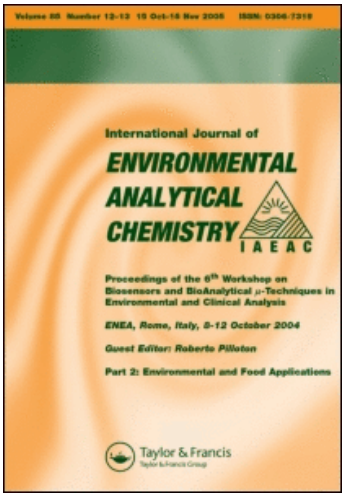


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# Direct Determination of Benzo(a)pyrene and Pyrene in Solid Environmental Samples by Jet-Cooled Spectroscopy

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# DIRECT DETERMINATION OF BENZO(A)PYRENE AND PYRENE IN SOLID ENVIRONMENTAL SAMPLES BY JET-COOLED SPECTROSCOPY

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We report the direct determination of two polycyclic aromatic hydrocarbons (PAH), Benzo(a)Pyrene [B(a)P] and Pyrene (Pyr), in solid environmental samples, i.e. a marine sediment and scrapings from the interior walls of a steel foundry, by the supersonic jet/laser induced fluorescence technique. We have found limits of detection (LOD) for these samples of 900 ng (1.8 ppm) for B(a)P and 200 ng (0.4 ppm) for Pyr. The LOD's for prepared solutions were 100 ng for B(a)P and 40 ng for Pyr. In validating the procedure we have also analyzed a standard mixture of PAH. The results of our analyses of the solid environmental samples agree well with those obtained by chromatography in other laboratories. We have found evidence of incomplete recovery of PAH from soil sediments by a prolonged low temperature Soxhlet extraction using methylene chloride.

KEY WORDS: Benzo(a)pyrene, pyrene, direct determination, jet-cooled spectroscopy.

## 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are widespread in the environments of industrialised countries and come largely from the combustion of carbon-containing fuels. Since some of them are carcinogenic and/or mutagenic to animal species, PAH's are subject to environmental monitoring in the atmosphere, bodies of water and the soil. For the most part, atmospheric PAH's appear as absorbed or adsorbed species on solid aerosol particles and samples of these are collected for analysis by drawing atmospheric air through filters, such as Hi-Vol filters.

The most common analytical techniques used are HPLC and GC, which are highly sensitive and selective. Each of these techniques requires a preliminary extraction of the sample with an organic solvent and an elaborate cleanup of the extracted fraction to remove species that are likely to cause interferences and/or deterioration of the chromatographic packing material. This preparatory procedure can often take several days to complete and may result in incomplete recovery of analyte from specific types of environmental samples, such as fly ash emitted by coal-fired power plants[1] and soils.[2] It would be advantageous,

therefore, to be able to analyze particulate and other solid samples directly; i.e., without subjecting the environmental sample to solvent extraction and cleanup.

In this report we describe the application of the technique of jet-cooled spectroscopy[3–7] to the direct analysis of PAH contained with environmental soil samples. In our version of the technique we load the solid sample directly into the stagnation chamber of a heated jet nozzle. The PAH vapour formed here is seeded into a supersonic expansion of argon and we monitor the PAH content of the beam formed by laser induced fluorescence (LIF). By loading the sample directly we avoid the problems associated with solvent extraction mentioned in the previous paragraph. We analyze directly two authentic environmental samples, one taken from a seabed sediment and the other from the interior walls of a local steel foundry. In addition we also analyze the Soxhlet extract of a soil sediment sample taken from the vicinity of a decommissioned coal gasification facility. One of the two representative and commonly encountered PAH's chosen for analysis, B(a)P, is a known carcinogen. The other, Pyr, is a non-carcinogen. To the best of our knowledge the work presented here is the first direct determination of environmental PAH, i.e. without preliminary solvent extraction, by the supersonic jet/LIF (SSJ/LIF) method.



## 2. EXPERIMENTAL

### *2.1 Apparatus and Procedure*

The essential elements of the SSJ/LIF experiment are (1) a pressurized sample chamber in which solid sample may be held and heated, (2) a nozzle which connects the sample chamber to a fluorescence cell, and (3) the evacuable fluorescence cell through which the laser beam is passed, intersecting the gas jet which issues from the nozzle.

The nozzle used in our experiments is a cylinder 27.5 cm in length and 3.1 cm in diameter. The forward end of the nozzle consists of a copper section the front face of which is pierced with a centred 0.32 mm diameter hole serving as the beam orifice. The copper section is wound with electrically insulated nichrome heating wire. This arrangement provides for rapid and uniform heating of the sample in the insert. The interior wall of the copper section is tapered to accommodate the conical end-piece of an insert, which holds the sample. A sample well capable of holding 0.5 g of solid or 0.7 mL. of liquid has been hollowed out of the end-piece. Gases are brought into the sample well through a 1 mm diameter duct in the end-piece. The end-piece is supported by a section of thin-walled stainless steel tubing, which minimizes thermal conductive losses from the sample. A vacuum seal between a wide section of the insert support tubing and the main body of the nozzle is effected by means of a Cajon fitting. A chromel–alumel thermocouple is silver-soldered to the rear of the end-piece.

The beam chamber is a 30 cm stainless steel cube evacuated by a 6″ oil diffusion pump backed by two mechanical pumps. A background pressure of less than 0.01 Torr is maintained when the stagnation pressure is as high as 1 atm.

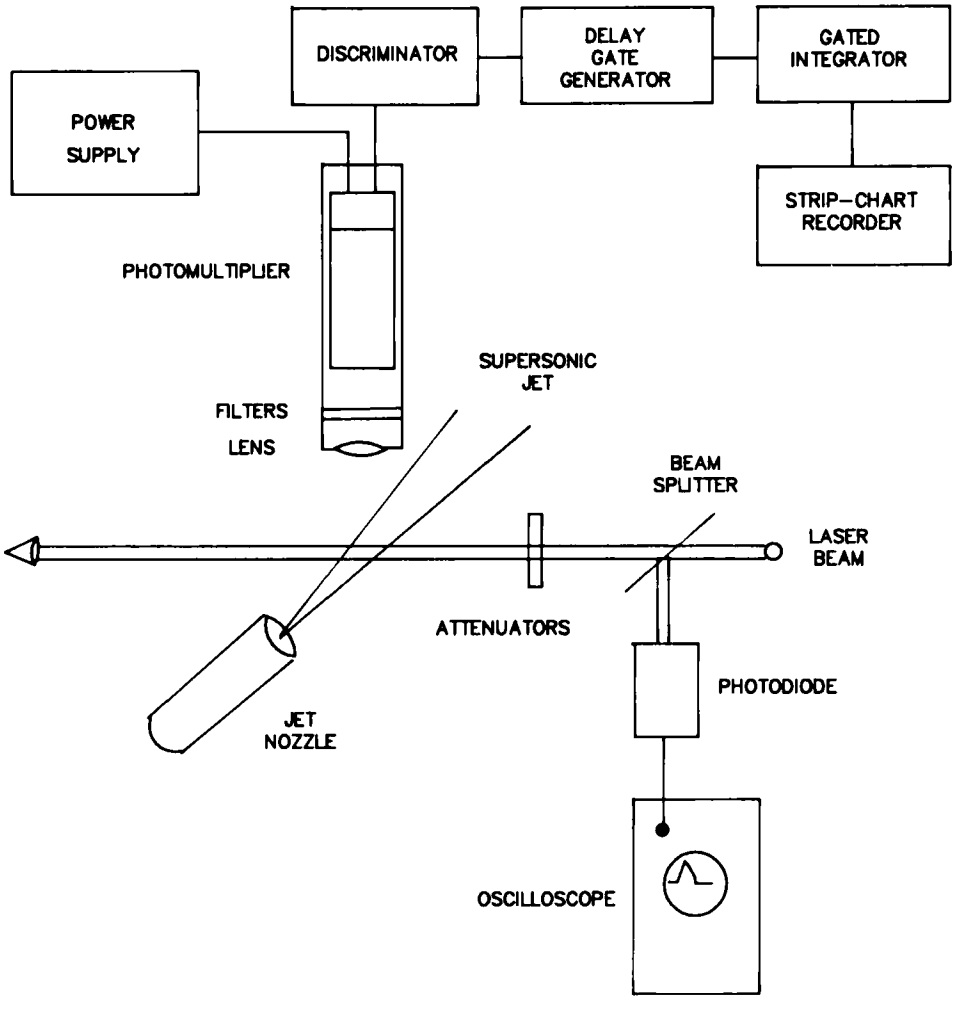


**Figure 1** Schematic representation of the apparatus.

Stagnation pressures, which are associated predominantly with the argon in the stagnation chamber, are kept in the range of 200 Torr to 1 atm and controlled to within 5%. However, the amplitude of the observed signal associated with a given sample is independent of the stagnation pressure over this range of pressures and depends only on the stagnation temperature. The nozzle is attached to the beam chamber by means of an O-ring seal which allows the nozzle to be moved relative to the probe laser beam. The laser beam enters and leaves the beam chamber by means of 0.5 m baffle arms to the ends of which are attached quartz windows at the Brewster's angle. The laser beam intersects the jet at a downstream distance of 10–50 nozzle diameters (3.2 to 17 mm).

Figure 1 is a schematic representation of the apparatus. An EMI 6256 photomultiplier is used to detect the LIF, which is collected by an f/1.3 lens

mounted parallel to the plane of intersection of the laser beam and supersonic jet. The signal from the photomultiplier is averaged by a boxcar gated integrator and displayed on a chart recorder. With an integrator gate width of 150 ns and time constants lying between 2 and 5 $\mu$s, signal to noise improvement ratios of between 5 and 8 are obtained. The delay time between the laser pulse and the onset of the gate pulse is chosen as a compromise determined by the radiative lifetime of the PAH and the need to minimize background radiation associated with the laser beam. Neutral density filters and/or wire mesh screens are used to attenuate the laser beam as required to prevent photomultiplier saturation.

When solid environmental samples are placed in the sample insert, they are wetted with acetone or toluene and then dried prior to insertion into the nozzle as a precaution against particles being swept by the carrier gas into the orifice. After being loaded directly into the stagnation chamber of the beam nozzle, the sample is heated to a temperature in the range of 220–375 °C in order to vaporize the PAH material present. Oven temperatures of less than 220 °C produce low yields, whereas temperatures higher than 375 °C cause the sample insert to stick in the nozzle, a mechanical problem. A measurable LIF signal appears in less than 20 s after the sample is loaded into the pre-heated nozzle and persists for 5–30 minutes. Quantitative analyses are carried out by alternating standard and unknown samples and comparing LIF-time integrals as discussed below.



Most of the data discussed in this paper have been obtained with a home-built dye laser based on the grazing-incidence grating design of Littman[8] and pumped with a nitrogen laser. A laser linewidth of 0.011 nm and pulse energies of 10–20 $\mu$J are typical of this arrangement. Some of the data have been obtained with a modified Lambda-Physik FL2000 dye laser also pumped with a nitrogen laser. This dye laser was operated with a linewidth of 0.06 nm and energies of 10–20 $\mu$J.

Laser excitation spectra of pure jet-cooled B(a)P and Pyr were obtained in separate experiments and served in the selection of laser wavelengths for use in our quantitative determinations. These spectra were found to agree in all respects with published jet-cooled spectra of these molecules.[9,10] At the outset of each series of experiments pure PAH was loaded into the jet nozzle, the laser was tuned to the wavelength of a known transition of the PAH to be determined close to the $S_0 \rightarrow S_1$ origin where spectral features are well separated, and the LIF signal was maximized with regard to the peak of the chosen feature. The wavelengths normally employed were 386.74 nm for B(a)P and 367.44 nm for Pyr.[10]

A marine sediment sample, designated HS-3, was purchased from the Atlantic Research Laboratory of the National Research Council of Canada Laboratories in Halifax, Nova Scotia, Canada. Another sample consisted of scrapings from the interior walls of the Dofasco Steel Foundry in Hamilton, Ontario, Canada. In addition, liquid samples were analyzed to calibrate the SSJ/LIF technique. These consisted of a standard mixture of ten PAH's dissolved in toluene (Supelco) and an extract of a sediment sample obtained by low temperature Soxhlet extraction with methylene chloride. The latter sample was in the form of a solution containing considerable solid suspended matter and was provided to us by the Trace Organics Laboratory of the Ontario Ministry of the Environment (OME) located in Toronto, Ontario, Canada. In both cases experimental aliquots were

measured with the aid of an Eppendorf pipette and the solvent was removed by evaporation prior to insertion into the nozzle.

### 2.2 *Spectroscopic Selectivity*

The utility of the SSJ/LIF method as an analytical procedure depends upon the degree of its success in achieving simultaneously both adequate selectivity and high sensitivity. In this experiment selectivity is provided by the tunability of the LIF source, its linewidth and the width of the absorption feature. An LIF excitation spectrum of a low temperature PAH vapor consists of a series of narrow line-like features which correspond to unresolved rotational line envelopes at the vibronic origins of the many allowed electronic transitions of the PAH. In our experiment the widths of these features are approximately 0.02% of the fundamental laser frequency, substantially wider than the laser linewidth. This resolution makes it possible to discriminate very effectively against interference by any other PAH.

In the work reported here the laser wavelength was set with the use of our authentic sample of the PAH concerned, B(a)P or Pyr. As mentioned above, these wavelengths were in agreement with literature values.[9,10] In addition, and as mentioned below for each sample, there is other evidence which confirms an identification made on the basis of the laser wavelength. This includes (1) the agreement of analyses for a given PAH made at alternative spectral features for that PAH, (2) the agreement of measured fluorescence lifetime for a particular PAH with those reported in the literature for that PAH, and, (3) the agreement of analyses for a given PAH by the SSJ/LIF procedure with those obtained by alternative techniques on the same sample. For most samples, but not for all, tuning the laser wavelength away from the center wavelength of an LIF feature by a linewidth eliminated the LIF signal. When this was not the case a correction was made as described below.



### 2.3 *LIF-Time Integrals and Detection Limits*

Typical LIF signals from standard and environmental samples are displayed in Figure 2. In each case the total amount of PAH is about 10 $\mu$g, but the peak observed for the solution sample is both higher and sharper than that observed for a solid environmental sample. The differences in the appearance of the signal peaks are related to the differences in the nature of the two types of sample. The PAH from the solution sample is distributed as a thin film over the walls of the sample well following the evaporation of the solvent and its heat capacity is negligible compared to that of the insert end-piece. This means that the PAH is flash-heated and the vapour is evolved very rapidly so that it comes out of the orifice in a comparatively short burst. On the other hand the environmental sample is composed primarily of a solid matrix of low volatility and thermal conductivity. A longer heating time is required before the sample is brought to a temperature at which a significant vapour pressure of the PAH is produced and the PAH vapour must diffuse through a relatively thick layer of particulate matter

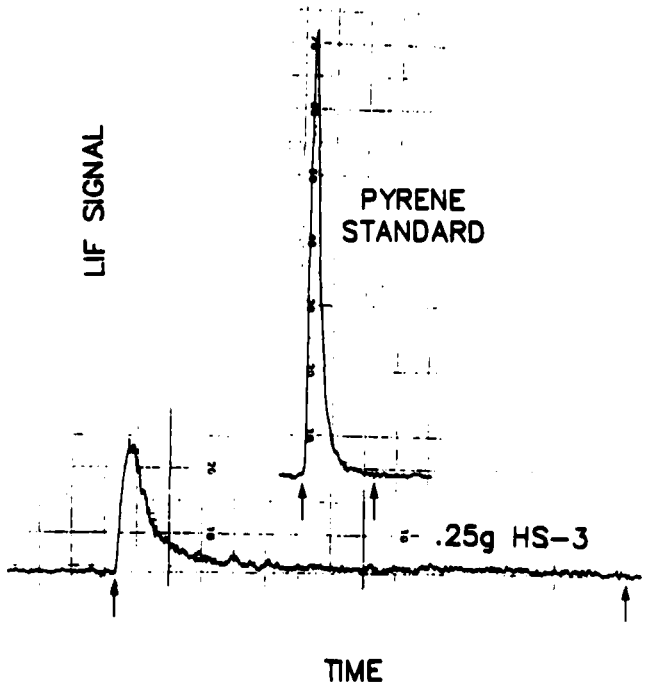


**Figure 2** Representative recorder traces of the LIF signals obtained from pyrene in a standard sample and in 0.25 g of the HS-3 sea sediment sample. The pyrene standard contains 10 $\mu$g of Pyr and the HS-3 sample contains 9.6 $\mu$g. The arrows indicate limits of integration of the observed LIF signal.



before it can mix with the carrier gas. As a consequence the observed peak has a smaller amplitude and persists over a longer interval.

The integration limits for the LIF-time integral must be established with some care for persistent low-amplitude signals. When it was judged that all the PAH had been evolved from the sample, the sample insert was removed from the nozzle. The absence of a detectible decrease in the baseline signal following the removal confirmed the essentially complete vaporization of recoverable-PAH from the sample. Only under these circumstances was the signal integration performed. Since LIF signal amplitudes were very small in the far tail of the trace, errors associated with misassigning the upper limit of integration were expected to be small and not the chief source of uncertainty in the quantitative analysis. This was confirmed by varying the upper limit of the integration from the positions indicated by the arrows in Figure 2.

Figure 3 shows the time-integral of the LIF signal intensity corrected for background signal plotted against the total amount of PAH in the sample insert for standard solutions of both B(a)P and Pyr in toluene. As can be seen the time-integral of the LIF signal varies linearly with the amount of PAH up to 140 $\mu$g of PAH. Limits of detection (LOD) for Pyr are found to be 40 ng when solutions are analyzed and about 200 ng for the solid environmental samples analyzed here. The

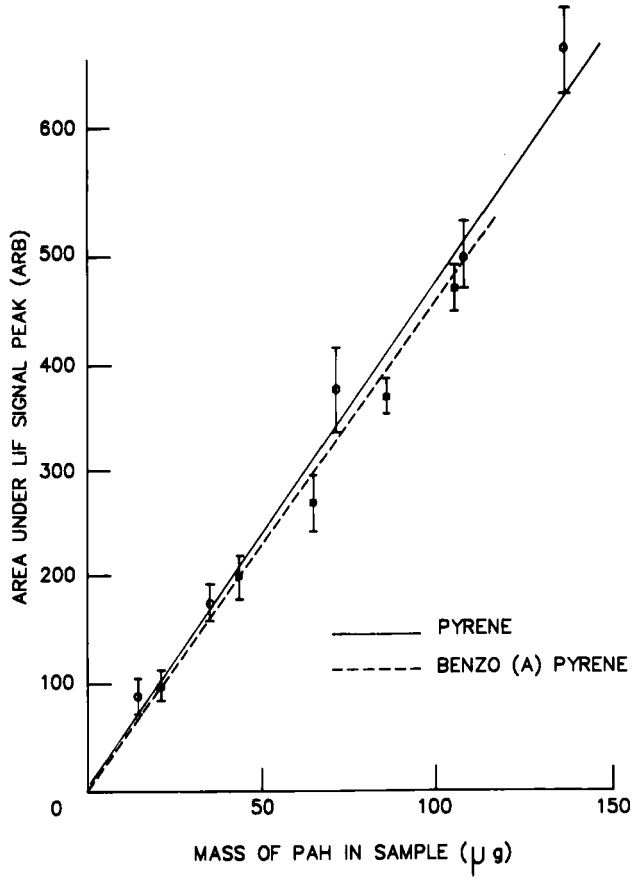


**Figure 3** Plots of the areas under the LIF signal peaks for Pyr and B(a)P as a function of added pure PAH solid. The ordinate scale is arbitrary and does not reflect the absolute sensitivities of the two PAH's. The straight lines shown were fitted to the data by linear regression based on the assignment of equal statistical weights to the data points. ○ Pyrene; □ Benzo(a)Pyrene.

LOD's for B(a)P are 100 ng (solutions) and 900 ng (environmental samples). The LOD's were determined by measuring the ratio of the peak amplitude of the LIF signal to the baseline noise amplitude for samples containing a few micro-grams of a given PAH (S/N) and then calculating the amount of PAH that would produce a S/N of 3. On the assumption that 0.5 g environmental samples are loaded into the nozzle these figures can be expressed as 0.4 ppm for Pyr and 1.8 ppm for B(a)P.

## 3. RESULTS AND DISCUSSION

The results obtained in this work are presented in Table 1. In each case the result

**Table 1** Results of analyses (PAH concentration in ppm)[a]

| *Sample* | *Benzo(a)pyrene* | | *Pyrene* | |
|---|---|---|---|---|
| | *This laboratory* | *Other laboratory* | *This laboratory* | *Other laboratory* |
| Supelco[b] | 0.49(0.03) | [b] | 0.49(0.03) | [b] |
| HS-3 | 7.6(0.9) | 7.4(3.6)[c] | 33.7(1.5) | 39.0(9.0)[c] |
| Dofasco | < 1.8 | 1.1[d] | 3.8(0.3) | 4.2[d] |
| SP45-0141 | 180 | 102[e] | 700 | 371[e] |
| OW50-0026 | 143 | 24[e] | 245 | 53[e] |

[a]Figures in parentheses are single standard deviations.

[b]Concentrations are given in mg/ml. Nominal concentration given by Supelco was 0.5 mg/ml.

[c]The HS-3 sample is marine sediment material purchased from the National Research Council of Canada Laboratories in Halifax, Nova Scotia. The quoted results come from HPLC analysis carried out there.

[d]These results were obtained in the Department of Biochemistry at McMaster University, Hamilton, Canada by GC/MS.[11] The sample was provided by Professor D. Bryant from McMaster University and the results are included with the approval of Dr. E. Gibson, Head of Occupational Health, Dofasco Steel Foundry, Hamilton.

[e]These are sediment samples from Kettle Creek, Ontario provided to us by the Trace Organic Laboratory of the Ontario Ministry of the Environment located in Metropolitan Toronto. The analytical results were obtained by HPLC.

obtained in another laboratory by an alternative technique is given for comparison.

### *3.1 The Supelco Standard Sample*

This sample is a commercially available mixture of ten PAH's dissolved in toluene at a stated concentration of 0.5 mg/ml. In our analysis of this sample we found a residual LIF signal when the laser was tuned away from the absorption features chosen for both Pyr and B(a)P. The contribution of this unidentified fluorescence source(s) to the Pyr LIF signal was short-lived and was eliminated by setting the delay between the laser pulse and the signal integration to 1 $\mu$s. This is possible in the case of Pyr because of its rather long radiative lifetime of 1.4 $\mu$s.[10] The much shorter radiative lifetime of B(a)P of 0.27 $\mu$s[9] prevented the use of this technique during its analysis. Thus in this case we corrected for the interfering fluorescence source by determining the value of the LIF-time integral at a wavelength 0.1 nm off-resonance and subtracting this (70%) correction from the value obtained on-resonance. The calculated concentration was in good agreement with that given by the supplier.

### *3.2 The HS-3 Marine Sediment Sample*

This sample was a marine sediment reference material purchased from the Marine Analytical Chemistry Standards Program of the National Research Council of Canada laboratory in Halifax, N.S. The sample is a fairly complex mixture in which NRCC identified 16 PAH's. A correction (45%) for the contribution of a non-resonant fluorescence signal during the B(a)P analysis was made for this sample as described previously for the Supelco sample. Our analysis for B(a)P and Pyr are in good agreement with those obtained by NRCC through an HPLC procedure. To confirm that all the recoverable-PAH had been removed from the

sample during an analysis the residue remaining in the sample well was itself reanalysed by pulverizing and reheating. No further detectible PAH was evolved from the residue during this procedure.

### *3.3 The Dofasco Sample*

This sample was obtained from the Dofasco Steel Foundry in Hamilton, Ontario and is material which had deposited over time upon the foundry walls. Thirty-three compounds were identified in this sample by a combination of GC/MS and HPLC.[11] Nevertheless our analyses for B(a)P and Pyr are in good agreement with those found by alternative techniques. As one test for retention of PAH in the soil matrix, a sample was prepared with PAH added in amounts several times in excess of the natural content. This sample was analysed and the residue was analysed a second time as was done with the HS-3 sample. Again it was found that no PAH could be detected in the second heating procedure. Recovery studies were not conducted for the HS-3 or Dofasco samples as they could not have served as reliable tests for the presence of PAH which was undetectible due to matrix retention. The agreement of our results for each of these samples with results obtained by the independent analyses given in Table 1 suggests that all the PAH content was analyzed by our procedure.



### *3.4 The Kettle Creek Samples*

These two samples were provided by the Trace Organics Laboratory of the Ontario Ministry of the Environment, Toronto, Ontario. Identified by sample numbers SP45-0141 and OW50-0026, these were soil samples drawn from the vicinity of a decommissioned coal gasification facility. The HPLC analysis conducted by the OME identified 25 PAH's in these samples. The samples were received in the form of so-called raw extracts; i.e., as fractions obtained from a 24 hour methylene chloride Soxhlet extraction of the dried soil at about 90 °C. These raw extracts contained large amounts of solid matter suspended in the solvent. Our analysis includes both dissolved PAH's and any undissolved PAH remaining on or in the fine particles making up the suspension. The OME analysis involved further extraction and clean-up prior to analysis.

The fact that the SSJ/LIF results were much higher than the OME results suggested that the extraction of PAH from the sediment may have been incomplete. Consequently the raw extract was centrifuged at 100000 G for 30 min to separate the suspended matter from the solvent substrate. This measure was only partially successful, since the substrate continued to have a cloudy appearance. SSJ/LIF analysis of the substrate indicated a 20% reduction in B(a)P. A small solid residue was also observed at the bottom of the centrifuge tube, but there was not enough of it for us to analyze. Thus, while we have shown that some PAH must have remained in the suspended solids, we have not shown that these carried sufficient PAH to account for the observed discrepancies between SSJ/LIF and OME results possibly because we were unable to completely separate the suspended solids.

To investigate alternate origins of the discrepancies we searched for spectroscopic interferences from other species by detuning the laser wavelength, but found none. In addition, we repeated our analyses at a second resonance wavelength for each of B(a)P and Pyr in each sample and obtained the same results. The B(a)P/Pyr ratios in both the OME and SSJ/LIF determinations are roughly equal, which, given the lack of evidence for spectroscopic interference, supports the supposition stated earlier that the observed discrepancies between SSJ/LIF and OME results can be ascribed to either incomplete solvent extraction of PAH from the original sediment or loss of PAH during the extractive process.

Such a possibility is supported by recent reports on the efficiencies of some common methods of extraction based on solvents. It has been argued that prolonged low temperature (90 °C) solvent extraction of certain solid environmental samples, a favored procedure in many environmental laboratories, may not be very efficient and that destruction of PAH may occur in the hot solvent.[12] Both Renkes *et al.*[12] and Junk and Richard[13] point to inconsistent recoveries of PAH reported for various extraction procedures. Efficiencies of extraction are often dependent on the solvent chosen and the temperature at which the extraction is carried out. In addition, the type of sample being subjected to extraction is often an important factor. For example, efficient recovery of PAH from fly ash has proven to be especially difficult.[1] Moreover it has been shown that PAH can be recovered more effectively from smaller solid particles than from larger solid particles[12] and from more heavily loaded particulates than from lightly loaded particulates.[10]



## 4. CONCLUSION

We have shown for two PAH's that the SSJ/LIF technique is precise and accurate. In principle this technique should also be useful in analysis for other organic materials commonly found in the environment. As a direct technique it avoids the potential loss of analyte characteristic of other techniques that require preliminary extractions and clean-ups. By eliminating the prolonged preparation of samples required for HPLC, GC and related methods the SSJ/LIF technique can be characterised as "fast" in the sense that the period between the collection of a sample and its analysis for a specific PAH is greatly reduced. The sensitivities that we have found for PAH's in solutions fall within the range of sensitivities reported by other investigators who introduced their samples into supersonic nozzles from GC[3,4,6] or HPLC[7] columns. In all these cases the samples were originally injected into the chromatographic columns in the form of solutions.

The sensitivity for analysis of PAH in solid samples was found to be between one and two orders of magnitude lower in solid environmental samples. This loss of sensitivity can in principle be recovered by improving the efficiency of the light collection optics and/or by increasing the local beam density. Spangler and Pratt[14] report a 25-fold improvement in light collection efficiency compared to a three-lens collection system used previously, when they mounted a commercially available

ellipsoidal mirror co-axially with their jet nozzle. Stiller and Johnston[15] have brought about a 30-fold increase in local particle density by surrounding their nozzle with a co-axial conical sheath through which they flowed a rare gas. The sheath flow concentrates the jet flow close to the flow axis and thereby reduces the rate at which the axial beam density decreases with distance downstream from the nozzle. By making these improvements it should be possible to reduce the LOD to the range of 40–2000 pg for solution samples and 0.2–9 ng for solid environmental samples.

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