# Optimizing Solvent Selection and Data Reduction Workflows for GC×GC Fire Debris Analysis

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## Introduction

**What are Ignitable Liquid Residues (ILRs)?**

- Chemical remains of ignitable liquids (IL) (e.g., gasoline or diesel) that did not fully burn during a fire
- ILRs are usually petroleum-based products and contain complex mixtures of volatile chemicals, like hydrocarbons

**Forensic Analysis of ILRs**

- Collection of porous materials like wood from the fire's point of origin
  - Must be stored in airtight containers to prevent volatile ILR from evaporation
- Passive headspace extraction onto activate charcoal strips (ACS) is used to extract ILRs from debris, and dichloromethane (DCM) is used to extracts ILRs from charcoal strips
- Emerging is the use of two-dimensional gas chromatography – time of fight - mass spectrometry (GC×GC-TOFMS), with higher separation and resolution
- Resulting chromatograms presents a pattern of peaks which can be used to identified specific type of accelerant used

**Chemometrics**

- The discipline that focuses on the application of statistical and mathematical methods to analyze chemical data and extract meaningful information (Bovens, 2019)
- Helps make sense of large datasets from analytical instruments, find pattens, and classify samples

## Purpose

**AIM 1**: Develop a streamlined workflow using chemometric tools to analyze large data sets and reveal underlying patterns and relationships.

**AIM 2**: Determine how different extraction solvents influence ILR extraction outcomes through chemometric analysis.

## Conclusions

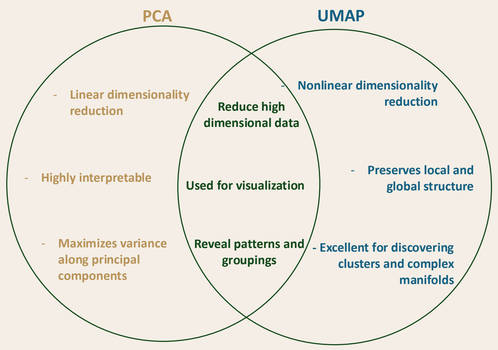


Figure 3. Comparison of PCA vs. UMAP

- This study demonstrated that the use of chemometrics can be integrated into a data processing workflow to better understand data sets and create a streamlined process
- Using UMAP, patterns identified that were not originally seen in PCA lead to the preferred solvents of ILR extraction being hexane and methanol. Since UMAP allowed visualization of local and global structures, groupings of gasoline samples allowed for better analysis of solvent effect

## References

1. Armstrong G, Martino C, Rahman G, Gonzalez A, Vázquez-Baeza Y, Mishne G, Knight R. Uniform Manifold Approximation and Projection (UMAP) Reveals Composite Patterns and Resolves Visualization Artifacts in Microbiome Data. mSystems. 2021 Oct 26;6(5):e0069121. doi: 10.1128/mSystems.00691-21. Epub 2021 Oct 5. PMID: 34609167; PMCID: PMC8547469.
2. Yadav et al., A Forensic Approach to Evaluate the Effect of Different Matrices and Extraction Solvents for the Identification of Diesel Residue in Simulated Arson by GC–MS, *Chromatographia,* Volume 84, 2021.
3. Bovens, M., et al. "Chemometrics in Forensic Chemistry — part I: Implications to the forensic workflow." Forensic Science International, vol. 301, Aug. 2019, pp. 82–90, https://doi.org/10.1016/j.forsciint.2019.05.030.

## Methods

**Sample Preparation**

- Wood chips were burnt in a controlled fashion and were used as the fire debris matrix, ½ cup of debris was placed into each 12 oz. Mason jar
- For experimental samples, 0.5 mL of gasoline, kerosene, or diesel was added to the debris, the matrix blanks had no IL present. Headspace extraction was then performed using ACS
- Each IL class had 5 replicates for each solvent, 20 samples per solvent, for a total of 100 total samples
- Solvents used were hexane, pentane, isopropanol, diethyl ether, and methanol (Yadav et. al, 2021).

**Analytical Instrumentation**

- LECO corporation BTX4D GC×GC-TOFMS with Paradigm Shift™ reverse fill-flush (RFF) flow modulator

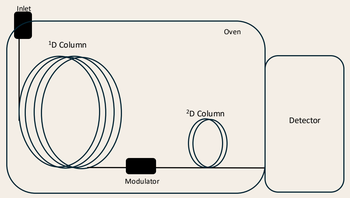


Figure 1. GC×GC Schematic


Figure 2. Fire debris sample preparation, sample wood matrix in respective jars

**Software**

- ChromaTOF Sync 2D (LECO corporation)
- R Statistical Software

**Dataset Preparation**

- All chromatograms were pre-processed using Sync 2D. This software aligns complex data, deconvolute peaks, and enable a non-targeted analysis. Once Sync 2D had process all 100 chromatograms, a compound list was generated. This unprocessed data set is what was used for to feed statical software programs like R statistical software
- In R, a total of 800 compounds was reduced to a focus set of 86 of the most influential compounds. These were compounds that had the most effect on solvent grouping
- Principal Component Analysis (PCA) and Uniform Manifold Approximation and Projection (UMAP) were compared. PCA is an unsupervised statical test that uses linear dimensionality reduction while UMAP is a nonlinear dimensionality reduction method that can reveals patterns that PCA may not display due to tight clustering. (Armstrong et.al, 2021)

## Results

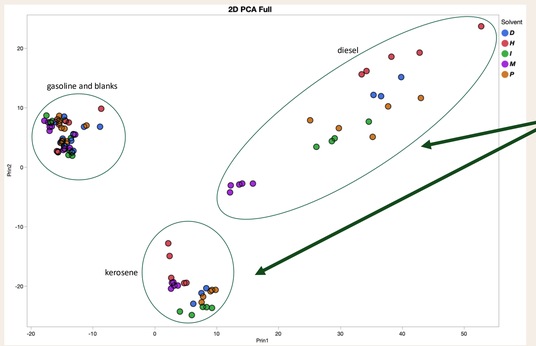


Figure 4. PCA Plot of raw data set (800)

- Colors are based on solvent choice
- Good grouping of kerosene samples, wide grouping of diesel samples, blanks and gasoline clustered tightly together
- Unable to determine characteristics of the blanks and gasoline grouping

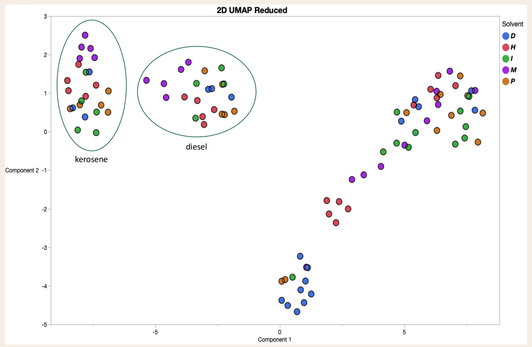


Figure 5. UMAP of focused data set (86)

- Kerosene and diesel showed tight clusters
- Diesel and kerosene samples clustered tightly together for all solvents except diethyl ether, whereas in the PCA the diethyl ether samples cause the diesel group to appear more dispersed.

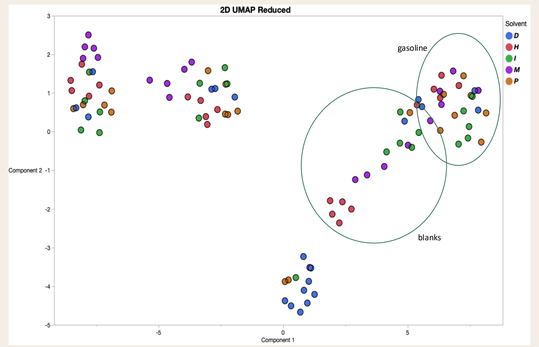


Figure 6. UMAP of focused data set (86)

- Gasoline and blank groupings are more dispersed
- Hexane and methanol (blanks and gasoline) samples tightly grouped
- Isopropanol did not group well with gasoline samples
- Pentane groups of blanks and gasoline grouped correctly but tightly

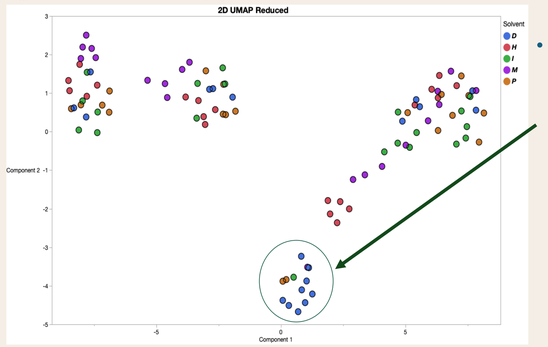


Figure 7. UMAP of focused data set (86)

- Diethyl ether solvent for all ILs did not group correctly but rather near the blanks suggesting low extraction of analytes