Using Fluorescence Emission-Excitation Matrices (EEMs) and Parallel Factor Analysis (PARAFAC) for Characterizing Petroleum Fractions

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ABSTRACT

This paper presents a rapid and objective approach for characterizing petroleum products and crude oil based on their polycyclic aromatic hydrocarbons (PAHs) composition. The method uses Fluorescence excitation-emission matrices (EEMs) combined with advanced multivariate statistical procedures: parallel factor analysis (PARAFAC) and soft independent method of class analogy (SIMCA) to identify the underlying components of the EEMs. The approach provides a fingerprinting for different petroleum products in solvents or mixed with soils. In this study, the method easily discriminated between the different samples of petroleum products: gas condensate, gasoline, diesel, flare pit residue, and heavy crude oil. Modeled PARAFAC components of various petroleum products and crude oil were compared to EEMs of standard PAHs. The comparisons indicated that the modeled components can be related to standard PAHs with similar fluorescence characteristics. The presence of predicted PARAFAC components was validated by laboratory chemical analysis results of the same petroleum products and crude oil samples.

RÉSUMÉ

Ce document présentera une démarche rapide et objective pour identifier les caractéristiques des produits pétroliers et du pétrole brut selon leurs compositions en hydrocarbure aromatique polycyclique (PAHs). La méthode de détection utilise des matrices d'excitation-émission (EEMs) par Fluorescence de pairs avec des procédures avancées de méthode à variables multiples tels que : l'analyse factorielle en parallèle (PARAFAC) et la méthode douce et indépendante de l'analogie des classes (SIMCA), pour identifier les composantes sous-jacentes des EEMs. L'approche fournit une table de références pour chaque produit pétroliers différents qui se retrouvent dans les solvants ou mélangé au sol. La méthode utilisée dans cette étude a pu facilement différencier les échantillons de produits pétroliers particuliers tels que : gaz à condensat, essence, diesel, résidu du puits de torche, et huile brut lourd. Les composantes des produits pétroliers et du pétrole brut utilisées comme modèle dans PARAFAC furent comparées avec les EEMs standard des PAHs. Les comparaisons démontrent que les composantes modelées concordent avec les PAHs standard qui ont des caractéristiques de fluorescences similaires. La présence des éléments PARAFAC prévus furent confirmé par les résultats en laboratoire de l'analyse chimique de ses mêmes échantillons de produits pétroliers et de pétrole brut.

1. INTRODUCTION

Various petroleum products and crude oil are frequently released into the natural environment through accidental spills, improper handling or leakage. Polycyclic aromatic hydrocarbons (PAHs) in these petroleum products are considered as significant environmental pollutants due to their potential carcinogenic or mutagenic properties. Therefore, reliable analytical methods for the continuous detection and characterization of these compounds on environmental aqueous or soil samples are of great interest (Bjorseth and Ramdahl, 1985). There is a need for improving existing methods for petroleum contaminants characterization and identification, which usually involve initial screening using gas chromatography-flame ionization detection (GC-FID) followed by more comprehensive analyses by gas chromatography/mass spectrometry (GC/MS) (Wang, et. al., 1999). In spite of their reliable selectivity and sensitivity features, these methods are based on time-consuming procedures and require an initial separation process due to spectral interferences of multi-component PAHs. Fluorescence spectroscopy is an efficient screening method that could complement current screening methods and could be used directly on various types of environmental samples as it does not require any pre-separation steps. It has been used for forensic analysis of oil and petroleum products for more than 20 years and successfully applied for the quantification of PAH compounds in petroleum products (Pharr, et. al., 1992). This work is being conducted in conjunction with the development of ultraviolet Induced fluorescence-cone penetration testing (UVIF-CPT) system that generates soil stratography and fluorescence profile data over contaminated sites to map the spatial distribution of contaminants (Alostaz, et. al., 2005). The generated data can be analyzed using the methodology described herein to rapidly discern different contaminant compounds during the contaminated site field investigation.

2. FLUORESCENCE SPECTROSCOPY

The fluorescing nature of petroleum products and crude oil is related to the electron structure and chemical bonds in their aromatic compounds constituents (i.e. compounds that have benzene ring (C_6H_6) as a basic structure). The benzene ring structure has double bonds, in which the first shared electrons pair forms an σ bond, while the second pair forms a Π bond. Electron pairs involved in Π bonding have weak binding forces. Therefore, when illuminated with sufficient energy (UV light), electrons engaged in Π bond(s) can absorb the induced energy (light photons) and get promoted to higher energy levels, from which they return to ground state through various non-radiative and radiative mechanisms including fluorescence. Due to the rigid structure of aromatic rings, they don not allow for efficient non-radiative relaxation and favor radiative mechanisms. That is why aromatic hydrocarbons have an intense fluorescing nature.

The fluorescence signal (spectrum) produced by a particular aromatic compound is unique because it reflects the compound's electron structure and can be used as a fingerprint to identify that compound. Emission fluorescence spectrum can be generated by scanning the spectral distribution of the emitted radiation (fluorescence of the illuminated hydrocarbons) at a particular exciting radiation (the source UV light) wavelength. Alternatively, in excitation fluorescence spectrum, the observation fluorescence wavelength is held constant while the fluorescence intensity is measured as a function of the excitation wavelength (Schulman, 1977). In multi-component mixtures, the overlap of fluorescence signals can be significant. Thus, alternative fluorescence analysis techniques, such as synchronous spectroscopy (Vo-Dinh, 1978), fluorescence emission-excitation matrices (EEMs) (Rho and Stuart 1978; and Vo-Dinh, 1982), and time resolved fluorescence spectroscopy (O'Connor and Phillips, 1984), might be used to resolve complex fluorescence signals.

2.1 Fluorescence Emission-Excitation Matrices (EEMs)

EEMs of a particular aromatic compound are collected by scanning its fluorescence spectra at different excitation wavelengths. The information from both the excitation spectrum and the emission spectrum are combined into a single display (Figure 1). That way, all information present in the excitation and emission fluorescence spectral features of the compound can be captured and presented in the form of a matrix. The data in an EEM is often visually presented in the form of a fluorescence contour plot that tends to separate different components of a multi-component system into isolated peaks, which helps to characterize these components (Figure 1) (Rho and Stuart, 1978; Vo-Dinh, 1982).

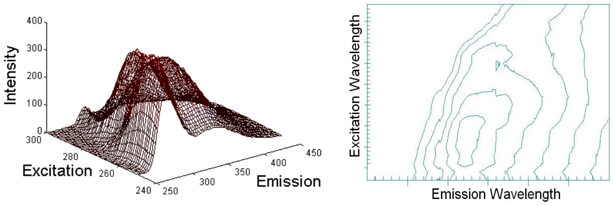

Figure 1. Excitation-Emission Matrix (EEM) (Adapted from Rho and Stuart, 1978).

Overlap in fluorescence signals can be severe in multi-component mixtures such as petroleum products that contain hundreds of individual PAHs, which produces complex EEMs that are difficult to interpret. Also quenching and energy-transfer processes can extensively affect fluorescence EEMs (Schulman, 1977). While the effect of quenching and energy-transfer processes on fluorescence of multi-component mixtures can be reduced by sample dilution, the complexity of fluorescence EEMs due to significant fluorescence signal overlap can be resolved by implementing advanced multivariate statistical techniques in Chemometrics.

3. MULTIVARIATE STATISTICAL TECHNIQUES

Chemometrics represents an interesting alternative for discrimination in multi-component sample. Multivariate statistical analysis techniques such as Parallel Factor Analysis (PARAFAC) and Soft Independent Method of Class Analogy (SIMCA) have been shown to be reliable tools to resolve multi-component mixtures of polycyclic aromatic hydrocarbons (Jiji, et. al., 1999; Pharr, et. al., 1992, Vogt and Sjoegren, 1989).

3.1 Parallel Factor Analysis (PARAFAC)

PARAFAC is multi-way decomposition technique that is suitable for decomposing three-dimensional fluorescence data generated from collecting fluorescence EEMs of a particular petroleum product at different concentrations into its underlying components. Figure 2 illustrates PARAFAC decomposition of fluorescence EEM belongs to four (4) components mixture.

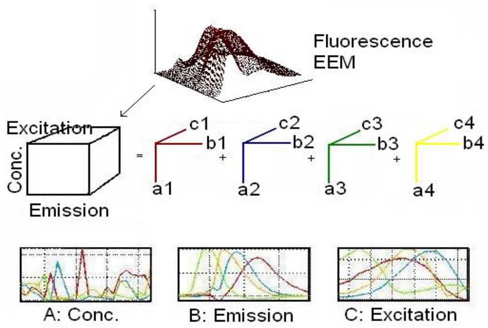

Figure 2. PARAFAC analysis of EEM data (Adapted from PLS-Toolbox manual, 2006)

Fluorescence EEMs can be arranged in a three-way array (X) of dimensions I × J × K, where I is the number of samples (at different concentrations), J the number of emission wavelengths, and K the number of excitation wavelengths. PARAFAC decomposes this array into three matrices: A (the score matrix), B, and C (loading matrices) with elements a_{if}, b_{jf}, and c_{kf}. The scores in a_{if} can be interpreted as the relative concentration of the analyte f in sample i. The vector b_f with elements b_{jf} is the estimated emission spectrum of that analyte and likewise c_f is the estimated excitation spectrum (Figure 2). Elements in X array can be modelled by PARAFAC as expressed in Equation 1, where F is the number of PARAFAC analytes and e_{ijk} represent the residual elements reflecting variability that can not be modelled:

$$x_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + e_{ijk} \qquad [1]$$

PARAFAC utilizes a least squares optimization technique, which, when given a series of measured data, attempts to find a function that closely approximates the data. It attempts to minimize the sum of the squares of the ordinate differences (residuals) between points generated by the function and corresponding points in the data (Bro and Andersen, 2003).

3.2 Soft Independent Method of Class Analogy (SIMCA)

SIMCA is a classification technique based on principal component analysis (PCA) models made for the groups of samples (classes). SIMCA constructs PCA models for each class and then projects new data to be classified onto the PCA models. By comparing the class models, the discrimination power of the variables can be estimated (Vogt and Sjoegren, 1989). Sample distances from each class are based on the Q and T^2 statistics. Therefore, samples close to a class (low Q and T^2) are considered belonging to that class. Large distances (high Q and T^2) suggest that a sample does not belong to that class. Therefore, in SIMCA it is possible for a sample to belong to one, none, or more than one class (PLS_ToolBox, 2006). The SIMCA method is robust for non-normal distributions (Vogt and Sjoegren, 1989). SIMCA can be used along with PARAFAC analysis to discriminate different types of petroleum products and crude oil based on their modeled factors.

4. EXPERIMENTAL WORK

Petroleum product samples used in this study are: 1) gas condensate, 2) gasoline, 3) diesel, 4) flare pit residue and 5) heavy crude oil. These samples were selected because they cover the typical range of petroleum contaminants that are usually encountered at upstream oil and gas sites. As well, they contain a variety of aromatic constituents with a wide range of aromatic ring sizes. Gasoline and Diesel samples used in this study were purchased from local market in Edmonton, AB. Gas condensate and flare pit residue samples were from two research sites in Alberta. The crude oil sample came from Cold Lake, AB, and was supplied by National Centre for Upgrading Technology (NCUT) laboratories, Edmonton. All samples were stored in airtight containers that were clearly marked and kept at the Applied Environmental Geochemistry Research Facility at the University of Alberta.

Along with non-diluted samples, a number of diluted samples of each petroleum product were prepared before proceeding with fluorescence measurements. Diluted sample had total concentrations that ranged from 0.5 to 800 ml/L. This wide range of concentrations was selected to provide a proper number of fluorescence EEMs for subsequent PARAFAC analysis and monitor the effect of fluorescence quenching and energy-transfer processes on the measured EEMs. In total 70 stock solution samples (including duplicates) of all petroleum products and crude oil were prepared. Hexane was used as a solvent to dilute gas condensate, gasoline and diesel samples. Chloroform was used to dilute flare pit residue and heavy crude oil due to presence of the larger PAHs in the flare pit residue or heavy crude oil samples that cannot be dissolved by Hexane.

Individual standards of PAHs were prepared including: BTEX compounds (Benzene, Toluene, Ethyl-Benzene and Xylenes), Naphthalene and Methyl-Naphthalene, Phenanthrene, Fluorene, Pyrene, Dibenzothiophene, Fluoranthene. These PAH compounds were selected because they most likely correspond to the major components of the analyzed petroleum products and crude oil, and their fluorescence signatures (EEMs) are needed to characterize the predicted components by PARAFAC analysis. In total 160 stock solution samples of individual PAH compounds were prepared with concentrations that ranged from 0.08 to 50 ml/L. For validation purposes, samples of gas condensate, gasoline, diesel, flare pit residue and heavy crude oil were sent to a commercial laboratory to be analyzed for their constituent BTEX and PAH compounds content.

Fluorescence EEMs were measured on a Varian Eclipse fluorescence spectrophotometer in the scan mode. Analyzed samples were prepared in both aqueous solutions (for baseline data) and were mixed with soils, to more closely represent actual conditions that may be encountered in the field. For aqueous solutions, 3 ml of each stock solution were transferred directly to the sample container to be analyzed. In soil mixtures, 3 ml of each stock solution were mixed with 5 gm of Ottawa Sand or 3 gm of Devon Silt, and then transferred to the sample container. The sample container was mounted in the spectrometer compartment on a solid sample holder that allows for front-face fluorescence detection. This set up was selected to permit fluorescence detection from soil and highly concentrated liquid samples that does not allow for regular right angle (90^o) fluorescence detection. A collection of emission scans from 250 to 600 nm with 1 nm increments was obtained at varying excitation wavelengths ranging from 240 to 450 nm with 10 nm increments. The bandwidths (silt width) were 5 nm for both excitation and emission for most scans, but were reduced to 2.5 nm when fluorescence intensity was out of range. The scan rate was 600 nm/min, which allowed a scan time of about 20 minutes per sample. Blank samples of Hexane and chloroform were analyzed each day, and a reference material (anthracene) was analyzed every day to monitor any variation in the spectrophotometer performance. A total of 210 fluorescence EEMs were collected for selected petroleum products and crude oil besides blanks and PAH standards.

5. RESULTS AND DISCUSSION

5.1 Fluorescence EEMs

Figure 3 illustrates the collected fluorescence EEMs for the analyzed petroleum products and crude oil in aqueous solutions (not diluted). Presented EEMs show that each of the analyzed petroleum products and crude oil have a unique fluorescence EEM with specific peak locations that can be utilized as a fingerprint for that particular compound. Emission peak locations in fluorescence EEMs varies among petroleum products and crude oil, which reflect the variation in their relative composition of PAHs. For instance, peaks in gas condensate fluorescence EEMs are mostly located at lower wavelengths (around 285 nm); while peaks in heavy crude oil fluorescence EEMs are mostly located at higher wavelengths (around 460 nm). These relative peak locations indicate that gas condensate is mostly composed of lighter aromatic compounds with 1 benzene ring that are known to fluoresce at 275-285 nm, while crude oil is mostly composed of heavier aromatic compounds with 3-4 benzene rings that are known to fluoresce at 360-480 (Berlman, 1971). Similarly, multiple peaks in gasoline and diesel fluorescence EEMs indicate that they are contain a wider range of aromatic compounds with varied numbers of benzene rings.

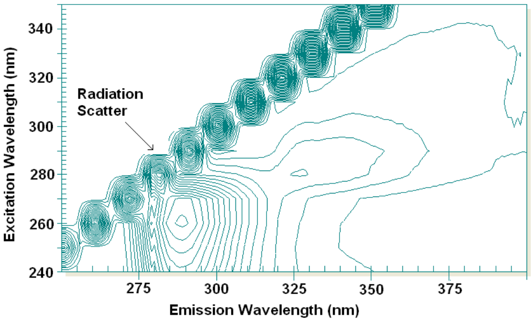

Figure 3a. Gas condensate EEM (not diluted)

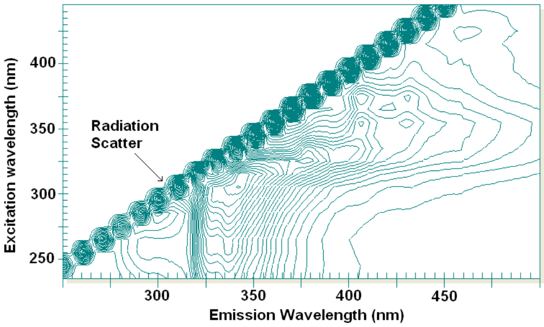

Figure 3b. Gasoline EEM (not diluted)

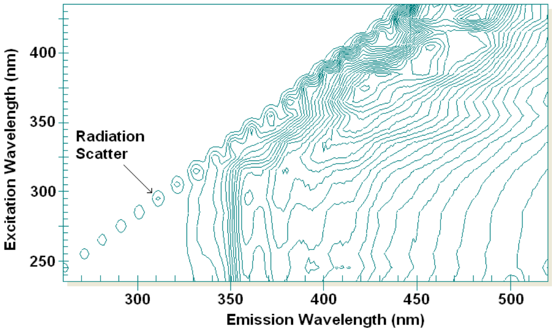

Figure 3c. Diesel EEM (not diluted)

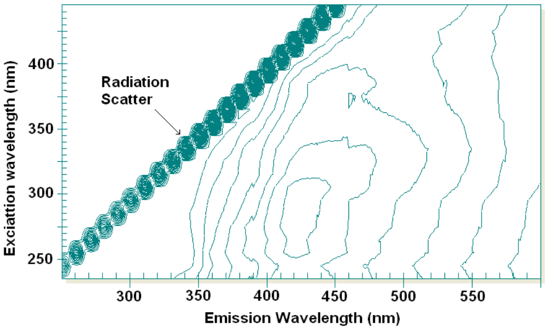

Figure 3d. Flare pit residue EEM (not diluted)

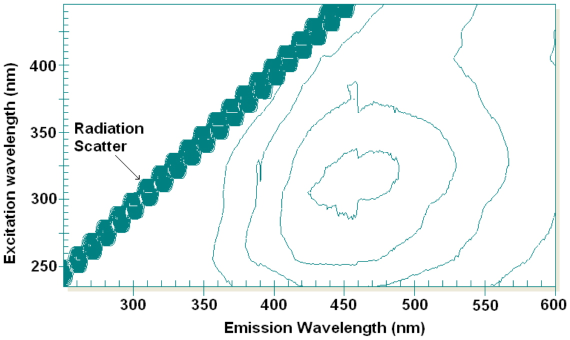

Figure 3e. Heavy Crude oil EEM (not diluted)

Examining collected Fluorescence EEMs of all analyzed samples revealed that EEMs of various petroleum products and crude oil maintained their unique structure and shape with minor variations, whether the analyzed sample was in aqueous solution or in a soil matrix. Figure 4 shows an example of the similarities of collected fluorescence EEMs of flare pit residue (not diluted) in liquid solution and mixed with sand and silt. This consistent appearance of fluorescence EEMs of petroleum products and crude oil in aqueous solution or in soil matrices opens the possibility for in situ detection and characterization of petroleum contaminants in environmental aqueous and soil samples.

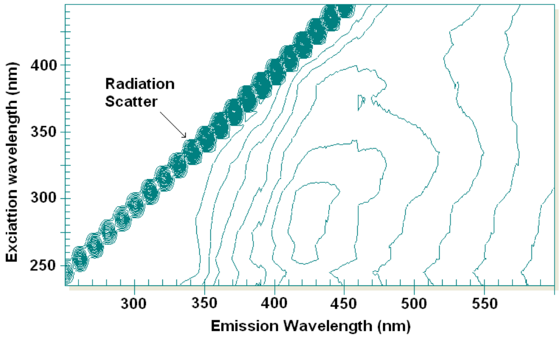

Figure 4a. Flare pit residue EEM

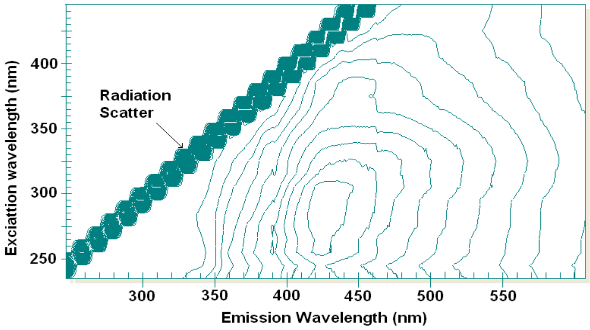

Figure 4b. Flare pit residue in silt EEM

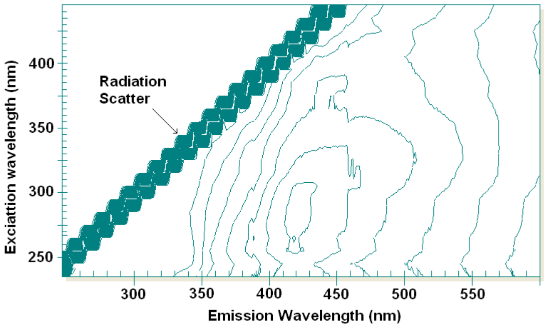

Figure 4c. Flare pit residue in sand EEM

Variations in fluorescence EEMs of a particular compound in aqueous solution and soil samples are related to attenuation in fluorescence intensity when fluorescing compounds are mixed with soil. Such attenuation might slightly weaken the presence of fluorescence peaks with low intensity, but will not alter their locations. Fluorescence attenuation occurs when a fluorescing analyte is mixed with soil, because the analyte molecules will disperse between soil particles, which causes fewer analyte molecules to be exposed to UV light so they could fluoresce. As soil particles size get smaller, they replace more fluorophore molecules per unit area, which results in less fluorescence intensity. That is why fluorescence attenuation is less significant in sand and more pronounced in silt.

In the field, the contaminants could be present as an aqueous solution or mixed with soils that may have a wide range of particles sizes, therefore fluorescence attenuation should not significantly affect the fluorescence EEMs capability to characterize various contaminants, however, it would require calibration when fluorescence intensities in EEMs are used to quantify analytes in aqueous solution or soil matrices.

5.2 PARAFAC Analysis

The PARAFAC models in this study generated spectral signatures of underlying PAH compounds for each different petroleum product analyzed. This then provides a library of PAH fluorescence signatures that may be used subsequently to identify unknown contamination in the subsurface. Described below are the model results compared to actual PAH compounds fluorescence spectra for the different petroleum compounds."

Data pre-processing is usually required before proceeding with PARAFAC analysis because experimental EEMs often deviate from trilinearity and are affected by scatter effects and measurement variability, which could lead to inaccurate model estimates. Radiation scatter in fluorescence measurements, especially in a front face setup, can be problematic because it is unrelated to the sample chemical composition and cannot be modeled adequately into a few PARAFAC factors. Raleigh and Raman scatter show up in three-way fluorescence data as diagonal lines across EEMs (denoted as Radiation Scatter in Figure 3). In this study, no Raman scatter was observed in blank solutions so was ignored. On the other hand, Raleigh scatter was detected in all collected EEMs as illustrated in Figure 3. Several methods have been used to reduce detrimental effects due to scatter (Andersen and Bro, 2003). In this study, scatter data within the diagonal lines across the EEMs were removed and missing values were inserted at appropriate locations. Inserting missing values instead of zeros in the scatter region was based on previous work by Andersen and Bro (2003) who argued that arbitrarily inserting zeros in this region of the EEM may interfere with the trilinearity of data. To ensure proper model estimation and to enhance the modeling process, certain constraints are usually applied. In the case of modeling fluorescence EEMs, “non-negativity” constraints are often enforced to the estimates of A, B, and C loadings. These constraints improve the stability of the modeling and are based on a priori knowledge that negative concentrations or fluorescence intensities are impossible (Bro, 1997).

The PARAFAC models were fitted Using MATLAB ver.7.1 using the PLS_toolbox 3.5. The convergence criteria and maximum number of iterations used throughout the modeling were 10^{-6}, 10^{-6} and 10,000, respectively. A large number of PARAFAC models were estimated for all analyzed samples in aqueous solutions and soil matrices using an increasing number of factors (from 1 to 5). Determination of the appropriate number of factors was mainly based on the number of iterations, core consistency, analysis of residuals (Andersen and Bro, 2003) and comparison of PARAFAC factors with fluorescence spectra of individual PAHs. Figure 5 illustrates the emission loadings of the PARAFAC modeled components for analyzed petroleum products and crude oil samples along with the associated fluorescence spectra of individual PAHs that are most related to predicted components collected during this study.

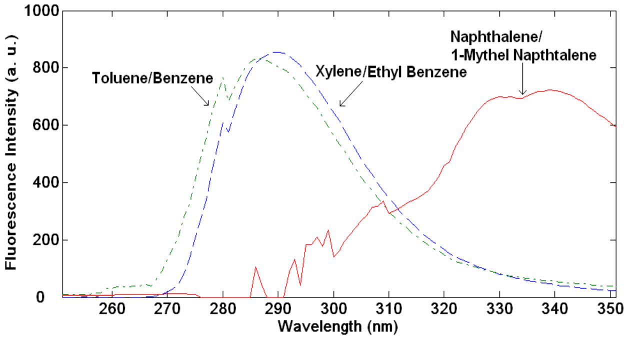

Figure 5a. PARAFAC model for Gas Condensate

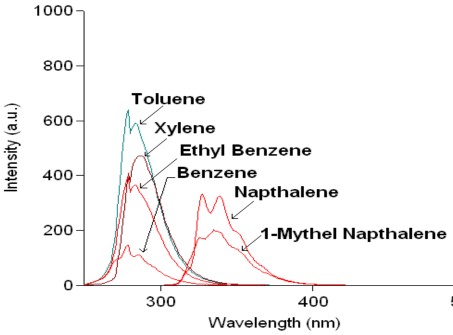

Figure 5b. Fluorescence spectra of PACs related to Gas Condensate

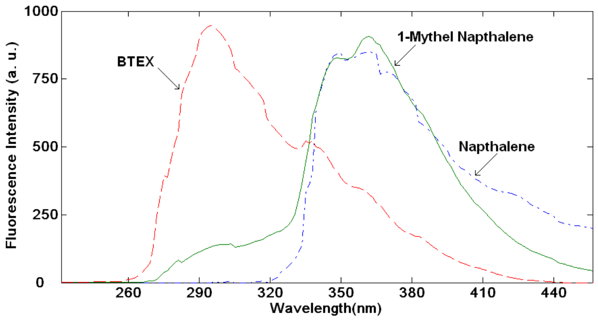

Figure 5c. PARAFAC model for Gasoline

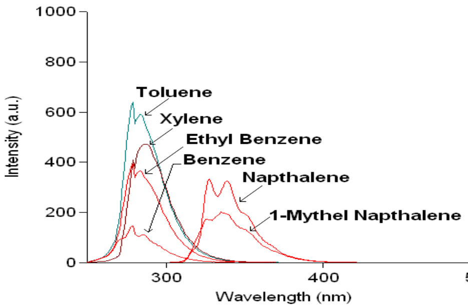

Figure 5d. Fluorescence spectra of PACs related to Gasoline

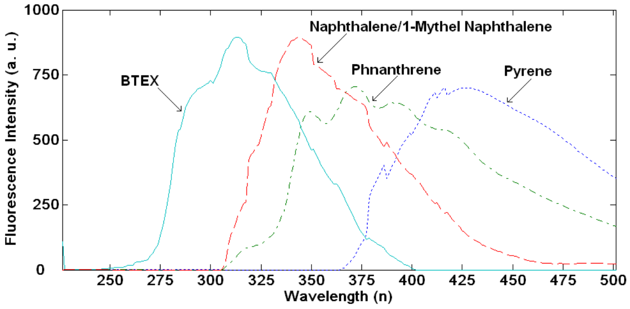

Figure 5e. PARAFAC model for Diesel

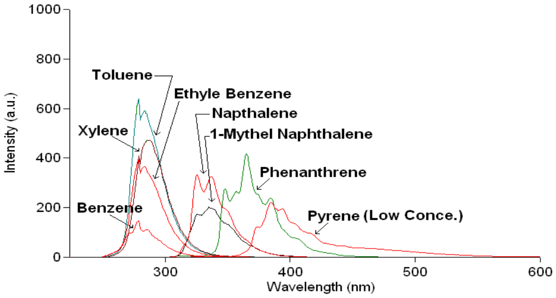

Figure 5f. Fluorescence spectra of PACs related to Diesel

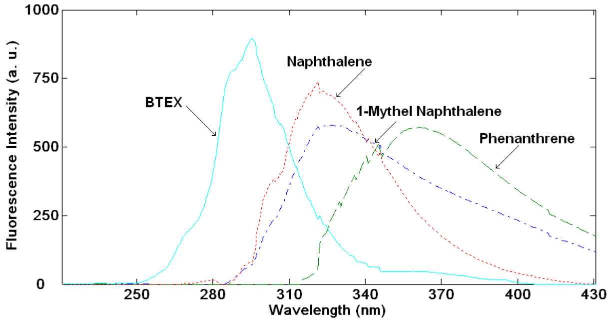

Figure 5g. PARAFAC model for Flare Pit Residue

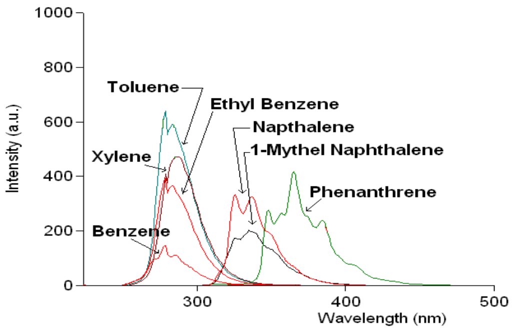

Figure 5h. Fluorescence spectra of PACs related to Flare Pit Residue

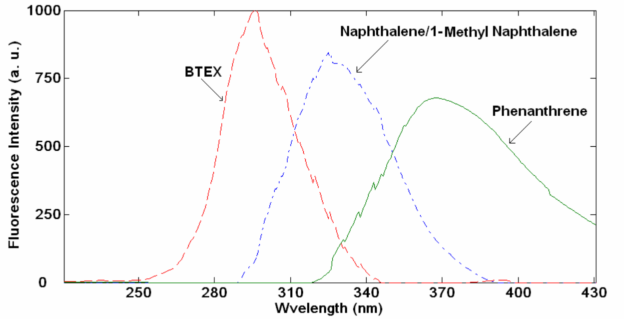

Figure 5i. PARAFAC model for Heavy Crude Oil

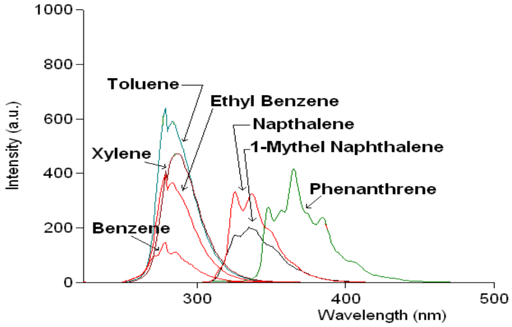

Figure 5j. Fluorescence spectra of PACs related to Heavy Crude Oil

Interpretation of factors in PARAFAC models was based on fluorescence characteristics of selected PAHs. The content of PAHs in analyzed petroleum products and crude oils is dominated by, BTEX compounds, naphthalene/methylnaphthalene, phenanthrene, and to lesser extent pyrene. Comparisons of the fluorescence characteristics of the PARAFAC factors and EEMs of individual PAHs indicate that each of the factors can be related to these main constituents. PARAFAC predicted components agreed with chemical analysis results for the aromatic composition of the analyzed samples that are listed in Table 1. Nevertheless, it was observed that PARAFAC might not be able to identify individual compounds that have very similar fluorescence spectra and it would usually characterize them under one class of compounds, such as BTEX and Naphthalene and Methyl Naphthalene compounds. PARAFAC is likely to extract a larger number of factors that are related to individual PAC compounds, even when their fluorescence spectra are similar, when more variation is included in the data set. For example, PARAFAC was able to identify more individual compounds in the BTEX class of compounds in the gas condensate sample due to variation in data, yet it was only able to identify the BTEX compounds as a class of compounds in other analyzed samples (Figure 5).

Table 1. Results of chemical analysis for aromatic compounds in the analyzed petroleum compounds

Sample	Total BTEX (mg/kg)	Naphthalene (mg/kg)	Benzo[e]pyrene (mg/kg)	Benzo(a)pyrene (mg/kg)
Gas Condensate	25675.00	9.40	0.00	0.00
Flare Pit residue	2582.00	461.00	18.50	1.80
Gasoline	151220.00	3230.00	0.00	0.00
Diesel	7337.00	1100.00	0.00	0.00
Crude Oil	9297.00	42.20	5.74	3.28

Sample	Perylene (mg/kg)	2-Methylnaphthalene (mg/kg)	Phenanthrene (mg/kg)	Pyrene (mg/kg)
Gas Condensate	0.00	5.60	5.60	0.00
Flare Pit residue	0.00	1180.00	1180.00	32.00
Gasoline	0.00	675.00	675.00	1.35
Diesel	0.00	5910.00	5910.00	82.10
Crude Oil	11.90	109.00	109.00	13.10

Being able to discriminate between fluorescence signatures (EEMs) of the analyzed petroleum and crude oil samples is of a great interest as it allows fast characterization of different petroleum contaminants in environmental samples (aqueous solutions or soil matrices), which could be even performed in situ. The ability to characterize petroleum product and crude oil samples depends on their relative composition of PAHs, which is reflected in the factors from PARAFAC analysis, and variation of scores of these factors for the analyzed samples. SIMCA analysis utilizes these variations to discriminate between various petroleum and crude oil samples.

To characterize samples analyzed in this study, PARAFAC estimated scores of various samples (in aqueous solutions and soil matrices) were normalized and classes were assigned to each sample (gas condensate, gasoline, diesel, flare pit residue and crude oil)., The SIMCA model was then fitted in MATLAB using a similar number of factors to the modelled PARAFAC components. After constructing a SIMCA model for each of the analyzed samples, scores of all samples were projected on the SIMCA model to investigate its ability to discriminate between various samples and assign a correct class for each one of them. With reasonable accuracy, the SIMCA model was able to discriminate and assign a correct class for gas condensate, gasoline and diesel samples (in aqueous solutions and soil matrices). SIMCA did not identify flare pit residue and crude oil samples to the same extent, due to the absence of distinguished and variations in the spectral features of their EEMs. The discrimination power of SIMCA could be enhanced by modifying its classification criteria and using larger fluorescence datasets for flare pit residue and crude oil samples.

6. CONCLUSIONS

An innovative characterization method for classification and matching of gas condensate, gasoline, diesel, flare pit residue and crude oil in aqueous solutions and soil matrices has been utilized in this study. It is based on multi-way decomposition of fluorescence EEMs by PARAFAC analysis and subsequent classification and matching of tested samples by SIMCA analysis. The PARAFAC estimated emission loadings were compared to the corresponding spectra of selected PAHs, and the results indicated that each of the estimated factors describe true chemical compound or groups of compounds with similar fluorescence spectra. It was found that BTEX compounds, naphthalene / methylnaphthalene, phenanthrene, and to lesser extent pyrene are the major components of the analyzed samples and chemical analysis results validated this finding. SIMCA demonstrated promising discrimination power to distinguish between different analyzed petroleum products and crude oil samples. Compared to visual comparison in the standard method for initial screening of petroleum samples, this approach is more objective and could be applied to various types of environmental samples without pre-separation steps. This method would allow quick and efficient characterization of different petroleum contaminates in aqueous or soil samples with minimum human intervention. In this procedure, measured EEMs are imported to MATLAB where they are modelled by PARAFAC, then, analyzed samples can be matched by SIMCA analysis to standard petroleum products and crude in a database based on their normalized scores.

7. ACKNOWLEDGMENTS

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