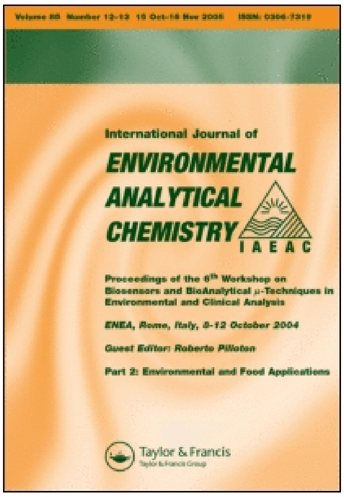

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

On the Determination of Benzo(a)pyrene in Atmospheric Aerosols Fractionated by a low Pressure Impactor, by TLC Separation and *in situ* Spectrophotofluorometry at the Picogram Level

Antonio H. Miguel[a][b]
[a] Instituro de Ouímica, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brasil [b] Departamento de Química, PUC, Rio de Janeiro, Brasil

To cite this Article Miguel, Antonio H.(1982) 'On the Determination of Benzo(a)pyrene in Atmospheric Aerosols Fractionated by a low Pressure Impactor, by TLC Separation and *in situ* Spectrophotofluorometry at the Picogram Level', International Journal of Environmental Analytical Chemistry, 12: 1, 17 — 25

To link to this Article: DOI: 10.1080/03067318208071567

URL: http://dx.doi.org/10.1080/03067318208071567

Intern. J. Environ. Anal. Chem., 1982, Vol. 12, pp. 17–25
0306-7319/82/1201-0017 $06.50/0

Printed in Great Britain

On the Determination of Benzo(a)pyrene in Atmospheric Aerosols Fractionated by a Low Pressure Impactor, by TLC Separation and *in situ* Spectrophotofluorometry at the Picogram Level[†]

ANTONIO H. MIGUEL[‡]
Instituto de Química, Universidade Federal do Rio de Janeiro, 21.941 Ilha do Fundão, Rio de Janeiro, Brasil

(*Received November 27, 1981*)

Urban aerosols were fractionated according to size by an eight-stage low pressure impactor with size resolution down to 0.05 μm diameter. Each stage of the impactor, containing picogram amounts of benzo(a)pyrene (BaP) and other polycyclic aromatic hydrocarbons (PAH) was ultrasonically extracted with benzene. After reduction to appropriate volumes, the extracts were spotted on a TLC plate and developed. The BaP spots were quantitated *in situ*, by finely focusing the TLC plate on the fluorescence excitation beam and measuring the resulting emission while scanning the plate. The regression lines passing thru the origins exhibited linear regression coefficients (R^2) between 0.9985 and 0.9996 for three-point BaP calibration data in the 100-1000 picogram range. The relative standard deviations varied between 3.4 and 12.9%, depending on the amount of BaP present. The detection limit for BaP is 5 picogram. The method allows the determination of typical atmospheric Bap size distributions with as little as 1.5 m^3 of sampled air.

KEY WORDS: Benzo(a)pyrene size distribution, low pressure impactor, TLC separation, *in situ* fluorescence, atmospheric aerosols.

[†] Presented at the Workshop on the Chemistry and Analysis of Hydrocarbons in the Environment, Barcelona, November 1981.

[‡] Present address: Departamento de Química, PUC, R. Marquês de S. Vicente, 225, Rio de Janeiro, 22.453, Brasil.

INTRODUCTION

Particle size and chemical composition of pollutants determine atmospheric extinction and transport, and deposition in the respiratory system. In addition, size data provide complimentary information regarding the source and mechanism of formation of toxic pollutant species.

Cascade impactors operating at atmospheric pressures have been used to fractionate PAH-containing ambient aerosols of aerodynamic diameter (d_p) larger than about 0.5 μm.[1-7] To obtain resolution below 0.5 μm, it is necessary to operate the impactors at reduced pressure.[8, 9] However, low pressure impactors operate at flow rates two to three orders of magnitude smaller (typically 1 l/min.). This limitation demands large aerosol volumes—which result in increased observation "time windows"—and analytic methods with PAH sensitivities at the picogram level for 24 hr samples.

Particle bounce and overloading are two of the most common sources of error in the fractionation of aerosols. Particle bounce during sampling increases with increasing particle size and loading of the impaction surface.[10] According to Fuchs,[10] many investigators have not paid sufficient attention to this fact, and this resulted in large discrepancies in the published size distribution data of pollutant aerosols.

For cascade impactors with single nozzles (this study), there are two ways of reducing particle bounce: (i) by sampling small aerosol volumes and, (ii) by using coated impaction surfaces. The first condition imposes a high sensitivity demand on the analytic method used to determine the species of interest. The second requires that the presence of the coating material does not interfere with the detection method.

Currently, there are two relatively inexpensive methods for the determination of PAH at the picogram level, namely high performance (pressure) liquid chromatography with fluorescence detection (HPLC-F) and thin layer chromatography with *in situ* spectrophotofluorometry (TLC-SPF). For samples collected with multi-stage cascade impactors (this study), the latter has two major advantages: (i) it is much faster—blanks and samples can be developed simultaneously in less than 1.5 hrs as compared with about 6.5 hrs required in the HPLC-F method. (ii) it provides confirmatory excitation and emission spectra of the separated PAH at the 50 to 100 picogram level.

In the following sections we report on an improved TLC-SPF method capable of determining picogram amounts of BaP and other PAH with high precision. This high sensitivity allows the use of low aerosol volumes in the determination of submicron PAH at low atmospheric levels. An illustrative example is given, where the submicron size distribution of atmospheric BaP was determined in a sampled air volume as small as 1.44 m^3.

EXPERIMENTAL

Aerosol collection

Aerosols were segregated according to size by an eight-stage low pressure impactor built from high density aluminum stock (Alcan type 7075-T6) according to design and construction tolerances reported elsewhere.[11] The impactor samples at a rate of 1 l/min and has 50% efficiency cutoffs of 4.0, 2.0, 1.0, 0.5, 0.26, 0.12, 0.075, and 0.050 μm d_p. A Leybold-Heraeus type S4A vacuum pump was used.

Particle bounce was reduced by a layer of Vaseline^R about 2-μm thick by 3 mm diameter. This layer was obtained by applying 0.5 μl of a 2% solution of Vaseline^R in toluene—using a Hamilton no. 7001 SN microliter syringe—and allowing it to evaporate.

Aerosol extraction

At the end of the sampling period, using a Pasteur pipette, the particle deposit was removed by drop-wise addition of about 300 μl of spectrograde benzene, while tilting the impaction disc. The resulting suspension was collected in a 1 ml amber Reacti-Vial™ (Pierce Chemical Co. no. 13097). After removal of all deposits, the vials were placed in an ultrasonic cleaner (Brosonic 220) and extracted for 30 min. The volume of each extract was then reduced to about 30 μl by flowing a stream of high grade nitrogen gas over their surface, at room temperature.

BaP analysis

Using 5 μl capillary pipettes, the extracts were spotted 0.7 cm apart and 1·5 cm from the bottom, on precoated TLC plates (21% acetylated cellulose, Schleicher and Schuel no. G1800/21 ac) cut into 20 × 4 cm pieces. The vials were rinsed three times with 5 μl of benzene also transferred to the same spot. BaP was separated from other PAH by development of the plates in the dark, in an equilibrated chamber containing 50 ml of a mixture of ethanol:toluene:water (17:4:4 (v/v). Plates containing BaP standards between 100 and 1000 picograms, spotted in the same manner with 5 μl pipettes were developed at the same time. The solvent front was allowed to travel 15 cm (~1 h 20 min) and the plates were removed and allowed to dry.

A Perkin-Elmer model MPF-2A Fluorescence Spectrophotometer was used. A spectrodensitometer with slide mechanism built from 0.64 cm dia. recorder slide bars permitted vertical (normal to the excitation beam) and horizontal movement (in the plane of the beam) of the TLC plate. Motorized vertical movement of the TLC plate was provided by an electric clock motor which scanned the plate at a rate of 1 mm/min in the direction of solvent migration. The horizontal movement was manual. The entire unit was assembled on the platform of the module normally used in phosphorescence measurements (with the cam motor removed), which is equipped with optical lenses (Figure 1). The TLC plate is viewed at a 45° angle from both the excitation and emission slits.

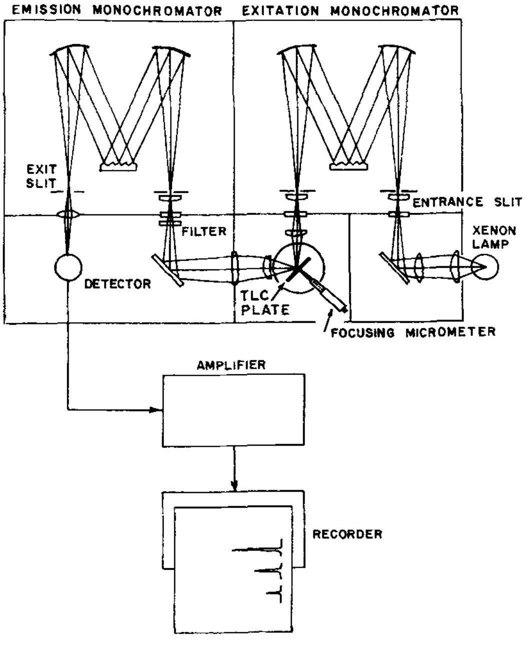

FIGURE 1 Schematic arrangement of the spectrophotofluorometer used, showing the TLC plate positioning and focusing micrometer.

After selection of the appropriate excitation and emission wavelengths and slits, the BaP spot is located and finely focused—using the straight micrometer shown in Figure 1—by optimizing the fluorescence emission intensity. Typical chromatograms are shown in Figure 2.

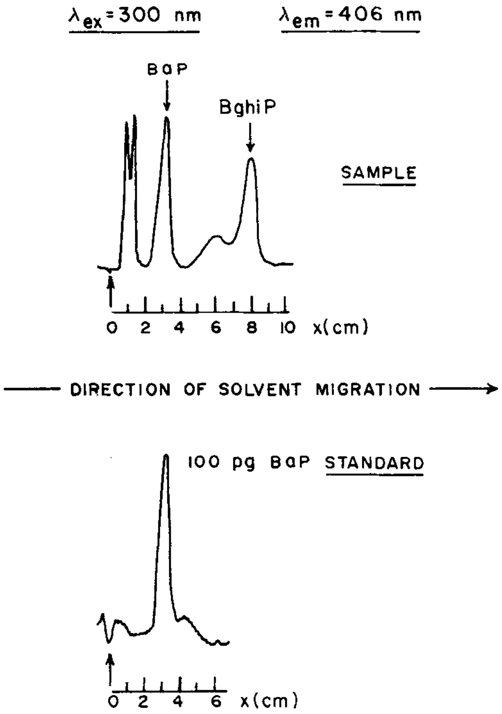

FIGURE 2 Typical TLC-SPF chromatograms. x = actual distance on the TLC plate.

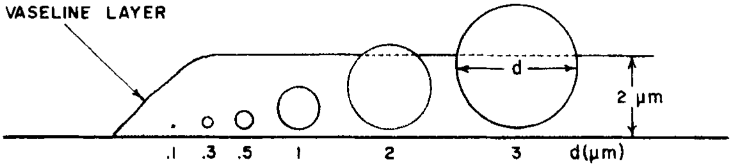

FIGURE 3 Representation of the sizes (μm) of deposited particles relative to a 2-μm thick layer of Vaseline coating.

RESULTS AND DISCUSSION

Collection efficiency

According to a model by Reischl and Johns,[12] the impaction area free of particle deposit decreases exponentially with the amount of aerosol sampled. Thus, for a coating layer 2-μm thick (Figure 3), particle bounce on the upper stages (cutoffs larger than 2 μm) will become critical only after monolayer coverage. This fact has been experimentally confirmed by current work of Hering and Friedlander.[13] Using an identical low pressure impactor, these investigators determined monolayer collection efficiencies of about 95% for polystyrene latex particles of 1.48 μm diameter collected on Vaseline coated surfaces. Collection efficiencies of submicron aerosols by the 2-μm Vaseline layer (Figure 3) should be greater than 95%, as a result of their embedding and retention by capillary forces.

TLC-SPF analysis

From the TLC-SPF chromatograms (Figure 2), either peak heights or areas of the spots can be used to plot the calibration curve and calculate the concentrations of the unknowns (provided that the same size pipettes are used for both sample and standard spotting). We found that, using either ordinate, the standard deviations of the calculated unknown concentrations were well within the standard deviation of the method.

The high precision of BaP analysis by this method is evidenced by correlation coefficients (R^2) between 0.9985 and 0.9996 (Table I) of linear regression lines passing thru the origins. Under the same operating conditions, calibration plots ran on separate plates also showed slope deviations within the standard deviation of the method (Table I).

TABLE I

BaP calibration data and linear regression coefficients $\lambda_{ex} = 300$ nm, $\lambda_{em} = 406$ nm, slits: ex = 14, em = 2.6 nm. Sensitivity = 3

BaP spotted, pg	Peak height,[a] cm	Peak height,[b] cm	Peak height,[c] cm
100	1.5	1.3	1.4
500	8.4	8.2	8.1
1,000	18.3	17.7	17.1
R^2	0.9985	0.9993	0.9996
intercept	−0.580	−0.669	−0.449
slope	0.0187	0.0183	0.0175

[a,b] Each set of standards applied on one plate.

[c] Each nominal standard (ran in duplicate) applied on three separate plates.

The relative standard deviations of several determinations varied between 3.4 and 12.9%, depending on the amount of BaP in the spot (Table II). The limit of detection—defined as a signal of amplitude twice the noise—is 5 picogram for BaP. Thus, to keep the RSDs near 5%, the

TABLE II

Reproductibility of the determinations as a function of BaP level[a]

pg found[b]	Ave. pg	Std. deviation	RSD, %
69, 61, 79	69.7	9.02	12.9
107, 103, 97	102.3	5.03	4.92
148, 139, 150	145.7	5.86	4.02
231, 228, 243	234.0	7.94	3.39

[a] 1 μl aliquots of benzene extracts (20 min in ultrasound) of atmospheric particles collected on Hi-Vol glass fiber filters.

[b] Average of duplicate determinations.

amount of BaP collected on each stage of the impactor should be at least 20 times this limit. BaP in solvent and Vaseline blanks were below the detection limit.

The stability of BaP during fluorescence analysis was investigated by exposing a spot containing 500 picograms of this PAH to UV light of 300 nm under normal analytic conditions. After 30 min of continuous exposure, about 20% of the original BaP had photodecomposed or evaporated from the plate. In the TLC-SPF method described, a full BaP chromatogram is obtained in about 30 sec. During this period, about 3 picograms of BaP is lost. For this reason, the TLC plate should be scanned as fast as the recording device response permits. This fact may well be the limiting factor for achieving lower PAH detection limits using the method described.

Treatment of BaP aerosol size distribution data

There are several ways of reporting data on chemical composition as a function of particle size. For cascade impactors with wide size resolution ranges, such as the low pressure impactor used in this study, the best way is to report concentrations and mass distribution functions with respect to particle size (Table III). From such data, physically meaningful histograms can be obtained by plotting $\Delta M/M \cdot \Delta \log d_p$ vs $\log d_p$ (Figure 4). For instance, the modal nature of the aerosol is clearly shown by these plots. Figure 4 represents a distribution for which about 60% of the BaP is in what has been called[14] the "accumulation" mode ($0.05 < d_p < 0.26\,\mu$m) whereas about 30% is in the "coarse" mode ($0.26 < d_p < 2\,\mu$m). Similar distributions were found in Pasadena (California) aerosols,[8] where an

TABLE III

BaP concentration and mass distribution function with respect to particle size[a]

d_p range,[b] μm	ng BaP	ΔM, ng/m^3	ΔM/MΔ log d_p
>4	0.13	0.090	0.184
2.0 -4.0	0.14	0.097	0.199
1.0 -2.0	0.13	0.090	0.184
0.5 -1.0	0.37	0.257	0.527
0.26 -0.5	0.21	0.146	0.317
0.12 -0.26	0.43	0.299	0.550
0.075-0.12	0.60	0.417	1.26
0.05 -0.075	0.33	0.229	0.804

[a] Aerosols sampled during a 24 hr period (Rio de Janeiro).

[b] The aerodynamic diameters refers to spherical particles of unit density. For other particle densities see ref. 11. The upper cutoff for the first stage was taken at 8 μm because particles larger than this size are not efficiently collected since sampling was not done isokinetically.

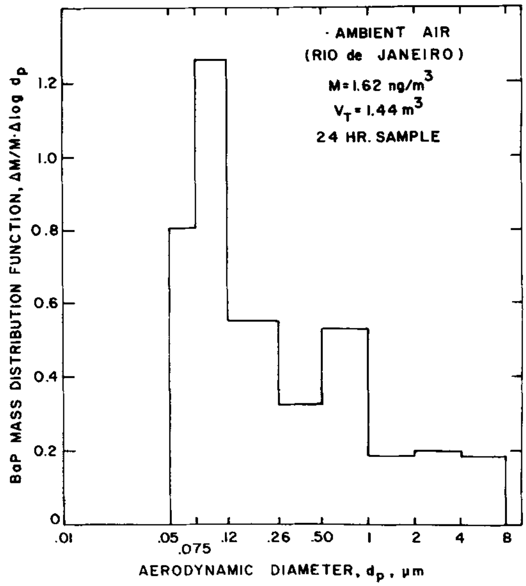

FIGURE 4 Distribution of BaP as a function of particle size. The distribution was normalized for M, the total BaP loading.

average of about 74 and 19% of the BaP was in the accumulation and coarse modes, respectively. These modal characteristics suggest similar sources of emission of this PAH into the atmosphere of the two cities.

Acknowledgements

The author wishes to express his gratitude to Celso Orsini (IF-USP, São Paulo) and Luiz C. Bouéres (Florida State University) for donation of the high density aluminum stock used in the construction of the low pressure impactor.

This research was supported in part by a grant from the National Research Council of Brasil (CNPq), FINEP and CEPG-UFRJ.

References

1. M. Kértesz-Sáringer, E. Mészáros and T. Varkonyi, *Atmos. Environ.* **5,** 429 (1971).
2. R. Starkey and J. Warpinski, *J. Envir. Hlth* **36,** 503 (1974).
3. A. Albagli, H. Oja and L. Dubois, *Envir. Lett.* **6,** 241 (1974).
4. R. C. Pierce and M. Katz, *Envir. Sci. Technol.* **9,** 347 (1975).
5. M. Katz and R. C. Pierce, *Polynuclear Aromatic Hydrocarbons: Chemistry, Metabolism, and Carcinogenesis* (Raven Press, New York, 1976), R. I. Freudenthal and P. W. Jones, Edrs., Vol. 1, pp. 413–429.
6. L. Van Vaeck and K. Van Cauwenberghe, *Atmos. Environ.* **12,** 2229 (1978).
7. M. Katz and C. Chan, *Envir. Sci. Technol.* **14,** 838 (1980).
8. A. H. Miguel and S. K. Friedlander, *Atmos. Environ.* **12,** 2407 (1978).
9. S. C. Stern, H. Zeller and A. I. Schekman, *Ind. Eng. Chem. Fundam.* **1,** 273 (1962).
10. N. A. Fuchs, *Fundamentals of Aerosol Science* (John Wiley and Sons, New York, 1978), Ed. by D. T. Shaw, Chap. 1, pp. 1-83.
11. S. V. Hering, S. K. Friedlander, J. J. Collins and L. W. Richards, *Envir. Sci. Technol.* **13,** 184 (1979).
12. G. P. Reischl and W. Johns, *Staub Reinhalt Luft* **38,** 55 (1978).
13. S. V. Hering and S. K. Friedlander, private communication (1981).
14. K. T. Whitby and G. M. Sverdrup, *California Aerosols: Their Physical and Chemical Characteristics.* (Particle Technology Laboratory Publication no. 347, 1978), Univ. of Minnesota.