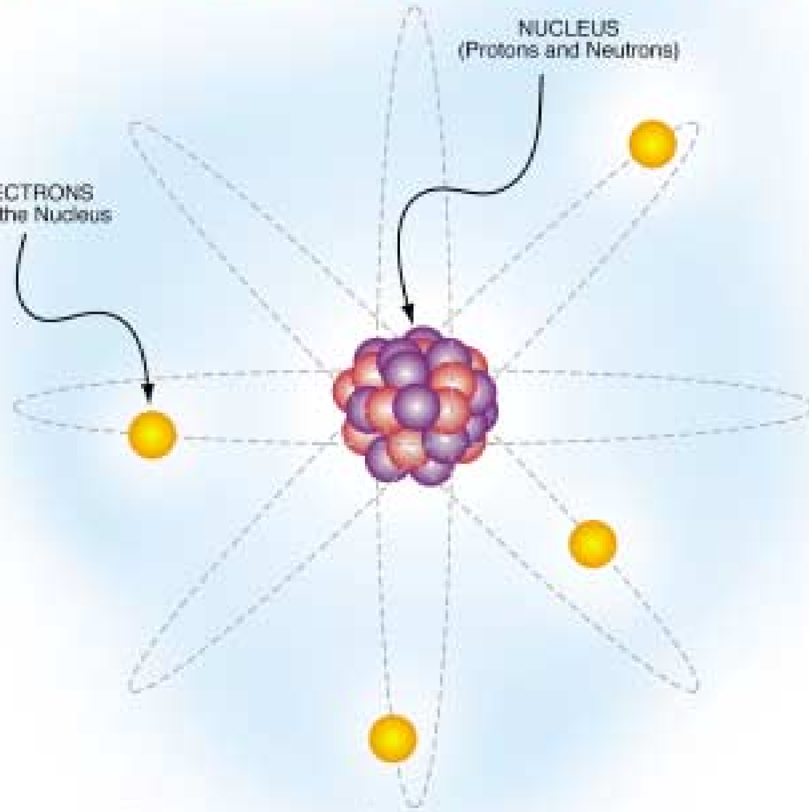
PUTTING THE ARSONIST AT THE SCENE:



"DNA" for the fire investigator?

Gas Chromatography/Isotope Ratio Mass Spectrometry

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The Age Old Problem with Arson

Face it, high among the frustrating situations arson investigators face is knowing who set a fire and how it was set, but lacking the quality evidence needed to pursue criminal charges or to deny a fraudulent insurance claim.

It's an old, but probably true, cliché that arson is the easiest crime to commit but the most difficult to solve. The arsonist usually works under cover of darkness, chooses the time of attack to minimize contact, usually gains entry through an entryway hidden from view, concocts a half-baked alibi that will stand up to a half-baked investigation and relies on the fire itself to destroy evidence of any link to the crime scene.

These strategies have worked distressingly well. According to the Federal Bureau of Investigation (FBI), arson has had the lowest clearance (arrest) rate of the eight major felonies measured by the Uniform Crime Reports with only approximately 2% of all known incendiary fires resulting in the conviction of a perpetrator for the crime of arson (Hall, 1995).

Taking a cue from television police dramas, today's trial courts and juries often demand physical and circumstantial evidence that positively links a suspect to a crime scene before they will deliver a verdict to convict. This unequivocal level of DNA-like forensic evidence has been historically hard to come by in arson investigation cases. However, this may be about to change.

A proven technology used in the petroleum industry and in basic science called Gas Chromatography/Isotope Ratio Mass Spectrometry (GC/IRMS) may become the next quantum leap for arson investigation. If GC/IRMS passes scientific and legal muster, it promises to take the public safety and insurance fraud effort to fight arson to an entirely new and more sophisticated level.

Traditional Method of Arson Debris Analysis

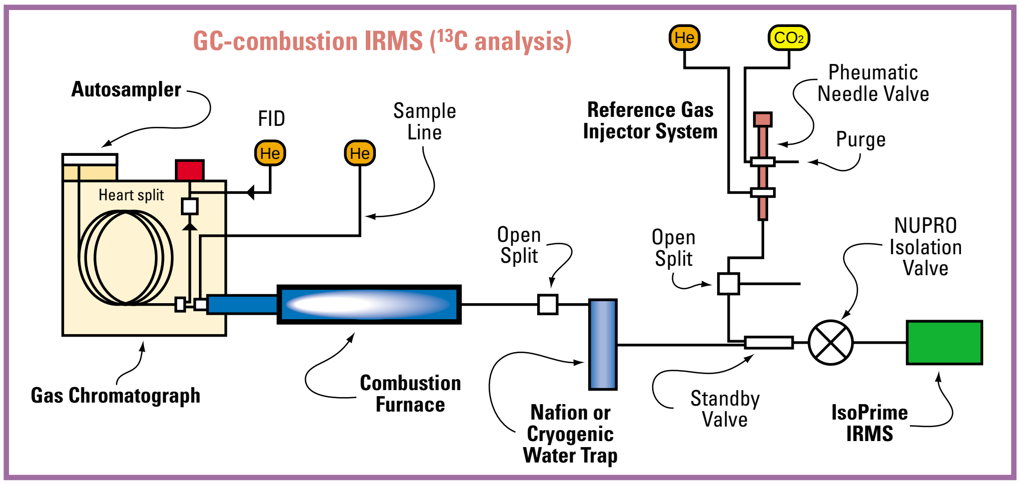
In modern forensic laboratories, trace analysis of fire-debris samples for ignitable liquid residue is typically performed by structural or, "organic" gas chromatography/mass spectrometry (GCMS). Using such equipment, forensic scientists can determine a sample's compound structure and relative concentrations and then identify or "fingerprint" specific organic compounds. These fingerprints, in turn, can be identified as specific classes of petroleum products by forensic chemists. In short, GCMS allows investigators to identify the type of accelerant used by an arsonist to ignite a fire.

New Method: GC/IRMS

Based on experience gained from the petroleum and pharmaceutical industries and a preliminary study of the stable carbon isotopic analyses from a number of controlled fire experiments, GC/IRMS technology promises to take the investigation a crucial step further by positively linking the accelerant from fire debris to accelerant identified in samples of the suspected arsonist's containers or clothing.

The GC/IRMS takes advantage of other types of tracers contained within the same analyte compounds, but which is not evaluated by structural GCMS, called stable isotopes. Taking experience gained from the petroleum and pharmaceutical industries and a preliminary study of the stable (carbon) isotope analysis from a number of controlled fire experiments, we demonstrate the potential for this type of analysis to link fire debris samples to accelerant samples from the container or clothes of a suspected arsonist. While we focus on carbon isotopes here, stable hydrogen isotopic composition also holds excellent promise as tracers of arson-related accelerants.

As the name of the instrument indicates, the gas chromatography/isotope-ratio mass spectrometer, the associated technique separates individual compounds by gas chromatography, combusts them into carbon dioxide peaks, and measures the isotopic composition of the resultant carbon dioxide peaks with a very precise isotope-ratio mass spectrometer *(Fig. 1)*. The precisely measured isotopic values can be used as "isotopic fingerprints" for a variety of purposes.



(Figure 1) A schematic diagram of a Micromass IsoPrime gas chromatograph/stable isotope-ratio mass spectrometer (GC/IRMS; www.micromass.co.uk). The three major components include: (i) a gas chromatograph where organic compounds are separated into individual peaks, (ii) a high-temperature (~900°C) combustion oven where individual chromatograph peaks are combusted into CO_2 and H_20, and (iii) an isotope-ratio mass spectrometer (IRMS) where the resulting $^{13}CO_2$ an $^{12}CO_2$ are separated and measured to give isotopic ratios for individual compounds.

The original and most significant purpose for such molecular isotope data was for tracing petroleum migration between subsurface reservoirs for the oil industry. In this application, billions of dollars of oil drilling decisions have been made on the basis of GC/IRMS data. A number of pharmaceutical companies are presently in a late research and development phase assessing the utility of stable isotopic "fingerprinting" of their pharmaceutical products (*e.g.*, Jasper *et al.*, 2001). Review of test data has convinced experts from the field that this method will provide them with a way of proving the source of counterfeit drugs by showing that they cannot have come from the actual manufacturer whose set of isotopic fingerprints are already known. Recently at an international Pharmaceutical Anti-counterfeiting Solutions meeting in Washington, DC, a US Food and Drug Administration official, acknowledging the likely utility of stable-isotopic fingerprinting, noted that he would "expect and accept" the very fine-scale isotopic variations that have been observed in pharmaceutical studies.

For the first time, GC/IRMS technology promises to provide fire and arson investigators with the ability to link together, with DNA-like specificity, (i) ignitable liquid accelerant residue recovered from burned flooring, (ii) partially-evaporated ignitable liquid accelerant residue from the arsonist's clothing, and (iii) the neat (i.e., "pure" or "unadulterated") liquid remaining in the accelerant container. Linkage of a specific accelerant at a fire scene to the accelerant in a container and accelerant found on the clothing of a suspected arsonist would make an extremely strong case.

Examples of the Types of Cases where GC-IRMS May Help

1. A business owner facing imminent bankruptcy lets himself into the rear door of his shop during pre-dawn hours. He pours gasoline on his business records, office furniture, and flooring and over goods in cardboard boxes in the warehouse on his way out. The ensuing fire destroys the building but investigators successfully recover ignitable liquid samples that help establish the arson. Further examination of the samples by GC/IRMS positively link the accelerant residue from the scene with evaporated gasoline residue found on the suspect's shoes and trousers, to the gas container seized from his vehicle and even to a specific gasoline station where investigators can prove he purchased gasoline before the fire.

2. A disgruntled employee brings a pint container of paint thinner into a basement storage room at work and sprays it onto upholstered chairs and carpeting before setting the hotel on fire. The container, later recovered from a trash can, contained the suspect's fingerprints. GC/IRMS linked the neat sample remaining in the can with residue recovered on the suspect's clothing and residue recovered from the carpet in the storage room. Fingerprints connect the suspect to the accelerant container and stable isotope analysis connects the accelerant bottle to the fire debris accelerant.

3. A large textile mill that had been converted for use by a dozen independent small businesses sustains a serious fire. Subsequent investigation reveals that an employee of one of the businesses that manufactured custom paint had improperly disposed of a gallon of a paint-contaminated petroleum-based solvent by putting it into the building trash compactor designed for disposal of paper waste. GC/IRMS analysis positively links this residue with unique samples taken from the company's off-site stock.

The Basics

The GC/IRMS method relies on identification of special types of elemental subspecies called "stable isotopes" (molecular-weight variants of common elements; also see definition below) in samples sent for laboratory analysis. A quick review of some basic chemistry would be helpful at this point.

The Basics

- All physical matter is made up of atoms.
- All atoms are composed of combinations of three basic particles: protons (+ charge), electrons (- charge) and neutrons (no charge). The number of each type of particle present in the atomic structure of an element results in physical and chemical properties that are unique to that element.
    - An element is defined as a pure substance that cannot be decomposed into simpler substances by ordinary (non-nuclear) chemical means.

- Most substances are combinations of atoms into molecules or compounds. For example, nearly all ignitable liquids (accelerants) are mixtures of low (<150 atomic mass units) molecular weight compounds that are typically composed of combinations of two-to-three elements: hydrogen, carbon, and sometimes oxygen.
- Molecule—The smallest particle of a pure substance (or, compound) that can exist and still retain the physical and chemical properties of the substance, such as H_2O.
- Stable isotopes of the same element have the same chemical properties but slightly different physical properties—notably, their mass, which is determined by the variable number of neutrons.
- The compositions of protons, neutrons, and electrons are the same between different elements. The number of each type of sub-atomic particle in an atom's structure determines the physical and chemical properties that vary from one element (or, one isotope) to the next. For example, the composition of the individual protons and neutrons in helium and gold are identical, but the number of each present largely determines the structure of the atom and its chemical properties.
- The masses of atoms of a given element change as the number of neutrons change, so that certain elements can have more than one isotope.
- An isotope of a given element (e.g., carbon, hydrogen, nitrogen etc.) is determined by its number of protons and neutrons, thus specific isotopes can be considered as individual "species" of one element with a slightly different mass that causes it to have slightly different chemical behavior.
- How isotopes are formed. All matter [*i.e.*, stable isotopes and the parents of radioactive ("unstable") isotopes] was formed at the origin of the Universe ("the Big Bang") about 4.5 billion years ago. This matter has dispersed to form planets and all of their physical components.
- For perspective, there are 112 elements known so far, 62 of which have a total of 252 stable isotopes. For general purposes, one can infer that every pair of stable isotopes could be used as a tracer of chemical processes and/or chemical identity.

Stable Isotopes

What are stable isotopes? Simply put, they are non-radioactive elements. More pointedly, the term stable isotope refers to a given atom's mass. While the number of protons defines an element [e.g., carbon (6) vs. nitrogen (7) vs. hydrogen (1)], the number of neutrons defines which isotope (*i.e.*, of which mass) of the element is being referred to. As a most relevant example for present purposes, carbon-12 (denoted ^{12}C) has six protons and six neutrons. The addition of one more neutron makes ^{13}C. For reference, ^{12}C comprises 98.89% of all naturally occurring carbon and ^{13}C comprises 1.11%.

To be useful as a tracer, one needs a pair of isotopes (*e.g.*, ^{12}C and ^{13}C) to form a ratio (*viz.*, $^{13}C/^{12}C$). (For perspective, note that the irmGCMS averages the $^{13}C/^{12}C$ ratios of enormous numbers of individual $^{12}CO_2$ and $^{13}CO_2$ molecules to produce a single isotopic ratio.) The variation in that ratio is the tracer of interest here. As you will see, a typical petroleum-derived accelerant has tens of individual compounds each with tens of individually-measurable isotopic ratios intrinsic to them, yielding highly-specific tracers. Fortunately, the ratio of these and other isotopes are highly variable in nature. That variation—caused by a number of processes—yields a wide variety in the isotopic compositions of individual compounds in given samples.

How This Technology was Developed

The main line of the history of online isotope organic chemistry extends back to a late 1980s joint venture in which the basic science (biogeochemistry) community, the petroleum industry, and a major instrument firm cooperated to solve an important problem (Fig. 2; Hayes *et al.*, 1990; Freedman *et al.*, 1998). The problem was imaging and quantifying the migration of petroleum in subsurface geological formations. Decades' worth of GCMS data could not provide the resolution that scientists needed to positively differentiate one petroleum source from another. From earlier offline analyses of light hydrocarbon gases, geochemists inferred that higher molecular-weight hydrocarbons should also reveal highly-specific isotopic compositions that have been used in the search for petroleum. This same technology is now being employed to fingerprint accelerant gasoline samples in experiments described in the associated web pages.

(Figure 2) Professor John M. Hayes, now the Director of the Woods Hole Oceanographic Institution's Accelerator Mass Spectrometry Laboratory, pioneered the development of the gas chromatograph/isotope-ratio mass spectrometer (GC/IRMS) largely in the late 1980s in a collaboration between basic science (biogeochemistry at Indiana University, Bloomington, Indiana) and industry (Chevron Oil and Finnigan Instruments).

Specificity

The specificity of the combined isotopic fingerprint of a number of molecular isotopic analyses can be compared to the number of combinations on a combination lock. Consider a combination lock (or slot machine) with 4 tumblers each of which has 10 numbers. Then, that lock (or slot machine) has 10^4—or, 10,000 combinations (or possibilities).

Most ignitable liquids used as fire accelerants contain a complex mixture of 50-100 or more individual compounds that can be chromatographically separated (*e.g.*, Smallwood *et al.*, 2001 and refs. therein). With that, one can combine the specificities of even a few of the compounds from an accelerant analysis to generate an estimate of the overall specificity. For example, if one measures the carbon isotopic composition ($\delta^{13}C$) of only five compounds, with each compound having 67 significantly different isotopic variations, the combined specificity would be $\sim(1/67)^5$, or ~1 in 1.4 billion – on the scale of the specificity of DNA analysis. That is, to a first-order estimate, there would be only about a 1-in-1.4 billion chance that a random accelerant sample (say, gasoline from another gas station etc.) would be identical to that associated with a given arson event.

Status of the Technique

Molecular isotope mass spectrometry (via GC/IRMS) is in a mid-research-and-development phase for applications to solving cases of arson. The GC/IRMS instrument has been commercially-available for approximately ten years with many techniques evolved for the analysis of petroleum-based hydrocarbons. Preliminary fire experiments indicate high specificity in identifying original accelerants, with degrading specificity under conditions of increasing combustion (from 0% up to 90% evaporation).

We would like to partner with the proper organizations (*e.g.*, insurance companies, government *etc.*) to refine the molecular-isotopic analysis of fire-debris accelerant to test the limits of this technique as a method for solving arson cases. The application and use of the molecular isotopic technique described in this article is subject to a US pending patent and patent applications in the other G8 countries and in Australia.

Conclusion

Molecular isotope analysis, typically performed on a GC/IRMS, will require further scientific testing and peer review before the courts will accept it as evidence in arson cases, as they have in cases of food adulteration and in athletic doping. The GC/IRMS method as applied to arson is in a relatively early stage, but initial experiments are promising with a technology that has been fully implemented in both the basic sciences and in the petroleum industry and is in the mid-to-late research and development stages in the pharmaceutical industry. Experts in arson debris analysis are impressed with the procedure's performance on several tests run to date. We expect that as the efficacy of this method is established in arson investigation federal and state level forensic laboratories, it will help mount an effective response to arson.

GC/IRMS is a proven analytical method that we believe will have a tremendous positive impact on arson investigation and related forensic applications in the near future. To exploit this potential, leaders in the public safety and property insurance fields should provide for expert review of the scientific paper on this process that will soon be available at **www.interfire.org** and at **www.MolecularIsotopes.com**.

Comments addressed to the authors or to *Fire & Arson Investigator* magazine are invited.

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About the Authors

Dr. John P. Jasper is a partner of Arson Stable Isotope Analysis (ASIA), a joint venture with EFT Analytical Chemists, Inc. that is developing the use of molecular isotopic tracers of arson.

Dr. Jasper is an organic and stable isotope chemist who has worked in the fields of marine organic chemistry and in analytical pharmacology. He earned a B.A. in Geophysical Sciences and Biological Sciences from the University of Chicago in 1981. He earned a Ph.D. in Marine Organic Chemistry from the Massachusetts Institute of Technology/Woods Hole Oceanographic Institution (MIT/WHOI) Joint Program in Chemical Oceanography where he quantified the relationship between bulk terrigenous and marine organic matter and specific organic compounds in the Quaternary Gulf of Mexico. As a Postdoctoral Fellow and Scientist at Indiana University with Prof. J. M. Hayes, he co-developed the use of molecular isotopes via GC/IRMS to reconstruct paleoenvironmental CO_2 levels over the last 250,000 years. He then worked in pharmaceutical industry with Pfizer, Inc. and Drumbeat Dimensions, Inc. He is now the Chief Scientific Officer of Molecular Isotope Technologies, LLC (www.MolecularIsotopes.com).

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John Edwards is a former Special Agent and forensic chemist with the North Carolina State Bureau of Investigation. John has conducted research on various topics including the affects of weathering on petroleum products. He is a co-owner of EFT Analytical Chemists, Inc. and specializes in the detection and identification of ignitable liquid residues in fire debris. He is a partner in Arson Stable Isotope Analysis (ASIA). He has testified numerous times as an expert witness in civil and criminal courts. He has also taught classes for the N.C. Chapter of the International Association of Arson Investigators and the state Fire Marshal's Office on fire behavior, collection and preservation of evidence, and origin and cause determination.

Edwards was graduated from Barton College with a Bachelor of Science degree in Chemistry that included advanced studies in organic, inorganic, and analytical chemistry. He has also completed studies in "Basic Chromatography" at the Federal Bureau of Investigation Academy, "Detection and Identification of Accelerants Found in Arson Debris" at the US Treasury Alcohol Tobacco and Firearms National Laboratory, and advanced studies in criminal and scientific investigation at the SBI Academy.

He is currently a member of the International Association of Arson Investigators, North Carolina Chapter of the International Association of Arson Investigators, and the Nashville Fire Department.

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Larry Ford is a retired Special Agent and Forensic Chemist with the North Carolina State Bureau of Investigation (NCSBI). He has conducted research and development on crime scene techniques that have improved the ability of investigators to detect and identify fraudulent fires and fire setters. He has also conducted research to improve laboratory testing of fire evidence. Larry has worked closely with the NCSBI Canine Accelerant Detection program and has conducted initial training and re-certification testing for over ten years. In addition to working as the Assistant Supervisor of the Trace Evidence section in the NCSBI Crime Laboratory, he was also responsible for the chemical and analytical examination of fire evidence from cases throughout North Carolina. He has testified over two hundred times as an expert witness in State and Federal, criminal and civil courts. As a certified instructor he has taught numerous classes for the NCSBI, the N.C. Justice Academy, and the N.C. Chapter of the International Association of Arson Investigators.

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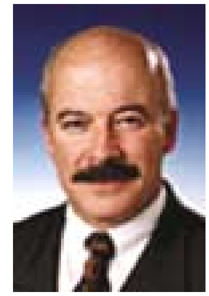
Larry is currently a forensic chemist and co-owner of EFT Analytical Chemists where he continues to conduct research on various fire topics and to analyze evidence. He is a partner in Arson Stable Isotope Analysis (ASIA). He is a graduate of Appalachian State University with a Bachelor of Arts degree in Chemistry. He is a member of the International Association of Arson Investigators (IAAI) and the American Academy of Forensic Sciences. Larry is a charter member of the North Carolina Chapter of the IAAI and has served as President, 1st and 2nd Vice President. On October 17, 2000, he was elected as an Honorary Life member of the NCIAAI.

Robert Corry is an Assistant Vice President and Fire Investigation Specialist in the Property Claims Division, based in American Re-Insurance's Hartford, Connecticut office. Bob's responsibilities include consulting with clients on arson and fire loss claims and providing educational programs on arson investigation and defense, and underwriting against arson.



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Bob served on the Massachusetts State Police from 1974 until his retirement in 1997. From 1982 until 1997 he was assigned to the Massachusetts State Fire Marshal's Office (SFMO). Bob was a fire and arson investigator assigned to the Hampden County District Attorney's Office for 10 years conducting fire, arson and bomb investigations in 26 communities, and was Detective Lieutenant and Commanding Officer of the statewide SFMO Fire, Arson and Explosion Investigation Unit – the largest unit in the state police – from 1992 until 1997. In addition, Bob was an Accelerant Detection Canine handler from 1990 until 1992.

Bob has been the principle developer of arson training programs and publications, including the Pocket Guide to Accelerant Evidence Collection. In addition, he lectures on fire/arson investigation, interview & interrogation techniques, and criminal investigation techniques to the Massachusetts state and local police and fire academies, the National Fire Academy, and the FBI National Academy.

A member of the Massachusetts Chapter of the International Association of Arson Investigators, Bob served as the group's Vice President in 1987 and President from 1988 until 1990. He is also a member of the National Fire Protection Association. Bob earned a Bachelor of Science in Criminology from Northeastern University and a Master of Science in Criminal Justice Studies from American International College. He served the U.S. Army from 1966 through 1970, where his last assignment was Captain, 173rd Airborne Brigade in Vietnam.