



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Application of infrared spectrum for rapid classification of dominant petroleum hydrocarbon fractions for contaminated site assessment

Liang Wang^{a,b,*}, Ying Cheng^{a,b}, Dane Lamb^{a,b}, Raja Dharmarajan^{a,b}, Sreenivasulu Chadalavada^b, Ravi Naidu^{a,b}^a Global Centre for Environmental Remediation, Research and Innovation Division, University of Newcastle, Callaghan, NSW 2308, Australia^b CRC for Contamination Assessment and Remediation of Environment, University of Newcastle, Callaghan, NSW 2308, Australia

ARTICLE INFO

Article history:

Received 20 July 2018

Received in revised form 13 September 2018

Accepted 14 September 2018

Available online 15 September 2018

Keywords:

Handheld FTIR

Carbon chain length (C_n)

Petroleum hydrocarbon

Alkanes

Rapid site assessment

ABSTRACT

In this study, the infrared spectrum ($4000\text{--}400\text{ cm}^{-1}$) was applied to identify and classify the different alkanes based on carbon chain length (C_n). It was found there were two bands coherent to the doublet at location 2954 and 2872 cm^{-1} , respectively can be applied to identify the fraction of carbon chains. From C_{20} to C_{37} , by the increase of the C_n , the intensities of the two bands were reduced as demonstrated. There were another two doublets existed at the region from 1480 to 1450 cm^{-1} and the region at 750 and 730 cm^{-1} . It was observed the intensity of one coherent band at each of these regions was increased following the increase on the C_n . The bands center at 1462 and 730 cm^{-1} were increased from C_{20} to C_{37} . The intensity ratio of the coherent bands can be applied to identify the C_n . Successfully identify four different petroleum products with different fractions of carbon chains in soil samples, is evidence the theory can be applied to investigate the fraction of carbon chains in soil. Coupling with handheld FTIR, it is possible to rapidly estimate the dominant fraction of C_n in soil in field.

© 2018 Published by Elsevier B.V.

1. Introduction

Petroleum is comprised of highly complex and varied mixtures of hydrocarbons [1]. For example, crude oil can consist of hundreds of individual petroleum hydrocarbon (PHC) compounds that represent from 50 to 98% of the total weight of crude oil [2]. The PHC fractions are defined by chemical structure, carbon number, and structure-activity relationships [3]. Equivalent carbon numbers (C_n) are used to describe the PHC fractions, which are based on a range of physical-chemical properties and simple partitioning models [4]. The chains under C_7 , called naphthas, which are normally used as dry cleaning solvents, are very light and easily vaporised. The chains from C_7 to C_{11} are normally blended and used for petrol, which is more volatile than water. The sequence that follows is kerosene, from C_{12} to C_{15} , and then diesel and other heavier fuel oils, from C_{12} to C_{30} . Lubricating oils, such as engine and motor oils, have carbon chains above C_{30} . Hydrocarbons with higher carbon fractions, or longer the carbon chains, are considered as heavier fractions of PHCs. The heavier fractions of PHCs have high viscosity, density, boiling points and long residence times in soil [3].

When an oil spill or leakage occurs on land, the sequestration and diffusion of PHCs are subject to physical, chemical, and biological processes that further change their composition, toxicity, and distribution (partitioning) within soil, and are referred to as weathering processes

[5]. The highly volatile fractions of PHCs will evaporate into the gas phase of the porous medium and may be lost to the atmosphere, adsorbed on to soil solids, or dissolved into soil water or groundwater [6]. Less volatile PHCs will diffuse as oil or non-aqueous liquid (NAPLs) forms, through the porous medium and be trapped in pores or adsorbed at mineral and organic matter surfaces. Linear compounds up to C_{30} , for example, may dissipate within a month by volatilisation, decomposition and degradation. By contrast, those with up to C_{37} need at least 200 days. Indeed, the tar fraction consisting of long and complex chains can persist for years [7]. Investigating the carbon fractions in a PHC contaminated site can provide valuable site assessment information for remediation.

To measure the fractions of C_n of PHC contaminants in soil, they need to be extracted by standardised soil extraction procedures before instrumental analysis. For volatile compounds, such as BTEX and petrol, methanol extraction is suggested under EPA method 5035, or direct headspace analysis can be performed. For semi-volatile compounds Soxhlet, sonication and supercritical fluid extractions (SFE) are commonly employed [1]. High-performance liquid chromatography (HPLC) and gas chromatography (GC) are the commonly used instrumental techniques for PHC analyses. GC with mass spectrometry (GC/MS) or flame ionisation detection (GC/FID) are preferably used for individual PHC component determinations [8]. However, these approaches suffer from disadvantages compared with online *in situ* monitoring, including the associated laboratory costs and lengthy processing time, sample degradation and cross contamination. In addition, these conventional methodologies provide only a 'snapshot' in time. Consequently,

* Corresponding author at: Global Centre for Environmental Remediation, Research and Innovation Division, University of Newcastle, Callaghan, NSW 2308, Australia.

E-mail address: Liang.Wang@newcastle.edu.au (L. Wang).

these methods require frequent sampling intervals to provide representative temporal variations in PHC levels. An alternative method for measuring PHCs is to use an infrared (IR) technique, such as EPA method 8440, whereby the PHCs are identified by their spectral bands. The analysis time and cost of IR methods are typically far less than the GC and HPLC based methodologies.

Nevertheless, the major disadvantage of Fourier Transformed IR (FTIR) is that the spectrum line shape (band) typically consists of a series of more or less overlapping bands representing absorbed or scattered individual molecules, which can be considered as interferences [9–12]. Extracting the information and identifying the components from an overlapping IR spectrum is a key challenge to analysing a sample with an unknown mixture of PHCs. Czarnecki and Ozaki noted that the separation of very overlapping bands requires both an experienced researcher and some knowledge about the system being studied [12]. Therefore, infrared analyses in the region of 4000 to 400 cm^{-1} are commonly used for such chemical structure studies.

Irrespective of the length of the carbon chains, all the PHC fractions have similar band patterns in infrared spectral modes. As demonstrated, a similar doublet IR band between 3000 and 2800 cm^{-1} , and a smaller single band between 1500 and 1450 cm^{-1} presented for all the long-chain alkanes. These IR bands indicate the vibration of carbon hydrogen bindings. Therefore, the slight difference of PHC fractions in the mid-IR 'fingerprint' region (1500–700 cm^{-1}) become crucial for PHC determination. However, the signals at the mid-IR 'fingerprint' region are significantly weaker than higher wavelength regions. Additionally, they possess low signal to noise ratios with intensive bands overlapping. Hence, there have only been limited studies on applying these spectral techniques for determination of PHC fractions.

Coupling with a handheld FTIR, this study demonstrated a rapid PHC fraction classification method for *in situ* PHC weathering assessment. Long chain alkanes from Icosane (C_{20}) to heptatriacontane (C_{37}) have been investigated using the infrared spectral signals. A novel infrared spectral data processing method was applied to automatically baseline correct and band decompose the IR spectra without visual inspection. Quantitative analysis for each alkane was investigated using the decomposed sub-bands. Orthogonal experimental design (OED) was applied to generate the alkane mixtures with designed heterogeneous concentrations [14].

2. Methodology

2.1. Apparatus

Pure chemicals of the alkanes: icosane (C_{20}), hexacosane (C_{26}), octacosane (C_{28}), dotriacontane (C_{32}) and heptatriacontane (C_{37}) were obtained from Sigma Aldrich. The pure alkane chemicals were added into hexane (95%, Sigma Aldrich) to create 20 mL of 10 g/L standard solutions for C_{20} to C_{32} , and 5 g/L for C_{37} , respectively. It was observed that the alkanes with higher carbon chain numbers have lower a dissolution rate in hexane. 5 g/L C_{37} solutions needed to be prepared with the assistance of ultrasonic vibrations. The individual alkanes were spiked into potassium bromide (KBr) for characteristic sub-band identification.

All the samples were measured triplicated using a handheld FTIR (Agilent 4300), with an 8 cm^{-1} resolution, 32 sample scans, 64 background scans were co-added in the infrared 4000 to 600 cm^{-1} region, at a scanning velocity of 2.5 kHz, and 255 beam energy. All measurements for the spiked soil samples were made in diffuse reflectance infrared spectroscopy (DRIFTS) mode, sample non-destructively. It should be mentioned that there are several levels of spectral resolution: from 8 to 2 cm^{-1} . The lower the number present, the higher resolutions, and the detection limits and spectral features for a given compound can be improved through higher resolutions which need high-resolution interferometers. However, the relative cost to incorporate such a system for field monitoring would be exorbitant. Further, it would take a considerable amount of time for a scan and obtain point data for

computational analysis. The sensitivity level chosen for this experiment is appropriate for reduced downtime and rapid screening for field related applications. With setting the resolution at 8 cm^{-1} , one measurement can be completed within thirty seconds with 32 scans. The infrared spectrum data can be obtained using Agilent Microlab PC software (Agilent). The spectrum data was transferred to the Resolutions Pro FTIR software for observation. The spectrum data was saved in comma separated value format (CSV), which is editable using Excel 2013. MATLAB R2016b was applied for method implementation, data processing, and analysis.

2.2. Baseline Correction

In this study, a new baseline correction method, computational recursion, was developed and applied to automated baseline correction for MIR (4000 to 400 cm^{-1}) spectra. The algorithm developed will run through all the spectral details and locate the lowest valley; then the baseline can be simply drawn by connecting the valleys to each side of the spectrum using straight lines. If any part of the spectrum is intersected by the straight lines after baseline correction, the spectrum will create negative absorbance values. In this case, the algorithm will be recursively run for the spectral regions where the intersecting straight lines connected. This simple and rapid baseline correction method can be applied to any IR spectral region, without any intervention. Furthermore, since all the PHCs have similar spectral features, the adopted baseline correction method can give unified baseline corrected IR data for all of the analytes of interest.

2.3. Band Decomposition

Automatic band decomposition method was applied in this study. The sub-bands were established using a second derivation curve (SDC). The band number can be controlled by eliminating the number of SDC valleys [13]. The dominant bands from the original spectrum were presented as the lower valleys in the SDC. The small valleys, representing secondary bands, could be eliminated using a Gaussian low pass filter, with a standard deviation 1.5. The spectrum band can be properly decomposed using Gaussian curves, which the amplitude, width, and location were optimized using Monte Carlo algorithm (MCA), which is a heuristic algorithm based on randomness and statistics to get an optimisation result.

3. Results and Discussion

3.1. Alkane Determination

The measurements for alkane identification was conducted using four different alkanes, C_{20} , C_{26} , C_{32} and C_{37} with the concentration of 5000 ppm for each alkane, respectively. To prepare these standards, the pure alkane chemicals were diluted with potassium bromide (KBr). The four alkanes' spectra after background subtraction and baseline correction are shown in Fig. 1.a. According to the similarity of the IR bands in the entire region indicates the alkanes have identical molecular structures. The doublet observed between 3000 and 2800 cm^{-1} , which is the evidence of carbon hydrogen bonding for long-chain alkanes due to —C—H stretching vibrations. From the Fig. 1.b, it is found there were two bands coherent to the doublet at location 2954 and 2872 cm^{-1} , respectively. From C_{20} to C_{37} , by the increase of the C_n , the intensities of the two bands were reduced as demonstrated. This phenomenon matched the similar results from Snyder and co-workers, when they are comparing the Raman spectrum data of C_8 and C_{20} [14,15]. As demonstrated in one of their figures, both the spectra of C_8 and C_{20} contained all the similar bands, including the bands at location 2954 and 2872 cm^{-1} . It is observed the band intensities of the C_{20} were less than C_8 at these two locations [14]. On the opposite, there were another two doublets existed in the region from 1480 to 1450 cm^{-1} and the

Download English Version:

<https://daneshyari.com/en/article/10147305>

Download Persian Version:

<https://daneshyari.com/article/10147305>

[Daneshyari.com](https://daneshyari.com)