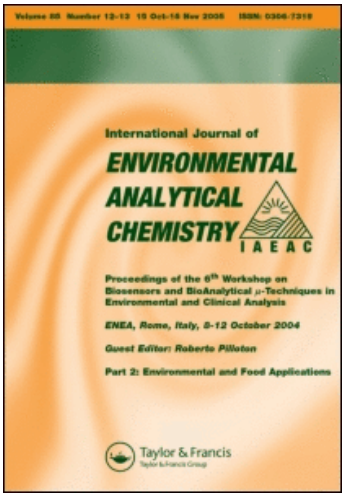

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Chemical Imaging for PAH Analysis in Particulate Materials

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CHEMICAL IMAGING FOR PAH ANALYSIS IN PARTICULATE MATERIALS

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Chemical imaging is a new analytical science, related to a combination of spatial and chemical resolutions. Several new chemical imaging tools have been developed and applied to environmental analysis. The advantages of such methods, which provide simultaneous morphological/geometrical and chemical speciation, are pointed out and exemplified in several environmental analytical applications. These include fast analysis of PAH contaminated aerosols at low concentrations, analysis of contaminated quartz sand particles, as well as improvement of laser induced fluorescence detection of PAH compounds in natural water, in the presence of various microparticles. It is shown that chemical imaging has a considerable potential in environmental applications and can provide detailed and unique information when particulate materials are concerned.

Keywords: Analysis; aerosol; sand; particulates; imaging; fluorescence

INTRODUCTION

One of the most challenging tasks of modern analytical chemistry is concerned with environmental analysis, where on-line and in-situ capabilities must be coupled with extremely low limits of detection. While traditional analytical chemistry has been focused mainly on separation techniques, modern environmental analysis requires sensitive speciation directly performed on complex mixtures. Successful accomplishing of these tasks must be based on acquisition of numerous additional data from the systems in hand, which is required for characterization and compensation for matrix effects. Chemical imaging has the potential of providing this sort of extra information needed.

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Chemical imaging actually provides analytical vision in the sense that simultaneous chemical and spatial information are obtainable. It combines the capability of spectroscopy for chemical analysis with the power of visualization. The result of chemical imaging is a 2D image of an object with full spectrum at each of its pixels.

Moreover, chemical imaging may supply environmental analysis with valuable information, which can, in some cases, be used for identification of the polluting sources. In these cases, chemical imaging does not only improve sensitivity and limits of detection, but serves also in an exploratory mode, which is of considerable environmental importance.

In this paper we report the development of imaging tools and their application to analysis of particulate materials of environmental interest. We address the issues of analysis of PAH contaminated aerosols and quartz sand particles, as well as PAH analysis in the liquid phase in the presence of microparticles. In the former application, we collect aerosols on filters and perform direct PAH analysis using UV light induced fluorescence collected by an imaging technique. In the later case, we model the emitted laser induced fluorescence in the presence of microparticles suspension, accounting for the absorption and scattering of the laser and the PAH fluorescence.

The proposed imaging techniques are not expected to replace the traditional methods for PAH analysis in environmental samples, but to provide additional information for fast analysis. The commonly used methods involve chromatographic separation followed by mass or optical spectrometric detection.[1-2] These methods usually provide accurate results, however, they are expensive and time consuming. Other modern techniques for aerosol analysis involve laser desorption/ionization coupled with time-of-flight mass spectrometry,[3-4] or electron emission.[5] Fluorescence PAH analysis in solutions is also a well established method and investigation of the solid state spectroscopy of some of these compounds was approached too[6-7]. Several imaging techniques have been evaluated for their analytical capabilities, especially for Raman spectroscopy[8-12] but also for fluorescence[13-15]. Most methods were based on optical filter application, which provide only limited information, however, full spectra were also obtained using acousto-optical tunable devices (at a much reduced light throughput and sensitivity)[16-20].

EXPERIMENTAL

Experimental setup

A new imaging device was employed for this study, namely, microscopic imaging by Fourier transform fluorescence. It was described in previous reports[21,22].

The system consists of a UV fluorescence microscope (Axiolab, Carl Ziess, Germany) coupled to an imaging FT spectrometer and a CCD detector (FIPA 20, Green Vision Systems, Israel).

In this system, the examined sample is irradiated by UV light of a high-pressure mercury lamp, through the microscope objective (360±10 nm). The image of the emitted fluorescence is transferred to the CCD detector through an imaging FT spectrometer, such that at each step of the interferometer a 2D CCD interference image is obtained. This measuring protocol ends up with a series of imaging interferograms, all originated from the same sample and at the same location.

Once the imaging interferograms are collected, Fourier transform is performed at each of their pixels, resulting in a combination of spectral and spatial resolution. Actually, full spectrum is obtained at each pixel of the CCD image of the object, enabling chemical speciation of the fluorescing PAH compounds there.

The imaging laser induced fluorescence was excited by the forth harmonic generation of a Nd:YAG laser (Minilite, Continuum USA, 266 nm, 3 mJ in 5 ns at 10 Hz).

Fluorescence lifetime measurements

Lifetime measurements were carried our using a gated intensified photodiode array detector (Princeton Instruments, USA), coupled to a spectrometer (Acton Research, USA). Spectra were acquired at a series of delays after the laser shot, at a temporal resolution of 1 ns. In these experiments, a nitrogen flow was passed through the measurement chamber (1×1 cm cuvette) in order to reduce the oxygen concentration. This flow was continued until no change in the fluorescence lifetime was observed, and the final reading was taken at this point. Particulates (at a series of concentrations) were stirred in the measurement chamber during the measurement.

Sample preparation

PAH contamination was produced with pyrene, coronene (Aldrich, 99%) and perylene (Fluka, 99%). Polydispersed aerosols were produced by an atomizer, coupled with a long (80 cm) drier. Aerosol sampling was performed on fiber filters (Staplex TFAG41). Particulate quartz in the size range of 50–100 μm were obtained by grinding quartz using a mortar and sieving through a 150 mesh (100 μm) sieve followed by a 300 mesh (50 μm) sieve (A.J. Levy, Israel).

Reference analysis

Generally, reference analysis was performed by extraction of the contaminated material in acetonitrile (Bio-Lab Ltd, Israel) followed by a concentration process and finally a fluorescence measurement (Perkin Elmer 50LB). Calibration was carried out by standard PAH solutions in the same concentration range as the examined samples. Particle size distribution of solids were obtained by SEM method, while their distributions in liquids were measured by means of a particle size analyzer (Coulter LS230, 0.04 0 2000 μm).

RESULTS AND DISCUSSION

Analysis of PAH aerosols in a mixture

Figure 1a shows the integrated fluorescence imaging of a filter contaminated with PAH aerosols (a mixture of perylene and coronene). The image was acquired using a x20 UV objective, such than an area of 64×23 μm is inspected. Our imaging technique provides full fluorescence spectrum at each pixel (at a spectral resolution of 5–10 nm), thus a reasonable speciation of each of the observed peaks is possible. For the purpose of single particle speciation and, finally, for its PAH content quantification, a classification algorithm is needed. In this research, where only simple aerosol mixtures were concerned, the classification was based on presentation of the spectrum at each pixel as a linear combination of base-spectra corresponding to pure PAH aerosols. A "library" of solid particulate PAH spectra was compiled for this purpose. The classification at each pixel was performed according to the expansion coefficient in the above mentioned spectral superposition.

The results of the classification algorithm applied to the above data are shown in Figure 1b. Here, the separation of the PAH compounds present on the aerosol collecting filter is clearly observed.

The next step is quantification of the PAH compounds on the collecting filter and comparison to traditional reference analysis of the same samples. Prior to this, classification of all PAH compounds is completed present is required. Quantification is based on the so called "fluorescence volume", which is an integral of the fluorescence intensity over the area corresponding to a particular PAH compound. After the fluorescence volume is calculated for each compound of interest, the filter is randomly moved and a new chemical image is acquired, such that a proper sampling of the filter is obtained. At the end, distributions of particle

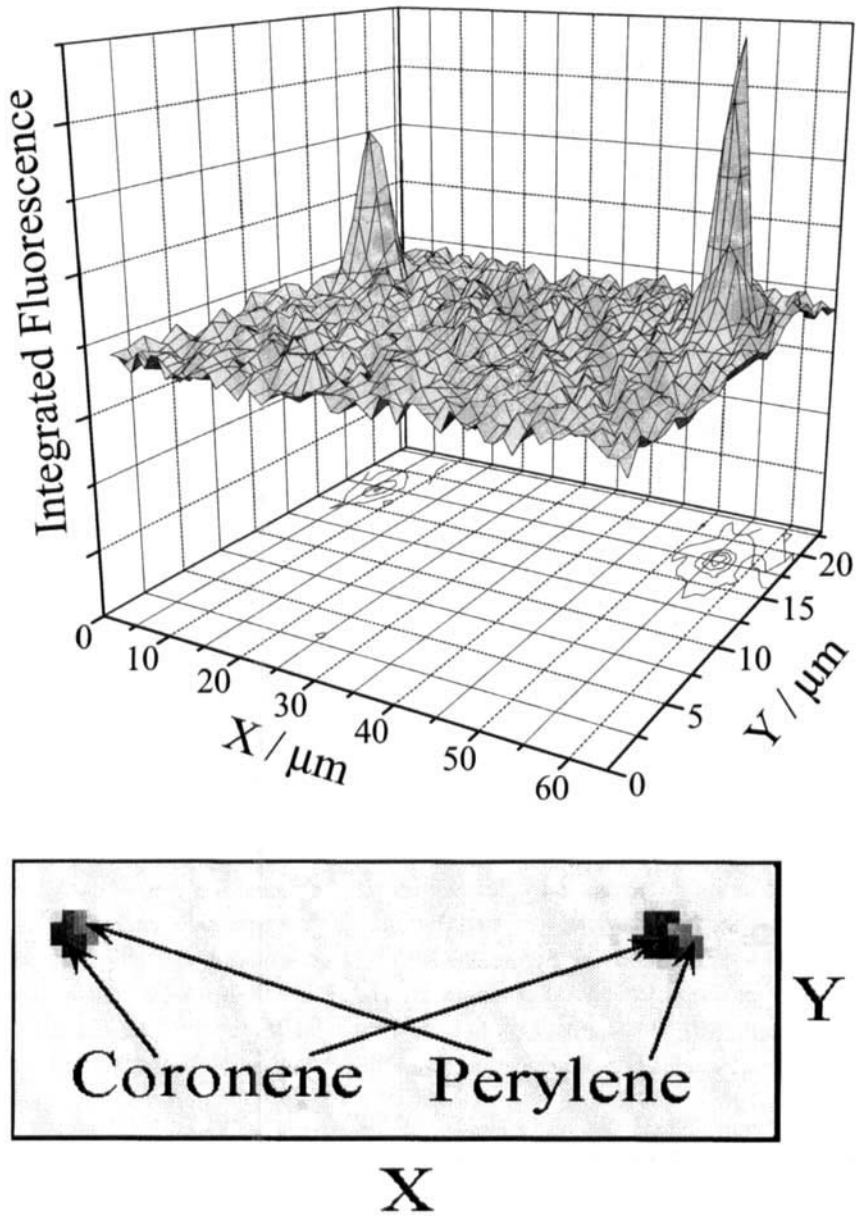

FIGURE 1 (a) 2D wavelength integrated fluorescence imaging map, obtained from a PAH aerosol contaminated filter. (b) The result of PAH classification applied to the same image, indicating the speciation of the two compounds in the aerosol particles

size and volume are obtained and the integrated fluorescence volume per square cm is calculated.

It should be noted that the collecting filter is far from being a flat sampling substrate, at the microscopic scale relevant to this measurement. Thus, re-focusing is required at each sampling position. It seems that results can be further improved by a proper correction for out-of-focus effects even at a single chemical image. Further investigation of this point is under progress.

The integrated fluorescence volumes were compared to classical results, as following: Each filter was divided into two equal parts: One was used for chemical imaging and the other was extracted in a small volume of organic solvents. The extract was examined by a sensitive fluorimeter and absolute concentrations were obtained by a pre-prepared calibration plot in the same concentration range.

The above procedure enabled comparison of the PAH quantification obtained by chemical imaging with traditional analysis of the same samples, and representative results are shown in Figure 2. Here, analysis of perylene in such PAH mixed-aerosols is shown. Linear calibrations were obtained, with calculated 95% confidence interval LODs as low as 5–10 ng cm^{-2} [21]. These figures correspond to an ambient air PAH concentration of 1–2 $\mu g\ m^{-3}$, collected on a standard filter during one second only. A comparison of these results to the current air-quality standards, regarding the presence of class B carcinogenic compounds, indicates that the sensitivity of this method is adequate for on line air analysis. It means that this method can, in principle, be used for PAH emission control, however, further investigation is still needed for establishing a standard measurement scheme.

When larger aerosol particulates are concerned, imaging and analysis of PAH adsorbed to single aerosol-particles is possible. Chemical imaging of such contaminated aerosol particle, (excited by the forth harmonic generation of a Nd:YAG laser) is shown in Figure 3a. The color presentation of this image indicate the location of the PAH compounds. The result of the classification algorithm applied to this aerosol particle is shown at Figure 3b. These findings suggest that single aerosol inspection is possible using the proposed technique.

Analysis of PAH contaminated sand particulates

Quartz sand particles can also be analyzed by this chemical imaging technique. For this study, such particles were contaminated with PAH compounds and then introduced under the imaging microscope. [22] A representative fluorescence image of a sand particle is shown in Figure 4. The 2D surface of the integrated fluorescence intensity originating from the same particle is shown in Figure 5,

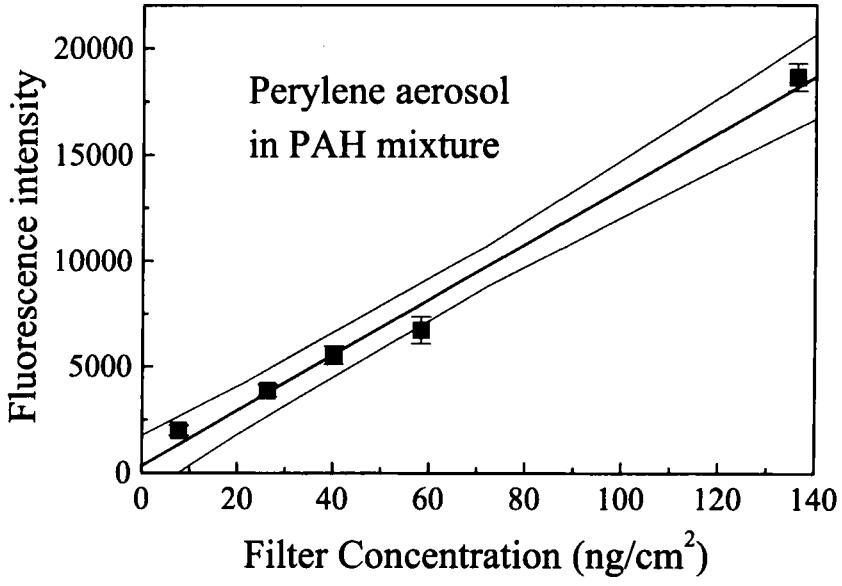

FIGURE 2 Calibration plot for quantification of perylene in air contaminated with a mixture of PAH aerosols

together with the results of the classification procedure which successfully resolved pyrene and perylene contamination on this particle.

Application of the above quantification algorithm to PAH on quartz sand particles also provided linear calibration plots. [22] The detection limits, based on 95% confidence intervals, were 1.5 – 3.5 pg, (depending on the analyzed compound). The data from quartz particulates were more spread than those obtained from similar aerosol analysis. The reason is that the number of sand particulates sampled is smaller than the number of aerosol particles, due to the much larger size of the former. Moreover, when analysis of individual sand particles is concerned, the fluorescence light reflected out of the detector's area, by the mirror-like particle's facets, may become significant. Similar arguments are applicable to the excitation light hitting the quartz surface at critical angles.

Analysis of PAH mixture

In the above study, we produced the PAH contamination in such a way that each individual microscopic deposition was composed of a single compound. When multi-component contamination was concerned, the samples were exposed to a

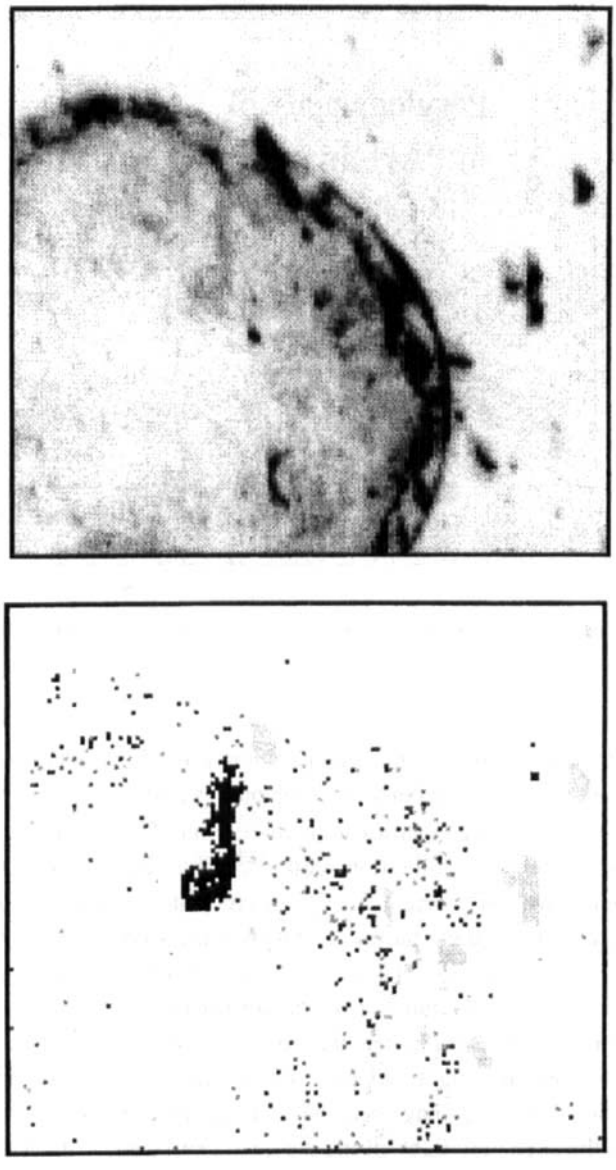

FIGURE 3 Chemical imaging of a single contaminated aerosol particle (a) and the resulted PAH classification (b)

series of such depositions. We are now interested in a more complex situation, where each individual microscopic crystalline is composed of a mixture of PAH

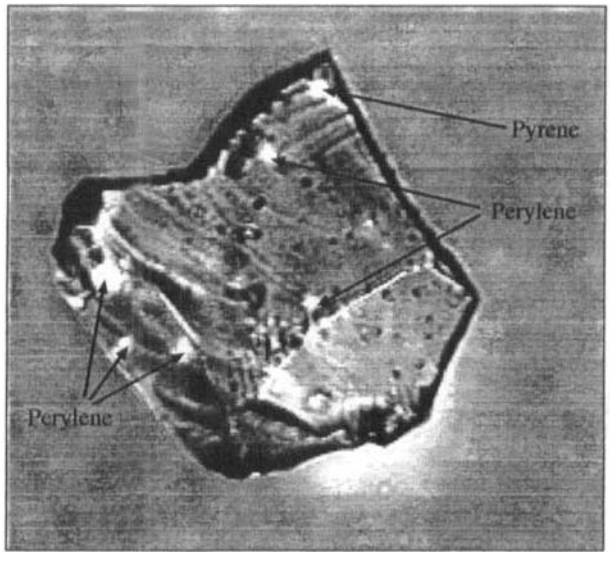

FIGURE 4 Chemical imaging of a single sand particle, indicating the location of the PAH compounds

compounds. Due to thermodynamic considerations, many PAH compounds do not crystallize together. However, several compounds, such as anthracene and pyrene do form, at some extent, a solid mixture. An example of the solid-state fluorescence spectrum of a single crystallite composed of these two compounds is shown in Figure 6, together with the corresponding spectra of the pure compounds. It can be seen that the spectrum of the solid mixture appears like a combination of the spectra of the pure components. Unfortunately, the actual mixture spectrum cannot be exactly described as a linear combination of the spectra of the pure ingredients. It means that complex internal matrix effects are involved in this case. Therefore, a simple quantification in such cases is not possible, and multivariate analysis is required.

LIF in microparticles suspension environment

Laser induced fluorescence is a sensitive analytical technique for PAH analysis in the liquid phase, however, its on-line applicability to environmental samples is limited by the yet unsolved complications, which are due to the presence of microparticles. The idea behind this study is that imaging data may provide the required additional information for understanding the effects due to the presence

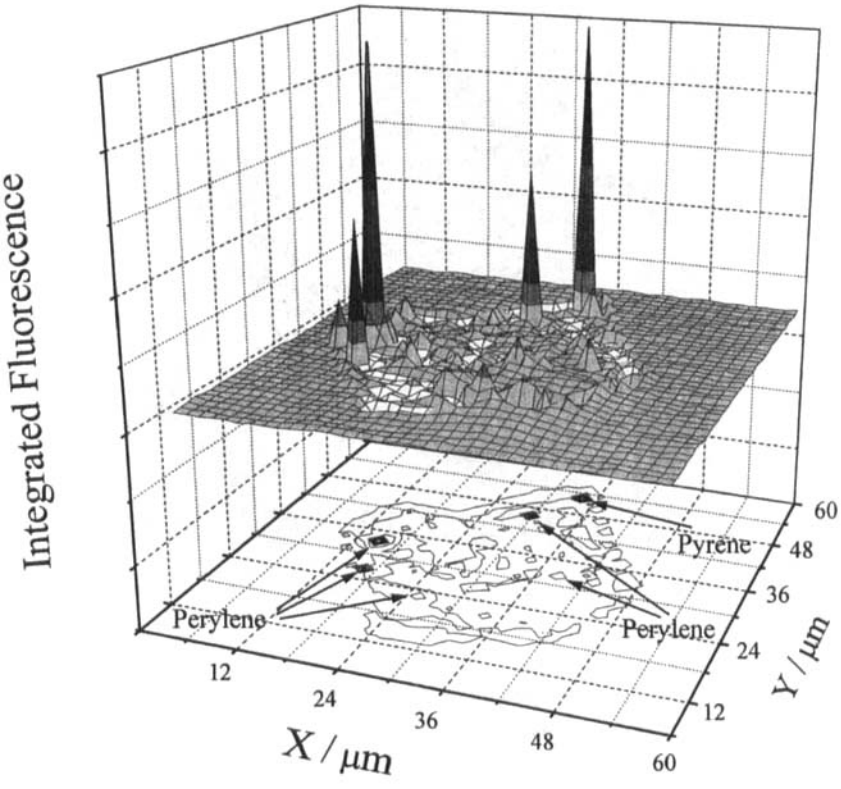

FIGURE 5 The wavelength integrated fluorescence intensity of the same sand particle shown in Figure 4, together with the classification results

of microparticles suspension, and for their compensation. Thus, we were interested in fluorescence analysis of PAH in solutions, in the presence of several micro-particulate matrices.

Series of 1.4 μg/g perylene solutions were prepared, in various micro-suspensions of graphite, carbon, alumina and silica. The imaging LIF from these samples were measured and analyzed. Such images, representing the limiting cases of white (left) and black (right) particulates, as well as low (top) and high (bottom) particulate concentrations, are shown in Figure 7. Clearly, several physical phenomena are involved: As the concentration of microparticles is increased, the laser light is absorbed and its depth penetration is reduced, Thus, a general fluorescence decay is expected and observed is this case. A rather exponential decay curve is observed, when the integrated fluorescence intensity is measured, provided that the detector can observe the whole fluorescence interaction-volume.

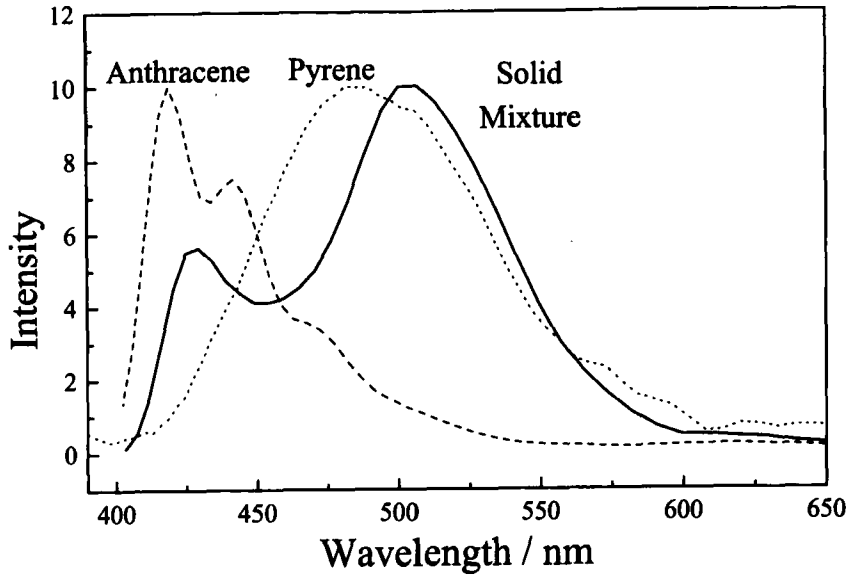

FIGURE 6 Fluorescence spectra of a solid mixture of anthracene and pyrene, together with the spectra of the pure compounds

This simple Bear-Lambert model correctly describes the behavior of the LIF signals in the presence of black particles.

When white (or light reflecting) microparticles are present, the situation is more complex. We, actually, observed (for the first time) an initial fluorescence gain, which is followed by, a quite expected, exponential decay. The physical grounds of this initial gain, occurring at small white microparticles concentration, is probably due to the scattering of the laser light, which, in turn, has a higher probability of exciting PAH molecules. In other words, the scattering of the laser light by the microparticles, actually elongate the optical path of the laser, and more fluorescence can be observed from the solution (provided that the detector's collection angle is wide enough). This insight is supported by the LIF imaging, as shown in the above Figure.

Quantitative description of the above physical understanding requires modeling under certain assumptions. Such a model can be developed in terms of the absorption coefficients of the PAH compounds, of the microparticles and the scattering coefficient of the microparticles present. We can start with the one-dimensional equations already established by Kubelka for spectroscopy in diffusive media.[23] It has been shown there, that a one-dimensional model,

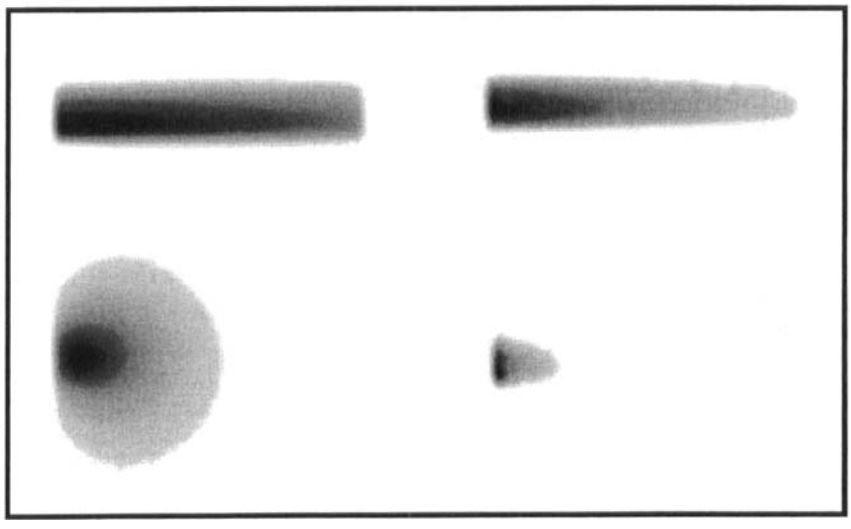

FIGURE 7 LIF imaging of PAH compounds in increasing microparticles suspension concentration (from top to bottom). The effects due to black particulates (left) and of white particulates (right) are shown

based on the solution of coupled differential equations, leads to an expression for the fluorescence in terms of the absorption and scattering coefficients: $F = (1 - T - R)$. The transmitance (T) and the reflectance (R) are calculated in terms of the absorption and scattering coefficients and geometrical parameters.

The above-mentioned one-dimensional model cannot account for any fluorescence gain (which originated from the 2D nature of the system). We expanded the model such that these effects can be accounted for and described the observed integrated fluorescence by the following expression: [24]

$$F = (I_0 \varepsilon_c C)/(\varepsilon_c C + \varepsilon_m m)\,[1 - T - R + \xi R(1 - T_d - R_d)]$$

Here, C is the concentration of the fluorescing PAH compound and ε_c is its absorption coefficient, m is the microparticles concentration and ε_m is their absorption coefficient. We assume that a fraction (ξ) of the initially reflected light, undergoes the same process of absorption, scattering and transmission as the main beam. However, it is now in the perpendicular direction and is related to different geometrical parameters (designated by "d", and representing the axis perpendicular to the laser beam and pointing toward the detector.

Application of this simple model quantitatively describes the fluorescence gain and the following exponential decay. Since the functions T and R both depend on

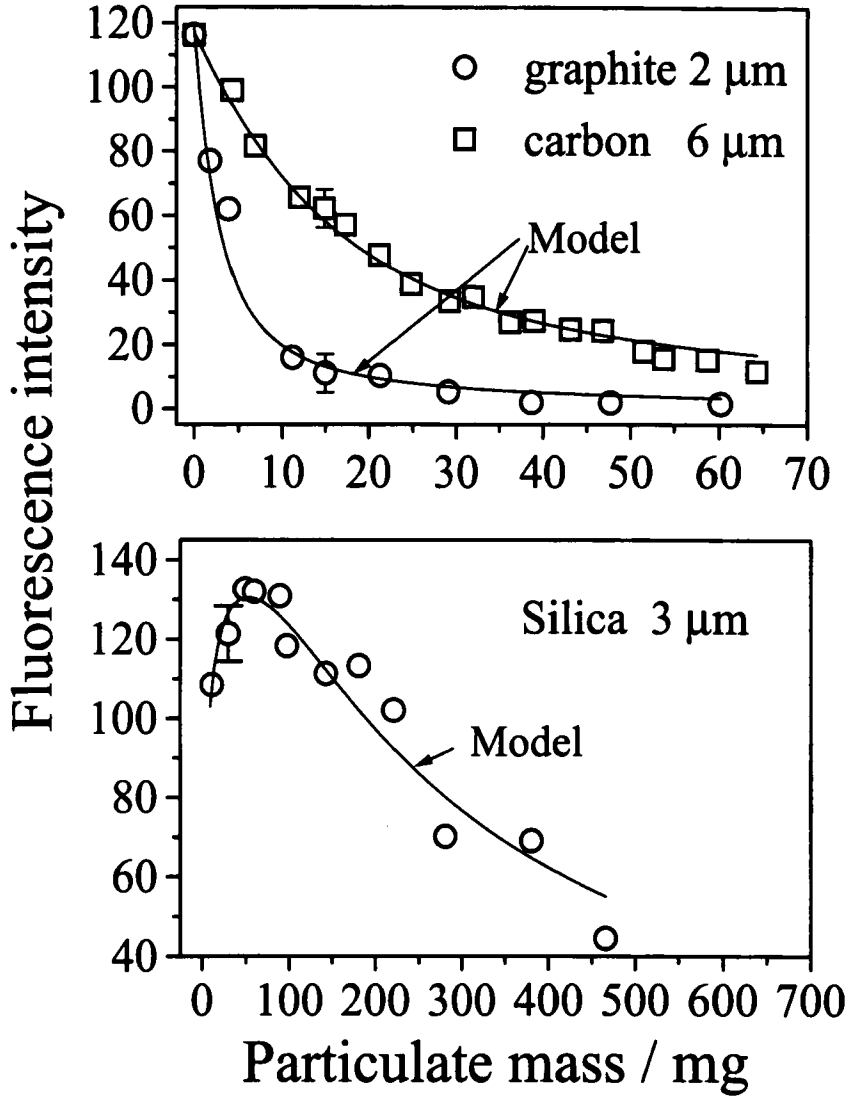

FIGURE 8 Experimental results of integrated LIF signals from PAH compounds in the presence various particulates. The particulates mass per 10 ml is indicated. The solid curves show the results of the proposed model

the scattering and absorption coefficients of the involved species, this model can be applied to any given solution and micro-suspension. Some experimental

results, together with the results of this model, are shown in Figure 8. We see that the experimental data are correctly modeled, so that the concentration of a fluorescing compound can be extracted (as a fitting parameter) and its quantitative analysis can be carried out in the micro-suspension environment.

LIF lifetimes in microparticles suspension environment

Fluorescence lifetimes are often used for resolution of complex PAH mixtures, since the spectral data is not sufficient when partially overlapping peaks are concerned. We report (as far as we know, for the first time) a systematic change in the observed fluorescence lifetime as a function of the suspension mass. In these measurements, the quenching effect of oxygen was reduced by a continuos nitrogen flow through the fluorescence chamber, as described in the experimental Section. The results obtained for two representative particulates are shown in Figure 9. Somewhat surprisingly, the fluorescence lifetimes become longer in the presence of the micro-particulates, under the conditions of our experiment. These findings may be attributed to several phenomena involved in this experiment, however, they are not yet completely understood and are currently under investigation. Possible effects due to the adsorption of oxygen to the suspension particulates are considered.

CONCLUSIONS

Several chemical imaging applications were revised. In all cases, the imaging information provided additional insight to the physical phenomena involved and resulted in improved trace analysis. The imaging of contaminated aerosols provided linear calibration plots and quantification limits in the ng cm^{-2} range. Analysis of single aerosol particles is possible, which implies a possible correlation between the chemical-morphological characteristics and the emission source. Analysis of PAH compounds on single quartz sand particles is also feasible. The problems due to formation of solid PAH mixtures were pointed out.

The imaging of laser induced fluorescence of PAH in microparticles suspension environment revealed an initial signal gain, followed by an exponential decay. The origin of this particulate-dependent fluorescence characteristics was explained in terms of the absorption and scattering coefficients of the suspended material, such that their effect can be readily compensated for. New results regarding the change in the fluorescence lifetime due to the presence of particulate materials were reported.

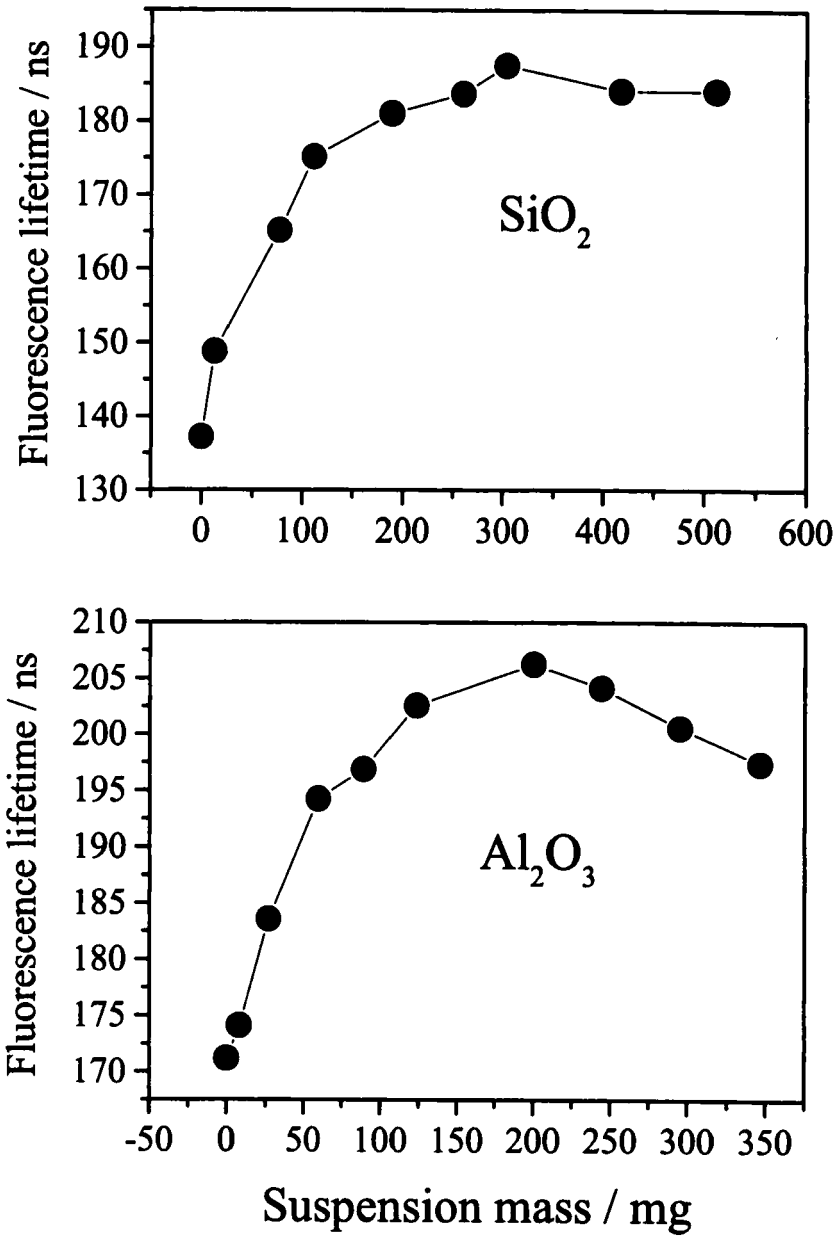

FIGURE 9 Fluorescence lifetime as a function the suspension mass (per 10 ml) in the measurement chamber, for two particulate species

Our study suggests that an on-line PAH control is feasible using this method. Some of the involved matrix effects, but by no means all of them, have been understood and can be compensated for. There are some evidences that the solid state fluorescence of PAH compounds is influenced by some matrixes. For example, for yet not understood reasons, the fluorescence quantum efficiency of pyrene layer on a carbon core is reduced. Therefore, further investigation of matrix effects is of relevance to this method, and is currently being carried out in our laboratory.

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