Analysis of Petroleum Products for Forensic and Environmental Applications

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Abstract

In both forensic and environmental applications, it is often important to identify ignitable liquid (IL) residues, to find a suspect or to clean up an oil spill. The ASTM method is commonly used; the extraction methods vary, but the data collection is the same. The instrument used in the ASTM method is gas chromatography mass spectroscopy (GC-MS), which allows a visual identification of the IL contaminating the sample. In this study, the use of Fourier transform infrared spectrometry (FTIR) was used in conjunction with chemometric analysis. Samples were prepared were to simulate an oil spill in natural waters. Two chemometric analysis methods were used: principal component analysis (PCA) and alternating least squares (ALS) to assist in the identification of the contaminant. The FTIR spectra were hard to visually identify, but when paired with PCA and ALS allowed the identification of gasoline and diesel contamination. The use of ALS and PCA together also allowed the identification of blank samples. The use of FTIR with chemometric analysis was found to faster and more efficient, and an accurate method of analysis, when compared to GC-MS.

Introduction

What

- Petroleum-based products include fuels, plastics, asphalt, and etc.
- Common fuels: gasoline, kerosene, and diesel [2]
- Gasoline is a complex mixture of organic substances and some trace inorganic substances obtained from petroleum [3]
- Gasoline, kerosene, and diesel have different organic and inorganic composition [4]

Why

- Forensic application: gasoline, kerosene, and diesel are most commonly used as accelerants in arson [2]
- Environmental application: oil spills can contaminate water and food supplies [2]

How

- Gas chromatography-mass spectroscopy (GC-MS): separates the mixture into its individual components
- Fourier transform infrared spectroscopy (FTIR): organic compound analysis
- Chemometric analysis: mathematical tool to analyze data

Experimental

Standards

- Various petroleum products were volumetrically diluted to 25% v/v solutions, using pentane as the solvent.
- The diluted and neat samples were analyzed using a Thermo Nicolet iS10 FTIR spectrometer with a horizonal attenuated total reflectance (HATR) accessory.

Water

- Water samples collected from:
  - Atlantic ocean (Virginia Beach, VA)
  - Pamunkey River (New Kent, VA)
  - Swift Creek Reservoir (Chesterfield, VA)
- The water samples were contaminated with gasoline and extracted with pentane.
- After extraction the samples were evaporated by rotary evaporation on an ice bath the residue analyzed by FTIR.

Chemometric Analysis

- All data analysis was performed in Matlab R2016b using in-house algorithms for principle component analysis (PCA) and the MCR-ALS toolbox available for free download (https://mcrals.wordpress.com/).

Conclusion

- FTIR is a **fast and inexpensive** way to analyze solutions and when paired with chemometric analysis can **group known solutions** and can help **classify unknown solutions**.
- Even though PCA was able to efficiently classify known solutions, it lacked accurately grouping unknown solutions on its own
- This study shows that using **ALS together with PCA** to analyze FTIR spectra has the ability to identify IL residues in **unknown contaminated samples**.

Results and Discussion

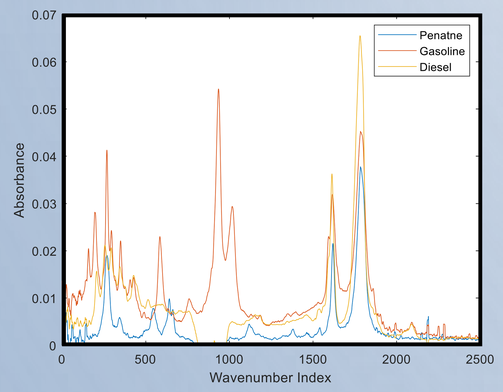

Figure 1
Fingerprinted spectrum of gasoline, diesel, and pentane spectra. Data was converted from %transmittance to absorbance**.**

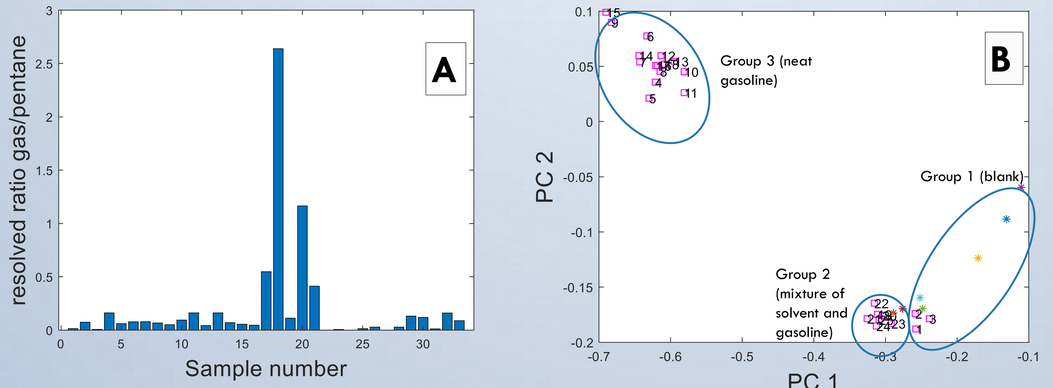

Figure 2
A. Resolved ALS results for unknown samples, using neat gasoline and solvent as initial estimate. The resolved ratio indicates that a mixture is either positive for gasoline (i.e. samples 17 – 21) or is a match to the solvent only.
B. A PCA plot showing the three possible groups identified. The asterisks (*) represent unknown samples. A match to group 2 or 3 is considered positive for gasoline.

Table 1
A MATLAB program was written to run the ALS and PCA analyses separately and give number values according to the results. Three classifications were allowed: blank, mixture (solvent plus contaminant), and neat contaminant.

Classification	Result
1 (blank)	Negative
2 (mixture of solvent and gasoline)	Positive
3 (neat gasoline)	Positive

Table 2
By using the MATLAB program the sensitivity and specificity of PCA and ALS were calculated as a percentage of true positives (specificity) and true negatives (sensitivity). PCA proved to have a better sensitivity than ALS alone.

	PCA Results	ALS Results
specificity	100	100
sensitivity	70	50

References

1. https://www.energy.gov/articles/hows-and-whys-replacing-whole-barrel
2. A.M. Huppa, L.J. Marshall, D.I. Campbell, R.W. Smith, V.L. McGuffina, Chemometric of diesel fuel for forensic and environmental applications, Analytica Chemica Acta. 606 (2008) 159-171.
3. J.M. Paulo, J. E.M. Barros, P. J.S. Barbeira, A PLS regression model using flame spectroscopy emission for determination of octane numbers in gasoline, Fuel 176 (2016) 216–221.
4. M. Khanmohammadi, A. B. Garmarudi, M. Guardia, Characterization of petroleum based products by infrared spectroscopy and chemometrics, Trends in Analytical Chemistry 35 (2012) 135-14
5. Ghali S, Harvey A, McCrillis K, Porter S. (2020) Analysis of Petroleum Products for Forensic and Environmental Applications. *INCITE Journal of Undergraduate Scholarship, In Press.*