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THE SOLID-MATRIX ROOM-TEMPERATURE LUMINESCENCE DETECTION AND CHARACTERIZATION OF POLYAROMATIC HYDROCARBONS WITHOUT A HEAVY ATOM

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Summary—A selective and sensitive method to detect polyaromatic hydrocarbons (PAH) using a new solid-matrix room-temperature luminescence technique is presented. The solid-matrix room-temperature fluorescence (SMRTF) and phosphorescence (SMRTP) of PAH can be readily obtained by adsorbing a PAH on Whatman 1PS filter paper. Strong phosphorescence can be detected without adding a heavy atom. Detection limits, ranging from 0.12 to 18 ng, were obtained for several PAH.

Solid-matrix room-temperature fluorescence (SMRTF) and phosphorescence (SMRTP) are selective and sensitive methods for the detection and characterization of organic compounds at trace levels.[1–4] Hurtubise and Ramasamy[5] recently showed that in many cases solid-matrix luminescence gives greater fluorescence and phosphorescence quantum yields at room temperature than the corresponding solution quantum yields at low temperature. The environment of the lumiphor is very important for obtaining strong luminescence with solid matrices.[6–29] Interactions such as hydrogen bond formation between the lumiphor and the solid matrix are important in obtaining strong solid-matrix luminescence.[7] To enhance the phosphorescence of lumiphors on solid matrices, various heavy atom salts can be used.[10,12–25,27–29] Solid-matrices, micelle and surfactant systems are also very effective for RTP detection when a heavy-atom salt is present.[24,25] Tjioe and Hurtubise[29] recently compared the relative enhancement of the RTP of tetrol isomers using sodium halide salts and thallium acetate. These tetrols are hydrolysis products from benzo[a]pyrene-DNA adducts. Their results indicated that thallium acetate was very effective in enhancing the SMRTP of the tetrols. They showed that thallium acetate enhanced the RTP signals of the tetrols on Whatman No. 1 filter paper by more than ten times compared to the halide salts. By adding acetic acid to the solvent, and thus improving the solubility of thallium acetate, they obtained picogram limits of detection for a tetrol with SMRTP. In addition, they introduced Whatman 1PS filter paper which did not require the addition of a heavy atom to obtain RTP signals from the adsorbed tetrols. They showed that it was possible to obtain a phosphorescence spectra of a tetrol with only 100 pg, or even less sample, using the Whatman 1PS filter paper. Strong SMRTF of the tetrols could also be obtained using this type of filter paper. Five picograms of sample were sufficient for obtaining a SMRTF spectra of a tetrol.

Many PAH exhibit strong fluorescence without a heavy atom salt. However, to obtain strong SMRTP from a PAH, a heavy atom salt is normally required.[7,8,12,15,17,18,22,23] Without the presence of a heavy atom, the SMRTP of PAH are generally extremely weak at room temperature.

To further investigate the analytical potential of Whatman 1PS filter paper, the SMRTF and SMRTP detection limits of several representative PAH were obtained without the addition of any thallium salts or other heavy atom salts. Whatman 1PS filter paper is a water repellent paper that has been used for the partition of phases in place of conventional separatory funnels. It can separate aqueous from water immiscible solvents. The paper is impregnated with a special silicone, and the paper contains a tin complex to enhance the stability of the paper.[30]

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EXPERIMENTAL

Reagents and apparatus

Triphenylene was purchased from ICN Pharmaceutical Co., Plainsview, NJ, U.S.A. Other PAH were purchased from Aldrich Chemical Co., Milwaukee, WI, U.S.A. The anthracene was 98%+ pure, and naphthalene and pyrene were 99%+ pure. Benzo[a]pyrene and phenanthrene were 99%+ and 99.5%+ pure, respectively. Both were gold-label grade chemicals. Methanol (Photrex grade), water (HPLC grade) and cyclohexane (HPLC grade) were purchased from Baker (Phillipsburg, NJ).

Whatman 1PS filter paper was purchased through Fisher Scientific Co., Pittsburgh, PA, U.S.A. All luminescence measurements were obtained from a Perkin-Elmer LS-5 spectrometer. The excitation source was a pulsed xenon lamp which was pulsed at line frequency. The SMRTP signals were detected with a 0.5 msec delay and a 9.5 msec gatewidth.

Procedures

Whatman 1PS filter paper was developed in absolute methanol three times to move impurities to the top of the filter paper and dried at 110° for 30 min to minimize its moisture content. Circular discs that were 3.18 mm in diameter were cut out from the developed paper and fitted into a blackened brass sample holder. The holder had a circular depression which was the same size in diameter as the filter paper disc. PAH were weighed and transferred into a 25-ml volumetric flask. Twenty milliliters of methanol was added to the flask, and the contents were sonicated for 15 min, or until the contents were completely dissolved. Water was then used to dilute the contents of the flask to 25 ml. The concentration of the stock solution was 0.012 mg/ml for anthracene, 0.0014 mg/ml for benzo[a]pyrene, 0.025 mg/ml for naphthalene, 0.0090 mg/ml for phenanthrene, 0.0018 mg/ml for pyrene, and 0.005 mg/ml for triphenylene. Similar concentrations for PAH solutions were made using cyclohexane as solvent.

One microliter of a PAH stock solution in methanol: water (80:20) was transferred to the surface of a filter paper disc in the sample holder with a Hamilton syringe. The Whatman 1PS filter paper contained silicone oil which is hydrophobic. Thus, the solution transferred to filter paper remained as a small droplet on the surface of the filter paper until the solvent was evaporated. The evaporation was accomplished by blowing a gentle stream of dry nitrogen gas on the surface of the drop for about 5 min. The sample holder containing the filter paper was placed into the sample compartment of the luminescence spectrometer, but dry nitrogen gas was flushed through the cell compartment for 45 min before the luminescence intensities were measured. The luminescence intensities of the PAH were measured at the excitation and emission wavelengths listed in Table 1. Also, the solid-matrix luminescence intensities of PAH were measured from samples adsorbed on 1PS paper from cyclohexane solutions under similar experimental conditions.

The limit of detection for each PAH was determined as defined in Ref. 31, where the luminescence intensity at the detection limit was equal to the average value of the blank filter paper samples treated with solvent plus three times the standard deviation of the blank.

$$X_L = \bar{X}_B + 3S_B$$

X_L = the luminescence intensity at the detection limit.
$\bar{X}_B$ = the average luminescence of the blank.
S_B = the standard deviation of the luminescence of the blank filter paper at the same experimental settings.

The amount of lumiphor at the detection limit was calculated from an equation in which the ratio of intensity to concentration of a standard near the detection limit was set equal to the ratio of the experimental intensity at the limit of detection to the concentration of the lumiphor at the limit of detection. The detection limits of the PAH were measured twice, or more, using the method described above, and average values of limit of detection are reported.

Table 1. Excitation and emission wavelengths of the PAH (nm)

	SMRTF		SMRTP	
PAH	Ex	Em	Ex	Em
1. Anthracene	358	403	—	—
2. Benzo[a]pyrene	295	403	—	—
3. Naphthalene	274	323	274	471
4. Phenanthrene	255	365	258	466
5. Pyrene	334	393	338	588
6. Triphenylene	258	354	262	464

Ex and Em represent the maximum excitation and emission wavelengths, respectively, for a PAH.

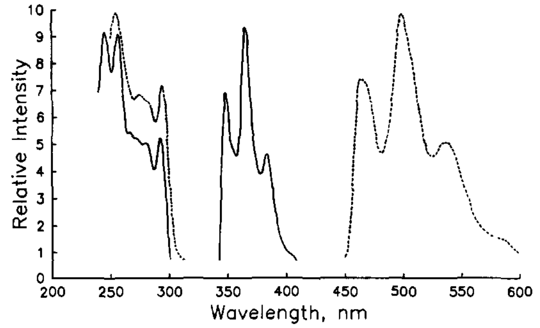

Fig. 1. Solid-matrix excitation, SMRTF, and SMRTP spectra of phenanthrene. The solid lines represent SMRTF and dotted lines represent SMRTP of the same sample spot on 1PS filter paper.

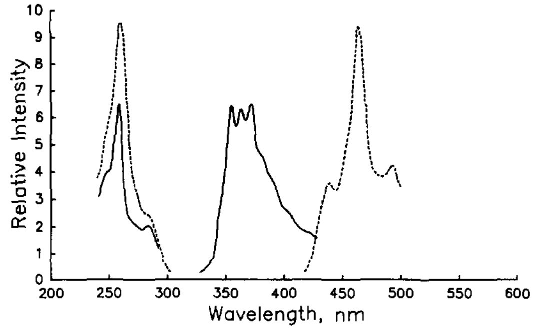

Fig. 2. Solid-matrix excitation, SMRTF and SMRTP spectra of triphenylene. The solid lines represent SMRTF and dotted lines represent SMRTP of the same sample spot on 1PS filter paper.

RESULTS AND DISCUSSION

The adsorbed PAH from cyclohexane solutions exhibited extremely weak luminescence intensities. The sample spot on the filter paper after drying could hardly be distinguished from the background when observed under a UV hand lamp. Therefore, the manner of the formation of a droplet on the surface of the filter paper was critical to the sensitivity of the method reported. The droplet from the methanol:water (80:20) solution formed primarily because the silicone oil in the filter paper matrix repels the water molecules in the solvent. The lumiphor molecules are therefore restricted from diffusing and penetrating into the filter paper matrix. Therefore, after evaporation, the phosphor molecules are held more rigidly and compactly near the top layer of the paper matrix, and thus they have the potential of giving strong phosphorescence.

The Whatman 1PS filter paper can significantly enhance both the fluorescence and phosphorescence signals of most of the PAH examined. The quantity required for obtaining the SMRTP spectra for naphthalene, phenanthrene, pyrene and triphenylene ranged from 1.8 to 18 ng. Even less sample was required for the SMRTF spectra. Figure 1 shows the room-temperature solid-matrix luminescence spectra of phenanthrene on Whatman 1PS filter paper. Figure 2 presents similar spectra for triphenylene.

It was very difficult to acquire SMRTP spectra of anthracene and benzo[a]pyrene because of the weak SMRTP signals obtained. Perry *et al.*[23] reported the SMRTP spectra of anthracene on Whatman No. 1 filter paper pretreated with thallium lauryl sulfate and also pretreated with thallium nitrate. Their report indicated that nanogram levels of anthracene were detectable by SMRTP with the heavy-atom enhancement. In this work, naphthalene exhibited a weak SMRTF signal after the solvent was evaporated. Thus, it was not possible to obtain useful SMRTF data from naphthalene. Interestingly, good SMRTF signals were observed before the droplet evaporated.

Detection limits of PAH on Whatman 1PS filter paper

Without the addition of heavy atoms, the detection limits given in Table 2 were obtained for the PAH using the Whatman 1PS filter paper as the solid matrix. Each detection limit represents the average of at least two measurements under identical experimental conditions. The standard deviation of the blank intensity of the filter paper was taken from the average of 5 measurements. As shown in Table 2, subnanogram detection limits were possible for phenanthrene, pyrene, and triphenylene by SMRTP. Also, subnanogram detection limits were obtained for benzo[a]pyrene, pyrene and triphenylene using SMRTF.

Table 2. The luminescence detection limits of PAH on Whatman 1PS paper

PAH	Detection limits SMRTF (*ng*)	SMRTP (*ng*)
1. Anthracene	1.6	—
2. Benzo[a]pyrene	0.12	—
3. Naphthalene	—	18
4. Phenanthrene	2.4	0.46
5. Pyrene	0.17	0.64
6. Triphenylene	0.91	0.29

CONCLUSIONS

In conjunction with previous work reported by Tjioe and Hurtubise,[29] the Whatman 1PS filter paper is shown to be a very promising solid matrix for obtaining the solid-matrix luminescence of several PAH. As noted previously, fluorescence spectra of tetrols could be obtained with as little as 5 picograms with this solid matrix.[29] In this work, the luminescence detection limits of the PAH were somewhat higher than those reported for tetrols. They ranged from 0.12 (SMRTF) to 18 ng (SMRTP) in comparison with 0.18 (SMRTF) to 3.3 pg (SM-RTP) for a tetrol. The tetrol exhibited a lower detection limit, possibly due to more extensive hydrogen-bonding interactions between the hydroxyl groups of the tetrols and those in the 1PS filter paper. Such interactions would permit the tetrols to be held more rigidly than the PAH.

When a nonpolar solvent such as cyclohexane was used to spot the PAH onto the 1PS paper, weaker luminescence intensities were observed. A binary solvent composed of a more polar component, such as water, and a less polar component, such as methanol, favored the strongest luminescence of the PAH. These results indicated that the more polar component of the solvent, being repelled by the hydrophobic filter paper media, was most likely involved in permitting the lumiphors to be positioned near the top of the filter paper. The size of the sample spot was considerably smaller than the size of a similar spot on Whatman No. 1 filter paper when observed under a UV hand lamp.

The analytical technique introduced in this report provides an economical way to characterize many PAH using both SMRTF and SM-RTP. The limit of detection was calculated to be within nanogram and subnanogram levels. For SMRTP, low limits of detection were obtained without the addition of a heavy atom. The Whatman 1PS filter paper is a new matrix for solid-phase luminescence analysis, and many of its properties still await further investigation. It has been reported that the Whatman 1PS filter paper contains a tin complex which gives stability to the paper.[30] Possibly the tin complex participates in enhancing the RTP of the PAH.

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