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Detection and Classification of Ignitable Liquid Residues in the Presence of Matrix Interferences by Using Direct Analysis in Real Time Mass Spectrometry^{†,‡}

ABSTRACT: Conventional Gas Chromatography-Mass Spectrometry (GC-MS) methods for the analysis of ignitable liquids (ILs) are usually time-consuming, and the data produced are difficult to interpret. A fast IL screening method using direct analysis in real time mass spectrometry (DART-MS) is proposed in this study. GC-MS, QuickStrip DART-MS, and thermal desorption DART-MS methods were used to analyze neat ILs and thermal desorption DART-MS without extraction was used to analyze ILs on five substrates (e.g., carpet, wood, cloth, sand, and paper). Compared to GC-MS, DART-MS methods generated different spectral profiles for neat ILs with more peaks in the higher mass range and also provided better detection of less volatile compounds. ILs on substrates were successfully classified (98 \pm 1%) using partial least squares discriminant analysis (PLS-DA) models based on thermal desorption DART-MS data. This study shows that DART-MS has great potential for the high-throughput screening of ILs on substrates.

KEYWORDS: forensic science, direct analysis in real time mass spectrometry, ignitable liquids, arson, classification, chemometrics

The identification of ignitable liquids (ILs) is significant in arson investigations and is typically performed using gas chromatography-mass spectrometry (GC-MS) as described in the ASTM Standard Method E1618-14 (1). However, differences in chromatographic conditions and columns can lead to variations in retention times for ILs from one laboratory to another (2), making interlaboratory comparison of GC-MS profiles challenging. Also, the nature of electron ionization tends to fragment the compounds, so the molecular ions of larger molecular weight compounds are usually low or even unobservable in the GC-MS spectra. In addition, compounds in the same category (e.g., alkane, alkene, and aromatic) produce similar mass spectra by GC-MS because of similar fragmentation patterns generated by the electron ionization source.

The total ion spectrum (TIS), which is the averaged mass spectrum across the chromatographic profile, has been

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systematically evaluated by Sigman and coworkers for the classification and discrimination of IL samples with different chemometric methods (2–5). TIS eliminates the influence of retention time shifts and reduces data size thus facilitates interlaboratory data comparison. Adutwum et al. introduced the segmented total ion spectrum (STIS) for analysis of ILs and demonstrated improved prediction accuracies relative to TIS (6). The success of using TIS or STIS data for IL classification indicates that mass spectrometry without chromatographic separation may provide sufficient information for the detection of ILs if the mass flux of material does not saturate the MS detection system.

Another crucial step when using conventional methods for IL residue identification on substrates (e.g., carpet, wood, cloth) is sample preparation. Standard methods for extraction of ILs from substrates prior to GC-MS analysis can be time-consuming. For example, the passive headspace concentration with activated charcoal method (ASTM E1412) is commonly used in forensic laboratories. The activated carbon strip is suspended into the headspace of a sealed heated can for 16–18 h (7). The compounds need to be recovered completely for pattern matching of the extracted IL with reference IL. Using this approach, certain compounds may not be extracted as well as others because of differences in their volatility, potentially skewing the IL pattern and making it difficult to compare it to a reference IL (1).

Solid phase microextraction (SPME) is an alternative extraction method, but the resulting IL residue patterns are dependent on factors such as extraction temperature, time, and SPME fiber coating type and thickness (8). For example, extraction temperature is critical because lower temperatures may be insufficient to volatilize less volatile compounds and higher temperatures may result in a significant discrimination against highly volatile

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compounds. The SPME extraction takes approximately 0.5–1 h depending on the heating method and the amount and type of matrix present in the can. For best results, the parameters should be optimized based on the type of IL or substrates, or both.

A simple and rapid screening method for the detection of IL residues is desirable in a forensic setting and could be achieved by using an ambient ionization method like direct analysis in real time mass spectrometry (DART-MS). DART-MS has been used for the analysis of petroleum products (9,10) and has demonstrated great potential for screening ILs because of several important features: minimal sample preparation, good sensitivity for both volatile and nonvolatile compounds, easy data interpretation (primarily $[M+H]^+$ ions), versatile modules for different matrices and types of samples, and relatively fast sample analysis (11). Moreover, in our laboratory, we recently found that DART-MS has the additional capability of detecting polymeric detergent additives in gasoline fuel which were not observed in GC-MS results (10).

Several DART-MS set-ups are available to meet the needs of analyzing samples in various forms, including QuickStrip, tweezer, and thermal desorption modules (Fig. 1*A* and *B*). For liquid samples, QuickStrip DART-MS has been shown to be an effective method for the analysis of neat ILs such as gasoline with good repeatability (10). Thermal desorption DART-MS has been used for the detection of drugs and metabolites (12,13), explosives (14,15), and automotive paints (16). Trade-offs of DART-MS compared to GC-MS are the loss of chromatographic information, potential ion suppression for MS detection, and increased complexity of mass spectral data. However, a temperature gradient can be applied in thermal desorption DART-MS which may preserve the information about the volatility of compounds in ILs and decrease the complexity of mass spectrum.

The objectives of the present study were to (i) examine the performance of thermal desorption DART-MS for the analysis of neat ILs and ILs on substrates (carpet, wood, sand, paper, and T-shirt material); (ii) compare results of thermal desorption DART-MS analysis to data generated using conventional GC-MS as well as QuickStrip and tweezer modules with DART-MS; and (iii) use partial least squares discriminant analysis (PLS-DA) on thermal desorption DART-MS data to classify ILs on different substrates.

Materials and Methods

Materials

Ignitable liquids including kerosene, diesel, japan drier, charcoal starter fluid, naphtha, prestain, lighter fluid, and unleaded gasoline were purchased from various local suppliers and gas stations. High point chestnut plank flooring and 100% PureColor[™] solution dyed BCF polyester carpet were acquired from a local home improvement store. Sand (50–70 mesh particle size) and carbon disulfide were purchased from Sigma-Aldrich, St. Louis, MO.

Instruments and Parameters

For DART-MS experiments in this study, a DART ion source (IonSense, Inc., Saugus, MA) was coupled to a Thermo LTQ XL mass spectrometer (Thermo Scientific, San Jose, CA). The ionization gas was helium for all the DART-MS experiments. The DART gas heater was set to 350°C, and the mass spectra were collected in an m/z range of 50–1000 in positive-ion mode. Quick-Strip, tweezer, and thermal desorption modules were used in this study for DART-MS analysis. For QuickStrip DART-MS analysis, an automated sample introduction apparatus consisting of a Linear Rail Enclosure that holds QuickStrip[™] sample cards was used (IonSense, Inc., Saugus, MA). QuickStrip[™] Sample Cards were purchased from IonSense, Inc. (Saugus, MA). The preloaded "OuickStrip" method was used: Heater Wait Time 30 sec; Sample Speed 0.5 mm/sec; Contact Closure Delay 5 sec; Standby Temperature 345°C. The tweezer module was set up by replacing the QuickStrip sample card holder with a tweezer holder. Most of the DART-MS parameters were the same as the QuickStrip module except the gas heater temperature which was set to 200°C. For thermal desorption analysis, the IonRocket temperature gradient system provided by BioChromato, Inc. (San Diego, CA) was used for DART-MS. The temperature program used was 25°C initial, hold for 1 min, ramp at 100°C/min to 600°C, hold for 1 min.

For GC-MS analysis, a Shimadzu QP2010S (Shimadzu, Kyoto, Japan) equipped with an auto sampler was used. The GC injector was set at 280°C and the analytes were separated on a SHRCI-5MS, 30 m × 0.25 mm ID capillary column chemically bonded with 5% diphenyl/95% dimethyl polysiloxane at 0.1 μ m film thickness (Shimadzu Scientific Instruments Inc. Columbia, MD). A constant helium flow of 1 mL/min was used, of which a fixed split of approximately 1:50 entered the column. The column temperature was programmed as follows: 50°C, hold for 1 min, ramp at 20°C/min to 280°C, hold for 10 min. The transfer line and ion source temperatures were both maintained at 280°C. Full scan mode was selected for the mass spectrometer and the scan range was from *m/z* 30 to 350.

Analysis of Neat ILs

Neat ILs were analyzed by GC-MS, QuickStrip DART-MS, and thermal desorption DART-MS and the mass spectral profiles



FIG. 1—Sample introducing strategies of the direct analysis in real time mass spectrometry (DART-MS) in this study. (A) QuickStrip module (Tweezer module if the sample card holder is replaced by tweezer holder); (B) thermal desorption module.

using these methods were compared. An aliquot of 20 μ L of IL was mixed with 1 mL of carbon disulfide before GC-MS analysis. For QuickStrip DART-MS, 3 μ L liquid samples were spotted onto QuickStripTM sample cards in triplicate. At least one blank spot on each sample card was analyzed for mass spectral background subtraction. For thermal desorption DART-MS, 3 μ L liquid samples were loaded onto disposable copper sample pots which were then place on the heating block. A glass T-junction was positioned over the copper sample pot, and the compounds were thermally desorbed from the samples and then analyzed directly by DART-MS.

Analysis of ILs on Substrates

Ignitable liquids on substrates were analyzed using both the tweezer and thermal desorption modules with DART-MS, and the resulting mass spectra were compared to each other and to spectral profiles of neat ILs. Five substrates, including carpet, wood flooring, sand, paper, and T-shirt material (97% cotton and 3% elastane) were tested. Samples were cut and placed directly into the reservoir of the copper sample pot for thermal desorption analysis, except for wood flooring samples. For these, Q-swabs were used to collect the residue of ILs from the surface of the flooring, and then the tips were cut off and analyzed in the copper sample pots. When using the tweezer module, each sample was held by a clean tweezer which was then placed onto the tweezer holder for DART-MS analysis.

Data Format

For data collected by DART-MS analysis with QuickStrip and tweezer modules, the background spectrum was first subtracted then the average mass spectrum for each sample was exported to Excel with Xcalibur 2.1 software (Thermo Scientific, Waltham, MA). For data collected by thermal desorption DART-MS analysis, the average mass spectra of desired time/temperature windows were exported to Excel without background subtraction. The data were binned by m/z from 50 to 1000 with 0.5 increments and then normalized to unit vector length (17) for further chemometric analysis in SIMCA-P (version 13.0 Umetrics, Sweden). MATLAB R2017a (MathWorks Inc., Natick, MA) was used for validation of the chemometric models.

Results and Discussion

Source Temperature Effect for DART-MS with QuickStrip Module

Source temperature is an important factor that affects ionization efficiency when using the DART ion source. The hot metastable helium gas stream vaporizes the compounds on the QuickStrip sample cards and then ionizes them. Therefore, with higher temperatures of the helium gas, there is an increased chance of detecting less volatile compounds. However, if the temperature is too high, some compounds may be vaporized too fast and enter into the air instead of being captured by the mass spectrometer. In a preliminary study, 150, 250, 350, and 450°C temperatures were tested for all different ILs. The 350°C temperature was found to provide the highest response based on total ion current (TIC) and was adopted for analysis of all samples in this study by QuickStrip DART-MS.

However, it is interesting to note how the source temperature affected the mass spectral profile for certain ILs. For example, n-alkanes (C₈-C₁₆), aromatics, chlorinated alkanes, and glycol ethers were found to be the major components in Crown paint thinner samples based on GC-MS data. The abundance of these peaks in DART-MS spectra were dependent on the temperature used for the DART ion source (Fig. 2). The peak clusters for xylenes (e.g., m/z 107.0, $C_8H_{11}^+$) and N-methylanilines (e.g., m/z122.1, $C_8H_{12}N^+$ and m/z 136.1, $C_9H_{14}N^+$) were the dominant peaks when the ion source temperature was set to 150°C in Crown paint thinner samples. As the ion source temperature increased, the relative abundance of these peaks decreased, but simultaneously less volatile compounds were observed. Chlorinated alkanes (e.g., m/z 162.1, $C_0H_{10}Cl^+$; m/z 176.1, $C_{10}H_{21}Cl^+$; m/z 190.2, $C_{11}H_{23}Cl^+$; and m/z 204.2, $C_{12}H_{25}Cl^+$) were the major ions in DART-MS spectra when the ion source temperature was increased to 350°C. Additionally, glycol ethers (e.g., m/z 299.1, C₂₀H₄₃O⁺) appeared to be significant ions in the mass spectral profiles when the temperature was increased to 450°C. These data indicate that the ion source temperature may be optimized in consonance with the ions of interest.

Comparison of DART-MS and GC-MS Data for Neat IL Analysis

Comparable results were achieved for all of the ILs in the study when comparing GC-MS and DART-MS mass spectral profiles. The DART-MS spectral profiles were very different from GC-MS spectral profiles and more characteristic ions were found in thermal desorption DART-MS spectra than in Quick-Strip DART-MS spectra. As an example, based on the GC-MS data, kerosene contained mainly alkanes with some minor aromatic and oxygenated components. The average mass spectrum for kerosene GC-MS data was dominated by m/z 43, 57, 71, 85, etc., which are common alkane ions observed in ILs (18). A representative mass spectrum for kerosene analyzed by DART-MS with QuickStrip module is shown in Figure S1. In comparison with GC-MS, more peaks can be observed in the higher mass range, for example, m/z 189.1, 230.2, 244.2, 263.2, 295.2, 431.4, and 589.6. A group of peaks, for example, *m/z* 176.1, 190.1, 204.2, 218.2, 232.2, and 246.2 are different by 14 Da (-CH₂), which is the common repeating unit for alkane, alkene, and aromatic compounds in ILs.

A representative thermal desorption DART-MS TIC for kerosene is shown in Fig. 3A and the average mass spectra for different time windows are shown in Fig. 3B. Similar to the QuickStrip DART-MS data, higher masses (>m/z 100) were found in these mass spectra relative to the GC-MS data and most of the ions in the QuickStrip DART-MS spectra can also be observed in thermal desorption DART-MS spectra. Furthermore, more compounds were detected and significantly different profiles were observed with respect to the temperature gradient in thermal desorption DART-MS spectra. From 0 to 1 min, the sample pot was unheated, so only highly volatile compounds were detected by the mass spectrometer. The resulting mass spectrum consisted of clusters of peaks with differences of 14 Da. From 1 to 2 min, more peaks appeared as the sample pot started to heat (100°C/min from 25°C). For example, m/z 263.2 and 295.2 were emerging in this temperature range and both peaks also existed in the QuickStrip DART-MS spectra. From 2 to 3 min (100 to 200°C), m/z 263.2 and 295.2 and several new peaks became major peaks in the mass spectrum and m/z 309.2 started to emerge. From 3 to 4 min (200 to 300°C), m/z 309.2 became one of the highest peaks in the mass spectrum and additional higher mass peaks (>m/z 350) also came out at this temperature window.



FIG. 2—Ion source temperature optimization for the analysis of Crown paint thinner liquid by QuickStrip direct analysis in real time mass spectrometry (DART-MS): total ion current (TIC) (top) and mass spectrum for each temperature, respectively (bottom). Note: m/z 282.3 was an interference ion which was found in different ignitable liquids (IL) mass spectra.

As the temperature continued to increase, there was a relative decrease in the abundance of lower mass peaks and increase in higher mass peaks. For the higher mass region, a peak cluster with 14 and 18 Da repeating units can be found which was observed to contain unresolved ion clusters. The "space charge effect" in an ion trap MS analyzer could cause unresolved ion clusters (19), therefore, tests were performed by analyzing kerosene diluted 10-fold with pentane or decreasing the ion injection time, and similar mass spectra were achieved, which indicated that the space charge effect was not the issue. Another reason for these unresolved ion clusters could be the highly complex mixtures in the sample. As a heavy petroleum distillate, the chemical composition of kerosene is very complex, which may result in the complicated mass spectrum. In general, peaks with lower masses were mainly observed at lower temperatures and compounds with higher masses were identified at higher temperature in thermal desorption DART-MS spectra. This observation agrees with the common rule for organic molecules: for molecules with a given functional group, boiling point increases with molecular weight.

Interferences of Substrate Matrix

Tweezer Module with DART-MS—Figure 4 shows the average mass spectra for neat gasoline analyzed by QuickStrip DART-MS, and blank carpet piles and carpet piles with gasoline spikes analyzed by DART-MS with the tweezer module. The carpet

used in this study was made of polyester and ion clusters with 44 Da repeating units were formed in the mass spectra, corresponding to the mass of ethylene glycol units ($-OCH_2CH_2-$), which are raw materials used in the synthesis of polyester (20).

There are two clusters of ions in the DART-MS spectrum for gasoline neat liquid: m/z 202.2–272.2 with 14 Da repeat units corresponding to the mass of methylene units (–CH₂–) and m/z 284.4–956.4 with 56 and 58 Da repeat units corresponding to the mass of isobutylene (–CH₂–C(CH₃)₂–) and ether groups (–CH (CH₃)–CH₂–O–), respectively (10). For gasoline spiked carpet piles, characteristic ions for carpet including m/z 283.2, 327.3, 344.3, 371.3, and 388.3, and ions for gasoline such as m/z 216.2, 230.2, and 244.2 were detected. However, it was noticed that the other set of characteristic ions with the 56 and 58 Da repeat units found in gasoline neat liquid samples were not seen in this mass spectrum. These ions, corresponding to proprietary fuel additives, are important characteristic features for gasoline, and they were found to be gasoline brand dependent (10).

There are several possible reasons for not detecting fuel additive ions. First, the boiling points of fuel additives such as polyisobutylene (PIB) succinimides and polyether amines are usually higher than 250°C (21) and the temperature of the helium gas stream decreases dramatically with increasing sample gap distance when using the tweezer module. For instance, sample gap distance in our experiment was about 5 mm and the temperature of the gas stream at this distance was about 227°C (Temperature data from DART ion source user manual) when the DART ion



FIG. 3—Analysis of kerosene by thermal desorption direct analysis in real time mass spectrometry (DART-MS): total ion current (TIC) (A) and mass spectra for different time/temperature windows (B).



FIG. 4—Analysis of gasoline on carpet substrate by direct analysis in real time mass spectrometry (DART-MS) with tweezer module. Top: total ion current (TIC). Bottom: Mass spectra for blank carpet piles, carpet piles with gasoline spike, and neat gasoline liquid (Note: neat gasoline was analyzed by QuickStrip DART-MS).

source temperature was set to 350°C. This temperature may be insufficient to evaporate the fuel additive compounds. Second, these polymeric additives may tend to bond to the polymer of carpet fibers, which makes it even harder to be detected. In addition, ion suppression effect was observed in this study and less volatile fuel additives could be suppressed more significantly than the volatile compounds. With the DART ion source, the protonated molecule $[M + H]^+$ is produced by proton transfer between the molecule and ionized water clusters. The compounds may compete for the limited number of ionized water clusters formed by reactions between atmospheric moisture and

helium in the 2^{3} S state (22). The carpet piles with IL spikes introduced a complex compound mixture to the DART ion source where competition occurred. The volatile compounds are expected to be ionized faster, since they can be released from substrates more easily.

Similar interference from the carpet matrix was found with other ILs and examples of kerosene and paint thinner are shown in Figures S2 and S3. Background spectral subtraction is critical to observe the characteristic peaks in some IL samples. For example, when spiked onto carpet, the characteristic ions such as m/z 277.3 and 319.4 for Gulf Charcoal Starter cannot be

observed because ions from carpet fibers dominate the spectrum. However, the characteristic ions stand out after subtracting the mass spectrum for blank carpet fibers (Figure S4). Background subtraction is important especially for the analysis of trace levels of ILs or ILs with low volatility when using the DART-MS tweezer module.

Although our results indicated that the ILs on substrates could be analyzed directly by DART-MS with the tweezer module, it was still challenging. The major difficulty was the immobilization of substrates, such as sand and carpet, in the helium stream between the DART ion source and MS orifice. When the DART ion source was attached to the mass spectrometer, the curtain plate needed to be taken off and there was no curtain gas to prevent the contamination of the instrument. Therefore, the fine fibers from carpet or fine sand particles might accumulate at or even fly into the ion transfer capillary of the mass spectrometer which would contaminate and damage the instrument. In addition, the distance from the sample to the DART ion source nozzle cap and ceramic tube affected the signals, so the variance of this parameter should be minimized to achieve satisfactory reproducibility. The tweezer module for the DART ion source was available in our lab to hold the sample object at a relatively consistent position, however, the irregular shapes of sample objects disturbed the helium flow and affected the analysis. Therefore, the position of the tweezer module was adjusted for every individual sample to ensure the sample was contacted by the helium stream from the DART ion source thoroughly and the average mass spectrum was used for data analysis. This step typically required several minutes. After about 20 analyses of carpet samples, fine carpet fibers were found around the orifice of mass spectrometer, indicating that special care needed to be taken when using this method. The analyses of ILs on other substrates such as wood floor and paper were also attempted but were unsuccessful. These sample objects disturbed the helium gas stream significantly and the residues were not detected by DART-MS.

Thermal Desorption DART-MS—For neat gasoline analyzed by thermal desorption DART-MS, there were three groups of characteristic peaks: a) a group of volatile compounds with 14 Da repeat units which were detected at room temperature, for example, m/z91.0, 105.1, 119.1, and 133.1; b) another group of compounds with 14 Da repeat units which were usually detected between 200 to 300°C, for example., *m/z* 202.2, 216.2, 230.3, and 244.3; and c) fuel additives such as fuel detergent peaks which were commonly detected between 320 to 450°C, for example, m/z 627.3, 685.4, 743.4, and 801.4. Figure 5 shows the results of thermal desorption DART-MS analysis for gasoline residues on wood flooring. All three groups of compounds were detected at different temperatures. It is worth noting that only some of these characteristic ions can be detected on carpet substrate. For example, compounds in groups a and b for gasoline residues were found in the mass spectra of carpet samples and peaks in group c were not observed. The polyester carpet fibers started to pyrolyze at 300°C, therefore, peaks in group c were suppressed by the dominant peaks from pyrolyzed polyester in the mass spectra.

All three groups of gasoline characteristic ions were found in the mass spectra of the other four substrates analyzed by thermal desorption DART-MS. The substrates interfered with the gasoline residue results differently, dependent on the complexity of compounds released from the substrate materials at different temperatures. The coexisting compounds from the substrate can suppress or mask the signals of targeted ions originated from ILs and complicate the mass spectra. The peaks at the lower mass range were found to be more susceptible to interference. Generally, the clustered ions in the high-mass range, such as fuel additive ions, are easier to observe and more reliable as evidence for gasoline residues on substrates, if available. In addition, the heat exchange efficiency for the materials of substrates is different which may cause a slight change in retention time.

The other ILs were also analyzed on different substrates by using thermal desorption DART-MS, and similar success was achieved.



FIG. 5—Analysis of gasoline residues on wood floor substrate by the thermal desorption direct analysis in real time mass spectrometry (DART-MS): total ion current (TIC) (A) and mass spectra for at different time/temperature windows (B). Note: Two clusters of peaks associated with fuel additive compounds are labeled with triangles and stars.



FIG. 6—Multistep classification with partial least squares discriminant analysis (PLS-DA) models for ignitable liquids (ILs) on substrates. (Classification rates with 95% confidence intervals were obtained from 100 bootstrapped Latin partitions).

TABLE 1—Partial least squares discriminant analysis (PLS-DA) classification rates with 95% confident intervals obtained by 100 bootstrapped Latin partitions.

IL names	IL Type	Carpet	Wood Floor	Paper	T-Shirt	Sand	Overall
KS VMP naphtha	LPD	100 ± 0	100 ± 0	74 ± 4	99 ± 1	100 ± 0	95 ± 13
Gulf charcoal starter	LPD	99 ± 1	99.7 ± 0.7	88 ± 6	100 ± 0	100 ± 0	97 ± 6
Zippo lighter fluid	LPD	84 ± 7	100 ± 0	100 ± 0	100 ± 0	100 ± 0	97 ± 8
Crown paint thinner	MPD	100 ± 0	96 ± 2	100 ± 0	100 ± 0	100 ± 0	99 ± 2
KS paint thinner	MPD	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0
Japan drier	MPD	100 ± 0	99.7 ± 0.7	99.7 ± 0.7	100 ± 0	100 ± 0	99.6 ± 0.2
Kerosene	HPD	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0
Diesel	HPD	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0
Gasoline	GAS	70 ± 9	100 ± 0	100 ± 0	100 ± 0	100 ± 0	96 ± 15
Overall		95 ± 8	99.5 ± 0.9	96 ± 6	99.9 ± 0.2	100 ± 0	98 ± 1

HPD, heavy petroleum distillates; LPD, light petroleum distillates; MPD, medium petroleum distillates.

The comparison of characteristic ions for selected ILs (e.g., KS paint thinner, Speedway diesel, and Zippo lighter fluid) by DART-MS with QuickStrip and thermal desorption modules are summarized in Table S1. The characteristic ions are dependent on the types of the substrates and the DART-MS modules. Therefore, the use of a combination of multiple characteristic ions for the identification of ILs is more reliable than relying on a single ion.

Compared with QuickStrip DART-MS, there are several advantages to the direct analysis of ILs on substrates by thermal desorption DART-MS. First, more types of substrates can be analyzed directly regardless of their shapes and materials as long as they can be cut into small pieces. Since the sample objects are not directly in contact with the helium gas stream from the DART ion source, the immobilization of the samples is easier. Second, similar to GC-MS, the thermal desorption DART-MS provides information associated with chemical volatilities in the data which could aid in confirming or refuting ambiguous signals for the identification of ILs. Third, more characteristic

features can be detected with stronger signals which can be critical in the case where an IL is present at a very low concentration. The compounds on the substrates are separated and analyzed based on volatility and boiling points, therefore, the ion suppression effect for the analytes is less when compared with QuickStrip DART-MS. Fourth, the sample introduction process is more friendly to the mass spectrometer. The sample objects are not exposed directly in front of orifice of the mass spectrometer, so it is unlikely to contaminate the MS instrument. Last but not least, the temperature of the thermal desorption device can be set up to 600°C, which enables the detection of less volatile compounds in ILs on substrates, such as fuel additives in gasoline.

Although thermal desorption DART-MS does not need extra sample extraction and chromatographic separation for the detection of IL on substrates, it partially preserves advantages of extraction and separation. For GC-MS analysis, the volatile compounds are thermally desorbed from substrates and extracted with an

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activated carbon strip or SPME fiber and a compromised temperature is usually selected for the extraction of a series of compounds with different volatility. When using thermal desorption DART-MS, there is no discrimination against either low or high volatility compounds because compounds from both IL residues and substrate matrices are vaporized along the temperature gradient, allowing more complete profiles for ILs to be produced.

Classification of IL with the Interference of Substrates

All nine ILs on five different substrates (e.g., carpet, wood flooring, sand, paper, and T-shirt material) were analyzed using thermal desorption DART-MS in triplicate. One gasoline on carpet replicate and one Zippo lighter fluid on carpet replicate were discarded because part of the data collection for these two samples was conducted using nitrogen as the ionization gas stream by accident. Therefore, there were 133 data objects (9 ILs \times 5 substrates \times 3 replicates -2 = 133) for chemometric analysis. As a commonly used data representation for IL classification (2,6,23), TIS was constructed by averaging the mass spectrum across the retention time range between 0-5 min and was used for the construction of partial least squares discriminant analysis (PLS-DA) models. In PLS-DA, the latent variables are optimized to have maximum covariance between the X- and the Y-scores and then are used for regression with a dependent variable Y. The classification of 9 ILs could theoretically be implemented by using one PLS-DA model in a single step (Figure S5). However, multistep classification strategy was adopted for this study because it was found to be more effective at teasing out the differences in the features among objects that belonged to different classes (Fig. 6). In previous studies, multistep classification strategies were used for the classification of ILs (3,4) and natural products (24), which could obviate "the small sample size problem" and benefit the parameter optimizations in data processing. In the present study, four Latin partitions were bootstrapped 100 times to evaluate the PLS-DA models and the pooled classification rates with 95% confidence intervals were calculated by averaging across the 100 bootstraps. The Latin partition method randomly divided the data sets into training (75%) and prediction (25%) sets and each sample was used once and only once for prediction. The method allowed an unbiased and generalized evaluation of chemometric models (17).

The classification results are summarized in Table 1. The overall classification rates for all ILs are above 95%, and the interference of substrate matrices is dependent on the types of substrates and ILs. For Crown paint thinner, kerosene, and diesel, 100% classification rates were achieved no matter the types of substrates tested. The classification of gasoline and Zippo lighter fluid was significantly undermined by the interference of carpet matrices with classification rates of $70 \pm 9\%$ and $84 \pm 7\%$, respectively. As discussed in the previous section, polyester peaks from carpet fibers caused serious interference for characteristic peaks in gasoline DART-MS spectra, especially the fuel additive peaks. For carpet substrates, the mass peaks for the compounds in ILs which were desorbed at 300°C or higher were significantly suppressed by pyrolyzed polyester from carpet. KS VMP naphtha and Gulf charcoal starter tend to be misclassified to each other on paper substrates with classification rates of $74 \pm 4\%$ and $88 \pm 6\%$, respectively. However, both ILs were accurately classified with the interference of the other four substrates (≥99% classification rates). In addition, 96% classification rates were achieved for all the ILs on wood floor, T-shirt material or sand substrates. To conclude, classification of ILs using PLS-DA models with thermal desorption DART-MS data, even

with the interference of different substrates, demonstrated promising results with an overall classification rate of $98 \pm 1\%$.

Conclusion

In this study, it was demonstrated that DART-MS can be used to analyze IL residues on substrates without complicated extraction and chromatographic separation, which could significantly increase sample throughput and simplify interlaboratory comparisons. QuickStrip DART-MS was found to be effective when analyzing neat ILs, while analysis of ILs on substrates by DART-MS with the tweezer module was found to be hampered by background interference as well as potential contamination of instrument. Thermal desorption DART-MS demonstrated the potential for the detection of neat ILs and IL residues even with the interference of different substrates. Also, ILs on substrates were successfully classified using PLS-DA models with thermal desorption DART-MS data with an overall classification rate at $98 \pm 1\%$. Compared with traditional GC-MS methods, this method is fast, simple, and reproducible, allowing for easy comparisons and interpretation between samples. It can also provide complementary information to GC-MS analysis in some instances. Based on the results presented, DART-MS shows great potential for the high-throughput analysis of various types of ILs on different substrates.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Figure S1. The QuickStrip DART-MS spectrum for kerosene neat liquid.

Figure S2. Analysis of kerosene on carpet substrate by DART-MS with tweezer module.

Figure S3. Analysis of paint thinner on carpet substrate by DART-MS with tweezer module.

Figure S4. Analysis of charcoal starter on carpet substrate by DART-MS with tweezer module.

Figure S5. One-step classification with PLS-DA model for ILs on substrates.

Table S1. Characteristic ions for the four ILs.