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 $\delta^{13}C$ 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 $\delta^{13}C$ 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.

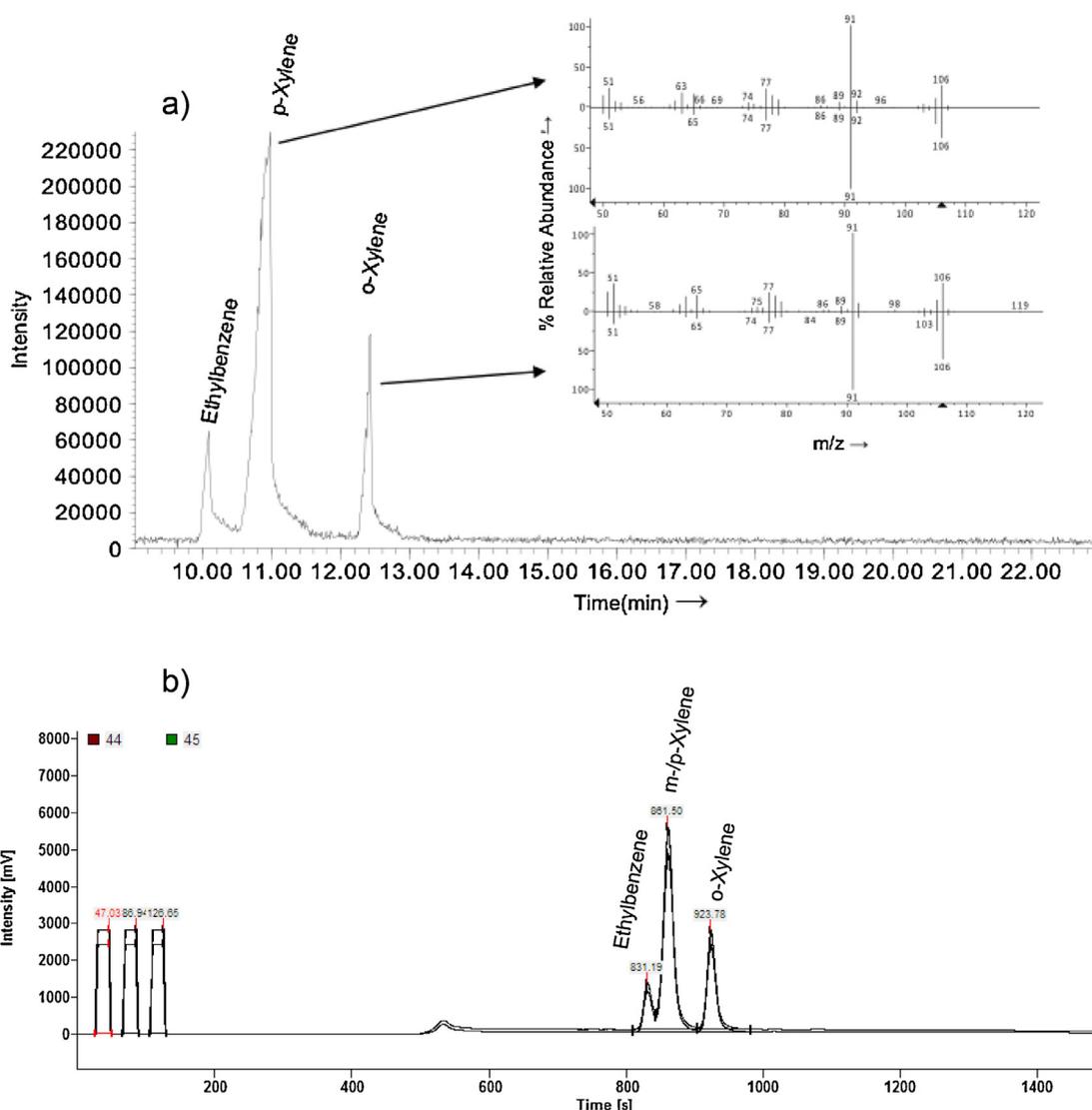|	Program 1: Goof Off and WD-40	Program 2: lighter fluid and turpentine
Initial temperature	35 °C	35 °C
Initial hold time (min)	5	5
Temperature ramp 1	5 °C/min	5 °C/min to 90 °C
Temperature ramp 2	NA	20 °C/min
Final temperature	250 °C	270 °C
Final hold time (min)	5	1
Total run time (min)	53	26

Fig. 1. Chromatograms of (a) TIC of Goof Off sample A obtained with the single quadrupole in EI mode, and (b) the concurrently acquired GC–IRMS chromatogram showing only m/z 44. Inserts show NIST head-to-tail spectra comparisons for two major peaks.

are provided in Table 1. Bulk $\delta^{13}C$ values were determined from replicate aliquots of the neat samples. For compound-specific $\delta^{13}C$ measurements, four replicate liquid samples were prepared from each sample by dissolving 1 mL of the liquid sample to 10 mL hexane (Sigma–Aldrich, St. Louis, Missouri). Both the Goof Off® and the WD-40 samples were further diluted 1:1000 using hexane.

2.2. Simulated fire debris

Carpet samples were prepared by placing 5 cm × 5 cm squares of carpet into separate glass jars. The Berber-style carpet used was of unknown origin and was tested for background levels of volatile organics. Analysis of unburned and burned carpet swatches revealed that peaks were not present at retention times or abundance levels that interfered with the IRMS analyses.

New carpet samples were then dipped into beakers containing the ignitable liquid samples. The excess liquid was drained from each sample and a Bunsen burner was used to ignite each carpet sample in a Pyrex container in a fume hood. Each sample was allowed to burn until it self-extinguished. All of the ignitable liquids produced fuel-rich yellow flames and left large soot deposits on the walls of the Pyrex jars. The backing of the carpet warped substantially during the tests and the fibers of the carpet were either consumed entirely or melted onto the backing. After cooling, approximately 2 cm × 2 cm pieces of the burned material were cut from the charred remains and placed into glass vials. The 2 cm × 2 cm charred remains were then extracted with 1.5 mL of hexane under sonication for 10 min. After sonication, the samples were vortexed for 5 min. After settling, the hexane layer was decanted, filtered with 4 µm filters, and placed in 1.5 mL autosampler vials for analysis.
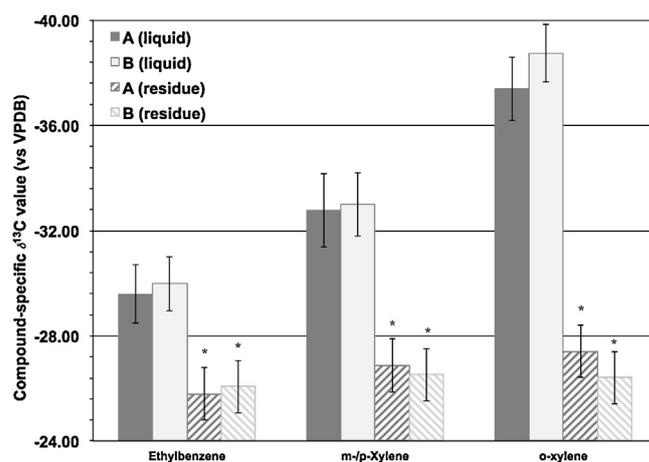

Fig. 2. Bar graph showing the mean $\delta^{13}C$ values for 3 major peaks for two Goof Off® samples (A & B) with error bars showing the 95% CI. Pre-combustion, $N = 20$ (5 subsamples × 4 replicate measurements of each sub-sample); post-combustion residue, $N = 3$ (1 sample × 3 replicate measurements). Isotope ratios were measured from the bulk samples and from residues of each sample extracted from post-combustion carpet swatches (labeled residue in the key). Compound specific $\delta^{13}C$ values that are significantly different (at $p < 0.05$) pre- and post-combustion are labeled with an asterisk.

2.2.1. Gas chromatography–mass spectrometry/isotope ratio mass spectrometry

GC–MS/IRMS analyses were performed using a single quadrupole mass spectrometer (HP5970B, Hewlett Packard (now Agilent Technologies), Santa Clara, CA, USA) and an isotope ratio mass spectrometer (Delta Plus Advantage, Thermo Finnigan (Now Thermo Scientific), Waltham, Massachusetts) used in combination with a gas chromatograph (Trace GC) equipped with an autosampler (AS3000), as described previously [50–52]. The GC column used was a DB-5, 30 m × 0.25 mm × 0.25 μm stationary phase (J & W Scientific, Folsom, CA, USA) and the effluent was split using a low-dead-volume X-connector so that ∼10% of the effluent flowed to the single quadrupole mass spectrometer for structural elucidation and ∼90% flowed to the IRMS for isotopic analysis. The combustion oven temperature was held at 940 °C and the reduction oven was held at 650 °C. Data acquisition was carried out using the standard software of the instrument, Isodat 2.0 Software.

Two different GC temperature programs were used depending on the analyte of interest. The details are provided in Table 2. For both temperature ramps, the injector temperature was set at 270 °C and the helium carrier gas flow rate was 1.5 mL/min. A volume of 1 μL was injected in split mode (10:1) using the autosampler. The auxiliary transfer line temperature was set at 280 °C. Electron ionization (EI) spectra were recorded with an electron energy of 70 eV in full scan mode over the range m/z 30–500 using the standard software for data analysis (ChemStation). Individual components in the chromatograms were determined by searching the 1995 NIST/EPA/NIH library. Identities were established manually from a combination of the Kovats retention indices and fragmentation pattern matching scores. The retention indices were established by injecting a standard mixture of n-alkanes (Sigma–Aldrich, St. Louis, MO, USA). The designation of specific compound identity to a peak in a complex mixture assumes that although co-elution can never be ruled out, one compound strongly dominated the mass spectra across each identified peak. In these cases, based on mass balance considerations, co-elution of a minor component at the same retention time as a major constituent is not expected to significantly influence the isotope ratio measurement of the major component of each peak.

2.2.2. Bulk isotope ratio mass spectrometry

Bulk carbon isotope measurements were made on precisely weighed samples (∼1 mg) that were placed in tin capsules in a Costech ECS 4010 elemental analyzer (EA) (Costech Inc., Winter Springs, FL, USA). The EA was coupled via a Conflo III interface to the Delta Plus Advantage. Data acquisition was carried out using Isodat 2.0 software, and extracted using Isodat 3.0. During both the GC and EA analyses, high-purity gases from Airgas (Parkersburg, WV) were used: >99.9999% He, 99.999% N_2, 99.997% CO_2, 99.999% O_2. The reference cylinder of CO_2 gas and the isotopic linearity of the instrument were determined from a two point calibration
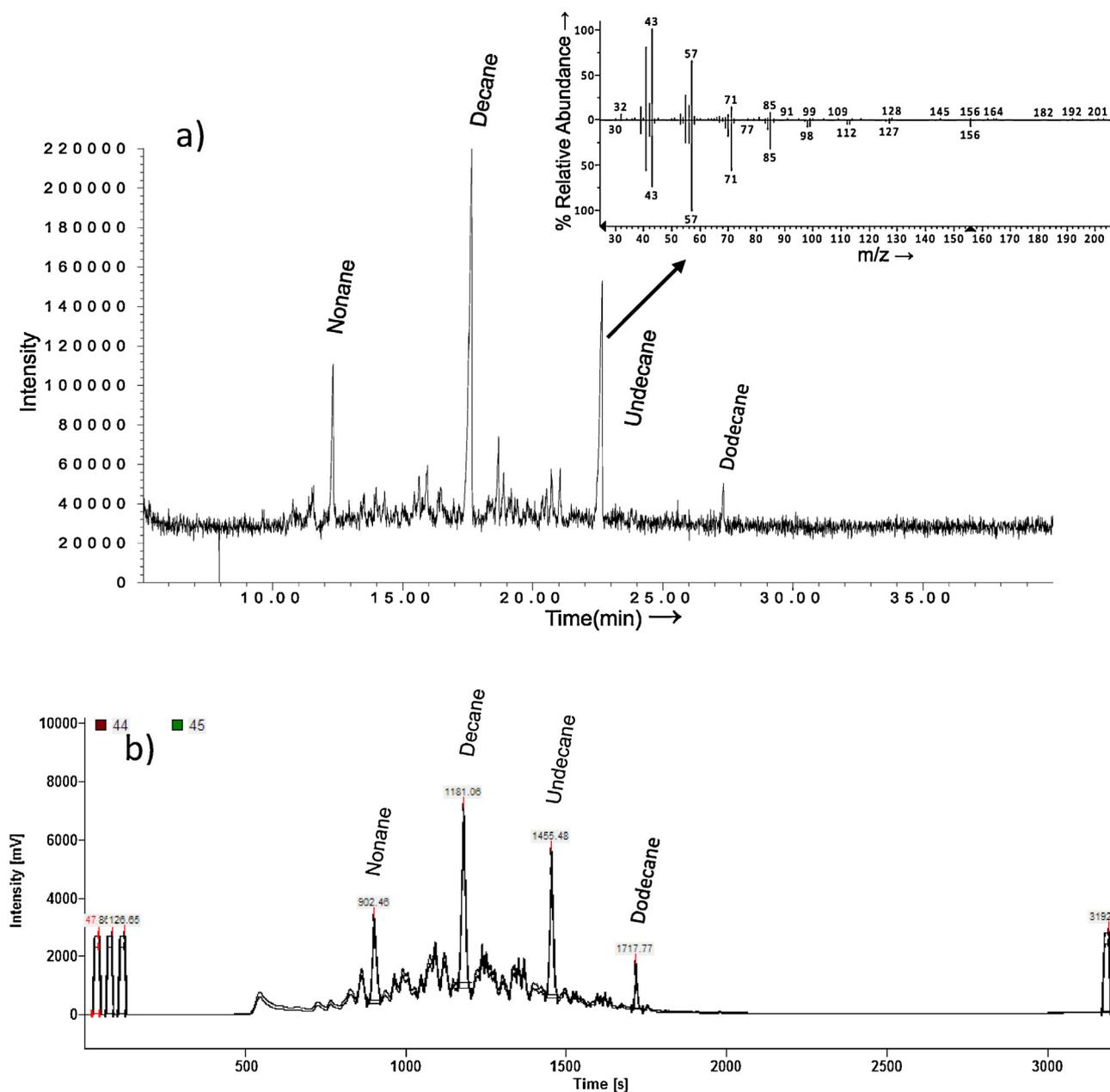

Fig. 3. Chromatograms of (a) TIC of WD-40 sample B obtained with the single quadrupole in EI mode, and (b) the concurrently acquired GC-IRMS chromatogram showing only m/z 44. Inserts show NIST head-to-tail spectra comparisons for each major peak.

curve using replicate analyses of United States Geological Survey standards USGS40 and USGS41 [53–55]. All ratios were corrected for ^{17}O in the standard manner using the Isodat 3.0 software.

2.2.3. Compound-specific isotope ratio mass spectrometry

In GC-C-IRMS mode, the reference gas CO_2 and isotopic linearity of the instrument were established using the identical treatment approach [56] in which a three point calibration curve of replicate measurements of three different isotope standards [54,55] were established in GC-C-IRMS mode. These standards included caffeine (IAEA-600, $\delta^{13}C = -27.77‰$), n-Pentadecane C_{15} (Chiron International Standards, Laramie, Wyoming, $\delta^{13}C = -30.22‰$) and n-Eicosane C_{20} (Chiron, $\delta^{13}C = -33.06‰$). Although these standards only covered a relatively narrow range of delta values (5.3‰), they effectively bracketed most of the sample measurements and provided a more robust normalization of the delta scale than could a one-point referencing strategy. This referencing approach for GC-C-IRMS mode is slightly different from our previous studies [51], but does not significantly affect the statistical outcomes of the previous or current results. Pulses of the same CO_2 reference gas during the analysis of each sample provided the reference ratios from which the compound-specific isotope ratios could be compared. All ratios were corrected for ^{17}O in the standard manner and were calculated using the Isodat 3.0 software.

To improve the accuracy and precision of the measurements and eliminate any error due to misbalance, each sample was adjusted (via dilution) so that the CO_2 signal amplitudes for the relevant analytes were within a factor of 4 of the CO_2 reference gas [57].

3. Results and discussion

3.1. Goof Off®

The Goof Off® samples had three distinctive chromatographic peaks and each component was used independently to establish possible differences in the $\delta^{13}C$ values of the samples. The single quadrupole confirmed the identity of the three resolvable peaks as ethylbenzene (peak 1), m-/p-Xylene (peak 2), and o-Xylene (peak 3) using a combination of the NIST database matching (as shown in Fig. 1a) and the retention indices. Unfortunately, the Goof Off® samples were taken without consent by a third party before bulk isotope measurements could be made.

A typical chromatogram obtained on the IRMS is shown in Fig. 1b. To establish the sources of variance (random error) in the measurements, five replicate aliquots of each sample were each analyzed four times ($N = 20$ for each sample). One-way analysis of variance (ANOVA) tests were performed to compare the means of the within-sample and between-sample variation of the $\delta^{13}C$ values for each peak. No significant differences were found for within-sample means. The within-sample $\delta^{13}C$ values for each component were then pooled to enable a T-test comparison between the two samples. The average (pooled) $\delta^{13}C$ values and error (95% CI) for each component in sample A were $-29.6 \pm 1.1‰$ (ethylbenzene), $-32.8 \pm 1.4‰$ (m-/p-xylene), and $-37.4 \pm 1.2‰$ (o-xylene). The $\delta^{13}C$ values and 95% CI for each peak in sample B were $-30.0 \pm 1.0‰$ (ethylbenzene), $-33.0 \pm 1.2‰$ (m-/p-xylene), and $-38.8 \pm 1.1‰$ (o-xylene).

Post hoc ANOVA tests, including Tukey's honestly significance difference test (Tukey's HSD), revealed no significant differences between any pair-wise comparison of the peaks in samples A and B. Fig. 2 is a bar graph of the pooled mean $\delta^{13}C$ values and the 95% CI for each component in the two samples of Goof Off®. The error bars show 95% confidence intervals (CI). After combustion, the weathered samples provided isotope ratios that were approximately 4, 6, and 11‰ less negative than the neat liquid for ethyl benzene, m-/p xylene and o-xylene, respectively. A paired T-test was conducted to test the correlation between the mean isotope ratios of each compound before and after combustion. The results showed a significant difference ($P = 0.004$, two-tailed) between the post- and pre-combustion means, with a mean enrichment of ^{13}C of $7.2 \pm 3.5‰$ (95% CI). However, the correlation co-efficient between the pre- and post-combustion means was 0.75 and was not significant at the 95% confidence interval ($p = 0.09$, $N = 6$). The r-squared value of

0.56 indicates that the isotope ratio of an unburned compound explains approximately 56% of the variance of the isotope ratio of the burned compound.

The confidence interval for the degree of fractionation in the pair-wise comparison was 3.9–10.6‰ (95% CI). The large confidence interval ($\pm 3.5‰$, 95% CI) for the change in isotope ratio during combustion therefore provides a very large range of possible pre-combustion values that could have provided a certain post-combustion value. This variance would make it very unlikely that one could link a post-combustion residue to a specific pre-combustion liquid, unless the isotope ratios of the pre-combustion compounds in the comparison samples were different by more than 7‰. This unlikely scenario makes it difficult to expect that a questioned post-combustion residue could be linked reliably to a specific liquid using compound specific isotope analysis.

3.2. Lubricant WD-40

WD-40 samples A and B had bulk $\delta^{13}C$ values of $-27.4 \pm 0.2‰$ (95% CI, $N = 5$) and $27.4 \pm 0.3‰$ (95% CI, $N = 5$). These bulk isotope ratios are not significantly different ($p = 0.76$, 2-tailed T-test). The samples are therefore indistinguishable based on the bulk carbon isotope ratios alone. On the GC, each sample had four major peaks eluting at 902, 1180 s, 1450 s, 1719 s, and many minor peaks. Unresolved and low-intensity peaks (<1000 mV) were not used for isotope comparisons [57]. The retention indices and single quadrupole EI fragmentation patterns confirmed the identity of these three peaks as nonane (peak 1), decane (peak 2), and undecane (peak 3), and dodecane (peak 4) as shown in Fig. 3a. The concurrent profile for m/z 44 on the IRMS is shown for comparison in Fig. 3b. Sample A contained a wider n-alkane distribution, including more dodecane and tridecane, so was actually readily distinguishable from sample B based on the n-alkane distribution alone. However, we continued with the isotopic comparison for evaluative purposes of this project.

Five replicate aliquots of each liquid sample were each analyzed four times each ($N = 20$ for each sample). One-way ANOVA tests were performed to compare the means of the within-vial and between-vial variation of the $\delta^{13}C$ values for each peak for each sample. Replicate analyses of the sub-samples showed that the within-vial means were not significantly different at the 95% CI, thereby indicating that the majority of the random error stems from instrumental and data manipulation sources of error, not in
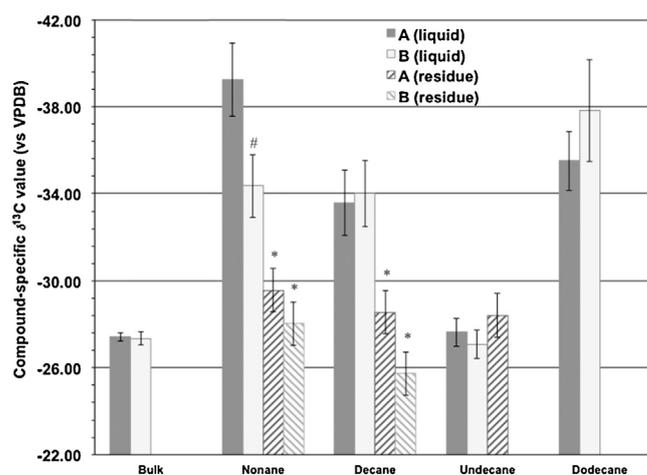

Fig. 4. Bar graph showing the mean $\delta^{13}C$ values for 3 major peaks for two WD-40 samples (A & B) with error bars showing the 95% CI. $N = 20$ (5 subsamples × 4 replicate measurements of each sub-sample). Compound-specific means that are significantly different between A and B at $p < 0.05$ are labeled with a hash symbol. Compound specific $\delta^{13}C$ values that are significantly different (at $p < 0.05$) pre- and post-combustion are labeled with an asterisk.

the sample. The $\delta^{13}C$ values for each within-sample compound were then pooled. The pooled $\delta^{13}C$ values and 95% CI ($N = 20$) for each major component in sample A were $-39.2 \pm 1.7‰$ (nonane), $-33.6 \pm 1.5‰$ (decane), $-27.6 \pm 0.6‰$ (undecane), and $-35.5 \pm 1.4‰$, respectively. The $\delta^{13}C$ values and 95% CI ($N = 20$) for each peak in sample B were $-34.4 \pm 1.4‰$ (nonane), $-34.0 \pm 1.5‰$ (decane), $-27.1 \pm 0.7‰$ (undecane), and $-37.8 \pm 2.3‰$, respectively. The relative precision in replicate analyses is somewhat worse than for Goof Off® and turpentine, presumably because of inadequate peak separation. Co-elution is more likely around the nonane and decane peak relative to the undecane peak, which could explain the better precision for C_{11}, but this does not explain the poor precision for dodecane, which is fairly well resolved.

A bar graph comparing the sample means and 95% CIs for samples A and B before and after combustion are shown in Fig. 4. One-way ANOVA comparisons of uncombusted within-sample and between-sample comparisons provided significant differences for nonane and undecane. However, post hoc Tukey's HSD analysis showed that only undecane provided consistent significant differences between every pair-wise comparison between each of the sub-samples (vials) of samples A and B. For the two liquid samples of WD-40 studied, compound-specific IRMS (of undecane) is therefore able to exclude the two samples as common in origin whereas bulk IRMS could not distinguish between these two samples. Because only three variables (peaks) were compared in this application, and because only one of the variables (undecane) was the major discriminating variable, principal component analysis was not attempted. Presumably, if more variables were considered for comparison, multivariate analysis could be a more valuable tool for separating the samples.

After extracting residues of samples A and B from post-combusted carpet samples, nonane shows a significant increase (i.e. less negative) in $\delta^{13}C$ values for both samples. The post-combusted isotope ratio values of nonane were $-29.6 \pm 0.8‰$ for sample A and $-28.0 \pm 0.5‰$ for sample B ($n = 3$ for each sample), which represents a change of +9.7 and +6.3‰, respectively, relative to the pre-combusted samples. Decane underwent similarly large fractionation of +10.7‰ and +8.6‰ for samples A and B, respectively.
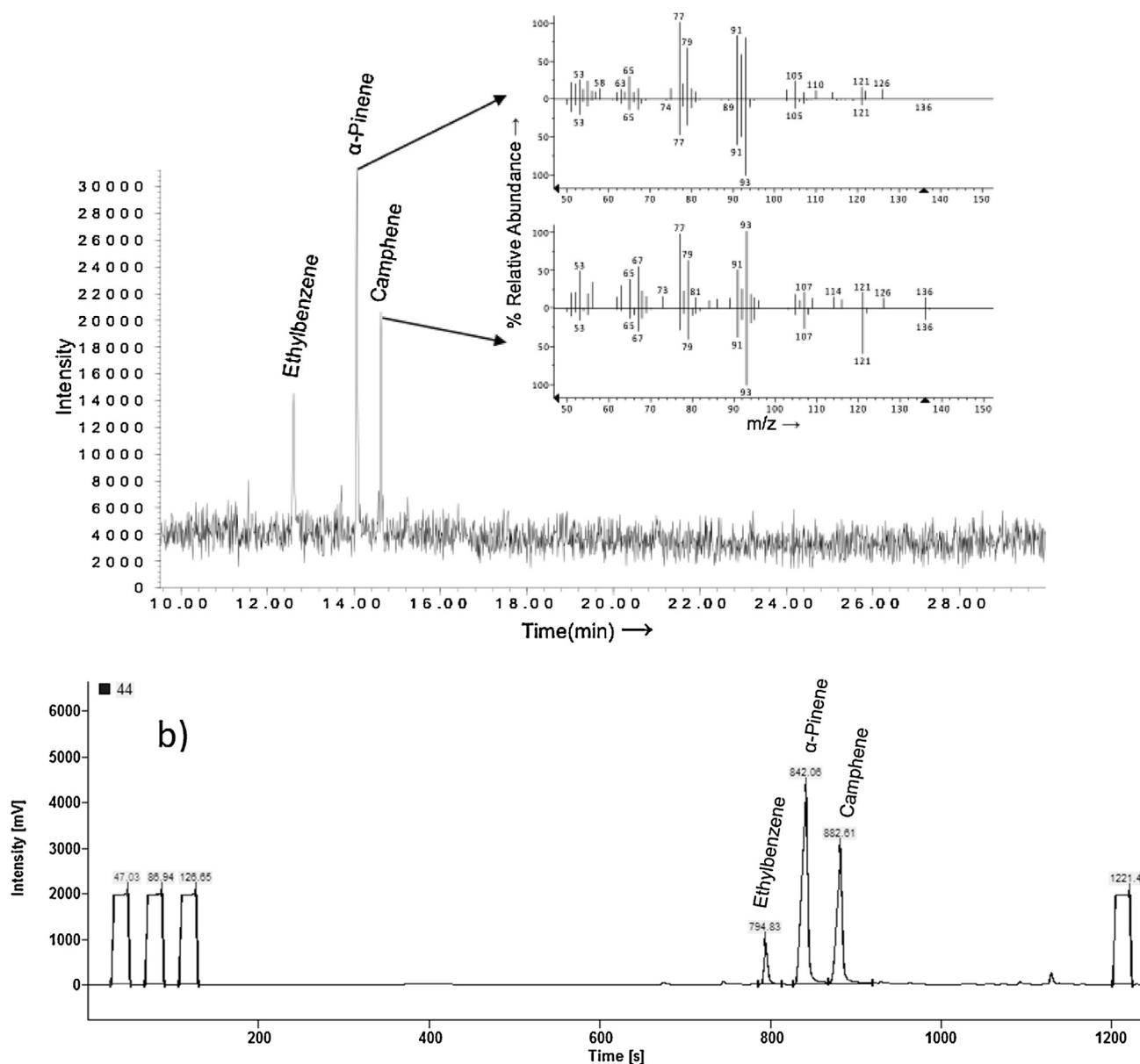

Fig. 5. Chromatograms of (a) TIC of turpentine sample B obtained with the single quadrupole in EI mode, and (b) the concurrently acquired GC-IRMS chromatogram showing only m/z 44. Inserts show NIST head-to-tail spectra comparisons for each major peak.

On the other hand, undecane did not undergo any significant fractionation following combustion. Dodecane was not quantifiable the post-combustion residues. The large range of fractionation (0–10.7‰) makes it difficult to image a scenario in which post-combustion residues in a complex mixture such as a medium petroleum distillate (like WD-40) could be reliably linked to a given source.

3.3. Turpentine

Turpentine samples A and B had bulk $\delta^{13}C$ values of $-31.6 \pm 0.4‰$ (95% CI, $N = 5$) and $-31.4 \pm 0.2‰$ (95% CI, $N = 5$). These samples are not significantly different ($p = 0.41$, two-tailed T-test) and therefore indistinguishable based on the bulk carbon isotope ratios alone. The turpentine samples had three major constituents which were identified as ethylbenzene (peak 1), α-pinene (peak 2), and camphene (peak 3), as seen in Fig. 5a. As before, one-way ANOVA tests were performed to compare the means of the within-vial and between-vial variation of the $\delta^{13}C$ values for each peak. Again, no significant differences were found for within-sample means so all the within-sample $\delta^{13}C$ values were pooled.

The $\delta^{13}C$ values and 95% CI for each component in turpentine sample A were $-34.3 \pm 0.5‰$ (ethylbenzene), $-29.2 \pm 0.2‰$ (α-pinene), and $-31.3 \pm 0.4‰$ (camphene). The $\delta^{13}C$ values and 95% CI for each peak in sample B was $-33.4 \pm 0.6‰$ (ethylbenzene), $-27.2 \pm 0.2‰$ (α-pinene), and $-29.0 \pm 1.3‰$ (camphene). The means and confidence intervals are plotted in Fig. 5. One-way ANOVA was performed on all three peaks of the two samples of turpentine to establish the sources of variance and any significant differences between the sample means. For between-sample ANOVA, all three peaks were significantly different between the two samples ($p = 0.025$, $<1 \times 10^{-10}$ and 0.002, respectively), as displayed in Fig. 6.

Following the combustion procedure, α-pinene was the only constituent to be recovered consistently from each of the replicates. The mean $\delta^{13}C$ values and 95% CI for α-pinene in post-combustion residues were $-28.7 \pm 0.5‰$ and $-26.4 \pm 1.2‰$ for samples A and B, respectively. Assuming equal variances, a two-tailed T-test between the sample means of the liquid and post-combustion residues of α-pinene showed no significance difference a the 95% confidence interval for sample A ($p = 0.06$) and a significant difference for sample B ($p = 0.003$), although they showed similar fractionation effects. Combustion had a much smaller size-effect on the enrichment of ^{13}C in α-pinene here than for the various compounds in Goof Off® and WD-40. For example, the average fractionation for α-pinene was $+0.5‰$ for sample A (not significant) and $+0.7‰$ for sample B (significant at $p = 0.003$). These results indicate that post-combustion residues for α-pinene relatively enrichment in ^{13}C, which my or may not be significantly different from the liquid origin.
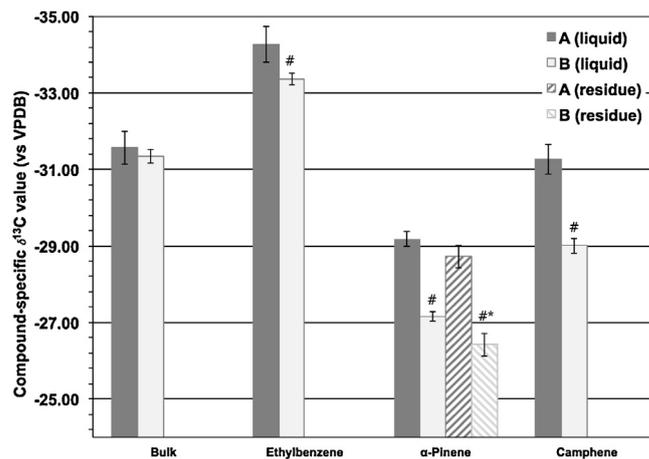

Fig. 6. Bar graph showing $\delta^{13}C$ for 3 peaks from turpentine samples A & B with error bars showing the 95% CI ($N = 12$). Compound-specific means that are significantly different at $p < 0.05$ are labeled with a hash symbol. Compound specific $\delta^{13}C$ values that are significantly different (at $p < 0.05$) pre- and post-combustion are labeled with an asterisk. Some residues were of too low abundance to provide reliable isotope ratio measurements.

3.4. Lighter fluid

Similar to WD-40, charcoal lighter fluid samples A and B also had three major peaks as well as numerous other minor peaks. We did not evaluate peaks with an intensity less than 1000 mV on the IRMS. The results are shown in Fig. 7. Three major peaks are identified as nonane, decane, and undecane, but undecance provided standard deviations on the order of 2–3 per mil within each sample so was not used in the comparisons. The $\delta^{13}C$ values and 95% CI for each component in sample A were $-25.1 \pm 1.2‰$ (nonane), $-23.1 \pm 0.7‰$ (decane). The $\delta^{13}C$ values and 95% CI for each peak in of sample B was $-26.0 \pm 1.2‰$ (nonane), $-23.2 \pm 0.7‰$ (decane). The results are plotted in Fig. 8. Peak intensities for the post-combustion residues were too small for reliable isotope ratio measurements to be conducted, so are not plotted. One-way ANOVA tests were performed on the two peaks of the two samples of charcoal lighter fluid using the sample as the fixed factor. The results indicated that neither the bulk, nonane nor decane values are significantly different between the two samples at the 95% confidence interval. However, more conventional GC-FID or GC–MS methods could easily differentiate the two samples because of the visually obvious difference in the relative abundance of the various n-alkanes. These results indicate that complex sample such as lighter fuels and WD-40 are difficult to analyze using compound-specific isotope ratio mass spectrometry, and that determining or excluding common origin is
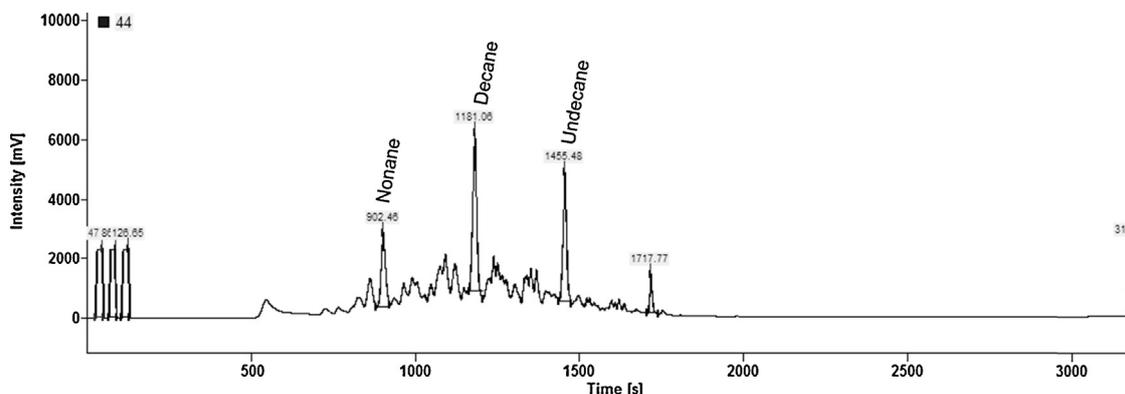

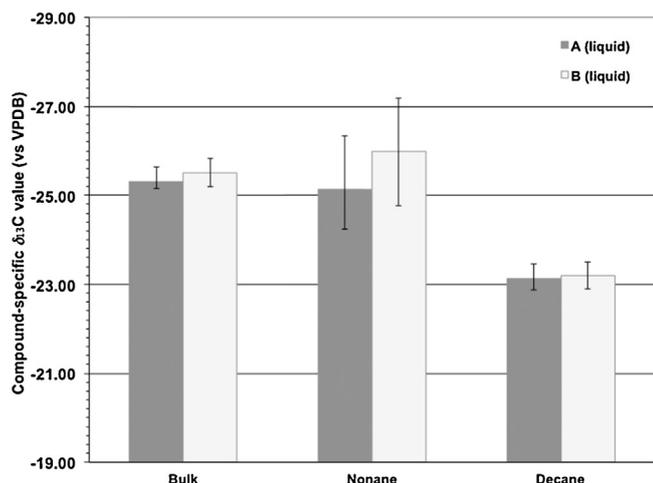**Fig. 7.** GC-IRMS Chromatogram showing m/z 44 of charcoal lighter fluid.

Fig. 8. Bar graph showing $\delta^{13}C$ for 3 peaks from charcoal lighter fluid samples A & B with error bars representing a 95% C.I. Residues were of too low abundance to provide reliable isotope ratio measurements.

less reliable than would using conventional pattern-recognition algorithms based on easy-to-perform GC-FID or GC/MS.

3.4.1. Fractionation prediction model

A regression analysis was performed on all the pair-wise measurements that were available for the non-combusted liquid and post-combustion residues. The comparison included six compounds from Goof Off® samples (three from sample A and three from sample B), five compounds from WD-40 (three from sample A and two from sample B), and two compounds from turpentine (α-pinene in sample A and B). Compounds from samples A and B were considered independent measurements because the compounds often started with significantly different isotope ratios. Thirteen pair-wise comparisons were available for the analysis and are plotted in Fig. 9. A linear regression analysis shows a very weak correlation of 0.06 ($R^2 = 0.04$), which did not exceed significance at the 95% CL. Despite the weak correlation, a two-tailed paired t-test did show a significant difference between the pre- and post-combustion residues ($p < 0.0003$). The average degree of fractionation was 5.6‰ with a 95% confidence interval of 2.4‰ ($N = 13$). The post-combustion residues were exclusively less negative than the pre-combusted compounds, in agreement
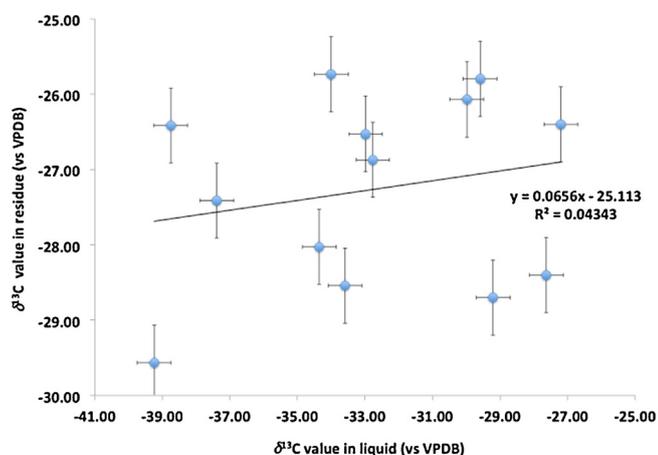
with almost all previous evaporation fractionation studies, which show enrichment in ^{13}C in the residues. These results indicate that there is no reliable model by which one can predict the degree of fractionation of a specific compound during relatively realistic combustion conditions. Whereas more controlled weathering experiments apparently show a stronger correlation and better prediction models [34–37,40,41], the simulated fire conditions tested here seem to provide many additional sources of variance that have not yet been understood in a predictable sense.

4. Conclusions

Our results on the effect of combustion on the shift in compound-specific $\delta^{13}C$ values are qualitatively similar to the carbon isotope fractionation observed during controlled weathering experiments by different groups [34–37,40,41]. In our experiments, compound-specific changes in $\delta^{13}C$ values from 0 to +10‰ were observed during the combustion procedure, depending on the liquids and compounds studied. In no cases were post-combustion residues of a given compound (or peak) isotopically enriched in ^{12}C relative to the liquid sample for the same compound (or peak). In the absence of additional controlled studies, the variance in the degree of fractionation of different compounds during combustion makes the comparison of liquid samples to real post-combustion residues presently unreliable. Whereas compound-specific isotopic analysis has the ability to distinguish between different sources of ignitable liquids, the same is not necessarily true for post-combustion residues. Conventional pattern-recognition and chemometric approaches are therefore considerably more reliable for the comparison of pre- and post-combustion or weathered ignitable liquids [7,26,31,58]. This work provides a current limitation in the application of IRMS to fire debris, which may be overcome by better chromatographic resolution, better sensitivity, or a better understanding of chemical-specific isotopic fractionation caused during pyrolysis and combustion.

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Fig. 9. Scatter plot of $\delta^{13}C$ values of seven different compounds in five different liquid samples showing the lack of correlation between pre- and post-combustion isotope ratios. $N = 20$ in liquid samples, $N = 3$ in post-combustion residues. Error bars show the average pooled 95% CI.

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