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Analysis of household ignitable liquids and their post-combustion weathered residues using compound-specific gas chromatography-combustion-isotope ratio mass spectrometry

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ABSTRACT

The continuing rise in home and vehicular arson cases involving the use of ignitable liquids continues to be an area of concern for criminal and civil investigators. In this study, the compound-specific δ^{13}C values of various components of four flammable household chemicals were measured using a single quadrupole mass spectrometer and an isotope ratio mass spectrometer as simultaneous detectors for a gas chromatograph. Whereas compound-specific carbon isotope ratios were able to discriminate between different sources of neat (pre-combustion) ignitable liquids, analyses of the post-combustion residues were problematic. Weathering caused by combustion resulted in a significant increase in the ^{13}C content of specific peaks relative to the neat liquids (i.e. less negative delta values) such that the isotopic comparison of pre- and post-combustion residues resulted in fractionation ranging from 0 to +10‰. Because of the current lack of understanding of isotopic fractionation during combustion, and because of problems encountered with co-elution in the more complex samples, compound-specific IRMS does not appear to be suitable for fire debris analysis. The comparison of non-combusted or non-weathered ignitable liquids is much more reliable, especially for relatively simple mixtures, and is best suited for exclusionary purposes until such time as a comprehensive database of samples is developed. Without a measure of the population variance, one cannot presently predict the false positive identification rate for the comparison of two ignitable liquids; i.e. the probability that two random ignitable liquid samples have indistinguishable isotope ratios.

1. Introduction

The current increase in home foreclosures in the United States, combined with the plunging real estate market, has lead to a significant rise in insurance fraud. According to Allstate Insurance Company spokesman Mike Siemienas, in California alone, the State's insurance division reports that the number of questionable residential fires in 2007 increased by 76% over 2006 [1]. Alabama's Chief Fire Inspector proposed a 400% increase in people using arson to collect insurance on houses that would otherwise be foreclosed [2]. According to the National Fire Protection Association, 20% of all fires are caused by arsonists [3]. Unfortunately, homes are not the only targets for arsonists as vehicular arson cases are also becoming more common [4]. Additionally, farmers have targeted valuable farm equipment in an attempt to collect on their insurance policies [3].

The hyphenated technique of GC–MS has long been a gold standard in forensic science and serves as a category A, or confirmatory method of analysis according to SWGDRUG [5], SWGFEX [6] and ASTM guidelines [7], and fire debris analysts have long-recognized the need to distinguish between different sources of evidentiary material [8–10]. The presence of background residues and pyrolytic products resulting from the combustion of synthetic materials are known to cause complications in data interpretation [11–13] and ASTM guidelines provide recommendations for interpreting fire debris samples to prevent misinterpretation [7].

Volatiles from freshly printed newspaper, newly lacquered furniture, paint spray, and paraffins in shoe polish can all be confused with mineral turpentine [14]. According to a study by Fernandes et al. [14], volatile residues in burnt household items such as printed materials, adhesives, finishes, flooring, etc. could be

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Table 1
Details of samples used for pair-wise comparisons of household chemicals.

	Goof-Off® sample A	Goof-Off® sample B	WD-40 sample A	WD-40 sample B	Lighter fluid sample A	Lighter fluid sample B	Turpentine sample A	Turpentine sample B
Source	Lilly Industries, Grand Rapids MI, USA		WD 40 Company, San Diego, CA, USA		The Kindsford Products Co., Oakland, CA, USA		WM Barr & Co., Memphis, TN, USA	PSC, Pearland, TX, USA
Lot #	E202E34904	A116E12215	4040M	2343G	M28185A1313	M25325B0834	804–166	804-01B
Mass/Vol	125 mL	474 mL	56 g	226 g	946 mL	946 mL	946 mL	946 mL

mistaken for commonly used fire accelerants. A study by Whyte et al. [15] showed that substrate porosity and accelerant volatility and the temperature of materials during combustion were key factors in determining the volatile organic profile of the fire debris. These authors also showed that the samples did not need to be fresh in order to be useful for analysis [15]. Another concern addressed by Ren and Bertsch [16] was the influence of water on the recovery of accelerants. Their results showed that water caused a slight shift toward larger molecular weight components. Similar effects are seen with natural and enhanced weathering, but the overall influence was only moderate. Furton and Almirall and coworkers have also provided a body of work examining different extraction procedures – such as solid-phase microextraction (SPME) – and analysis methods for the interpretation of ignitable liquid residues [13,17–20].

A complete study on the influence of factors such as type of accelerant used, type of burned material, time between starting and extinguishing of the fire and availability of air on the possibility of detection of accelerant traces was completed by Borusiewicz et al. [21]. Their results showed that among the investigated factors, the kind of burned material was the most important factor influencing the recovery of ignitable liquid residues. Pert et al. [22] provided a report on analytical techniques for ignitable liquid residues, and a complete review of fire investigation and ignitable liquid residue analysis was conducted by Sandercock [23]. Two- and three-dimensional gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) were the most commonly used instrument for the detection of trace residues.

Although gasoline accounts for most arson cases, we chose to study household chemicals and potential ignitable liquids outside the more common gasoline, light and medium distillates. Complex distillates, like gasoline, contain many variable components with which to discriminate between sources. For such complex samples, where chromatographic resolution of all the components is difficult and pattern matching is necessary, chemometric analysis of chromatographic data has proven to be quite reliable for classification and discrimination [14,24–29]. In an apparently simpler approach, Sigman's group has shown that a summed mass spectrum approach – essentially averaging mass spectra across an entire GC chromatogram and ignoring chromatographic information – can effectively classify ignitable liquids according to the widely accepted ASTM classification scheme [30–32].

Recently, Lee and coworkers reported using stable isotope ratios to discriminate gasoline samples on the basis of their origin [33]. They investigated the bulk and compound-specific isotopic compositions of gasoline produced by four oil companies in South Korea. However, when ignitable liquid residues are found on a suspect or in fire debris, it is useful to have a means to compare a known non-combusted sample to a questioned post-combusted sample. Several groups have investigated the effects of weathering on the compound-specific isotope ratios of compounds present in petroleum distillates and gasoline [34–40]. In addition to weathering, biodegradation has been shown to be involved with altering the relative distribution of components in petroleum distillates [41–45], and may or may not influence the isotope ratios [39,41,46]. Unfortunately, controlled weathering almost invariably involves longer evaporation times at lower temperatures than real fire conditions and in no way captures effects or sources of variance expected in realistic conditions, such as pyrolysis. To the best of our knowledge, such studies on compound-specific carbon isotope ratios have not been extended to weathering and fractionation induced via combustion [9].

The main goal of this work was to test the hypothesis that compound-specific isotope analysis can be used to predict the pre-combustion liquid sources from post-combustion residues. To test this hypothesis, we simulated fire debris by burning pieces of carpet that had been saturated in different ignitable liquids. We then used liquid extraction of the charred debris to collect any unburned residues and prevent any isotopic fractionation that might occur due to headspace sampling methods. As described by others [47–49], we split the GC effluent to analyze the separated components on two concurrent mass spectrometer systems: a single quadrupole mass spectrometer with an electron ionization source to confirm the identity of each compound in each sample and an isotope ratio mass spectrometer (IRMS) to simultaneously determine the δ^{13}C values of each compound in the same sample. Although dual detectors are not necessary, there are quality assurance, time and cost benefits to inject one sample and obtain results that simultaneously confirm the identity and provide the isotope ratios. Many laboratories function perfectly adequately by performing compound identification and compound-specific isotope ratio analyses on two different, but similarly configured, GC instruments. Two of the four ignitable liquids in this study are much simpler than typical petroleum distillate classes and do not have as many components for discrimination by chemometric methods. For these simple ignitable liquids especially, isotope ratio data can provide an additional layer of discrimination between liquid samples that is not afforded by other means. However, as our data shows, isotopic fractionation caused by weathering during a fire can complicate comparisons of pre-combustion liquids to post-combustion residues.

2. Materials and methods

2.1. Chemicals

Samples of common flammable household chemicals (other than class 2–3 distillates) including specialty solvents and lubricants were purchased from local home improvement stores and hardware stores in southeastern Ohio. The details

Table 2
Details of temperature ramps used for the separation of different samples.

	Program 1: Goof Off and WD-40	Program 2: lighter fluid and turpentine
Initial temperature	35 °C	35 °C
Initial hold time (min)	5	5
Temperature ramp 1	5 °C/min	5 °C/min to 90 °C
Temperature ramp 2	NA	20 °C/min
Final temperature	250 °C	270 °C
Final hold time (min)	5	1
Total run time (min)	53	26