

Interpretation of PAH fluorescence spectra on Al₂O₃ and SiO₂ using Laser based spectroscopy

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1. Introduction

Among various spectroscopic techniques, Laser-Induced Fluorescence(LIF) is distinguished by its high sensitivity and selectivity for detecting aromatic compounds. In contrast to LIF applications for monitoring of aquatic system, the heterogeneity and the opacity of soil matrices is still a considerable experimental challenge for the qualitative and quantitative interpretations of LIF results obtained for soil system. (Loehmannsroebe *et al*, 1996).

LIF results are expressed as functions of wavelength, time and intensity. For characteristic wavelength range corresponding to the specific analytes, integrated intensity is easily considered as an indicator of the concentration of contaminant. The widely varying photophysical properties of analytes and matrices strongly influence the fluorescence signal obtained. These affecting factors change not only the fluorescence intensity but also fluorescence spectral signature (Lieberman *et al.*, 1998). Therefore, for more accurate interpretation of LIF results and, it is necessary to study the effect of a soil matrix on the fluorescence spectral signatures of PAHs. For more accurate interpretation of LIF results, In this study, solid media with different matrix conditions such as polarity, mineralogy and grain size as well as solvent addition effect was studied in terms of fluorescence spectral signature.

2. Materials and Methods

Aluminum oxide and quartz showing uniform color and single representative mineralogy were used for LIF test to investigate the soil media type effect on the fluorescence spectra. Also, Anthracene was selected as representative Polycyclic aromatic hydrocarbons (PAHs) because of its characteristic fluorescence spectra. PAHs are major components of gasoline and other fuels, which are therefore very common environmental pollutants. These reagents were purchased from Sigma Chemical Co. Two soil media were used to determine the influence of soil properties on the fluorescence signatures of PAHs.

Keyword: Laser Induced Fluorescence(LIF), PAH, Al₂O₃, SiO₂

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These were selected to represent the different soil surface area and mineralogy, i.e., soil media type. For the preparation of PAH contaminated soil media, Fifty grams of soil were mixed with 10ml of spiking solution where PAH, anthracene, was dissolved in dichloromethane. To achieve homogeneous condition, spiking procedures was thoroughly carried out through several steps. The contaminated soils were placed in the fume hood for 3 day to evaporate dichloromethane. The fiber-optic probe was dipped into soil sample, rinsed with ethanol and distilled water, and cleaned with a fine laboratory wiping tissue after each measurement.

The original spectra from LIF system are time resolved spectra between 0 and 50ns over the wavelength range between 258 and 607nm. For the entire soil sample, at least five measurements were performed and averaged to avoid the heterogeneity of soil matrix. The total fluorescence intensity and spectral signature is generally obtained by the integrated spectra for the total time interval between 0 and 50ns. In addition, the fluorescent intensity was obtained by integrating the spectra for the wavelength coverage of each PAH.

3. Results and Discussion

Matrix properties that affect LIF sensitivity include soil grain size, mineralogy, moisture content, and surface area. Each of these factors influences the relative amount of analyte that is adsorbed on or absorbed into soil. Only the relative fraction of analyte that is optically accessible at the window of the probe can contribute to the fluorescence signal (Bujewski and Rutherford, 1997). Of the influencing factors mentioned above, the dominant variable appears to be soil surface area. LIF sensitivity to PAHs on soil has been shown to be inversely proportional to the available surface area of the soil substrate.

At a given concentration of 150mg PAH/kg dry soil, the fluorescence spectra of anthracene indicated that different soil media type showed different spectral signature implying the different interaction between soil media and contaminants(Figure 1) and it can affected the total fluorescence intensity extracted from the fluorescence curve for wavelength coverage.

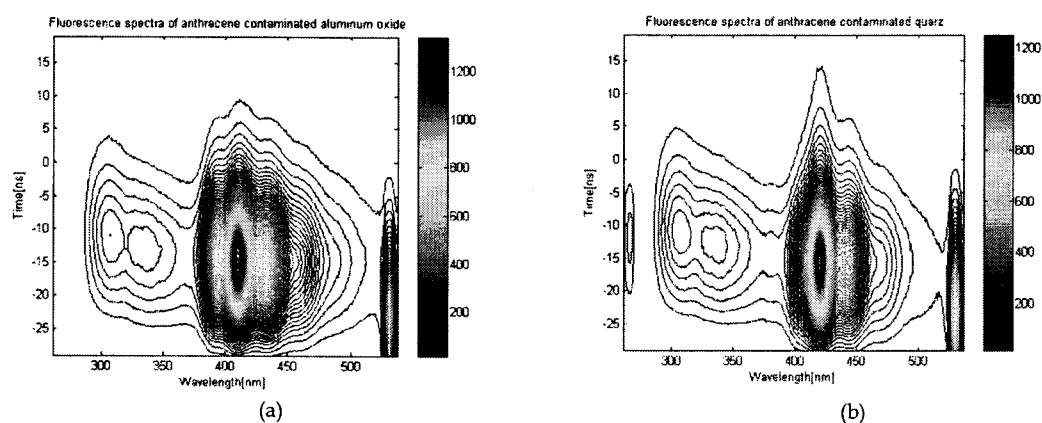


Fig 1. The fluorescence of anthracene on (a) aluminum oxide and (b) quartz

In case of quartz, the first peak (bending mode) of fluorescence was deteriorated and it can be explained as the suppression of bending of molecules by the strong binding of PAH on soil surface. Also, the extraction of PAH from the contaminated soil showed recovered fluorescence spectra by comparison of the fluorescence spectra of PAH on aluminum oxide and in solvent meaning that the PAH was not destroyed. Therefore, this observation imply that the fluorescence spectra signature according to the soil media type should be carefully considered when it is used as the contaminant indicator with the expression of relative quantities of PAH presented in the soil sites of interest.

In addition, For adsorbed PAH on soil media, the effect of solvent addition was evaluated. The added solvent increased fluorescence intensity and spectral structure of adsorbed PAH is getting similar to the fluorescence of dissolved PAH in solvent because the contaminant is start to dissolved in added solvent. In other words, the phase of contaminants in soil media was changed from adsorbed phase on surface to dissolved phase in solvent resulting in free bending mode of contaminant molecules, which is shown in dissovled PAH in solvent. Therefore by comparing the fluorescence spectra of PAH in solvent and on soil, it is possible to deduce the state of contaminants and interaction taking place in soil media. It means that LIF monitoring can give the information related the phase of contaminant as well as the relative concentration of PAH in soil environment.

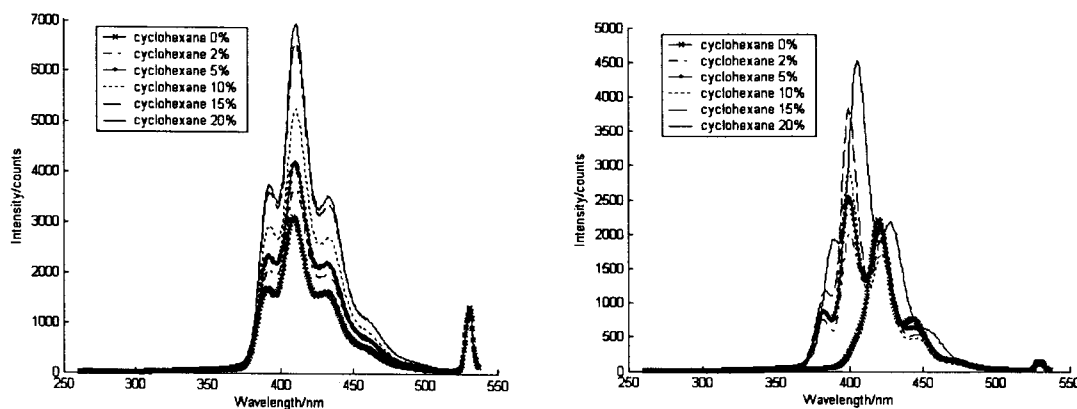


Fig 2. The fluorescence of anthracene contaminated (a) aluminum oxide and (b) quartz as solvent addition

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