



**ARSON
STABLE ISOTOPE
ANALYSIS**



A Novel Method for Arson Accelerant Analysis: Gas Chromatography/Isotope Ratio Mass Spectrometry

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Abstract

Stable isotopes are natural tracers that are ubiquitous in virtually all organic matter, including petroleum-based accelerants. The development of the gas chromatograph - isotope-ratio mass spectrometer (GC-IRMS), primarily for the petroleum industry to trace the subsurface migration of petroleum, generated an instrument that is useful for the high-precision tracing of molecular organic components back to their origins. We present here a reconnaissance overview of molecular isotope chemistry and preliminary isotopic results from several fire experiments. The importance of more detailed molecular isotopic studies of arson is recognized. This scientific article was substantially the basis for an article on the detection of arson by molecular isotopes (Jasper et al., 2002).

Introduction

Trace analysis of fire debris is typically performed by structural (or organic) gas chromatography/mass spectrometry (GCMS) that provides compound pattern recognition (i.e., boiling point range and relative concentration) and chemical composition and compound structure (ASTM E 1387; ASTM E 1618). When analyzed through various pattern recognition techniques, they provide a means by which to identify (or "fingerprint") accelerants or ignitable liquid samples. Another type of tracer contained within the same analyte compounds, but which is not evaluated by structural GCMS is stable isotopic composition. With evidence from both the petroleum and pharmaceutical industry and a preliminary study of the stable (carbon) isotope analysis of simulated fire experiments, we will show some of the potential for this analysis to connect fire debris samples to accelerant samples from containers or clothes of suspected arsonists.

The history of online isotope organic chemistry extends back to the late 1980's when a joint venture between the basic science (biogeochemistry) community, the petroleum industry, and a major instrument firm cooperated to solve an important problem (Hayes et al., 1990). The problem was imaging and quantifying the migration of petroleum in subsurface geological formations. Decades' worth of GCMS data were not providing the resolution to permit the intended differentiation of 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 could be used in the search for petroleum. Since the early 1990's, GC-IRMS analyses have become a standard measurement in the petroleum industry for tracing ("fingerprinting") petroleum and reconstructing their subsurface migration. In the near subsurface environment, the molecular isotopic composition of the refined gasoline-additive methyl tertiary butyl ether (MTBE) is being explored to trace the origin of gasoline that has leaked into many ground waters (Smallwood et al., 2001). Given the ubiquity of stable isotopes, one of the first publicly-released studies of the use of stable isotopes (of carbon, nitrogen, oxygen, and hydrogen) to trace the identity of pharmaceuticals showed that the combined use of isotopes gives a highly specific tracer of product identity in an area termed "Isotopic Product Integrity" (Jasper et al., 2001).

Stable Isotopes

What are stable isotopes? Simply put, they are all 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%. (By the way, radioactive ^{14}C comprises only about 1 part per trillion of the total natural carbon.) To a good first approximation, your bodily carbon is ~99% ^{12}C and ~1% ^{13}C .

To be useful as a tracer, one needs a pair of isotopes (e.g., ^{12}C and ^{13}C) to form a ratio (viz., $^{13}\text{C}/^{12}\text{C}$). The variation in that ratio is the tracer of interest here. Fortunately, the ratio of these and other isotopes are highly variable in nature. That variation - caused by a number of processes - yields a highly specific tracer that is endemic to every organic compound.

Dynamic Range

How specific is this tracer that is fundamental to every organic compound? Based on the chemist's standard idea of dynamic range (observed range/1s pooled standard deviation of the measurement), we can estimate the specificity of typical molecular carbon isotope analyses at ~67 - i.e., by GC-IRMS, we can measure 67 discrete units across the typical range of naturally-varying carbon-based material. Note that bulk materials -- versus chromatographically-purified compounds -- can be measured to a much higher dynamic range of ~1500 because of the higher precision of a dual inlet mass spectrometer (cf. Jasper, 1999 and refs. therein).

Specificity

The specificity of the combined isotopic fingerprint of a number of molecular isotopic analyses can be considered as close analogy to the combination on a combination lock. Consider a combination lock with 4 tumblers each of which has 10 numbers. That lock has 10^4 (or, 10,000) combinations. We will see that the specificity (or, "number of combinations") of a molecular isotopic analysis of a given accelerant can be estimated by the inverse of the dynamic range (DR) raised to the power of the number of compounds (n), thus specificity = $(1/\text{DR})^n$, as illustrated below.

Recall that most accelerants contain a complex mixture of 50-100 individual compounds that can be chromatographically separated (e.g., Smallwood et al., 2002 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 ($\delta^{13}\text{C}$) of only five compounds, each with a dynamic range of 67 (based on typical petroleum compound 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, 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.

Instrumentation

Jasper (1999) reviewed the four main types of isotope mass spectrometers (i) for bulk isotopic analysis: (a) the dual-inlet MS (for high precision, individual analyses), (b) the elemental analyzer/mass spectrometer (EAMS; a high throughput MS for automated, sequential, though less precise analyses) and (ii) for molecular isotope analyses: (a) the isotope ratio-monitoring gas chromatograph MS [irmGCMS, discussed here and in Hayes et al. (1990) and Freedman et al. (1997)], and (b) the isotope ratio-monitoring liquid chromatograph MS (irmLCMS). At base, the irmGCMS is composed of three major parts: a gas chromatograph, a combustion interface, and an isotope ratio mass spectrometer. As is typical, liquid samples are injected into the GC where the dissolved compounds are chromatographically separated into individual peaks. The purified individual compound peaks then elute into a high-temperature ("850°C") combustion oven where they are combusted into CO_2 , H_2O etc. After the online removal of H_2O , the purified CO_2 (composed of both $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$) is advected into the magnetic sector isotope-ratio mass spectrometer where the isotopomers are separated and the $^{13}\text{C}/^{12}\text{C}$ ratio of the CO_2 is measured. With that, the isotopic composition of each individual compound is measured. For perspective, a typical GC-IRMS instrument costs ~\$150-250k. Experience shows that most organizations initially contract out stable isotopic analyses to test their utility. Then, depending on the number of sample analyses etc., some will simply continue to contract out analyses, while others will purchase their own instruments.

Unit of Measurement

To maintain a very high degree of precision and therefore intercomparability between laboratories, isotopic results are reported as a part-per-thousand difference (δ) from an internationally-accepted standard:

$$\delta^{13}\text{C} (\text{‰}) = 1000[(R_{\text{smp}}/R_{\text{std}}) - 1]$$

where R = the $^{13}\text{C}/^{12}\text{C}$ ratio and the subscripts denote the sample and the isotopic standard. Carbon isotopic compositions are typically reported relative to that of a primary standard such as the Vienna PeeDee Belemnite (VPDB) carbonate standard from the International Atomic Energy Authority (IAEA) that defines the zero point on the δ scale of carbon isotopic abundances. Jasper (2001) recently defined quantitative methods for estimating molecular isotopic measurements and their statistical errors.

Preliminary Experimental Arson Case Study

To perform a preliminary test of the utility of molecular isotope analysis to trace the identity of a typical accelerant under simulated arson fire conditions, we performed isotopic analyses of three gasoline samples. The conditions under which the samples were treated were as follows: (i) untreated ("neat") sample of 87 octane gasoline (i.e., 0% evaporated, no fire) was used as a control, (ii) a petroleum-ether wash (ASTM E 1386) of burned, 50% residual (i.e., 50% evaporated) of the 87 octane gasoline extracted from burned carpet and padding was used to simulate a moderately-burned and concentrated fire-debris sample, and (iii) a dynamic headspace separation and concentration (ASTM E 1413) of burned, 10% residual (90% evaporated) 87 octane gasoline extracted from burned carpet and padding was used to simulate a severely-burned and low-concentration fire-debris sample.

These samples were subsequently analyzed by GCMS (for pattern recognition and structure) and irmGCMS (for isotopic composition). Briefly, the GCMS was a Hewlett-Packard MSD equipped with a 50 m DB-1 column. In this case the GC-IRMS was a Varian 3400 GC coupled to a Finnigan MAT 252 via a 950oC combustion furnace and a water trap.

The isotopic composition of 14 specific compounds (typical for arson analyses) was determined, typically in duplicate (Table 1).

Table 1.
 $\delta^{13}\text{C}$ of Accelerant Compounds of Fire Experiments

Compound Identification	$\delta^{13}\text{C-A}^a$	$\delta^{13}\text{C-C}^c$	$\delta^{13}\text{C-E}^e$	1s-A	1s-C	1s-E
	, vs VPDB			(,)		
A p/m-Xylene			-25.64			0.03
B n-Propylbenzene	-25.11	-24.50	-24.55	0.11	0.26	0.24
C 1-ethyl-2-methylbenzene	-26.60	-25.58	-25.92	0.20	0.25	0.22
D 1,3,5-Trimethylbenzene	-25.14	-24.46	-24.53	0.25	0.18	0.12
E 1-Methyl-2-ethylbenzene	-25.58	-25.02	-24.41	0.15	0.31	0.15
F 1,2,4-Trimethylbenzene	-26.71	-25.40	-26.76	0.01	0.00	0.00
Indane	-24.54	-24.13	-24.79	0.04	0.26	0.32
G 1,2-diethylbenzene/propylbenzene	-23.74	-24.50	-24.60	0.00	0.00	0.29
H 1,3-dimethyl-5-ethylbenzene	-25.46	-24.52	-25.01	0.23	0.54	0.32
I Unknown	-24.43	-23.50	-24.62	0.00	0.21	0.15
J 4-ethyl-1,2-dimethylbenzene	-24.11	-23.31	-23.58	0.24	0.30	0.20
K 1-methyl-2-ethylbenzene	-25.89	-25.43	-25.22	0.04	0.34	0.21

L 1,2,4,5-Tetramethylbenzene	-25.84	-24.51	-27.01	0.06	0.02	0.33
M 1,2,3,5-Tetramethylbenzene	-25.91	-24.56	-26.21	0.03	0.22	0.36
O 1-methylindane/2-ethyl-1,4-dimethylbenzene	-25.11	-25.47	-24.16	0.12	0.02	0.19

a,c,e: \bar{N} The experimental conditions experienced by samples A, C, E, and their respective pooled 1s standard deviations are explained in text.

In this case, the overall span of the molecular isotopic data was $\sim 4.0\text{‰}$ with an average 1s variance of 0.3‰ . To produce more generally realistic estimates of the dynamic range of a specific compound, we would need more isotopic measurements on other gasoline samples. As a first-order estimate, the carbon isotopic difference between US West Coast petroleum and Gulf Coast petroleum is $\sim 10\text{‰}$. With a typical 1s standard deviation of $\sim 0.25\text{‰}$, the dynamic range would be ~ 40 [N.B., $(1/40)^5$ equals about a 1 in 100 million chance of random reproduction of the exact same value].

Correlation Plots of Simulated Fire Scene Data

Three cross correlation plots of molecular isotope data generated from the analyses of the three preceding gasoline samples demonstrate that the degradation of isotopic signals under a preliminary set of experimental fire conditions (Fig. 1a-c).

All of the plots are constructed as comparisons to the carbon isotopic compositions ($\delta^{13}\text{C}$) to the control analyses of "neat" gasoline.

0% Evaporation: The Identity Plot

For illustrative and comparative purposes, the first crossplot of the $\delta^{13}\text{C}$ of all 14 compounds (Fig. 1a)

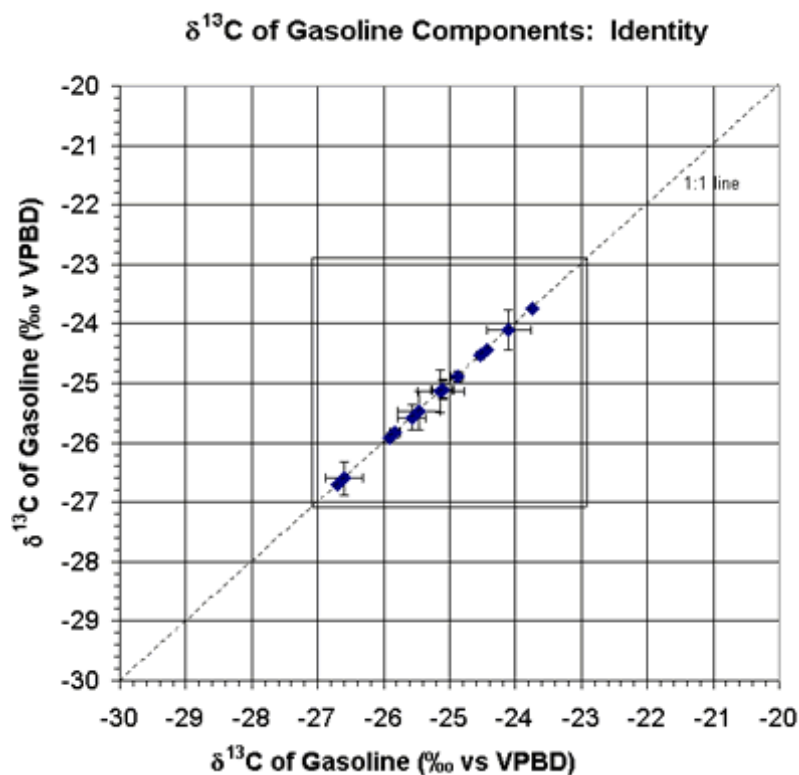


FIG 1a. An illustrative crossplot of the carbon isotopic composition ($\delta^{13}\text{C}$) of 14 compounds selected from the GC/IRMS analysis of 87 octane gasoline plotted against themselves to show both the identity (1:1) line and typical errors associated with the method.

is plotted against itself to illustrate an identity (1:1) plot with its attendant errors (or variances). For a highly specific identification of a very fresh (0% evaporated) accelerant sample versus a suspected

arsonists' sample (e.g., from a container in his automobile - or with his fingerprints on it!), such a plot with a high correlation would be an important first step in establishing a fire debris/arsonist connection. More refined analyses of point-by-point correlation could be made by a statistical test (Smallwood et al., 2001) which could be compounded in one estimate of probability by a method analogous to the dynamic range/specificity method discussed above (also see Jasper, 2001). Of course, in this example, the correlation is perfect ($r^2 = 1.000$) by definition given that it is an identity. As we will see, any degradation of the isotopic signal will result in a degradation of the correlation graph and attendant statistical correlation estimators.

50% Evaporation: Systematic Alteration of the Signal

The systematic alteration of the isotopic signal results in a general migration of the individual isotopic data points by $\sim 0.5\text{‰}$ above the 1:1 line in almost every case (Fig. 1b).

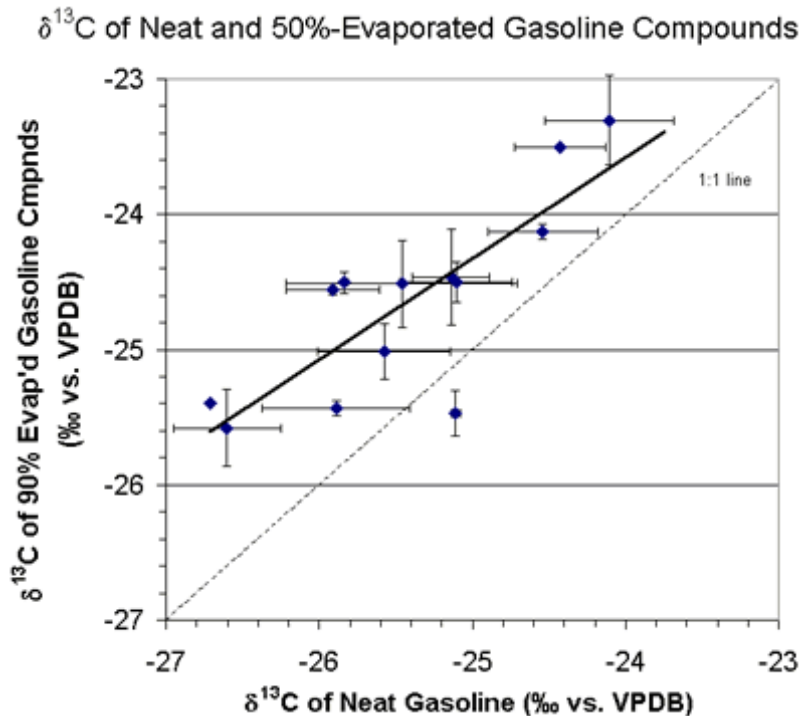


FIG 1b. A crossplot of 50% evaporated/combusted gasoline plotted against original neat gasoline source. Note the general $\sim 0.5\text{‰}$ enrichment of the experimentally altered gasoline is consistent with normal preferential removal of the light end - whether it is in molecular weight or in isotope mass.

(Fig. 1b) Expressed in isotopic terms, upon evaporation of the control sample, the individual compounds virtually all become more positive or "isotopically enriched" in the heavy component (viz., in ^{13}C relative to ^{12}C), in the vernacular of isotope chemists.

What does a 0.5‰ enrichment mean? Briefly, it means that the ^{13}C -depleted fraction of the original accelerant was preferentially evaporated, leaving behind a relatively ^{13}C -enriched fraction of that compound. For example, in the present experiments, n-propylbenzene migrated from an original (0% evaporated) carbon isotopic value of -25.0‰ to a 50% evaporated $\delta^{13}\text{C}$ value of -24.5‰ , thus becoming depleted by 0.5‰ - a small, but measurable change. This observation is consistent with basic isotopic and chemical principles and is exactly analogous to the debris chemists' everyday observation that the "light end" of accelerant chromatograms is significantly depressed by preferential evaporation of the volatile (low molecular weight) compounds.

90% Evaporation: Degradation of the Signal.

Ninety-percent evaporation of the original gasoline sample results in a notable degradation of the overall relationship of the original accelerant gasoline versus that of the experimentally-combusted sample. Despite the specific degradation, there remains a general correspondence (Fig. 1c)

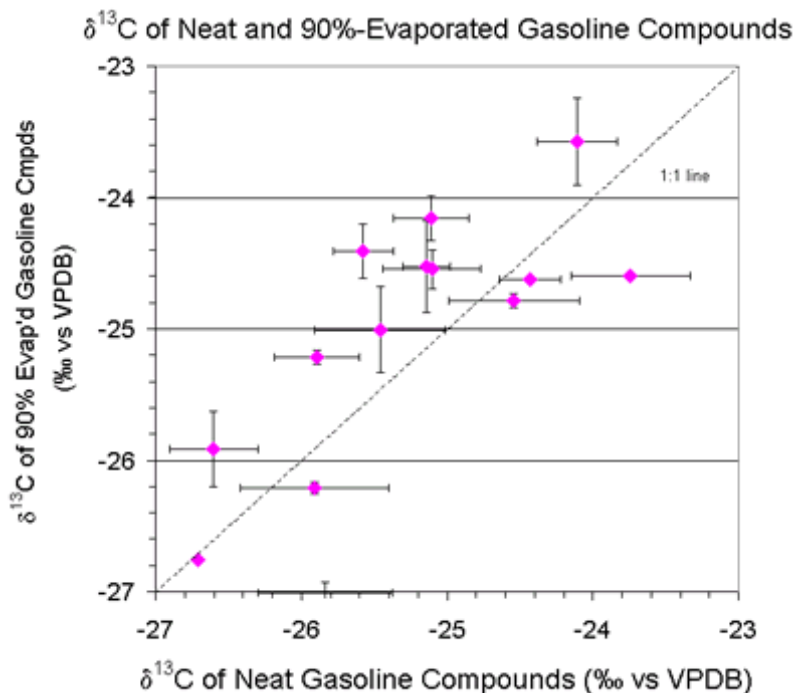


FIG 1c. A crossplot of 90% evaporated/combusted gasoline plotted against original neat gasoline source. At this high degree of evaporation (fractionation), there remains a general correspondence to the 1:1 relationship in slope as well as average isotopic value, but the relationship is degraded relative to the 50%-evaporated state. More intermediate steps in evaporation/combustion should better define the tracers' behavior under varying degree of combustion.

of the 90%-evaporated accelerant to the original (0%-evaporated) gasoline with both remaining in the isotopic range (-27‰ to -23.5‰). Remember that randomly chosen isotopic values of existing petroleums (i.e., the sources of most accelerants) can span 10‰ or more as compared to the 3.5‰, so that non-matching accelerant samples may readily evidence themselves.

Sample Evaporation: Isotopic Fractionation

A plot of carbon isotopic fractionation ($\Delta\delta^{13}\text{C}$) versus percent of sample evaporation shows that on average the residual gasoline was enriched in ^{13}C as the sample was partially evaporated. Between the neat (0% evaporated) gasoline and the 50% evaporated gasoline, eleven out of twelve compounds were isotopically enriched by $\sim 0.75\text{‰}$; one out of the twelve compounds demonstrates an anomalous depletion by -0.36‰ , a depletion that may be caused by a coeluting compound. By 90% evaporation, eight compounds demonstrate $\sim 0.75\text{‰}$ enrichment relative to the original gasoline; one compound shows no measurable fractionation; the remaining three compounds span depletions of $\sim -0.2\text{‰}$ to -1.2‰ . In summary, the general trend in residual gasoline-compound isotopic enrichment is the expected trend: isotopically-depleted (and therefore less massive) compounds preferentially evaporate from a parent liquid to the gas phase resulting in isotopic enrichment in the residual parent liquid. As noted below, more finely graded studies should permit better description of the isotopic fractionation trends with increasing evaporation.

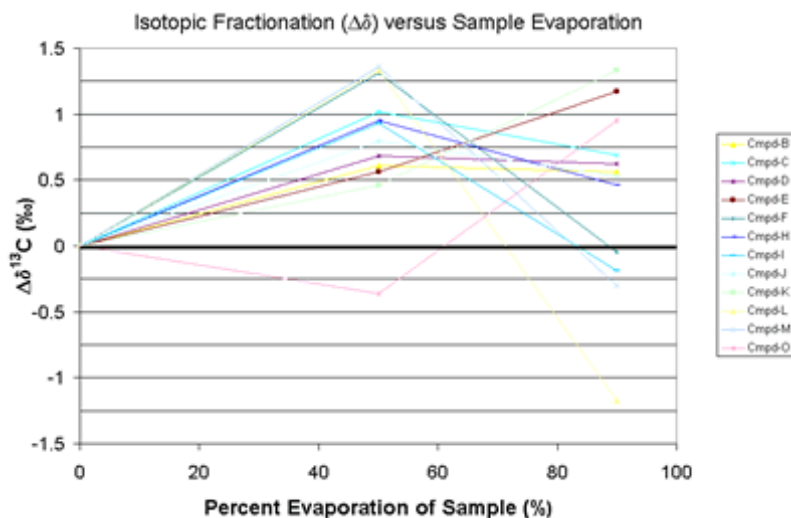


Fig.2. A plot of carbon isotopic fractionation ($\Delta\delta^{13}\text{C}$) versus percent of sample evaporation

Prospectus

The analysis of just one gasoline sample examined under these simulated fire scene conditions indicated some basic points about the utility of molecular isotope analysis (via irmGCMS). First the analysis of the control (0%) sample showed that within a given gasoline (accelerant) sample, there is a wide range of isotope values spanning many sample compound classes (14 reported here) - i.e., an isotopic fingerprint for many individual accelerants exists. The measurement errors were of reasonably small size, giving a useful dynamic range. Secondly, partial (50%) evaporation results in a systematic, predictable change in the system by a small amount (0.5-to-0.75‰) that is not much larger than the measurement error. The ^{13}C -enrichment of the evaporated accelerant is consistent with the evaporative removal of the "light end." While high (90%) fractional evaporation leads to scattering around the 1:1 line, the molecular isotopic composition of the combusted sample remains in the region of the original neat gasoline. The stepwise continuity of the relationship underscores the need for higher resolution studies of the effects of fractional evaporation (e.g., 0, 10, 20, ...80, 90, 95%) on molecular isotopic composition. Such studies should provide a more systematic and predictable relationship between original accelerant and fire debris-extracted components that have undergone varying degrees of combustion and evaporation.

Summary

A preliminary set of simulated fire scene experiments with a controlled accelerant provided an initial view of a prospective tool for fire debris chemists. Molecular isotope analysis via GC-IRMS provides a highly specific means of identifying petroleum hydrocarbons and other organic compounds and connecting them to their original sources. Results presented here on refined gasoline-accelerant showed (i) consistency with a decade's worth of molecular isotope data on crude petroleum analysis, (ii) systematic alteration of accelerant components under middling conditions of combustion and evaporation, and (iii) significant alteration of the isotopic signal under more severe conditions that should be more understandable with further controlled fire experiments. Molecular isotope analysis has contributed and promises to contribute great and previously unconsidered understanding to the areas of petroleum and environmental geochemistry, product identification etc. Since most accelerants are composed of petroleum byproducts, it is inevitable that their isotopic fingerprints are left wherever an arsonist leaves splashes of the crime. This project is a first application of molecular isotopic techniques to solving problems of arson. Further research is warranted.

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