A systematic study of the absorbance of the nitro functional group in the vacuum UV region.

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ABSTRACT: The nitro functional group (NO_2) features strongly in compounds such as explosives, pharmaceuticals, and fragrances. However, its gas phase absorbance characteristics in the vacuum UV region (120 – 200 nm) have not been systematically studied. Gas chromatography/vacuum UV spectroscopy (GC/VUV) was utilized to study the gas phase VUV spectra of various nitrated compounds (*e.g.*, nitrate esters (-R-O-NO_2), nitramines (R-N-NO_2), nitroaromatics (Ar-NO_2), and nitroalkanes (R-NO_2)). The nitro absorption maximum appeared over a wide range (170 – 270 nm) and its wavelength and intensity were highly dependent upon the structure of the rest of the molecule. For example, the nitroalkanes exhibited a trend in that the ratio of the relative absorption intensity between these two absorption features between the alkyl group (< 150 nm) and the nitro group (200 nm) increases as the molecular weight increases. It was observed that the addition of multiple nitro functional groups on benzene or toluene resulted in an increase in intensity and blue shift from approximately 240 nm to 210 nm. Nitrate esters exhibited an absorption between 170 nm to 210 nm and absorbance increased with increasing nitrogen content. The relative diversity of the spectra obtained was analyzed by Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA). These calculations revealed that the spectra of all the compounds analyzed could be reliably differentiated without any misclassifications.

KEYWORDS. Nitrated Compounds, Vacuum Ultraviolet Spectroscopy, Gas Chromatography.

1. INTRODUCTION

Since the development of the benchtop vacuum ultraviolet spectrometer as a detector for gas chromatography, GC/VUV has been utilized to study a variety of compounds in several applications.[1] One key advantage of GC/VUV is its spectral range (120 – 430 nm), which produces spectra that can differentiate compounds that are difficult or impossible to distinguish by mass spectrometry. Hence, there has been a focus in the literature on the discriminating power of GC/VUV in the analysis of structurally similar compounds and isomers.[2-17] Additionally, the differentiation of spectra based on structural classes has been studied. Most notably is attributing specific wavelength ranges to specific compound classes to create spectral filters (*i.e.*, aromatics, saturates, and di-olefins). This approach has been extended to the analysis and characterization of Paraffins, Isoparaffins, Olefins, Naphthenes and Aromatics (PIONA) in petroleum products.[18-20]

However, less has been written about differentiation of the same functional group or trends in spectra for different chemical structures.[21-23] To date, analysis of aromatic hydrocarbons in mineral oils,[24] organosilanes,[22] and alkanes[25] have revealed changes in VUV spectral features due to corresponding chemical structure changes. Other trends include a red shift with each of the following: increasing number of double bonds present,[26] increase in the number of aromatic rings,[5] and increase in the dihedral angle of polychlorinated biphenyls.[10] Additionally, the impact of silylation of cannabinoid spectra was also investigated in detail, attributing structural features (aromaticity, oxygenation, saturation/unsaturation) to specific wavelength ranges.[27] Similarly, GC/UV has been utilized to extensively characterize the UV spectra of various compounds; however, the minimum

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wavelength was limited to 168 nm.[28, 29] Furthermore, using GC/VUV to identify unknown compounds has been less explored.

In this work, the spectral characteristics of various nitrated compounds from differing structural classes (*i.e.*, nitrate esters, nitramines, nitroaromatics, and nitroalkanes) were investigated. Nitrated compounds are of interest in several areas of application including forensic science, environmental science, medicine, and flavors/fragrances.

Of the 24 compounds analyzed, only 11 have been analyzed by GC/VUV previously (Table 1). In addition, this is the first time that the mono-nitrotoluene structural isomers (2-nitrotoluene, 3-nitrotoluene, and 4-nitrotoluene) have been compared and differentiated by GC/VUV. The absorption band attributed to the nitro group was investigated for each structural class to assess its utility as a reliable marker. A figure characterizing the nitro group of nitroalkanes, nitrobenzenes, nitrotoluenes, and nitrate esters was also developed. Lastly, Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA) were completed to further investigate spectral differences of nitroaromatic, nitrate ester and nitramine compounds. All 12 compounds analyzed were successfully discriminated via LDA with an 80:20 validation: training set with zero misclassifications.

Table 1. Summary of previously analyzed compounds via GC/VUV. *approximation of absorbance maximum.

Compound	**MW (g/mol)**	**Abs. Max (nm)**	**Ref**
Nitromethane	61.0	130.6	[30, 31]
Nitrobenzene	123.1	178.75	[32]
2-Nitrotoluene	137.1	182.8	[30, 31]
Ethylene Glycol Dinitrate	152.1	134.9±0.2	[7]
2,4-Dinitrobenzene	182.1	166.8	[30, 31]
2,6-Dinitrobenzene	182.1	174.6	[30, 31]
Isosorbide Mononitrate	191.1	<125*	[33]
RDX	222.1	120	[33]
Nitroglycerine	227.1	134.9±0.2	[7]
Isosorbide Dinitrate	236.1	130-140*	[33]
Pentaerythritol Tetranitrate	316.1	136.1±0.4	[7]

2. MATERIALS AND METHODS

2.1 Chemicals. Nitroglycerine (1000 µg/mL in methanol), ethylene glycol dinitrate (1000 µg/mL in methanol), pentaerythritol tetranitrate (1000 µg/mL in methanol), EPA method 8330 calibration mix #1 (1000 µg/mL each in acetonitrile) and #2 (1000 µg/mL each in acetonitrile) were purchased from Restek. 2,3-dimethyl-2,3-dinitrobutane, musk xylene (1000 µg/ml in acetonitrile), nitromethane, nitroethane, and 1-nitropropane were purchased from Sigma-Aldrich. Isosorbide mononitrate was purchased from MEDCHEMEXPRESS LLC, isosorbide dinitrate was purchased from Cayman Chemical, and nitroquinoline was purchased from Santa Cruz Biotechnology. Methanol (optima LC/MS), chloroform (stabilized HPLC grade), and acetonitrile (HPLC Grade) were purchased from Fischer Scientific.

2.2 Sample Preparation. A 1000 ppm standard of 2,3-dimethyl-2,3-dinitrobutane was prepared in methanol. 1000 ppm standards of isosorbide mononitrate and isosorbide dinitrate were each made by dissolving in chloroform. A 1000 ppm standard of nitroquinoline was created by dissolving in acetonitrile. Nitroglycerine, ethylene glycol dinitrate, pentaerythritol tetranitrate, EPA 8330 calibration mix #1 and #2, and musk xylene standards were analyzed as received. 1000 ppm standards of nitromethane, nitroethane, and 1-nitropropane were prepared in methanol.

2.3 Gas Chromatography. An Agilent 7890B series GC equipped with a multimode inlet and Agilent 7390 autosampler was utilized with hydrogen carrier gas at 3.2 mL/min and a splitless ramped inlet temperature program (50 °C ramped to 280°C at 900°C/min). A Restek Rtx®-5MS column (15 m x 0.32 mm x 0.25 µm) was utilized for analysis of the EPA 8330 and remaining compounds, other than the nitroalkanes. The EPA 8330 calibration mix 1 and 2 were analyzed with an oven program of 50°C held for 2 min, ramped 10°C/min to 170°C then 20°C/min to 240°C. The remainder of the compounds (other than the nitroalkanes) were analyzed with a splitless injection and an oven program of 50°C held for 0.5 min, ramped at 20°C/min to 200°C.
A flow rate of 2.5 mL/min was utilized for the nitroalkanes with a 5:1 split injection at 200°C and an HP-5MS UI column (30 m x 0.25 mm ID x 0.25 µm). An isothermal oven program of 45°C for 3 min was utilized to resolve nitromethane from the solvent front.

2.4 Vacuum Ultraviolet Spectroscopy. GC effluent was directed into a VUV Analytics VGA-101 VUV spectrometer. All experiments were run with a spectral range of 120 nm to 430 nm with a 4.5 Hz scan rate, nitrogen make-up gas at a pressure of 0.35 psi, and a deuterium lamp as the light source. Nitroalkane and nitroaromatic compounds were analyzed at a transfer line and flow cell temperature of 300°C, while nitrate ester and nitramine compounds were analyzed at 200°C due to their thermal decomposition at higher temperatures.[7, 34] Spectra obtained for PCA and LDA analysis were obtained at a flow cell temperature of 300°C.

2.5 Principal Component Analysis and Discriminant Analysis. JMP Pro 15 by SAS Institute was utilized to complete Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA). For PCA analysis, spectra were normalized via the square root of the sum of squares normalization. The spectra were then truncated to 120 nm - 300 nm. Five replicates of each compound were acquired. The first four principal components were utilized for LDA.

3. RESULTS AND DISCUSSION

3.1 Nitroalkanes. The VUV spectra of four nitroalkanes are similar with absorption features around 200 nm and below 150 nm (Fig. 1). The ratio of the relative absorption intensity between these two absorption features (< 150 nm / 200 nm) increases as the molecular weight increases (r = 0.81). When compared to the VUV spectra of their corresponding alkanes (not shown), these spectra confirm that the contribution of the alkyl nitro group in gas phase VUV spectra is a single broad absorption that appears between 185 and 215 nm. This was confirmed previously via experimental and computational analysis of nitromethane as the $\pi^* \leftarrow \pi$ transition associated with the nitro group.[35-37]

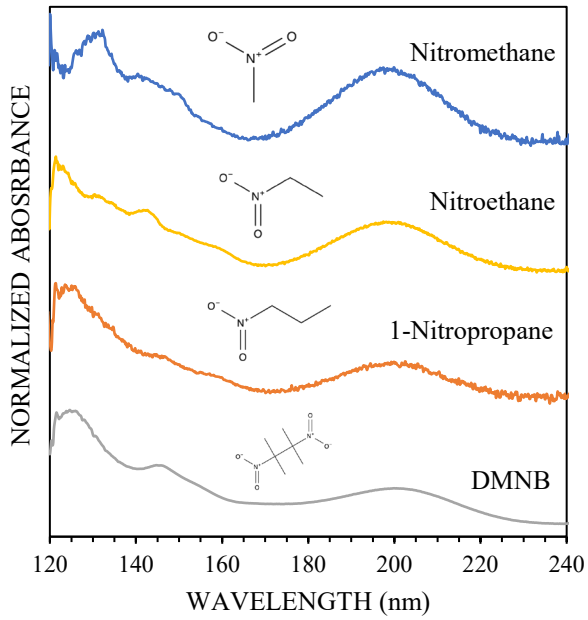
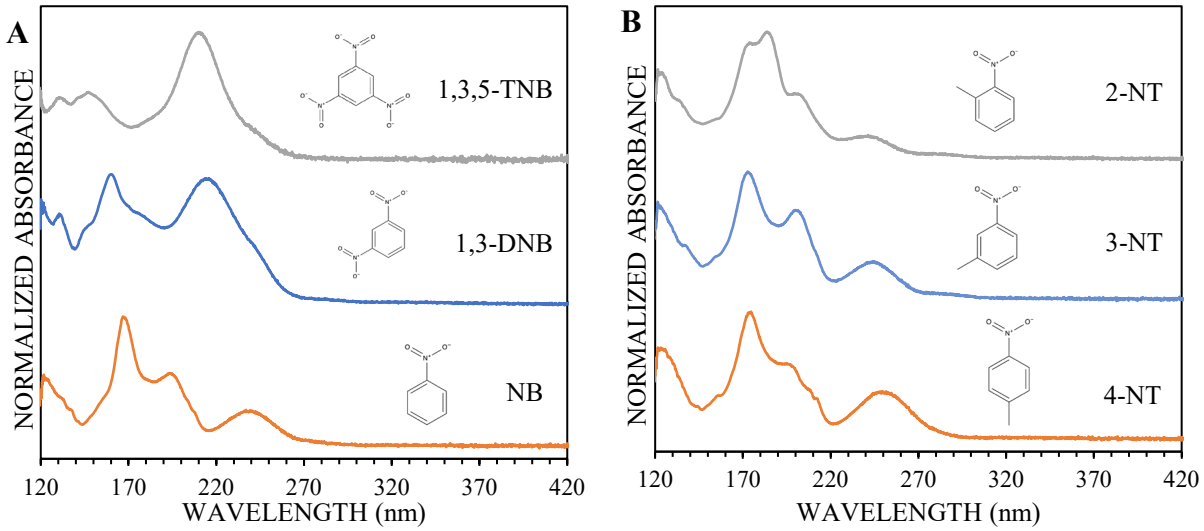


FIGURE 1. Nitroalkane VUV spectra at 300 °C.

3.2 Nitroaromatics. VUV spectra of the nitroaromatics are organized by similar structures (*i.e.*, nitrobenzenes (Fig. 2A), mononitrotoluenes (Fig. 2B), and di- and tri- nitrotoluenes (Figure 2C)). More complex structures that did not correspond to these categories are grouped into Fig. 2D.
In nitrobenzenes (Figure 2A), the nitro functional group generates a broad absorption around 240 nm. As additional nitro groups are added, this absorption increases in intensity and exhibits a blue shift, appearing at the shoulder of the absorption band at 210 nm in trinitrobenzene. This absorption band has been established for nitrobenzene as the $\pi^* \leftarrow \pi$ charge transfer transition from the benzene ring to the nitro group.[38-41]

Mononitrotoluenes (Figure 2B) have a similar broad absorption between 240 and 250 nm. A decrease in the absorption intensity of the nitro group charge transfer for 2-nitrotoluene is observed. This is attributed to the ortho position of the nitro group to the methyl group that sterically forces the nitro group out of plane and decreasing the energy of charge transfer state.[42-45] Similar to nitrobenzenes, as additional nitro groups are added to the toluene sub-structure (Figure 2C) the absorption increases in intensity and shifts to shorter wavelengths, appearing at 240 nm on the shoulder of the absorption band at 210 nm in 2,4,6-trinitrotoluene. The spectra of 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene became more complex with the addition of two nitro groups when compared to the VUV spectra of o-toluidine and p-toluidine (not shown), respectively. The nitrated VUV spectra of the toluidine compounds resulted in a more complex and broader absorption band around 215 nm due to increased overlapping of multiple absorption bands (Figure 2D).[46] Additionally, the presence of the nitro groups on musk xylene shifts the maximum absorbance to a slightly longer wavelength (198 nm for musk xylene) when compared to 5-tert-butyl-m-xylene (195 nm) (Figure 2C).[46]
Note that several compounds in this class exhibit EI mass spectra that are extremely similar (e.g., 2,4- and 2,6- dinitrotoluene[30] and 3- and 4- nitrotoluene). These compounds can be readily differentiated based upon their VUV spectra. This underscores the discriminating power of VUV spectroscopy as a detector for GC.



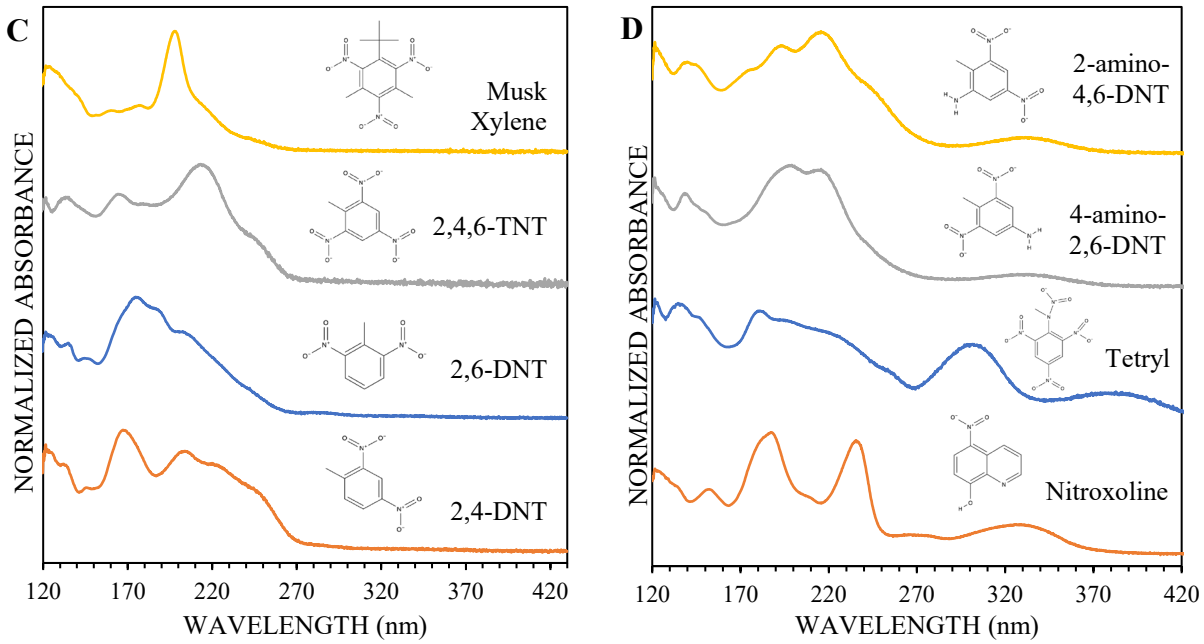


FIGURE 2. VUV spectra at 300°C of nitroaromatic compounds. Compounds are grouped by parent structure: A) nitrobenzenes, B) mononitrotoluenes, C) di- and tri- nitrotoluenes, and D) more complex nitroaromatics, where TNT = trinitrotoluene, DNT = dinitrotoluene, NT = nitrotoluene, TNB = trinitrobenzene, DNB = dinitrobenzene, and NB = nitrobenzene.

3.3 Nitrate Esters and Nitramines. Analysis of nitrate ester and nitramine compounds at higher VUV transfer and flow cell temperatures (e.g. >250°C) result in thermal decomposition.[7, 34] Therefore, these compounds were analyzed at 200°C to obtain intact spectra to investigate the nitro group absorption band (Fig. 3). Compared to the corresponding alkanes for the nitrate ester explosives (EGDN, NG, and PETN), an absorption band was observed between 170 nm and 210 nm that was attributed to the nitro groups. Relative absorbance increased with increase in percent nitrogen content (r = 0.86). Additionally, a blue shift is observed with the increase in nitro groups, with the exception of isosorbide mononitrate.

3.4 PCA and DA. Compounds analyzed for PCA and LDA were analyzed at 300°C to represent a realistic temperature encountered in realistic analyses (typical temperatures in literature are 275°C). The first four principal components captured >90% of the total variance (the cumulative percent variance for the first four principal components were 68.75%, 81.25%, 88.23%, and 92.64%, respectively). Therefore, these four principal components were selected for LDA analysis. Investigation of the factor loadings of the variables (the wavelength range from 125 nm to 240 nm) was utilized to understand the chemical differences of the compounds analyzed. Nitroaromatic compounds were distinguished from nitrate esters and nitramine compounds along principal component 1 (Fig. 4A). This also distinguished between intact compounds (nitroaromatics) and decomposed compounds (nitrate esters and nitramine). Principal component 2 discriminated within functional groups in which it is observed that nitroaromatics di- and tri- nitrotoluene have an absorbance at ~220 nm while this is absent for mono-nitrotoluenes. This is due to an overlapping of absorption bands in the di- and tri-nitrotoluenes as the nitro group absorption band shifted to lower wavelengths. Additionally, separation of EGDN, NG, and PETN from RDX, ISMN, and ISDN is apparent along principal component 2 due to presence of formaldehyde in the decomposition spectra as well as a broader absorption bands observed at <170 nm in the spectra of RDX, ISMN, and ISDN.

Utilizing an 80:20 validation, zero misclassifications were observed. Demonstrating clear discrimination between nitro compounds with similar chemical structures and the discriminating power of VUV (Fig. 4B).

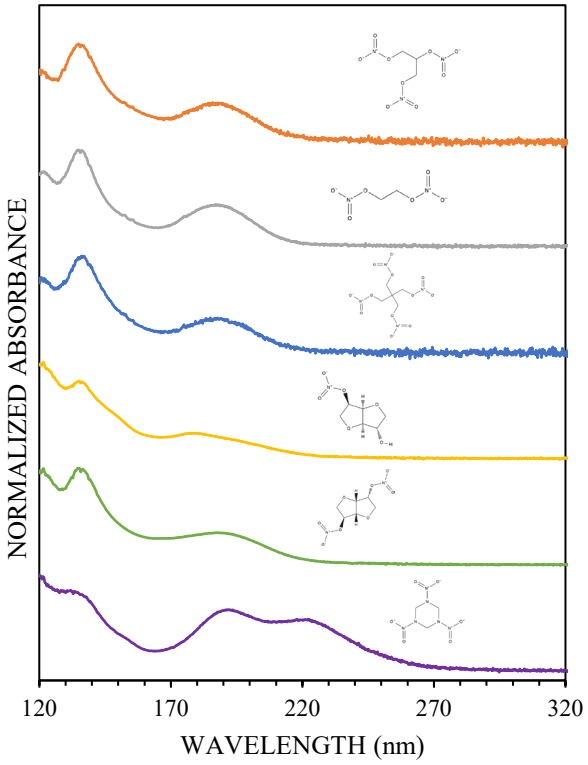
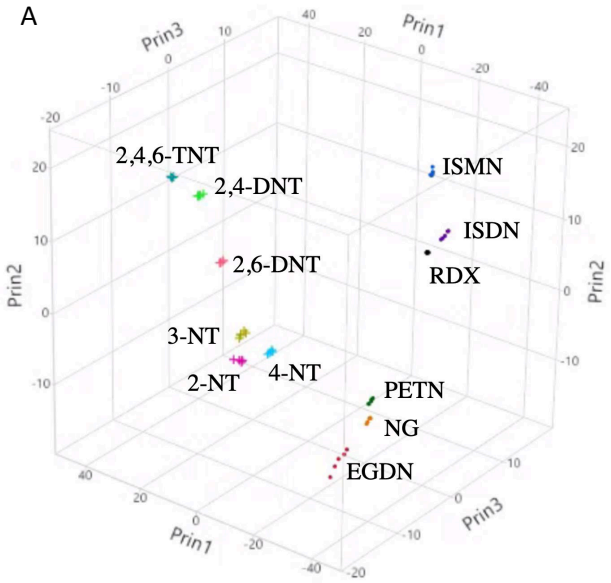


FIGURE 3. Nitrate ester and nitramine VUV intact spectra analyzed at 200°C.



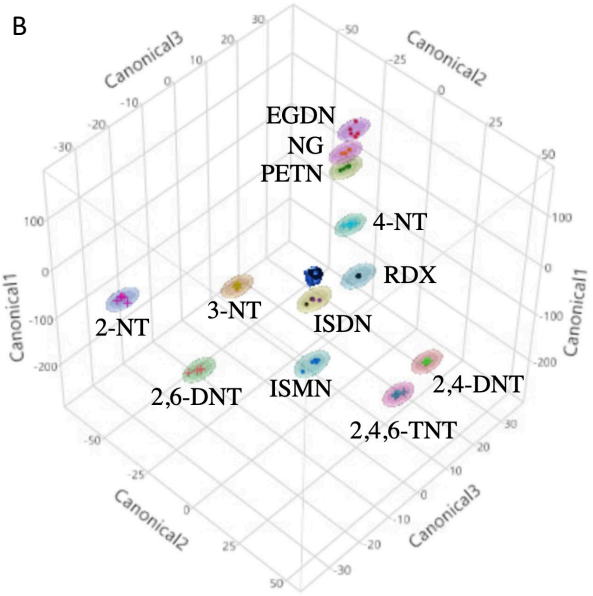


FIGURE 4. A. Three-dimensional factor score plot for five replicates of nitroaromatic, nitrate ester, and nitraime compounds. Cross markers denote nitroaromatic compounds while circle markers denote nitrate ester and nitramine compounds. B. Three-dimensional canonical plot for LDA based upon the first four principal components with 80:20 training:validation.

3.5 Nitro Group Absorption Classification. The nitro group absorption bands were investigated by structural class to establish structural information and potential for structural elucidation of unknown compounds. Nitrobenzenes and nitrotoluenes have nitro absorption band regions that are distinct from nitroalkanes and nitrate esters. However, nitrate esters and nitroalkanes overlap with nitroalkanes being slightly red shifted compared to the nitrate esters. Additionally, nitrobenzenes and nitrotoluenes overlap (to form a larger nitroaromatic group) with nitrobenzenes having a blue shift and narrower absorption band.

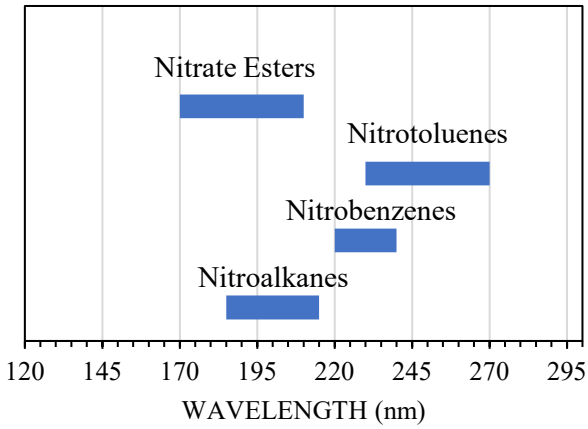


FIGURE 5. Absorption bands of the nitro group characterized by chemical structure.

4. CONCLUSIONS

Nitrated compounds were analyzed by GC/VUV to investigate the characteristic absorption of the nitro group in the wavelength region from 120 nm to 430 nm. Addition of nitro functional groups on benzene or toluene resulted in an increase in intensity and blue shift from approximately 240 nm to 210 nm for the nitro group absorption band. Nitroalkanes exhibited a trend in that the ratio of the relative absorption intensity between these two absorption features between the alkyl group (< 150 nm) and the nitro group (200 nm) increases as the molecular weight increases. In addition, the nitrate ester nitro group absorbs from 170 nm to 210 nm with an increased absorbance, relative to the primary absorption band, with the increase in percent nitrogen content. Analysis of the loading plots from PCA revealed

differences based on the chemical structure of the compounds with principal component 1 differentiating between nitroaromatics and nitrate ester and nitramine compounds, and principal component 2 differentiating EGDN, NG, and PETN from RDX, ISMN, and ISDN. Utilizing the first four principal components, LDA with an 80:20 validation resulted in successful discrimination of all compounds. Thus, further establishing the discriminating power of VUV to differentiate between nitrated compounds.

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Author Contributions
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Notes
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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REFERENCES

[1] K.A. Schug, I. Sawicki, D.D. Carlton, H. Fan, H.M. McNair, J.P. Nimmo, P. Kroll, J. Smuts, P. Walsh, D. Harrison, Vacuum Ultraviolet Detector for Gas Chromatography, Anal. Chem. (Washington, DC, U. S.), 86 (2014) 8329-8335.
[2] Z.R. Roberson, J.V. Goodpaster, Differentiation of Structurally Similar Phenethylamines via Gas Chromatography – Vacuum Ultraviolet Spectroscopy (GC – VUV), Forensic Chemistry, (2019) 100172.
[3] R.F. Kranenburg, A.R. García-Cicourel, C. Kukurin, H.-G. Janssen, P.J. Schoenmakers, A.C. van Asten, Distinguishing drug isomers in the forensic laboratory: GC–VUV in addition to GC–MS for orthogonal selectivity and the use of library match scores as a new source of information, Forensic Science International, 302 (2019) 109900.
[4] A. Hodgson, J. Cochran, Vacuum Ultraviolet Spectroscopy as a New Tool for GC Analysis of Terpenes in Flavors and Fragrances, Journal of AOAC International, 102 (2019) 655-658.
[5] B.M. Weber, P. Walsh, J.J. Harynuk, Determination of Hydrocarbon Group-Type of Diesel Fuels by Gas Chromatography with Vacuum Ultraviolet Detection, Analytical Chemistry, 88 (2016) 5809-5817.
[6] H. Fan, J. Smuts, L. Bai, P. Walsh, D.W. Armstrong, K.A. Schug, Gas chromatography-vacuum ultraviolet spectroscopy for analysis of fatty acid methyl esters, Food Chem., 194 (2016) 265-271.
[7] C.A. Cruse, J.V. Goodpaster, Generating highly specific spectra and identifying thermal decomposition products via Gas Chromatography/Vacuum Ultraviolet Spectroscopy (GC/VUV): Application to nitrate ester explosives, Talanta, 195 (2019) 580-586.
[8] H. Fan, J. Smuts, P. Walsh, D. Harrison, K.A. Schug, Gas chromatography–vacuum ultraviolet spectroscopy for multiclass pesticide identification, Journal of Chromatography A, 1389 (2015) 120-127.
[9] H. Fan, J. Smuts, L. Bai, P. Walsh, D.W. Armstrong, K.A. Schug, Gas chromatography–vacuum ultraviolet spectroscopy for analysis of fatty acid methyl esters, Food Chemistry, 194 (2016) 265-271.

[10] C. Qiu, J. Cochran, J. Smuts, P. Walsh, K.A. Schug, Gas chromatography-vacuum ultraviolet detection for classification and speciation of polychlorinated biphenyls in industrial mixtures, Journal of Chromatography A, 1490 (2017) 191-200.
[11] S. Buchalter, I. Marginean, J. Yohannan, I.S. Lurie, Gas chromatography with tandem cold electron ionization mass spectrometric detection and vacuum ultraviolet detection for the comprehensive analysis of fentanyl analogues, Journal of Chromatography A, (2019).
[12] R.F. Kranenburg, A.R. Garcia-Cicourel, C. Kukurin, H.G. Janssen, P.J. Schoenmakers, A.C. van Asten, Distinguishing drug isomers in the forensic laboratory: GC-VUV in addition to GC-MS for orthogonal selectivity and the use of library match scores as a new source of information, Forensic Sci Int, 302 (2019) 109900.
[13] Z.R. Roberson, J.V. Goodpaster, Differentiation of structurally similar phenethylamines via gas chromatography-vacuum ultraviolet spectroscopy (GC-VUV), Forensic Chem, 15 (2019) 100172.
[14] C. Qiu, J. Smuts, K.A. Schug, Analysis of terpenes and turpentines using gas chromatography with vacuum ultraviolet detection, J Sep Sci, 40 (2017) 869-877.
[15] J. Schenk, J.X. Mao, J. Smuts, P. Walsh, P. Kroll, K.A. Schug, Analysis and deconvolution of dimethylnaphthalene isomers using gas chromatography vacuum ultraviolet spectroscopy and theoretical computations, Anal Chim Acta, 945 (2016) 1-8.
[16] T. Groger, B. Gruber, D. Harrison, M. Saraji-Bozorgzad, M. Mthembu, A. Sutherland, R. Zimmermann, A Vacuum Ultraviolet Absorption Array Spectrometer as a Selective Detector for Comprehensive Two-Dimensional Gas Chromatography: Concept and First Results, Anal Chem, 88 (2016) 3031-3039.
[17] J.L. Tanen, I.S. Lurie, I. Marginean, Gas chromatography with dual cold electron ionization mass spectrometry and vacuum ultraviolet detection for the analysis of phenylethylamine analogues, Forensic Chem, 21 (2020) 100281.
[18] M.N. Dunkle, P. Pijcke, B. Winniford, G. Bellos, Quantification of the composition of liquid hydrocarbon streams: Comparing the GC-VUV to DHA and GCxGC, Journal of Chromatography A, 1587 (2019) 239-246.
[19] P. Walsh, M. Garbalena, K.A. Schug, Rapid Analysis and Time Interval Deconvolution for Comprehensive Fuel Compound Group Classification and Speciation Using Gas Chromatography-Vacuum Ultraviolet Spectroscopy, Anal. Chem. (Washington, DC, U. S.), 88 (2016) 11130-11138.
[20] J.X. Mao, P. Walsh, P. Kroll, K.A. Schug, Simulation of Vacuum Ultraviolet Absorption Spectra: Paraffin, Isoparaffin, Olefin, Naphthene, and Aromatic Hydrocarbon Class Compounds, Appl Spectrosc, 74 (2020) 72-80.
[21] L. Bai, J. Smuts, J. Schenk, J. Cochran, K.A. Schug, Comparison of GC-VUV, GC-FID, and comprehensive two-dimensional GC-MS for the characterization of weathered and unweathered diesel fuels, Fuel, 214 (2018) 521-527.
[22] C. Qiu, P. Asgari, X.J. Mao, J. Jeon, K.A. Schug, Gas chromatography-vacuum ultraviolet spectroscopic analysis of organosilanes, Talanta, 223 (2021) 121781.
[23] A.R. Garcia-Cicourel, H.G. Janssen, Direct analysis of aromatic hydrocarbons in purified mineral oils for foods and cosmetics applications using gas chromatography with vacuum ultraviolet detection, J Chromatogr A, 1590 (2019) 113-120.
[24] A.R. Garcia-Cicourel, H.-G. Janssen, Direct analysis of aromatic hydrocarbons in purified mineral oils for foods and cosmetics applications using gas chromatography with vacuum ultraviolet detection, J Chromatogr A, 1590 (2019) 113-120.
[25] J.X. Mao, P. Kroll, K.A. Schug, Vacuum ultraviolet absorbance of alkanes: an experimental and theoretical investigation, Structural Chemistry, (2019).
[26] C. Qiu, K.A. Schug, J. Smuts, Analysis of terpenes and turpentines using gas chromatography with vacuum ultraviolet detection, J Sep Sci, 40 (2017) 869-877.
[27] A. Leghissa, J. Smuts, C.L. Qiu, Z.L. Hildenbrand, K.A. Schug, Detection of cannabinoids and cannabinoid metabolites using gas chromatography with vacuum ultraviolet spectroscopy, Separation Science Plus, 1 (2018) 37-42.

[28] V. Lagesson, L. Lagesson-Andrasko, J. Andrasko, F. Baco, Identification of compounds and specific functional groups in the wavelength region 168–330 nm using gas chromatography with UV detection, Journal of Chromatography A, 867 (2000) 187-206.
[29] L. Lagesson-Andrasko, V. Lagesson, J. Andrasko, The Use of Gas-Phase UV Spectra in the 168−330-nm Wavelength Region for Analytical Purposes. 1. Qualitative Measurements, Analytical chemistry, 70 (1998) 819-826.
[30] R. Reiss, B. Gruber, S. Klingbeil, T. Groeger, S. Ehlert, R. Zimmermann, Evaluation and application of gas chromatography - vacuum ultraviolet spectroscopy for drug- and explosive precursors and examination of non-negative matrix factorization for deconvolution, Spectrochim. Acta, Part A, 219 (2019) 129-134.
[31] R. Reiss, B. Gruber, S. Klingbeil, T. Groger, S. Ehlert, R. Zimmermann, Supplementary Material: Evaluation and application of gas chromatography - vacuum ultraviolet spectroscopy for drug- and explosive precursors and examination of non-negative matrix factorization for deconvolution, Spectrochim Acta A Mol Biomol Spectrosc, 219 (2019) 129-134.
[32] C. Weston, J. Smuts, J.X. Mao, K.A. Schug, Investigation of gas phase absorption spectral similarity for stable-isotopically labeled compounds in the 125-240nm wavelength range, Talanta, 177 (2018) 41-46.
[33] C.A. Cruse, J.V. Goodpaster, Thermal and spectroscopic analysis of nitrated compounds and their break-down products using gas chromatography/vacuum UV spectroscopy (GC/VUV), Analytica Chimica Acta, 1143 (2021) 117-123.
[34] C.A. Cruse, J. Pu, J.V. Goodpaster, Identifying Thermal Decomposition Products of Nitrate Ester Explosives Using Gas Chromatography-Vacuum Ultraviolet Spectroscopy: An Experimental and Computational Study, Appl Spectrosc, (2020) 3702820915506.
[35] I.C. Walker, M.A.D. Fluendy, Spectroscopy and dynamics of nitromethane (CH3NO2) and its anionic states11Dedicated to Professor Aleksandar Stamatovic on the occasion of his 60th birthday, International Journal of Mass Spectrometry, 205 (2001) 171-182.
[36] W.M. Flicker, O.A. Mosher, A. Kuppermann, Investigation of low-lying electronic states in nitromethane by electron-impact spectroscopy, Chemical Physics Letters, 60 (1979) 518-522.
[37] M. Bazin, S. Ptasinska, A.D. Bass, L. Sanche, E. Burean, P. Swiderek, Electron induced dissociation in the condensed-phase nitromethane: II. Desorption of neutral fragments, Journal of Physics: Condensed Matter, 22 (2010) 084003.
[38] S. Krishnakumar, A.K. Das, P.J. Singh, A. Shastri, B.N. Rajasekhar, Experimental and computational studies on the electronic excited states of nitrobenzene, Journal of Quantitative Spectroscopy and Radiative Transfer, 184 (2016) 89-99.
[39] O. Kröhl, K. Malsch, P. Swiderek, The electronic states of nitrobenzene: electron-energy-loss spectroscopy and CASPT2 calculations, Physical Chemistry Chemical Physics, 2 (2000) 947-953.
[40] S. Nagakura, M. Kojima, Y. Maruyama, Electronic spectra and electronic structures of nitrobenzene and nitromesitylene, Journal of Molecular Spectroscopy, 13 (1964) 174-192.
[41] T. Ari, H. Güven, N. Ecevit, Electron energy-loss spectroscopy in monosubstituted benzenes, Journal of Electron Spectroscopy and Related Phenomena, 73 (1995) 13-23.
[42] W.G. Brown, H. Reagan, Steric Effects in the Ultraviolet Absorption Spectra of Aromatic Nitro Compounds, Journal of the American Chemical Society, 69 (1947) 1032-1033.
[43] W.R. Remington, The Effects of Steric Inhibition of Resonance on Ultraviolet Absorption Spectra1, Journal of the American Chemical Society, 67 (1945) 1838-1842.
[44] D.W. Sherwood, M. Calvin, Resonance in Substituted Biphenyls1a, Journal of the American Chemical Society, 64 (1942) 1350-1353.
[45] J. Clarkson, W.E. Smith, D.N. Batchelder, D.A. Smith, A.M. Coats, A theoretical study of the structure and vibrations of 2,4,6-trinitrotolune, Journal of Molecular Structure, 648 (2003) 203-214.
[46] VUVAnalytics, VUV Spectral Database, Austin, TX, 2018.