# Hyperspectral Imaging as a Method for Detecting and Visualizing Ignitable Liquid Residues

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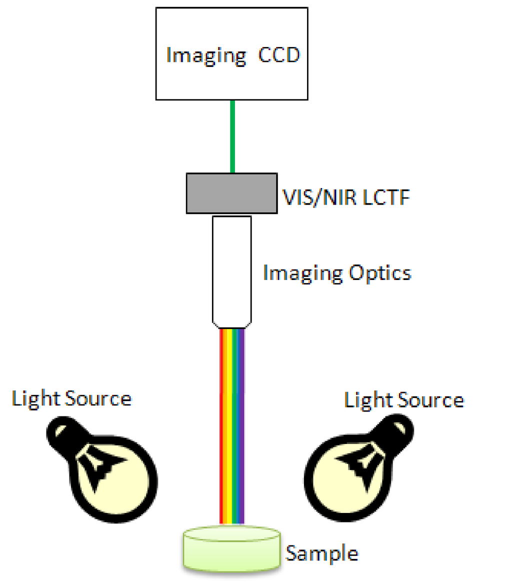
## Introduction

### Purpose

- The purpose of this study was to determine the capability of hyperspectral imaging (HSI) in the detection of ignitable liquid residues (ILR) on common unburned clothing fabrics, as well as on unburned carpeting.
  - The method's detection limits, discrimination ability, and visualization of aged samples were specifically evaluated.
- Arsonists typically use ignitable liquids as accelerants, so that the fire will quickly ignite and engulf the scene in flames.
  - Gasoline, kerosene, and diesel fuel are most often used because they are cheap, easily accessible in large amounts, and flammable[(1)].
- Due to federal mandate, dyes and markers, called 'tags,' are added to certain petroleum products during the refining process so that the products can be quickly distinguished visually[(2)].
- HSI was used to visualize the ILR stains by the fluorescence of these petroleum dyes and markers which are left behind after the hydrocarbons have evaporated.
- There are several methods currently in use for detecting and analyzing ILR, both in burned debris and on clothing as well as on other substrates. Most of these methods detect and analyze the hydrocarbon component of the ILR as opposed to detecting the tags[(3-12)].
  - In previous studies of ILR detection, volumes of gasoline under 100μL could not be detected after 24 hours of deposition on car carpet[(13)].
  - In a study examining gasoline detection on human hands, 500μL was found to be undetectable after two hours[(14)].
  - To date, there are no published accounts of using HSI for the analysis of ILR, specifically focusing on the dyes and additives in the stains.




| | |
|---|---|
| Binning | 1x1 |
| Averages | 1 |
| Exposure Time | 30 seconds/60 seconds |
| Speed/Gain | Hi/Hi |
| ROI Coordinates | Left=323, Right=843, Top=238, Bottom=735 (variable) |

**Figure 1.** Hyperspectral imaging schematic (Left)

**Table 1.** Data collection parameters used during experimentation (Right)

### Technology

- HSI technology provides data both in the form of digital images as well as chemical information in the form of a spectrum associated with the sample.
  - The spectral data is collected individually for each pixel. The intensity value of each pixel at each wavelength collected is recorded by the detector and projected as a spectrum.
  - The images are collected as a function of the wavelengths in the collection range which results in a stack of images, called a 'datacube'.
  - The images that make up the datacube are collected at manually chosen wavelength intervals throughout a selected region of data collection.
- Having multiple image frames to reference allows the maximum contrast between the sample and the background to be found and viewed.
- Minimal to no sample preparation is required.
- HSI is a nondestructive technology.
  - Since HSI analysis is nondestructive, it is a useful method of preliminary examination since it does not expend the sample which may be limited, allowing further testing by other instrumentation.

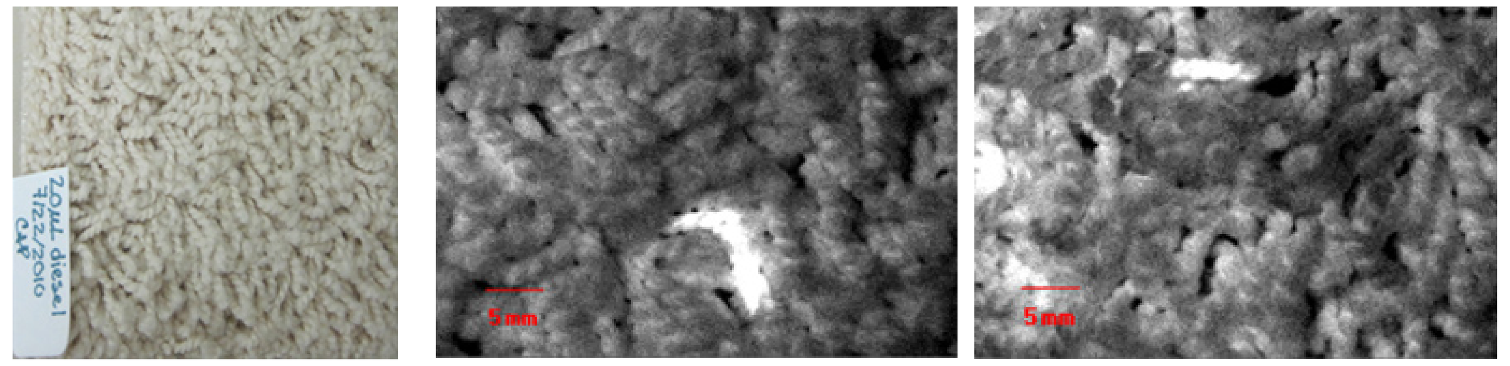



**Figure 2.** Left: Digital image of diesel fuel on carpet; Middle: HSI image 455nm illumination, 540nm frame of 20μL diesel fuel on carpet; Right: HSI image of 10μL diesel fuel on carpet 2.

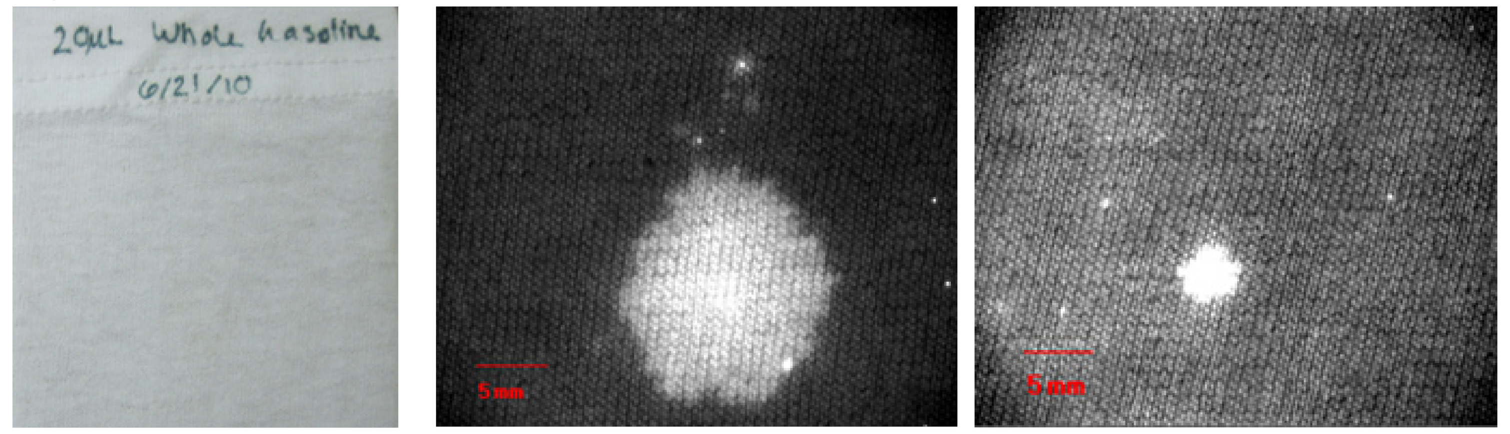



**Figure 3.** Left: Digital image of gasoline on a white cotton sample; Middle: HSI image, 455nm illumination, 600nm frame of 20μL gasoline on white cotton; Right: HSI image of 1μL gasoline on white cotton.

## Materials and Methods

### Instrument

- The instrument used for this experimentation was the CONDOR™ Hyperspectral Imaging System (ChemImage Corp, Pittsburgh, PA).
  - A Mini CrimeScope (MCS) 400 Series (SPEX, Edison, NJ) was used for sample illumination.
  - Tunable filter wheels included with the MCS offered specific illumination wavelengths at 300-400nm, 415nm, 445nm, 455nm, 515nm, 535nm, 555nm, and 600nm.
  - A liquid crystal tunable filter (LCTF) which selected the wavelength of light allowed to reach the camera at each frame of data collection.
  - A 1024x1024 pixel CCD camera (Princeton Instruments, Trenton, NJ) was used for image collection.
  - The instrument was controlled with ChemImage Xpert™ version 2.5.2 software (ChemImage Corporation, Pittsburgh, PA).

### Samples

- The ignitable liquid samples used were gasoline, kerosene, and diesel fuel, all colored, and an additional undyed sample of lighter fluid (Zippo).
  - The three dyed liquids were chosen because they are documented as the three most commonly used ignitable liquids in arson cases[(1)].
  - The undyed lighter fluid was chosen to act as a negative control as it was an undyed petroleum product.
- The substrates used were white cotton cut from a white cotton t-shirt (Hanes, ComfortSoft), black cotton cut from a black cotton t-shirt (Jerzees), and denim cut from a pair of shorts (Levi's). Three types of carpet were also used as substrates; Carpet 1 (Shaw brand, Inspired Touch style, Mirage color), Carpet 2 (Shaw brand, Alpine style, Moonlight color), and Carpet 3 (Shaw brand, Alpine style, Arrowhead color).
  - Fabrics and carpets were relevant substrates to be examined as they were cited in a study as being a highly submitted evidence type, second only to ashen debris, in one year of arson cases from a forensic laboratory[(15)].

### Experimental Design

- All data was collected in the form of fluorescence hyperspectral images.
- Before any sample data was collected, the liquids were allowed to evaporate from the substrate for at least 24 hours.
- First, the optimal illumination wavelengths for the ignitable liquid samples were determined.
  - Separate datasets were collected for each illumination wavelength option and mean intensity values were acquired.
  - The ignitable liquids were imaged on a nonfluorescent background, specifically an aluminum plate.
  - The collection range for each illumination wavelength remained constant for all following data collection.
  - Before any sample data was collected, a substrate blank dataset for each substrate was collected at the illumination wavelengths used in the experimentation.
- Experimental design continued in three levels.
- In the first level of experimentation, the lower limit of detection (LLOD) was determined by collecting datasets of decreasing volumes and dilutions of each liquid on each substrate.
  - The decreasing volumes examined were 20μL, 10μL, 5μL, 2μL, and 1μL.
  - The dilutions examined were 1:2, 1:5, 1:10, 1:25, and 1:30.
  - Also as part of the LLOD testing, duration samples were examined to determine the amount of time after deposition that a stain could still be imaged on each substrate.
  - Duration samples were made with 20μL aliquots of gasoline on both white cotton and denim substrates, and also 20μL aliquots of diesel fuel on white cotton. The duration samples were made in triplicates and datasets were collected weekly.
  - Processing steps were applied to the LLOD datasets in order to eliminate spectral interference from the substrate background and to improve image contrast between the ILR and the background by filtering noise.
    - Background division diminishes the background spectrum's influence on the overall spectrum which represents all the pixels of the image.
    - Normalization is a technique which corrects for the influence of image topography by scaling the spectral data to the same intensity scale.
- The second level of experimentation involved multi-stain samples to determine the ability of HSI to discriminate between different dyed liquids.
  - The liquids used for these samples were washer fluid, hydraulic fluid, two different antifreezes, motor oil, concentrated fire fighting foam, and transmission fluid.
    - These liquids were chosen because they were colored with dyes which may have fluoresced similarly to the dyes found in ignitable liquids.
  - 10μL of each of the dyed liquids along with 10μL of each gasoline and diesel fuel were pipetted onto white cotton, denim, and a swatch of carpet 1.
- The third level of experimentation dealt with the examination of blind samples.
  - The purpose of these tests was to determine the amount of time required for real world application when the area of liquid deposition was unknown, and also the success of visualizing all stains present, as well as the ability of HSI to distinguish stains of different compositions.
  - An additional processing step, principal component analysis (PCA), was used when analyzing the blind samples as a means of visualizing stains which were not revealed with the normalization and noise reduction filter processing.
    - PCA is a multivariate statistical method of analysis which emphasizes discrete differences in sample data[(16)].
- The collection parameters used for data collection are listed in Table 1.

## Results and Discussion

### Illumination Determination

- For each sample dataset, four regions of interest (ROI) were selected in the stain and a mean intensity range was documented. An additional ROI was taken from the non-fluorescent Aluminum background, and a signal to noise ratio was determined by averaging the intensities of the four sample ROIs and dividing the sample intensity value by the background intensity value.
- The illumination wavelengths which resulted in the highest intensity for both gasoline and diesel fuel were 445nm and 455nm, therefore they were used in all following data collection of gasoline and diesel fuel on the various substrates.
  - Data collected with 445nm illumination was collected from 480nm-720nm.
  - Data collected with 455nm illumination was collected from 510-720nm.
- Kerosene did not fluoresce significantly under any wavelength of illumination as all signal to noise ratio values are roughly 1.
  - Since the dyes and markers used in this sample of kerosene seemed to not be fluorescent, the kerosene sample was excluded from all further data collection.
- The sample of undyed lighter fluid also did not show any significant fluorescence under any of the illumination wavelengths.
  - The lack of fluorescence in the lighter fluid, however, was expected as that sample was void of any dyes and markers which might result in a fluorescent response.

### Lower Limit of Detection

- Gasoline and diesel fuel were both successfully visualized on white cotton and carpets 1-3.
- Only gasoline was visualized on denim.
- The smallest volumes and highest dilutions of gasoline and diesel fuel visualized on each substrate are listed in Table 2.
- Neither gasoline nor diesel fuel were able to be visualized on the black cotton substrate.
  - It is reported that when another dye is added to a fluorescent solution, if one of the dyes absorbs the wavelength of light that the other emits, the fluorescence can be diminished[(17)].
- The ILR spectral data collected seems to have been influenced by the fluorescence of the substrate onto which the liquids were deposited.
- This observation indicates that HSI should be used in conjunction with another method to confirm the presence of a specific ignitable liquid.
- Images were successfully acquired with all duration samples at four weeks after deposition, and the images did not show any fading due to time elapsed at the four week interval.
- The ability to visualize ILR stains weeks after deposition is extremely valuable, as traditional ILR detection techniques are useful only for a limited time before the hydrocarbon components evaporate.
- For evidence that is not packaged within the timeframe, or is not packaged correctly in airtight containers, HSI offers a technique to detect ILR stains when they may have otherwise been overlooked.

**Gasoline Fluorescence**

| Substrate | Smallest Volume | Highest Dilution |
|---|---|---|
| White Cotton | 1μL | 1:10 |
| Black Cotton | X | X |
| Denim | 1μL | X |
| Carpet 1 | 1μL | 1:10 |
| Carpet 2 | 1μL | X |
| Carpet 3 | 1μL | X |

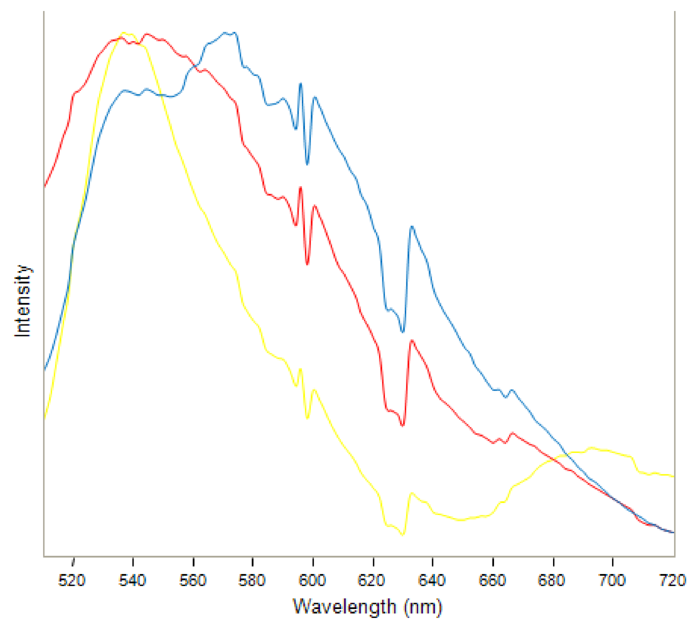
**Diesel Fluorescence**

| Substrate | Smallest Volume | Highest Dilution |
|---|---|---|
| White Cotton | 1μL | 1:30 |
| Black Cotton | X | X |
| Denim | X | X |
| Carpet 1 | 1μL | 1:30 |
| Carpet 2 | 10μL | 1:2 |
| Carpet 3 | 2μL | 1:2 |

**Table 2.** Left: results of LLOD tests for gasoline. Right: results of LLOD tests for diesel fuel

### Multi-Stain Samples

- Fluorescence HSI was able to visualize all the stains on the white cotton fabric, as well as on the carpet substrate.
- Five of the nine stains were visualized on the denim.
- All stains could be visibly distinguished from each other throughout the datacube.
- In Figure 4 below, gasoline, concentrated fire fighting foam, and Shellzone antifreeze can be seen at 530nm, 570nm, and 610nm.
  - In the 570nm frame, all three stains appear to be fluorescing similarly; however in the 530nm and 610nm frames, all three can be distinguished.
- When examining samples which may contain stains from multiple origins, it is especially advantageous to review images at multiple wavelengths.
- Additional data was collected at 2nm step sizes in order to get more specific spectra for the three liquids in the subset.
- Figure 4 shows the spectra collected for the gasoline, concentrated fire fighting foam, and the Shellzone anitfreeze; the three stains each gave distinctly different spectrums, especially at the beginning of the data collection range.



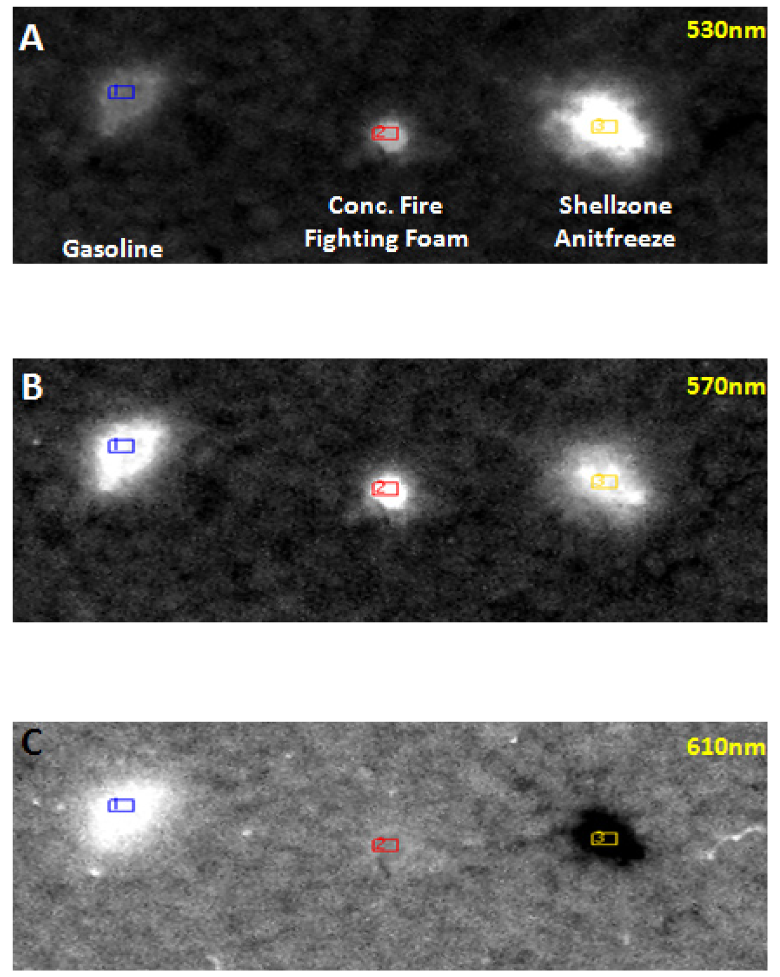




**Figure 4.** Spectra from the 2nm step size data collection of the multi-stain subset. The blue spectrum is representative of gasoline, the red spectrum is representative of concentrated fire fighting foam, and the yellow spectrum is representative of antifreeze. Figure A is the 530nm frame of the stain subset. Figure B is the 570nm frame of the subset. Figure C is the 610nm frame of the subset. 455nm illumination was used for this data collection.

### Blind Samples

- Blind samples were made on carpet 2, carpet 1, and denim substrates, along with an additional black leather glove substrate.
- The samples were specifically designed by a scientist other than the examiner to test the LLOD limits, stain differentiation, and the effects of the fire fighting foam on the visualization of gasoline.
- Volumes comparable to those listed as the LLOD volumes for gasoline and diesel fuel were successfully detected and visualized.
- Gasoline was successfully visualized even after fire fighting foam had been poured over the ILR.
- Stains of different chemical makeups were differentiated, and the PCA processing was able to successfully indicate that stains of the same substance were similar.
- PCA processing was also useful in one blind sample at revealing three stains in addition to those visualized with the traditional processing steps.
  - Kerosene stains were visualized with PCA, even though kerosene did not show any fluorescence throughout the dataset.
- Gasoline was successfully visualized on the black leather.
- Data collection time ranged from 11 to 25 minutes depending on the substrate type and the illumination wavelength used.
- Processing time was variable depending on the number of steps applied; however the average amount of time spent processing the data was an additional 10 minutes.
- For very large substrates, such as entire garments, the time required to analyze the item will increase depending on the size.

## Conclusions

- This study may be valuable to arson investigators, as fluorescence HSI methodology offers a novel, nondestructive method of detecting and visualizing ILR.
- Fluorescence HSI has proven to be successful at detecting and visualizing ILR stains on both clothing and carpeting.
- HSI could visualize stains as small as 1μL on multiple substrates, and dilutions of 1:30.
- HSI could also visualize stains which had been deposited four weeks prior to data collection.
  - Visualization weeks after deposition is especially valuable since methods of ILR detection which detect the hydrocarbon component of ILRs are limited by the hydrocarbon rate of evaporation. HSI could be especially valuable for detecting gasoline, as it is the quickest to evaporate of the three most commonly used ignitable liquids.
- HSI was successful at distinguishing, both visually and spectrally, between stains of different liquids, which is helpful in giving the examiner knowledge of how many different areas on a substrate need to be tested further.
  - Even with ILR samples that have been detected using other methods, especially GC-MS and SPME, the ILR visual provided by HSI could be helpful in determining if the response of the other instrument was from an actual ILR, or if it was due to a compound already integrated into the substrate during manufacturing, as mentioned in several publications[(18, 19)].
- Because HSI spectral data is broad and not specific enough to be used as a method to confirm the origin of a stain, fluorescence HSI methodology should be used in accompaniment with another method, such as Raman or MS, which can identify a class of petroleum products, or a certain dye as one that is used in a specific kind of petroleum product.
- The visual portion of the data provides the examiner with the knowledge of exactly where a stain is located on a substrate, so that only that area can be submitted for further testing.

### Future Work

- The next phase of experimentation will include the use of an instrument with a Raman detector.
- Raman spectral data is more specific than that given by fluorescence HSI alone, and therefore will promote the more specific qualification of residues detected.
- Examination of numerous samples of different brands and grades of gasoline and other ignitable liquids, in order to determine the ability of HSI to visualize and distinguish between different varieties of one type of ignitable liquid will be conducted.

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