

Chemosphere 42 (2001) 671-680

UV-visible spectroscopy of organic carbon particulate sampled from ethylene/air flames

L.A. Sgro^a, P. Minutolo^{a,b,*}, G. Basile^a, A. D'Alessio^a

^a Dipartimento di Ingegneria Chimica, Universita degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy ^b Istituto di Ricerche sulla Combustione, CNR, Piazzale Tecchio 80, 80125 Napoli, Italy

Abstract

A systematic comparison of spectra obtained with extra and in situ diagnostics in the soot preinception region of rich, premixed ethylene air flames suggests that combustion generated organic carbon (OC) particulate can be extracted from flames and isolated from other flame material for further chemical analysis. Both the trend with height above the burner and the form of UV fluorescence and absorption spectra from extra situ sampled material captured in water agree with those measured in situ. These results show that the OC particulate formed in flames is partially water soluble. However, the collection efficiency can be increased using less polar solvents, like acetonitrile and dichloromethane. The fluorescence spectra from the water samples are comprised both a naphthalene-like component and a broad band UV fluorescence component similar to that observed in situ which is attributed to flame generated OC particulate. The broad band UV fluorescence centered around 320 nm is also observed very early in flames and does not change considerably with increasing flame residence time. These results support previous hypotheses that the UV broad band fluorescence is from carbonaceous material comprised two-ring aromatics, formed earlier than soot in the flame, and is still present along with soot at higher heights or flame residence times. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Nanoparticles; Premixed flames; Soot; Soot precursors

1. Introduction

Recent findings from atmospheric science, toxicology, and epidemiology reveal the need to focus more research efforts toward characterizing and understanding the formation processes of the ultra fine $(d < 0.1 \ \mu\text{m})$ and water soluble fraction of particulate matter because of their possible effects on human health and the environment. Epidemiological studies report that the association between morbidity and/or mortality and particulate matter increases and becomes more statistically significant moving to smaller-sized particulate (Wilson and Spengler, 1996; Peters et al., 1997). The toxicological mechanism, though still unknown, is also thought to involve the ultrafine particles (Oberdorster et al., 1995; Donaldson et al., 1998). The interaction of small particles with water is also of interest to human health since water comprises 90% of the lung fluid, and the dose received from exposure depends partly on the hygroscopic nature of particles. Small particles that are partially water soluble may also significantly affect the albedo of our atmosphere because of their ability to contribute to cloud condensation (Cruz and Pandis, 1997; Seinfeld and Pandis, 1998).

In response to the need to better understand the toxic and radiative effects of particulate matter, recent research efforts in atmospheric chemistry are shifting toward characterizing organic carbon (OC) particulate rather than the previously well studied elemental carbon

^{*}Corresponding author. Tel.: +390-81-768-2246; fax: +390-81-593-6936.

E-mail address: minutolo@irc.irc.na.cnr.it (P. Minutolo).

(EC). EC is black material partially identified with soot that absorbs visible radiation and is hydrophobic. OC is transparent to visible radiation, less characterized chemically, more hydrophilic, and comprises more of the ultrafine fraction of atmospheric particulate than EC (Hildemann et al., 1991, 1994; Rogge et al., 1993; Saxena et al., 1995; Havers et al., 1998; Seinfeld and Pandis, 1998). The OC/EC ratio is often greater than 1 in urban environments.

In direct studies of combustion sources, organic particles one order of magnitude smaller than soot have been previously identified in rich non-sooting premixed flames and in the region prior to soot in slightly sooting flames using UV-visible optical diagnostics (Minutolo et al., 1994, 1996, 1998, 1999; Gambi, 1996; D'Alessio et al., 1998). Their optical properties suggest that these organic particles are molecular clusters or polymer-like particles, comprised 2-ring aromatic and aliphatic bonds. These organic particles become more aromatic with longer flame residence time (as observed by a measurable absorption in the visible), and eventually form primary soot particles. Studies of combustion systems that use only diagnostics in the visible to observe particle formation do not observe these organic 2-5 nm particles since they are initially transparent to visible light, and can only be detected with UV extinction and fluorescence. Others report comparable soot precursor material in diffusion flames using light scattering techniques (Santoro and Semerjian, 1984) and thermophoretic sampling followed by visualization with transmission electron microscopy (TEM) (Wesborg et al., 1973; Dobbins and Subramaniasiavam, 1994; Dobbins et al., 1995; Koylu et al., 1997).

Recently, extra situ sampling of this flame generated 2–5 nm organic particulate in water showed spectral features similar to those measured in situ, and promised as a method for isolating this material from other species in flames (Gambi, 1996; Minutolo et al., 1999) and in the exhausts of engines and industrial flames (Borghese and Merola, 1998; Merola et al., 1999) for chemical analysis. While earlier work showed qualitative similarities between in situ and extra situ spectra (Beretta et al., 1992; Minutolo et al., 1998), there is a lack of systematic development of the technique.

This paper examines the water solubility of combustion generated organic particulate matter by comparing the UV-visible spectra observed in situ in rich ethylene air flames with the spectra of extra situ sampled material trapped in water. We investigate the similarity between spectra obtained in situ and those obtained from the material sampled extra situ at various heights above the burner to evaluate the ability of the extra situ technique to isolate the 2–5 nm carbonaceous material, identified by broad band UV absorption and fluorescence features.

2. Experimental

Two laminar, premixed, sooting ethylene air flat flames (C/O = 0.77 and 0.92) are studied using in situ (Fig. 1(a)) and extra situ (Fig. 1(b)) sampling techniques. The flames are stabilized with a stainless steel plate (located 29 mm above the burner surface) on a capillary, water-cooled, burner (diameter = 5.6 cm). Other properties of these flames are listed in Table 1. Flame temperatures are measured using the Na D-line reversal method employing a calibrated tungsten strip lamp. Flow rates of the feed gasses to the burner are controlled with Brooks instruments mass flow controllers. The position of the flame front is measured by the maximum OH emission at 306.4 nm ($A^2\Sigma^+ \rightarrow X^2\Pi$).

We use the fourth harmonic of a pulsed Nd:YAG laser ($\lambda_0 = 266$ nm) as the light source for in situ laser light scattering (LLS) and laser induced fluorescence (LIF) for both in and extra situ samples (Fig. 1(a)). The laser beam is vertically polarized and focused to the center of the burner with a cylindrical lens. The laser pulse is attenuated to avoid photofragmentation or vaporization, and the energy of the laser is 0.2 mJ with a duration of 15 ns and a laser fluence of 1.7×10^5 W cm⁻², which is well below the fluence that causes the appearance of the C₂ swan bands emission signal. A high-pressure 150 W xenon lamp, filtered with a predispersing monochromator to avoid stray light, is used to



Fig. 1. Experimental set up (a) in situ laser light scattering and absorption and laser induced fluorescence for both in situ and extra situ samples. (b) extra situ isokinetic sampling.

Table 1 Flame properties, cold flow velocity = 7.5 cm s^{-1}

C/O = 0.77	C/O = 0.92
$\Phi = 2.31$	$\Phi = 2.76$
$T_{\text{max}} = 1700 \text{ K}$	$T_{\text{max}} = 1675 \text{ K}$
$Z_{\text{forme front}} = 0.75 \text{ mm}$	$Z_{\text{forme front}} = 1.5 \text{ mm}$

obtain in situ extinction measurements. The light signal, 90° for scattering and fluorescence, and line of sight for extinction, is focused on the entrance slit of a f/8.8 spectrometer, which has a focal length of 500 mm. A vertical polarization analyzer is placed in front of the entrance to the spectrometer for scattering and fluorescence measurements. An intensified coupled charged device (ICCD) camera is aligned to the exit of the spectrometer. A delay generator controls the ICCD exposure to synchronize the opening of the gate to the ICCD with the timing of the laser source, and a PC stores the signal from the ICCD.

We use an isokinetic water-cooled, stainless steel probe (ID 2 mm) to extract material from the flame that is transported through Teflon sampling lines and bubbled through a solvent in two water-cooled condensers connected in series (Fig. 1(b)). Extra situ extinction measurements are taken using a Hewlett-Packard 8452A spectrophotometer. Fluorescence spectra of extra situ samples are obtained with the same optical setup used for in situ measurements with a standard 1 cm pathlength quartz cell. Fluorescence measurements obtained by centering the water sample in the probe volume of the laser compare well with the fluorescence spectra obtained by a commercial Perkin-Elmer LS-50B spectrofluorimeter. Fluorescence and scattering signals are corrected for extinction (measured at the excitation wavelength 266 nm), for spectral response of the detection system measured with the calibrated tungsten strip lamp, and for changes in laser power using the measured and theoretical scattering cross-section at 266 nm of methane at ambient temperature. Therefore, reported scattering and fluorescence signals are in absolute units $(cm^{-1} sr^{-1})$. A 400 nm long pass filter is used when taking spectra in the visible to remove the 2nd order signal.

All of the samples reported in this paper were analyzed within a few hours of collection because we observed that the optical properties of the samples started changing at longer time. Some experiments were run to optimize the collection system to capture more material in less sampling time. For example, using a cone-shaped condenser rather than a larger, cylindrical one increased the transfer time for the sample inside the bubble to diffuse to the bubble surface and establish contact with the solvent. Increasing the amount of solvent also increases the transfer time, but decreases concentration due to dilution. The sampling time for all extra situ experiments in this study was 30 min, and 8 ml of solvent was used in each condenser.

To determine if the extra situ UV fluorescence and absorption signals are a byproduct of our sampling procedure, we ran a cold flow of only ethylene and another of air through the burner and the extra situ sampling system. After sampling for the same amount of time with the same flow rates used for the flame experiments, we found a barely detectable absorption signal and no fluorescence for both the air and ethylene flows. The UV fluorescence and absorption signals reported in this paper are found only when sampling material produced in flames.

3. Results

The light scattering and extinction measurements obtained as a function of height above the burner in the C/O = 0.92 flame are reported in Fig. 2. We subtract from the measured scattering (at 266 nm) and extinction (at 266 and 530) in situ, respectively, the scattering and extinction of gas phase components, calculated using their concentrations predicted by the premix model for CHEMKIN and their published cross-sections. Therefore, the excess extinction and scattering is the signal remaining after that expected from the gas phase species is subtracted (Fig. 2). The gas phase contribution to absorption is negligible for these rich flames (on the order of 10⁻⁴ cm⁻¹ in the UV) because there is no considerable amount of CO₂, which is highly absorbing in the UV at high temperature. Just above the flame front, an excess UV extinction and scattering are observed. The extinction increases with height above the burner (z)while the excess scattering signal remains constant until z = 5.5 mm, where a large increase in scattering, attributed to the onset of soot formation, is observed. Visible extinction is below the limit of detection for z < 3.5 mm.

The fluorescence spectra for the two examined flames at different heights above the burner obtained in situ are reported in Fig. 3. In situ fluorescence curves show a broad band in the UV centered around 320 nm that is constant with z. Also, a broad band in the visible peaking around 530 nm is observed for z > 3.5 mm that increases strongly as a function of z.

It is known that laser induced incandescence (LII) often interferes with LIF measurements (Ni et al., 1994). However, the low laser fluence of our attenuated laser beam and the shape of the fluorescence signal, which has a maximum at 530 nm for the C/O = 0.92 flames, suggest the signal is unlikely to be incandescence. Furthermore, the in situ signal at 530 nm is also detected in the presooting region (<5 mm), where the absorptivity/ emissivity in the visible of the OC particles is very low, and it is even less likely due to incandescence. To verify the nature of the visible laser induced signal, we



Fig. 2. In situ scattering (a) and extinction (b) measurements in excess of the calculated gas phase contribution for the C/O = 0.92 ethylene/air flame. *Note*: Both the raw scattering data, Q_{vv} , and the excess scattering signal after the gas phase contribution is subtracted are shown in (a). The gas phase contribution for extinction is negligible in these rich flames.

measured the time response of this signal at 530 nm, a parameter used to distinguish LIF from LII (Bengtsson and Alden, 1989; Vander Wal et al., 1997), at a height of 10 mm above the burner, well into the sooting region of the flame. The signal decay rate is an order of magnitude faster than that expected for LII signals, providing further evidence that the measured light comes from fluorescence rather than incandescence.

The fluorescence spectra from the extra situ material possess only a UV component which is more structured than the broad band UV fluorescence measured in situ, containing a series of sharp peaks at 320, 328, and 332 nm (Fig. 4). Also, unlike the UV fluorescence detected in situ, which does not change considerably with z, the extra situ fluorescence increases strongly as a function of z. The peaks at 320, 328, and 332 nm in the UV fluorescence spectra from the extra situ material are similar to those of naphthalene (Karcher, 1992). We estimate how much of the fluorescence from the extra situ sam-



Fig. 3. In situ scattering and fluorescence. Numbers near the curves indicate the height above the burner in mm (onset of soot formation occurs at z = 5.5 mm).

ples could be due to naphthalene by subtracting the fluorescence spectrum from a standard, created by saturating naphthalene in water (solubility = $30\,200 \ \mu g \ l^{-1}$) times a subtraction factor. This subtraction factor is evaluated by the disappearance of the peaks at 320, 328, and 332 nm from the fluorescence spectra. Fig. 5 shows the fluorescence curves of an extra situ sample (a), the amount of naphthalene estimated in the sample (b), the subtraction of these two curves (c), and the fluorescence measured in situ (d). There is considerable similarity between the fluorescence peaks in the 320-330 nm range in the total extra situ material sampled and naphthalene in water (Figs. 5(a) and (b)). Also, the form of the fluorescence spectrum after subtraction of naphthalene is very similar to the fluorescence measured in situ in flames (Figs. 5(c) and (d)).

Comparing the fluorescence spectrum of naphthalene (Fig. 5(b)) with those from the extra situ material (Figs. 5(a) and 4) reveals that naphthalene does not produce fluorescence at 300 nm, while both the sub-tracted (extra situ material – naphthalene) and the in situ curves do fluoresce at 300 nm. The monochromatic fluorescence at 300 nm can be tracked to determine the trend with height of the extra situ sampled material that



Fig. 4. Extra situ fluorescence. Numbers near the curves indicate the height above the burner (onset of soot formation occurs at z = 5.5 mm).

fluoresces similar to that observed in situ without the additional naphthalene-like fluorescence. Fig. 6 plots fluorescence at 300 nm along with that at 330 nm (where fluorescence is observed also for naphthalene) as a function of z. Fluorescence of the samples in the first condenser at 300 nm is relatively constant, showing a trend similar to the UV component of fluorescence observed in situ, but the 330 nm fluorescence shows a much stronger increase with z.

The material collected at z = 2 mm shows a broad band extinction in the UV that decays with wavelength similar to that observed in situ (Fig. 7). Also, the intensity of the absorption spectrum increases with height above the burner similarly for both in situ and extra situ measurements, providing evidence that the sampling procedure is able to isolate the material responsible for



Fig. 5. Fluorescence spectra of total extra situ sampled material at z = 3.5 m, C/O = 0.92 (a), naphthalene estimated in this sample (b), total material – naphthalene (c), and fluorescence measured in situ at the same height and flame conditions (d).



Fig. 6. Extra situ monochromatic fluorescence at 300 nm (open symbols) and 330 nm (filled symbols) vs. height above the burner for the first (squares) and second (circles) condensers.





the UV absorption in the flame. This is seen by the monochromatic extinction coefficients at 266 nm, which are reported in Fig. 8. The in situ and extra situ curves in Fig. 8 have different scales because of the different particle concentration. In the case of the water sample, the concentration depends on sampling time, dilution in water, and collection efficiency, which is in the order of a few percent.

At higher heights above the burner the intensity of the broad band absorption spectrum increases and three peaks at 220, 236 and 246 nm and a broader hump at 260–280 nm are present (Fig. 7). Using the estimated concentration of naphthalene in our samples, obtained from the samples' fluorescence spectra and the quantum yield and molar absorptivity of naphthalene obtained from the literature at 266 nm (Karcher, 1992), we can subtract the extinction expected from the naphthalene in the samples from the extinction spectra of the extra situ samples. Subtracting the naphthalene contribution changes the shape of the extinction spectra less noticeably than the fluorescence spectra. Just the small hump from 260 to 280 nm and part of the 220 nm peak, but



Fig. 8. Measured extinction coefficient, $K_{ext}(\lambda_0 = 266 \text{ nm})$, from material collected in the first and second condenser compared with in situ measurements. Extra situ K_{ext} is measured from material sampled for 30 min in 8 ml of water.

not all, can be attributed to naphthalene. In fact, a low concentration of naphthalene, with a low level absorption, can produce a relatively large fluorescence signal because of its rather large quantum efficiency (QE) (QE = 0.23) (Karcher, 1992).

The peaks in the extra situ extinction curves could be due to other PAHs also trapped in the water, but not to PAHs with more than two rings since we did not observe fluorescence in the visible in any of our samples. The spectra of the commonly reported species from chemical analyses of ethylene flames (Beretta et al., 1985; Petarca and Marconi, 1989; Ciajolo et al., 1994; Olten and Senkan, 1999) could not account for these peaks from our combined absorption and fluorescence measurements. The peaks at 236 and 246 nm may be due to similar material that produces a hump in the extinction spectra at 230 nm observed in situ in ethylene (Minutolo et al., 1998) and methane (Buchta et al., 1995) flames and at 240 nm in benzene flames (Minutolo et al., 1996). Increased spectral resolution of the in situ extinction spectra is needed to better resolve this 230-240 nm hump.

The (QE) can be calculated from measured extinction and fluorescence by

$$\mathrm{QE} = 4\pi rac{\int Q_{\mathrm{f}\lambda}^{\lambda_0} \,\mathrm{d}\lambda}{K_{\mathrm{ext}}^{\lambda_0}},$$

where $Q_{f\lambda}^{\lambda_0}$ is the fluorescence measured at wavelength, λ , excited at λ_0 , and $K_{ext}^{\lambda_0}$ is the measured extinction coefficient at λ_0 . We can calculate the QE of the UV broad band fluorescence in situ at z = 2 mm, where the sampled material does not fluoresce in the visible. The QE of the extra situ material is generally higher than that measured in situ, and it increases with height above the burner, approaching the QE of naphthalene, which is two orders of magnitude higher than that observed in situ. After subtracting the naphthalene from the extra situ spectra, the quantum yield no longer increases with z, and is one order of magnitude lower, closer to the value observed in situ (Table 2).

The fluorescence in the visible detected in situ that increases strongly as a function of height is not present in any of the extra situ samples. Visible fluorescence was also not detected in experiments using dichloromethane or acetonitrile as a solvent in the condensers instead of water. We flushed the lines and sample probe with different solvents, and analyzed the material trapped in the probe lines. Water flushes out material that absorbs/ fluoresces mostly in the UV, but less polar solvents collected material that absorbs/fluoresces both in the UV and the visible from the walls of the probe. The fluorescence of the total material trapped in the lines shows significant fluorescence in the visible in addition to the UV similar to that measured in situ, but with more structured peaks.

We also analyzed the material trapped in the second condenser connected in series. For both the flames, the fluorescence spectra from the second condenser do not exhibit the strong peaks similar to naphthalene observed in the spectra from material collected in the first condenser, and the fluorescence at 300 and 330 nm are relatively constant at various heights (Fig. 6). Similarly, the extinction spectra in the second condenser show the same trend with wavelength as the in situ spectra, and

 Table 2

 Differences in material collected with different solvents

Solvent	Fluores- cence at 300/330 nm	QE (calculated after subtracting the naphthalene
Dichloromethane	0.97	0.083
Acetonitrile	1.33	0.056
Water	0.51	0.053
In situ material Naphthalene		0.003 0.23

the peaks superimposed on the background UV absorption are less evident with respect to the first condenser (Fig. 7). These results suggest that the first condenser traps both materials that fluoresce similar to that observed in situ and a naphthalene-like fluorescing material. However, only the first kind of material is not completely collected by the first condenser and is also trapped in the second condenser.

We ran additional extra situ experiments using less polar solvents, acetonitrile and dichloromethane, in which we found extinction and fluorescence spectra similar to the hydrosol samples. No new peaks in the fluorescence spectra were found using different solvents, but the fluorescence intensities for the less polar solvents were higher. The QEs for the material collected by different solvents, water included, are similar when calculated after the subtraction of naphthalene. Therefore, also less polar solvents can collect the two kinds of materials collected by water: a naphthalene-like one and the broad band UV absorbing particles also detected in situ. The relative amounts of these two components collected depend on the solvent. This is shown in Table 2 from the ratio of the fluorescence intensity at 300 and 330 nm. These results suggest that while UV absorbing particles can be trapped in water in high enough concentration to be analyzed, less polar solvents can be used to increase collection efficiency.

4. Discussion

The main purpose of this study was to examine the ability of the sampling method to isolate organic particles formed in flames from other flame generated material and to examine the interaction of these particles with water. Elaboration of the in situ scattering and extinction measurements (Fig. 2) estimates a diameter of 2-3 nm for the particles, which are transparent in the visible and possess a broad band UV absorption and fluorescence spectra, in agreement with past results (Minutolo et al., 1998). The shape of the extra situ extinction spectra is similar to those observed in situ (Fig. 7), and also the profiles of intensity of extinction spectra versus z show the same trend (Fig. 8). These results strongly suggest that the 2–3 nm organic particles are captured in the samples.

Comparing the UV portion of the fluorescence curves of in and extra situ samples (Figs. 5 and 6) further suggests the 2–3 nm organic particles are isolated in the water samples with only one other interfering species whose fluorescence coincides with naphthalene. The in situ fluorescence in the UV is relatively constant as a function of height above the burner, while visible fluorescence increases strongly. After subtracting the naphthalene contribution, the extra situ fluorescence spectra closely resemble the in situ spectra in the UV (both shape and trend with z), even in flame conditions where visible fluorescence is observed in situ. This result further demonstrates the ability of the sampling procedure to isolate the particles, even when more aromatic material and also soot particles are present.

To separate the 2-5 nm particles from other flame generated material, we make use of the previous result that these particles have a very low coagulation rate in combustion conditions (Minutolo et al., 1999). Because of their small size and low coagulation rate (or sticking probability) this material would not be well captured by filters and may not stick to the walls of a cold trap. Since the cool walls of the probe and sample lines are, in effect, a sort of filter removing sticky material from our samples, we collect only the material that does not stick to them but is captured in the condensers. In this way, we isolate the 2-3 nm organic particles produced in flames, and analyze their spectral features. In studies that capture all condensable material formed in flames, the spectral features of the more sticky material that remains in the lines and probe mask the spectra of these nanoparticles.

By using water as a solvent, we are looking specifically at the material that is partially soluble in water. The fact that the water traps collect material with spectra similar to that in flame suggests the 2–3 nm organic particles formed in flame are partially water soluble. Furthermore, since water is able to flush the material that absorbs/ fluoresces in the UV but not in the visible from the probe sampling lines, we conclude that the 2–3 nm particles associated with the broad band UV extinction/fluorescence are more water soluble than the material that absorbs and fluoresces in the visible which is associated with the more aromatic or soot-like particles.

The main difference between in situ and extra situ fluorescence spectra is the presence in the extra situ spectra of a banded structure, which is coincident with that of naphthalene and absent in the spectra obtained in situ at high temperature. This feature is seen only in the first condenser.

One possible hypothesis for this spectral feature is that the increase of QE at low temperature with respect to the flame temperature is much larger for naphthalene than for the 2-3 nm particles, and the capturing efficiency for naphthalene is higher. We observed that the QE for the broad band UV fluorescence attributed to the 2-3 nm particles is one order of magnitude lower in situ at high temperature with respect to that observed extra situ. It is difficult to measure directly the change in QE of a pure PAH since it is not thermally stable and decomposes at temperatures much lower than flame temperatures. However, on the basis of a recent study that measured the lifetime of fluorescence (which is linearly related to the QE) of naphthalene in a wide range of temperature (Ossler, 1999), it seems probable that the QE of naphthalene would decrease more than one order of magnitude changing from room to flame temperatures. The fact that naphthalene peaks in fluorescence are seen only in the first condenser suggests it is more efficiently collected than the 2–3 nm particles, which break through to the second condenser in series and have a sampling efficiency on the order of a few percent. It is also not surprising that naphthalene is the only PAH identified in the spectra of our extra situ samples since the solubility in water of naphthalene is one order of magnitude higher than other PAHs reported in high concentration in ethylene air flames (Lee et al., 1981).

The experimental evidence can also be explained by the hypothesis that the PAHs seen in extra situ sampling separate or disaggregate during the sampling from the particles, while in the flame they are attached as a part of a polymeric structure of aromatic material joined by aliphatic bonding. These carbonaceous structures could be held together by weak bonds of aggregation rather than molecular bonds as is the case for asphaltenes (Sheu and Mullins, 1995). It may be that a similar bonding forms in the rich combustion of hydrocarbons at high temperatures, and these aggregates disassociate in solution at room temperature whereas in the flame, at high temperature, the reactions to form aggregates are faster than the destruction reactions. This point of view can explain both the large excess scattering signal observed in situ that, combined with UV extinction, comes from some 2-3 nm scatterer, with aliphatic and aromatic functionalities as well as the fact that the extra situ spectra contain signatures of naphthalene that are not observed in situ.

The other main difference between in situ and extra situ spectra is that the in situ fluorescence spectra possess visible fluorescence which is not observed in any of the extra situ samples collected in water or with less polar solvents. At high temperatures, fluorescence bands can be shifted to higher wavelengths. Specifically, the fluorescence peak of naphthalene is shifted about 50 nm into the visible going from room to flame temperature (Ossler, 1999). However, it is unlikely that the fluorescence in the visible observed in situ is solely a temperature effect because the UV fluorescence is also observed simultaneously with the visible fluorescence in situ and they have different trends with z. Also, the shift between the UV and visible fluorescence is too large (200 nm) to be an effect of temperature. The visible feature of the in situ spectra can instead be attributed to more aromatic particles that are filtered by the sampling line and are not collected in the condensers.

5. Conclusions and implications

In this paper, we show that extra situ sampling can isolate the 2–3 nm sized organic particulate, which is UV-absorbing and transparent to visible radiation, from other material generated in flames. Both the form and the trend with height of the UV absorption and fluorescence spectra of extra situ samples are similar to the spectra observed in situ from rich ethylene air flames. The intensity of the broad band UV fluorescence spectrum associated with 2 nm OC particulate does not change substantially with height. It is present even after the formation of soot, which implies that these OC particles can persist past the presoning regions of premixed flames and may be present in the exhaust of combustion systems. This result agrees with the findings of material with similar spectra in the exhaust of engines and industrial sized flames.

These combustion generated organic particles are more soluble in water than both soot particles and the more mature aromatic particles transforming into soot. The fact that this material interacts with water has implications for both the effects of this material on human health and on the radiative balance of the atmosphere. UV extinction and fluorescence spectra similar to those we observe here have been observed in atmospheric studies and in atmospheric water (Black and Christman, 1963; Perry et al., 1984; Havers et al., 1998; Zappoli et al., 1999). Recently this UV absorption/fluorescence in water was attributed to humic-like material with size ~ 3000 amu coming from biomass burning (Zappoli et al., 1999). The result that we can isolate combustion generated material collected in water with similar spectroscopic features implies that direct emissions of these 2 nm OC particles from combustion sources other than biomass may be an unaccounted source for the humiclike substances found in atmospheric waters.

A recent study using a similar collection technique to estimate the amount of OC particulate in the exhausts of engines and stationary sources shows that motor vehicles are likely an important source (Merola et al., 1999). Because of their small size and low tendency to coagulate, the detection of this material is difficult. Atmospheric studies using filters or mechanical devices such as the particle mobility analyzers that measure well particles with diameters greater than 10 nm would not detect this material.

Acknowledgements

Support for L.A. Sgro by the US Fulbright Fellowship is acknowledged. The authors thank Anna Ciajolo and Rosalba Barbella for helpful discussions regarding the experiments and the use of the spectrometer and spectrofluorometer, and Angela Violi for help with CHEMKIN.

References

Bengtsson, P., Alden, M., 1989. Application of a pulsed laser for soot measurements in premixed flames. Appl. Phys. B 48, 155.

- Beretta, F., Cincotti, V., D'Alessio, A., Menna, P, 1985. Ultraviolet and visible fluorescence in the fluorescence in the fuel pyrolysis regions of gaseous diffusion flames. Combust. Flame 61, 211–218.
- Beretta, F., D'Alessio, A., D'Orsi, A., Minutolo, P., 1992. UV and visible laser excited fluorescence from rich premixed and diffusion flames. Combust. Sci. Technol. 85, 455–470.
- Black, A.P., Christman, R.F., 1963. Characteristics of colored surface waters. J. Am. Water Works Assoc. 55, 753–770.
- Borghese, A., Merola, S.S., 1998. Detection of extremely fine carbonaceous particles in the exhausts of diesel and sparkignited IC engines, by means of broadband extinction and scattering spectroscopy in the UV band 190 nm–400 nm. In: Proceedings of the 27th International Symposium on Combustion. The Combustion Institute, pp. 2101–2109.
- Buchta, C., D'Alessio, A., D'Anna, A., Gambi, G., Minutolo, P., Russo, S., 1995. The optical characterization of high molecular mass carbonaceous structures produced in premixed laminar flames across the soot threshold limit. Planet. Space Sci. 43, 1227–1232.
- Ciajolo, A., D'Anna, A., Barbella, R., Tregrossi, A., 1994. The formation of aromatic carbon in sooting ethylene flames.
 In: Proceedings of the 25th International Symposium on Combustion. The Combustion Institute, pp. 679–685.
- Cruz, C.N., Pandis, S.N., 1997. A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei. Atmos. Environ. 31, 2205–2214.
- D'Alessio, A., D'Anna, A., Gambi, G., Minutolo, P., 1998. The spectroscopic characterization of UV absorbing nanoparticles in fuel rich soot forming flames. J. Aerosol Sci. 29, 397– 409.
- Dobbins, R.A., Subramaniasivam, H., 1994. Soot precursor particles in flames. In: Bockhorn, H. (Ed.), Soot Formation in Combustion. Springer, Heidelberg, pp. 290–301.
- Dobbins, R.A., Fletcher, R.A., Lu, W., 1995. Combust. Flame 100, 301–309.
- Gambi, G., 1996. Cinetica di Formazione di Strutture Carboniose di Alta Massa Molecolare in Fiamme, Ph.D. Thesis. Universita degli Studi di Napoli, Federico II, Napoli.
- Havers, N., Burba, P., Lambert, J., Klockow, D., 1998. Spectroscopic characterization of humic-like substances in airborne particulate matter. J. Atmos. Chem. 29, 45–54.
- Hildemann, L.M., Markowski, G.R., Cass, G.R., 1991. Chemical composition of emissions from urban sources of fine organic aerosol. Environ. Sci. Technol. 25, 744–759.
- Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1994. Seasonal trends in Los Angeles ambient organic aerosol observed by high-resolution gas chromatography. Aersol Sci. Technol. 20, 303–317.
- Karcher, W., 1992. Spectral Atlas of Polycyclic Aromatic Compounds. Kluwer, Dordrecht.
- Koylu, U.O., McEnally, C.S., Rosner, D.E., Pfefferle, L.D., 1997. Simultaneous measurements of soot volume fraction and particle size/measurements in flames using thermophoretic sampling technique. Combust. Flame 110, 494–507.
- Lee, M.L., Novotny, M.V., Bartle, K.D., 1981. Analytical Chemistry of Polycyclic Aromatic Compounds. Academic Press, New York.
- Merola, S.S., Allouis, C., Gambi, G., Beretta, F., Borghese, A., D'Alessio, A., 1999. Differential analysis of exhaust emitted by reciprocating engines and stationary burners, by means

of UV-visible extinction and scattering spectroscopy. In: Proceedings of the Sixth International Congress on Toxic Combustion Byproducts, Karlsruhe, Germany, 27–30 June.

- Minutolo, P., Gambi, G., D'Alessio, A., 1996. The optical band gap model in the interpretation of the UV-visible absorption spectra of rich premixed flames. In: Proceedings of the 26th International Symposium on Combustion, The Combustion Institute, pp. 951–957.
- Minutolo, P., Gambi, G., D'Alessio, A., 1998. Properties of carbonaceous nanoparticles in flat premixed C₂H₄/Air flames with C/O ranging from 0.4 to soot appearance limit. In: Proceedings of the 27th International Symposium on Combustion.
- Minutolo, P., Gambi, G., D'Alessio, A., Carlucci, S., 1999. Spectroscopic characterisation of carbonaceous nanoparticles in premixed flames. Atmos. Environ. 33, 2725–2732.
- Minutolo, P., Gambi, G., D'Alessio, A., D'Anna, A., 1994. Optical and spectroscopic characterization of rich premixed flames across the soot formation threshold. Combust. Sci. Technol. 101, 311–325.
- Ni, T., Gupta, S.B., Santoro, R.J., 1994. In: Proceedings of the 25th International Symposium on Combustion. The Combustion Institute, pp. 585–592.
- Olten, N., Senkan, S., 1999. Atmospheric pressure ethylene diffusion flame. Combust. Flame 118, 500–507.
- Ossler, F., 1999. Laser diagnostics in combustion elastic scattering and picosecond laser-induced fluorescence, Ph.D. Thesis, Lund University, Lund, Sweden.
- Perry, M.E., Elzerman, A.W., Overcamp, T.J., 1984. Solubility of atmospheric particulate matter. In: Durham, J.L. (Ed.), Chemistry of Particles, Fogs, and Rain. Butterworths, Stoneham, MA.
- Petarca, L., Marconi, F., 1989. Fluorescence spectra polycyclic aromatic specie in a N-heptane diffusion flame. Combust. Flame 78, 308–325.
- Peters, A., Wichmann, H.E., Tuch, T., Heinrich, J., Heyder, J., 1997. Respiratory effects are associated with the number of

ultrafine particles. Am. J. Respir. Crit. Care Med. 155, 1376–1383.

- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1993. Sources of fine organic aerosol. 2. noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks.. Environ. Sci. Technol. 27, 636–651.
- Santoro, R.J., Semerjian, H.G., 1984. Soot formation in diffusion flames: flow rate, fuel species, and temperature effects. In: Proceedings of the 20th International Symposium on Combusiton. The Combustion Institute, pp. 997–1006.
- Saxena, P., Hildemann, L.M., McMurry, P.H., Seinfeld, J.H., 1995. Organics alter hygroscopic behavior of atmospheric particles. J. Geophys. Res. 100, 18755–18770.
- Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. Wiley, New York.
- Sheu, E.Y., Mullins, O.C., 1995. Asphaltenes Fundamentals and Applications. Plenum Press, New York.
- Vander Wal, R.L., Jensen, K.A., Choi, M.Y., 1997. Simultaneous laser-induced emission of soot and polycyclic aromatic hydrocarbons within a gas-jet diffusion flame. Combust. Flame 109, 399–414.
- Wesborg, B.L., Howard, J.B., Williams, G.C., 1973. Physical mechanism in carbon formation in flames. In: Proceedings of the 14th International Symposium on Combustion. The Combustion Institute, pp. 929–940.
- Wilson, R., Spengler, J.D., 1996. Particles in our Air: Concentrations and Health Effects. Harvard University Press, Cambridge, MA.
- Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M.C., Gelencser, A., Kiss, G., Krivacsy, Z., Molnar, A., Meszaros, E., Hansson, H.-C., Rosman, K., Zebuhr, Y., 1999. Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. Atmos. Environ. 33, 2733–2743.