SURFACE PHOTOCHEMISTRY TECHNIQUES APPLIED TO THE STUDY OF ENVIRONMENTAL CARCINOGENS

Anabela Sousa De OLIVEIRA,[a]* Josino COSTA MOREIRA [b]
and Luis Filipe VIEIRA FERREIRA [a]

[a] Centro de Química-Física Molecular, Complexo Interdisciplinar do Instituto Superior Técnico, Universidade Técnica de Lisboa, Avenida Rovisco Pais 1049-001 Lisboa, Portugal
[b] Centro de Estudos da Saúde do Trabalhador e Ecologia Humana, Escola Nacional de Saúde Pública, Fundação Oswaldo Cruz, Rua Leopoldo de Bolhões, Rio de Janeiro, RJ, 21041-210, Brasil

Ground state diffuse reflectance, laser induced luminescence (using reflection geometry) and diffuse reflectance laser flash photolysis are the techniques used on surface photochemistry studies. These techniques conjugate the use powerful lasers as excitation sources and intensified charged coupled devices (ICCDs) as detectors and they are powerful and sensitive methods of analysis for the study of opaque heterogeneous samples (powdered solid samples).
These techniques can be used as rapid and low cost methods with excellent detection limits for monitoring the content of environmental carcinogens substances on either model or real solid samples. They are also very useful to follow degradation studies of the same substances.
This paper presents results obtained from different real and model samples containing polycyclic aromatic hydrocarbons (PAHs) on several surfaces using experimental set-ups available at the Surface Photochemistry Laboratory of CQFM.

INTRODUCTION

Chemical Environmental Carcinogens and Polycyclic Aromatic Hydrocarbons (Pahs)

Chemical Environmental Carcinogens [1,2] are chemical substances able to induce the appearance of cancer in men and/or animals. Although some environmental carcinogens have natural origin, most of them have anthropogenic origin, being produced intentionally or as non desirable by-product on several industrial / urban processes. In fact, environmental carcinogens of anthropogenic origin are a direct consequence of the recent industrial development, which is responsible for the great increase on pollution levels of different environmental compartment and their consequent negative impacts on all terrestrial ecosystems. Some chemical environmental carcinogens also possess high residence time on the environment and are therefore named **persistent organic pollutants (POPs)**. [1,3,4]

Polycyclic aromatic hydrocarbons (PAHs) [1,3,5] are a family of POPs of more than one hundred organic compounds, which contains two or more aromatic rings, (connected in a way that each aromatic ring shares two carbon atoms). PAHs may also present on their structure five carbon non-aromatic rings, fused with 6-carbon aromatic rings.

PAHs occur naturally on fossil fuels or as suspended particulate matter on urban atmosphere, originating from organic matter pyrolysis. As a matter of fact, combustion processes using fossil fuels on vehicles motor or for heating and energy production are the primary sources of PAHs, nevertheless other industrial processes, usually associated with the production of synthetic fuels or the production of secondary products of the petroleum industry, also contribute for they production. Although in much smaller amounts PAHs are formed also on the course of some food preparation processes as grilling, frying or roasting. The use of naked fires for heating or cooking proposes can be also a domestic source of

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* Corresponding authors: ASOliveira@ist.utl.pt

PAHs, also contributing for the increase of human exposition to this class of pollutants.

PAHs are considered to be toxic and some of them are already know as being carcinogenic to humans. This evidence was furnished by occupational studies on workers after inhalation or dermal exposure.[1,3,5,6] Benzo[a]pyrene is one of most known and studied PAHs since it was the first member of this family to be identified as being a strong carcinogenic agent.[3,5]

Usually when PAHs's molecular weight increases, melting and boiling point increase also, their water solubility decreases and increases their solubility on fat tissues. The danger of these compounds is therefore directly related with the increase of their molecular weight. Because, on environment PAHs are usually semi-volatile and posses low water solubility, they have high affinity for particulate matter.

From same source, PAHs are produced together but on variable concentrations and properties and effect of those mixtures change according to the PAHs present and to their relative concentrations. Although they have variable individual toxicological effects, 16 PAHs (see structures on Fig. 1) were identified by Environmental Protection Agency (EPA) from United States of America as prioritary for environmental monitoring.[5] PAHs integrate also the list of the most dangerous substances from Agency for Toxic Substances and Disease Registry (ATSDR)/EPA, being PAHs as a family, benzo[a]pyrene, benzo[b]fluoranthene and dibenzo[a,h]anthracene between the 20 first substances of the list from 2005.[7]
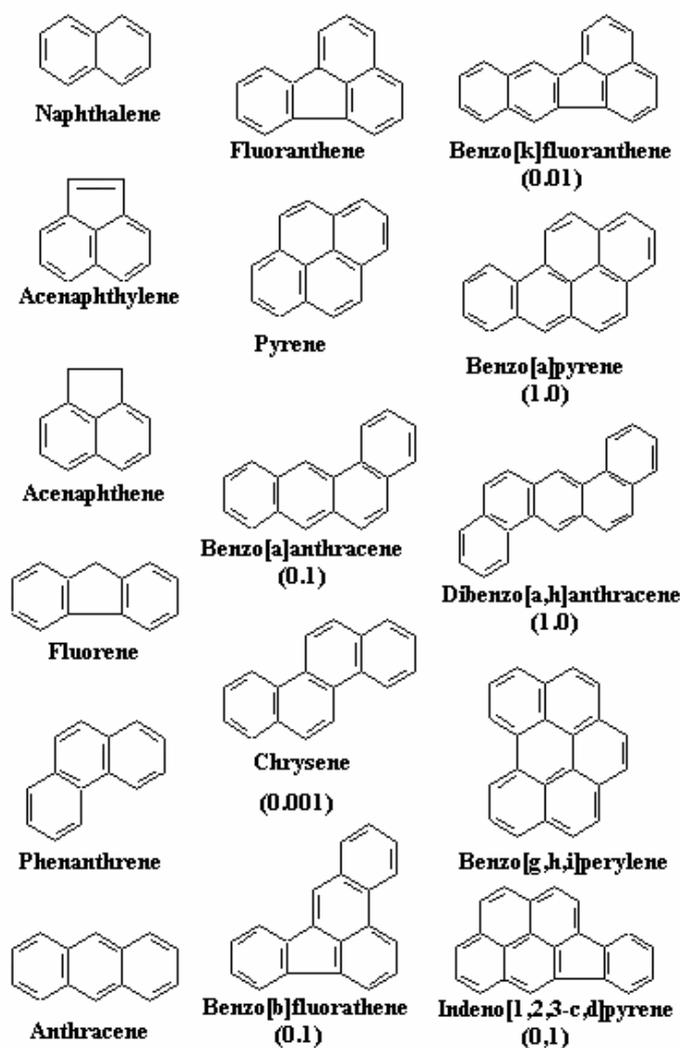

Fig. 1 – PAHs identified by Environmental Protection Agency (EPA) as prioritary organic pollutants for environmental monitoring. Toxic equivalent factors relatively to Benzo[a]pyreine are displayed in brackets for the PAHs which are probably carcinogenic to humans.[5, 6, 20]

Surface Photochemistry Techniques: Diffuse reflectance geometry for the study of reactions on surfaces [8, 9]

The growing interest on the photophysical and photochemical properties of heterogeneous systems, most of them opaque highly scattering solids, determined the strong interest that on last two decades was devoted to the implementation of new experimental techniques for their study.

Conventional techniques for absorption and emission studies on transparent medium, either in stationary or transient modes, always operate on the validity limit of Beer Law. When an incident radiation beam is transmitted through an absorbing transparent sample the beam decreases exponentially with the sample optical path whilst it is partially absorbed by the absorbing species present therein. The transmitted radiation, emerge from the sample with 180º angle with incident radiation. The difference of intensity between the two beams, (incident and transmitted) is the amount of radiation absorbed by the sample. After sample irradiation, if the absorbing species are also emissive them luminescence is emitted in all directions. When the initial excitation pulse comes from a source with high intensity and short duration, higher excited states are significatively populated and their transient absorptions can be measured following the variations on a monitoring light that crosses the sample. This is the basis of laser "flash-photolysis", a powerful technique developed in the 50's by G. Porter (Chemistry Nobel Prize, 1967).[10]

However, until now, all experimental set-ups described here are limited to the use of transmission geometry and therefore are not suitable for the analysis of non transparent systems *i.e.,* they can not analyze systems that are not crossed by light.

When light radiation reaches the surface of a powdered solid sample, the incident radiation is strongly attenuated due to simultaneous strong absorption and strong dispersion, as a consequence of the highly scattering nature of the sample. All the incident radiation is absorbed or dispersed before to completely cross the sample, there is no radiation transmitted trough the sample and only scattered radiation is observed. During the pathway of incident radiation through the sample, part of the incident radiation is absorbed by the absorbing species present in there, reason why once dispersed radiation emerges from the sample, it can be used to analyze and quantify the absorbing species

present on the sample in the same way that transmitted light is used for the analysis of transparent media.

Like that, it is possible to measure the ground state absorption of highly scattering solid samples, by measuring the reflectance of the sample as a function of the wavelength.[8,9,11] The reflectance of the sample is measured with the help of an integrating sphere internally coated with a high diffusing material (R $\cong$ 1), which collects efficiently all the scattered radiation that comes out in all direction from the sample surface. (Fig. 2a). Because ideal scatters and ideal absorbers does not exist, it is necessary to calibrate the light measuring system. The calibration of the integrating sphere is usually performed with the best white and black standards available which, from 200 to 1000 nm, typically display reflectance values of about 97-98% and 1-2%, (Fig. 2b), respectively.

Using reflection geometry (sample excitation and signal collection at the same sample side) and an intense excitation source, which is simultaneously short and monochromatic (typically a pulsed laser) it is also possible to observe luminescence originating from opaque solid samples. On our laboratory in Lisbon, the laser induced luminescence set-up uses an intensified charged coupled device with a minimum time gate of 2.2 ns, coupled to a time-delay unit, that enable to obtain immediately after a single laser shot a luminescence spectra (fluorescence or phosphorescence depending on the luminescence lifetime of the species being analyzed).

On the beginning of the 80's, F. Wilkinson and co-workers showed that laser flash-photolysis principles for the analysis of transparent media could be extended to the analysis of solid highly scattering opaque media, provided that the changes on the monitoring light level due to the absorption of transients generated following laser pulse excitation are measured in diffuse reflectance mode.[12] So, the geometry of the excitation beam, that of the analysing light and of detection system, relatively to the opaque sample has to be built in a way that any scattered light originated from laser or analysing light could reach the analysing monochromator and that the maximum of scattered light originated from the sample reach the entrance slit of the monochromator of analysis. As is evidenced at Fig. 3, the reflection geometry (very much different from the one used on the conventional transmission techniques) is the essential characteristic of both laser induced luminescence and laser flash photolysis in diffuse

reflectance mode. In fact, it is possible to transform a laser induced luminescence system on a laser flash photolysis system, only by adding to the laser

excitation-detection system on reflectance geometry an appropriated monitoring light, arranged also on reflection geometry.
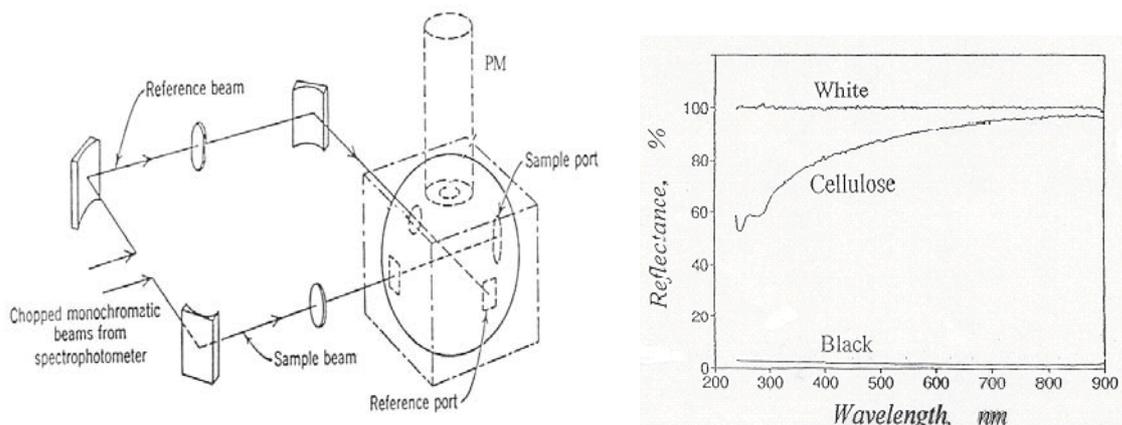

Fig. 2 – Ground state diffuse reflectance. **a)** Radiation optical path within the integration sphere of a diffuse reflectance spectrophotometer; **b)** Ground state diffuse reflectance spectra from a white standard, a black standard and for a microcrystalline cellulose sample.[8, 9]
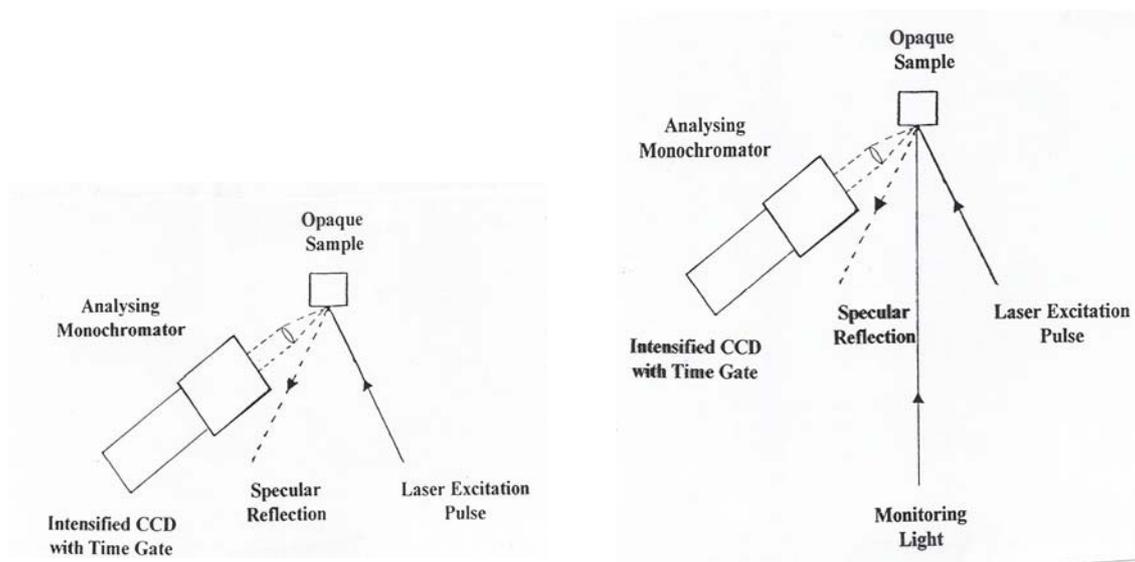

Fig. 3 – Reflection geometry for the analysis of opaque powdered samples by **a)** Laser induced luminescence and **b)** Diffuse reflectance laser flash-photolysis.

The use of diffuse reflectance and laser induced luminescence enabled already the study of numerous probes deposited or adsorbed on different opaque subtract, namely microcrystalline cellulose,[13,14] cyclodextrins,[15,16] calix[n]arenes,[17] silicas,[18] silicalite[15,16] and other zeolite like materials.[19] Recently we tested the use of these techniques to the study of chemical contaminant environmentally relevant on different solid supports [16,17,20-24] namely PAHs adsorbed on model and real solid samples.[20-23]

Laboratorial methods currently used on the determination of chemical environmental pollutants are expensive and time consuming, because on environment pollutants are usually present as complex mixtures or included on complex solid matrixes.[25] The more usual methods of analysis use particulate mater extraction with organic solvents, column or thin layer chromatography to eliminate interfering substances followed by detection after chromatographic separation (*e.g.* gas chromatography coupled to mass spectrometry (GC/MS) or high

performance liquid chromatography (HPLC)).[25] Therefore, it is important to find alternative simpler methods for detection and quantification of those substances, namely real samples direct analysis methods (preferentially field methods) that do not require the extraction of the substance to be analyzed from their natural matrix and that do no suffer with their interference.[20]

Room temperature luminescence is strongly dependent on probe-matrix interactions and can be strongly favoured by the rigid environment frequently enabled by deposition or inclusion on a solid support of the probe to be study.[1, 13-24] This fact can be successfully used on the determination of extremely low levels of luminescent probes, as PAHs, adsorbed on surfaces.[1,20-23]

When diffuse reflectance and luminescence from solids are combined with the use of powerful lasers as excitation source and intensified charged coupled devices cameras (ICCDs) as detectors, they constitute extremely powerful and sensitive methods of analysis, and they can be used as methods for solid substrates analysis with excellent detection limits.[1, 20]

RESULTS

Real environmental samples – Determination of total PAHs level on atmospheric particulate mater

Air pollution on urban areas is associated to the incomplete combustion of fossil fuels and to the consequent emission of carcinogenic compounds, like PAHs, which are considered target pollutants for environmental monitoring. Methods used on their detection are expensive and time consuming and use sophisticated methods of extraction followed by chromatographic detection.

We tested the use of ground state diffuse reflectance techniques and of time resolved fluorescence with intensified charged coupled device detection on the evaluation of PAHs from atmospheric particulate mater samples, collected at four collection points at Rio de Janeiro, Brazil.[20] As shows Fig. 4, the total PAHs content on atmospheric particulate measured by ground state diffuse reflectance and laser induced luminescence[20] is in good agreement with chromatographic results published before for the same samples and for a standard reference material (SRM 1648).[25] Ground state diffuse reflectance proved to be a good technique to the evaluation of

the total PAHs content in urban atmospheric particulate mater while laser induced luminescence appeared as a less efficient method due to the strong quenching effect promoted by the high black carbon content of the samples. As a matter of fact, for samples with high black carbon content it was not possible to fully correct the observed fluorescence extinction effect. This fact leaded us to the determination of lower PAHs levels than expected for the most contaminated samples and for the standard reference material. However, fluorescence still proved to be valid as analysing method on a local scale, provided the black carbon content of the samples is similar.

Our techniques proved to be a valid alternative to reduce the cost of air monitoring, with the advantage of being rapid and simple, enabling a large number of measurements in a short time.[20]

Model Samples – Photodegradation studies of pyrene on microcrystalline cellulose and silica

The study of powdered solid samples of pyrene adsorbed on microcrystalline cellulose and silica by surface photochemistry techniques enabled the acquisition of experimental evidence of a distinct photochemical behaviour of this PAH on the two substrates. The information obtained was extremely useful on the elucidation on the pyrene photodegradation mechanism on those substrates.[22]

Ground state absorption studies showed that at low concentrations pyrene is on the monomer form on both substrates. For high concentrations of pyrene on microcrystalline cellulose and silica different aggregated species where detected: for pyrene on microcrystalline cellulose ground state absorption spectra becomes broader and its maxima shifts to higher wavelengths. Pyrene adsorbed on silica presents a new band, shifted to the red relatively to the location of monomer absorption. On silica, the appearance of such bands is described on literature as originating from the formation of ground state dimers.

Laser induced luminescence studies showed that pyrene on microcrystalline cellulose presents only fluorescence from monomers, for the all range of concentrations investigated. For pyrene adsorbed on silica, we observe fluorescence arising from excimers from very low concentrations.

For the two substrates, diffuse reflectance laser flash-photolysis and photodegradation studies were performed for concentration where mainly monomers exist; we feared that dimers could trap all the energy furnished to the sample preventing its photodegradation.
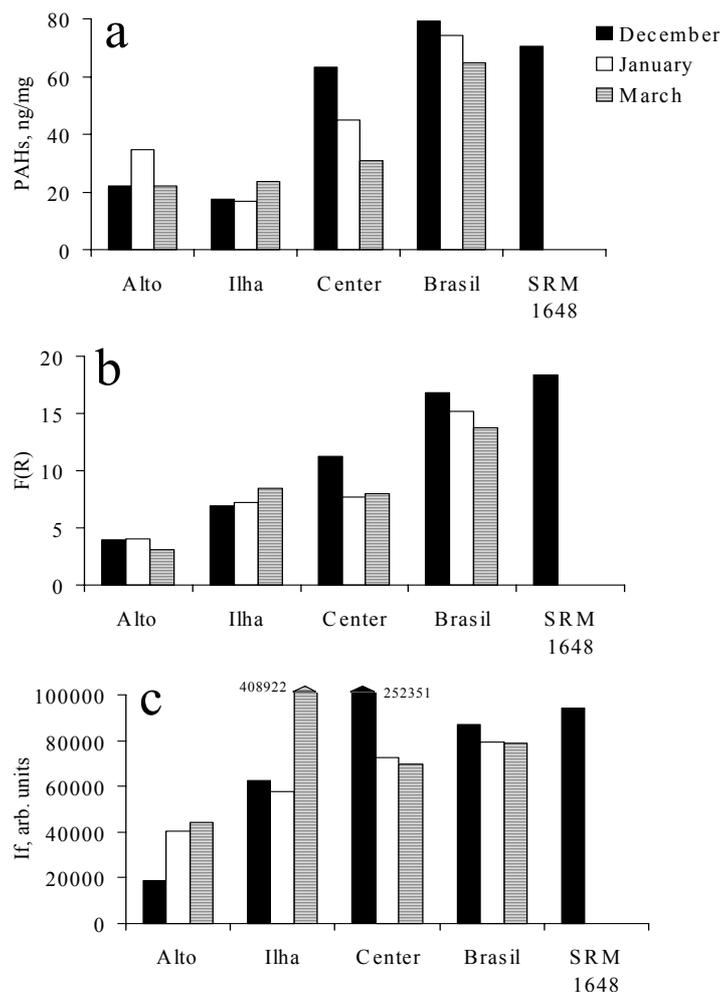
Fig. 4 – **a)** Total PAHs content, **b)** Remission function, **c)** Fluorescence intensity for urban atmospheric particulate samples from Rio de Janeiro and SRM 1648. Collection points in Rio de Janeiro city: Alto da Boa Vista, Ilha do Governador, Centro and Avenida Brasil.

Diffuse reflectance laser flash-photolysis studies showed that pyrene presents a distinct photochemistry on both substrates: while on silica only transient absorption from pyrene radical cation was observed, on microcrystalline cellulose we detected the simultaneous transient absorption of pyrene radical anion, pyrene radical cation and pyrene triplet. Fig. 5 presents the transient observed for both substrates.

On silica, in the presence of O_2, pyrene radical cation is formed by photoionization or from pyrene triplet, being O_2 the molecular species that receives the electron released on the reaction. On microcrystalline cellulose and in the absence of O_2, radical cation formation occurs in presence of another pyrene molecule which receives the e⁻ this turn, originating the simultaneous formation of pyrene radical anion.

Photodegradation studies followed from chromatographic analysis confirm the two distinct phtodegradation pathways on the two substrates: for pyrene included on microcrystalline cellulose polymer chains (*i.e.* in the absence of oxygen) the main observed product is hydroxypyrene; for pyrene on silica photodegradation showed to be very much efficient and it was almost impossible to detect hydroxypyrene.

Either on microcrystalline cellulose or on silica, the intermediate species that leads to photoproduct formation is pyrene radical cation. Hydroxypyrene can be easily formed from the radical cation, on both substrates. For pyrene deposited into microcrystalline cellulose polymer chains, and in oxygen absence, the oxidation of the formed hydroxypyrene is extremely slow. Nevertheless for pyrene on silica and in the presence of oxygen, almost all the hydroxypyrene previously formed is quickly oxidized origination other photodegradation studies.
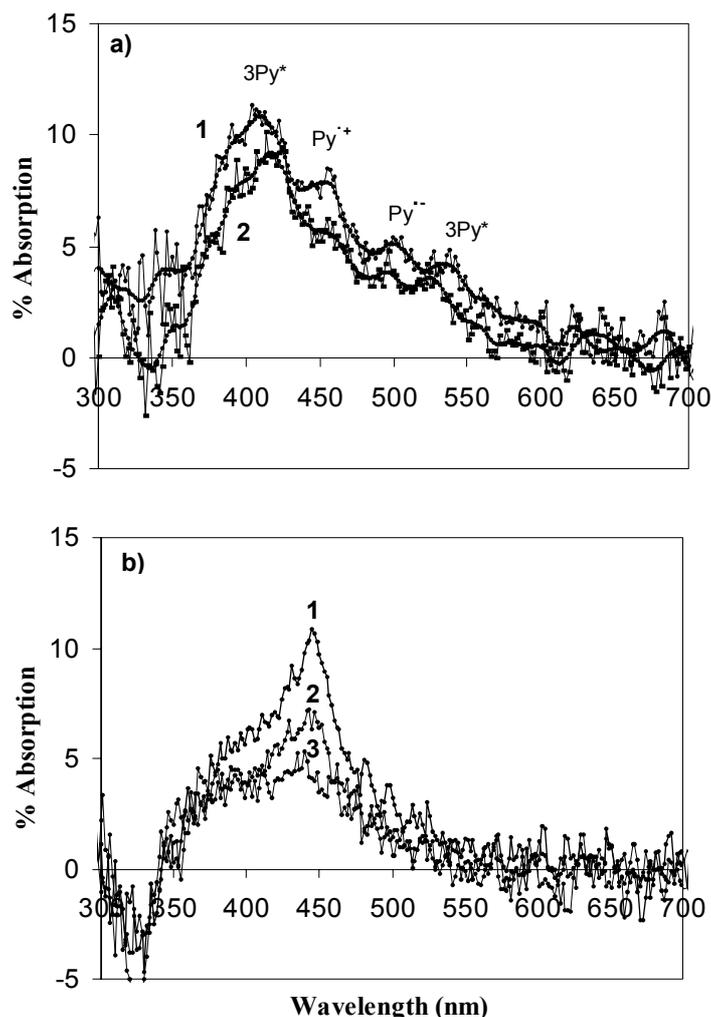
Fig. 5 – Time resolved transient absorption for **a)** Pyrene on microcrystalline cellulose (air equilibrated sample; 10 μmolg⁻¹). Curve 1 and 2 were registered 20 μs and 1ms after laser pulse. **b)** Pyrene on silica (argon purged sample; 0.1 μmolg⁻¹). Curves 1, 2 and 3 were registered 5 μs, 100 μs and 20 ms after laser pulse.

The use of surface photochemistry techniques for the detection and identification of intermediates and photoproducts, allied to chromatography, for product identification, showed to be complementary techniques on the study of the photodegradarion of pyrene on cellulose and silica.

Model Samples – Use of laser induced fluorescence for monitoring the laser photodegradation of nitropyrene on microcrystalline cellulose

We further investigate the photodegradation of nitropyrene adsorbed on microcrystalline cellulose when irradiated with a 355 nm (100mJ/pulse) pulse from a de Nd:Yag laser.[21] Fig. 6a presents the changes on fluorescence emission of a sample of nitropyrene deposited on cellulose with the number of laser shots. For the non-irradiated sample the simultaneous presence of monomers and excimers can be observed. After Nd:Yag laser irradiation the intensity of the excimer band decreases as the same time that from the monomer increases up to a maxima from what it also starts to decreases. Fig. 6b) shows excimer disappearance with the first 200 laser shots while Fig. 6c) puts in evidence the changes on monomer concentration with the increase of sample irradiation. The results show that is possible to use laser radiation for the efficiently destruction of chemical environmental carcinogens.

We further verify that the speed of the photodegradation of nitropyrene on microcrystalline

cellulose as well as that of several other PAHs on microcrystalline cellulose and silica[26] is much higher when samples contain also TiO_2. It is well known that TiO_2 in its anatase form it is a efficient catalyst for the photodegradation of organic compounds and that TiO_2 use lead to more efficient methods environmental remediation of persistent pollutants.[27-29] The mechanism of TiO_2 photocatalysis [28,29] is based on absorption of photons with enough energy to promote an electron from the valence band to the conduction band of the semiconductor ($E_{abs} \geq E_{band-gap}$), with the consequent creation of vacant places (holes) with oxidizing power on valence. These holes have potentials adequate to oxidize the water adsorbed on the TiO_2 surface and produce hydroxyl radicals. The later are able to promote oxidation reactions that lead to the destruction of the organic compound close nearby.
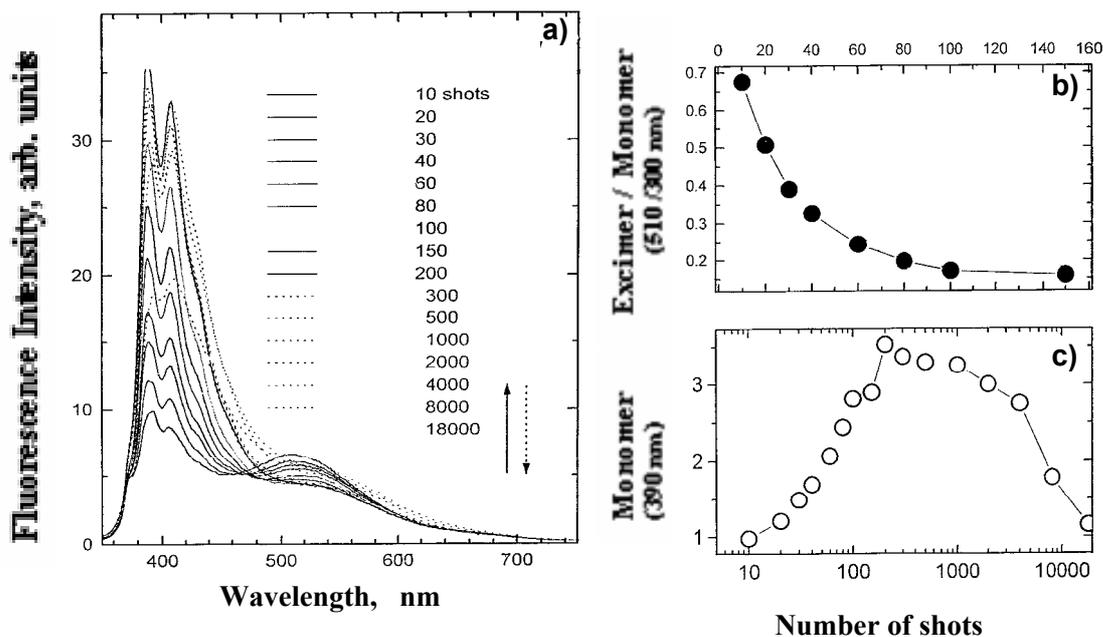

Fig. 6 – **a)** Changes on laser induced fluorescence (N_2 laser, 337 nm 1,6 mJ/pulse) of a 6 μmolg^{-1} sample of nitropyrene onto microcrystalline cellulose with the number of shots from a Nd:Yag laser (355 nm, 80mJ/pulse); Variation on the fluorescence intensity of the **b)** excimer and of the **c)** monomer.

The efficiency of surface photochemistry techniques to monitor PAHs photodegradation in the presence or absence of TiO_2 on the above mentioned solid supports and the use of laser radiation for the photodegradation of PAHs and other chemical compounds of environmentally relevant have shown to be very useful for environmental studies and very much promising for the development of methods able to destroy and/or monitor the destruction of that substances on different environmental compartments.

CONCLUSION

Diffuse reflectance techniques enables the direct study of photophysical processes on opaque heterogeneous systems (either real or model systems) avoiding the recurrent use of classic liquid model systems (transparent homogeneous systems). Ground state diffuse reflectance, laser induced luminescence and diffuse reflectance laser flash photolysis proved to be complementary techniques extremely useful on the study of probes adsorbed on solid supports and on the elucidation of their photodegradation mechanisms, namely on the study of polycyclic aromatic hydrocarbons deposited on different solid supports, either model or real.

Surface photochemistry techniques have shown to be valid alternatives to reduce environmental monitoring cost with the advantage of being quick and enabling a large number of determinations. Furthermore, there is a varied set of compact commercial components (lasers, CCDs, diffuse reflectance spectrophotometers) that can be easily

adapted to field analysis with excellent detection limits. Finally, laser radiation and/or TiO_2 can be used on the photodegradation of persistent environmental pollutants.

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