

presented in Table V. Good agreement is observed between the results found in this work and those found by flame AAS by other laboratories in the SOAP program. The results for Cr are consistently high, which had also been observed by us previously (2), but the reasons for this disparity are still not fully understood. The advantages of the present multielement system are illustrated by the analysis of the jet-engine oils. The rapid slewing rate of the monochromator and the maximum 10-sec measurement period, enable measurements to be made for five elements and an internal standard in little over 1 min (somewhat less when higher concentrations of wear metals are present). Even with triplicate measurements, the series of analyses summarized in Table V represents a measurement time of less than 1 hr, including the measurement of both standards and samples.

The problem of scattering of the incident radiation of particles in the flame was not encountered with either the pure aqueous solutions or with the oil samples. However, with "real" samples containing a high solids content, such scatter can be evident. Because a continuum source of excitation is used, this scatter is spread over all wavelengths and can be simply corrected for by making two measurements, one of which will normally be at the fluorescence wavelength, and the other at a nearby (e.g., within 1 nm) non-fluorescence wavelength. By a slight modification of the computer program, it is possible to make such off-wavelength background correction, and preliminary studies have indicated the effectiveness of this approach in the determination of trace metals in such matrices as blood serum and orange juice. The detection limits observed in these cases are somewhat poorer than those observed in pure solution because of the increased noise due to scatter in the system.

An additional potential source of systematic error is spectral interference due to overlap or close proximity of fluorescence lines (and/or absorption lines) of different elements. We have studied the fluorescence spectra of a large range of elements, and, in general, those spectra (also ab-

sorption spectra) are simple, consisting of only a few prominent lines, so that the chances of spectral overlap are small. Iron, cobalt, and nickel gave spectra containing 20 or more lines, but most of these were above 340 nm, away from the resonance lines of most elements. One of the iron lines overlaps the Cr 357.9-nm line, but interference here can be avoided by choosing the Cr 360.5-nm line with only a slight loss in sensitivity. At high concentrations of Mg, a line at 279.5 nm is evident due to fluorescence of Mg^{+} which overlaps the Mn 279.5-nm line, but again spectral interference can be avoided by using the Mn 280.1 line.

In summary, the system we have developed shows great potential as a technique for rapid, multielement analysis. The sensitivity for many elements is comparable to that obtained by other spectrometric techniques, with the added advantage that rapid measurements are possible. Only one source is required for a large number of elements and this shows good long and short term stability as well as ease of operation and long lifetime. The instrumental system is simple, flexible, and relatively inexpensive.

At present, the computer is primarily used for rapid data acquisition and future improvements could be made by modifying the program to further process the data, so that calibration curves could be determined, errors estimated, etc., and the analysis presented as a finished report.

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Determination of Atmospheric Isomeric Polycyclic Arenes by Thin-Layer Chromatography and Fluorescence Spectrophotometry

Ronald C. Pierce and Morris Katz¹

Centre for Research on Environmental Quality, T-115 Steacie Science Building, York University, 4700 Keele Street, Toronto, Ontario M3J 2R3, Canada

Polycyclic aromatic hydrocarbons (PAHs) having the same molecular weight and possessing similar structures have been difficult to separate quantitatively using standard chromatographic techniques. A thin-layer chromatographic procedure involving a preliminary group separation on aluminum oxide followed by resolution of the isomeric arenes on acetylated cellulose has been developed as an aid in the fractionation of three isomeric groups of polycyclic arenes present in ambient particulate matter. Five pentacyclic and seven hexacyclic arenes have been quantitatively isolated

using this procedure. Two-dimensional thin-layer chromatography on a composite plate of aluminum oxide:40% acetylated cellulose was also used for identification purposes. Thin-layer chromatography coupled with fluorescence spectrophotometry proved to be an effective analytical technique for the determination of isomeric PAH-content in atmospheric aerosols.

Polynuclear aromatic hydrocarbons (PAHs) have been studied extensively in recent years as a result of their occurrence in such diverse sources as automobile exhaust,

¹ Author to whom all correspondence should be directed.

Table I. R_B Values and Percent Recovery of Isomeric Arenes Separated by Thin-Layer Chromatography

Compound No.	Compound name	Acetylated cellulose (<i>n</i> -propanol:acetone:water)(2:1:1)			Aluminum oxide (hexane:ether)	Percent recovery ^a
		20%	30%	40%	(19:1)	
I	Benzo[<i>e</i>]pyrene	3.93	4.76	5.93	1.02	86.0 ± 5.3
II	Benzo[<i>a</i>]pyrene	1.00	1.00	1.00	1.00	85.2 ± 5.1
III	Benzo[<i>b</i>]fluoranthene	1.17	1.24	1.37	0.99	92.1 ± 3.5
IV	Benzo[<i>k</i>]fluoranthene	2.20	2.65	3.15	0.99	91.2 ± 3.7
V	Perylene	3.17	3.89	4.71	0.97	90.4 ± 4.6
VI	Dibenzo[<i>def,mno</i>]chrysene	1.17	1.32	1.67	0.90	90.9 ± 3.9
VII	Benzo[<i>ghi</i>]perylene	3.27	5.03	6.57	0.91	88.7 ± 4.0
VIII	Naphtho[1,2,3,4- <i>def</i>]chrysene	2.74	5.33	7.01	0.74	87.9 ± 5.5
IX	Benzo[<i>rst</i>]pentaphene	1.14	1.68	1.89	0.73	91.8 ± 4.2
X	Dibenzo[<i>b,def</i>]chrysene	0.27	0.33	0.40	0.73	89.8 ± 3.9
XI	Naphtho[2,1,8- <i>gra</i>]naphthacene	1.23	4.11	4.90	0.73	90.7 ± 5.1
XII	Dibenzo[<i>def,p</i>]chrysene	2.77	5.95	7.99	0.76	84.1 ± 6.2

^a Percent recovery ± reproducibility for two-step preliminary aluminum oxide-final cellulose acetate TLC.

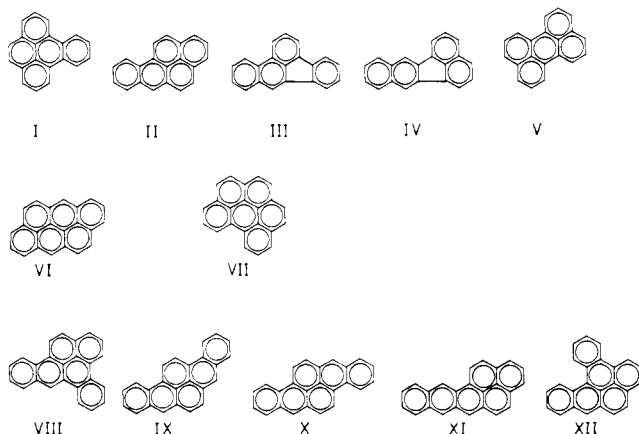


Figure 1. Chemical structures of isomeric polycyclic arenes (names given in Table I)

coal tars, atmospheric particulate matter, cigarette smoke, sediments, processed foods, and high-boiling petroleum distillates. Due to the complex chemical phenomena that may take place in a combustion process, the mixtures of resultant PAHs are extremely complex. PAH fractions recovered from airborne particulates have been shown (1) to contain over one hundred different PAH compounds. Certain PAHs have been known as potent tumor-producing agents in biological systems. However, not all isomers of a single aromatic group are carcinogens. It has been reported (2) that benzo[*a*]pyrene is a potent carcinogen whereas benzo[*e*]pyrene may have only weak carcinogenic properties. In addition, benzo[*rst*]pentaphene is a powerful carcinogen while naphtho[1,2,3,4-*gra*]chrysene is a mild carcinogen. Since small differences in the structure of PAHs may cause great differences in their tumorigenicity, it is of primary concern that attention should be focused on these hard-to-separate isomers. It has been recently reported (3) that approximately 70 to 90% of the total PAH content of airborne particulates was associated with aerosol particles in the "respirable size range" (less than 5.0- μ m diameter) (4). This fact has a significant bearing on inhalation health hazards associated with toxic airborne substances.

The lack of an effective separation scheme appears to be the most serious hindrance to a better understanding of the composition and possible carcinogenicity of PAHs derived from various combustion sources. The chromatographic separation of isomeric arenes containing five rings, the so-

called "benzpyrene fraction", employing thin-layer chromatography (5, 6), high-pressure liquid chromatography (7, 8), gel filtration, adsorption chromatography and charge-transfer complexation (9), and paper chromatography (10), has met with varying degrees of success. Isolation of the individual isomers by a combination of two or more of the above techniques has also been attempted. Although several investigators (11-14) have separated some isomeric arenes composed of six rings from other aromatic compounds, no study on the isolation of the individual members of this group has been reported.

A chromatographic procedure utilizing adsorption thin-layer chromatography for the group separation of the isomeric arenes followed by partition thin-layer chromatography for the resolution of the individual members of each isomeric group was developed. A total of twelve PAHs, five pentacyclics and seven hexacyclics, were efficiently resolved using this chromatographic technique. Spectral analysis of individual compounds was performed using fluorescence techniques. The quantitative determination of the individual isomeric arenes present in suspended particulate matter was also accomplished.

EXPERIMENTAL

Collection and Extraction of Organic Matter. Suspended particulate matter was collected with standard High-Volume air samplers (15). Ambient air samples were drawn through non-hydroscopic glass fiber filters of pH 6.5 at a controlled flow rate of 50 ft³/min (24 l./sec) for periods of 24 to 48 hr. Each filter was oriented in the horizontal plane (orthogonal to air flow) in the sampler and protected in a standard aluminum shelter. Airborne particulates were collected during four specific sampling periods representative of spring, summer, fall, and winter seasons at the York University sampling station in Toronto, Ontario. This sampling location may be described as a northern suburban-rural area of Toronto and, thus, particulate loading and PAH-concentrations are significantly lower than values obtained for a downtown urban area (3).

Before and after sample collection, each filter was conditioned at a constant relative humidity (50 ± 2%) and temperature (22 ± 2 °C) for 24 hr and then weighed to obtain the total weight of collected particulate matter. Specific particulate-laden filters, representative of sample collection during a particular season, were then composed and put in a Soxhlet apparatus. The benzene soluble fraction (BSF) was extracted with 250 ml of hot spectrograde benzene for 8 hr. The cooled BSF was then filtered through sintered glass and reduced to a volume of 50 ml by flash evaporation at a temperature below 40 °C. The remaining benzene was carefully evaporated under a stream of dry nitrogen at room temperature. The brown oily residue was redissolved in a known amount of spectrograde benzene and stored at -20 °C in the dark until analysis was performed.

Table II. Mass Concentrations of Ambient Aerosols Collected at York Sampling Site

Date	No. of samples	Mean mass concn, $\mu\text{g}/\text{m}^3$	Geometric standard deviation, \pm
16/06/72-21/06/72	4	78.0	31.6
5/08/72-14/08/72	7	54.2	24.2
14/11/72-9/12/72	6	43.8	13.0
13/03/73-19/03/73	10	95.0	32.3

Chromatographic Isolation and Spectral Analysis. All standard PAHs were purified through recrystallization and thin-layer chromatography on cellulose acetate where necessary. The chemical names of the PAHs were derived from the Ring Index (16) and are given in Table I with corresponding chemical structures in Figure 1. The polycyclic arenes investigated were pericondensed and all the hexacyclic arenes possessed a pyrene nucleus. All solvents employed were of spectrograde quality.

Preliminary adsorption thin-layer chromatography on neutral aluminum oxide using hexane:ether (19:1, V/V) as the mobile phase was employed to isolate the three isomeric groups of arenes from each other and also from other non-polar fluorescent organic compounds of different molecular weight. A slurry of 25 g of aluminum oxide G, Type E, 10-40 μm minimum grain size, supplied by Brinkmann of Canada Ltd., in 50 ml of distilled water was prepared in a blender (5 min at high speed) and spread on five 20-cm \times 20-cm clean glass plates with a Desaga spreader. The wet plates were then air-dried for $\frac{1}{2}$ hr and positioned vertically in a drying oven for 30 min at 110 $^{\circ}\text{C}$. The activated plates, of 250- μm thickness, were stored at a constant relative humidity of $50 \pm 2\%$ prior to use.

Aliquots of various BSFs were added 1.5 cm from the bottom of the thin-layer plate with the aid of a clean, disposable capillary pipet of 2.0 μl capacity (0.1-0.5 mg of BSF per spot). Samples of standard PAHs (2-5 μg per spot) were added to the origin of the same plate to be used as internal standards. After the solvent front was allowed to progress to a distance of 15 cm (~ 20 -30 min), the chromatogram was removed from the development chamber, dried, and viewed under a non-destructive long-wavelength ultraviolet light source. The perimeters of the fluorescent areas of internal standards and corresponding fluorescent areas of the PAHs isolated from the BSF were scribed, and the adsorbent, containing either standard or extract, was removed from the plate. The desired PAHs were eluted with 20-30 ml of hot spectrograde dichloromethane for 10 to 15 min and the solvent was evaporated under a stream of dry nitrogen. The residues were taken up in a specific volume of benzene.

Resolution of the individual arenes present in each isomeric group isolated by alumina TLC was accomplished using thin-layer plates prepared from cellulose of different degrees of acetylation (20, 30, and 40%) with *n*-propanol:acetone:water (2:1:1, V/V/V) as the developing phase. Acetylated cellulose plates were obtained by producing a slurry of 15 g of 20, 30, or 40% acetylated cellulose powder, obtained from Brinkmann of Canada Ltd., in 75 ml of absolute ethanol in a blender for 5 min. The resultant slurry was spread to a thickness of 250 μm on five 20-cm \times 20-cm glass plates. The acetylated cellulose plates were air-dried for $\frac{1}{2}$ hr and put in an oven at 40 $^{\circ}\text{C}$ for $\frac{1}{2}$ hr. The plates were then stored at a constant relative humidity of $50 \pm 2\%$. Spotting, development (2-3 hr) and detection were carried out as described above. Anhydrous diethyl ether (20-30 ml for $\frac{1}{2}$ hr) was used as the eluting agent in place of dichloromethane, as the latter solvent dissolves cellulose. After solvent evaporation, each residue recovered from the cellulose plate was taken up in a specific volume of spectrograde hexane for fluorescence analysis.

Because of the success of the above separation scheme, two-dimensional thin-layer chromatography using aluminum oxide:40% acetylated cellulose plates, prepared from a slurry of two parts by weight aluminum oxide and one part by weight 40% acetylated cellulose in 75 ml of absolute ethanol, was investigated. The freshly prepared layers, 250 μm thick, were air-dried for $\frac{1}{2}$ hr followed by oven-drying at 40 $^{\circ}\text{C}$ for $\frac{1}{2}$ hr. A spot of the appropriate aliquot (0.5 mg BSF) was applied to a corner of the composite plate. Development was performed in the first direction with hexane:ether (19:1) for 20-30 min, followed by drying and rotation of the chromatogram by 90 $^{\circ}$. The plate was then developed in the second direction for 2-3 hours with *n*-propanol:acetone:water (2:1:1). The

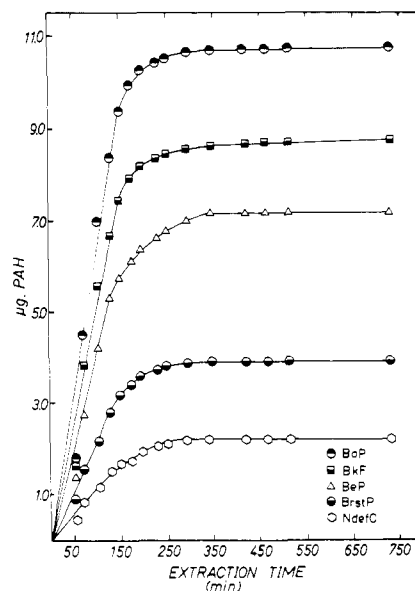


Figure 2. Extraction curves of benzo[a]pyrene (BaP), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[rs]pentaphene (BrstP), and naphtho[1,2,3,4-def]chrysene (NdefC)

resolved spots on the dried chromatogram were then removed from the plate and eluted with diethyl ether, as described previously.

The fluorescence excitation and emission spectra of each residue obtained from the above isolation procedures were recorded at room temperature on a Farrand MK1 spectrofluorimeter equipped with a high intensity xenon arc lamp, grating monochromators for wavelength selection in both excitation and emission modes of operation, a RCA 1P28 photomultiplier tube, and a Heath strip chart recorder. Wavelength resolution was achieved with the aid of slits of varying width from 1 to 20 nm. Both excitation and emission spectra were recorded at a scanning speed of 75 nm/min.

RESULTS AND DISCUSSION

Collection and Extraction of Organic Matter. Gravimetric analysis was performed on each particulate-laden filter and the geometric mean values of the mass concentrations together with the geometric standard deviations were statistically computed for each representative sampling period (see Table II). In general, relatively low concentrations of ambient particulates were recorded during the fall and winter periods at the York sampling site. However, significantly higher concentrations were reported for spring and summer samples. The seasonal variation in the mass concentration of ambient aerosols was partially due to a change in large particle emissions during specific seasonal periods. The size distributions of suspended particles were significantly altered by the influx of large particles due to reentrainment processes during spring and summer periods at this site (3). The geometric standard deviations, which represent the spread of values over the number of particulate samples analyzed, give an indication of the degree of variability for the different sampling periods.

Composites of particulate-laden filters were extracted with benzene for eight hours. An extraction curve for five of the compounds analyzed was prepared for a total extraction time of 21 hours and appears in Figure 2. Extraction of the desired PAHs was essentially complete after six hours. The initial slope of the extraction curve is affected by the amount of particulate matter and, in most cases, the amount of BSF to be removed. With low levels of particulate matter and correspondingly low PAH content, the initial slope of the curve becomes steeper, whereas with high levels of particulate matter and high PAH content, the initial slope becomes shallower. In addition, during the first hour of extraction, the curve deviates from linearity for

Table III. Fluorescence Excitation and Emission Spectra of Model PAHs^a

Compound No.	Fluorescence excitation spectra, wavelength, nm	Fluorescence emission spectra, wavelength, nm
I	274, 284, 300, 309, 324, <i>329</i> , 349 358, 366	389, 397, 410, 421
II	267, 286, 297, 333, 347, 365, 375 <i>381</i>	402, 407, 414, 424, 452
III	280, 293, <i>301</i> , 340, 349, 368	404, <i>424</i> , 446,
IV	267, 294, <i>305</i> , 323, 338, 350, 357 368, 377, 390	402, 409, 418, 425, 435, 454
V	365, 384, <i>407</i>	438, 444, 465, 500
VI	263, 293, <i>302</i> , 360, 377, 396, 402	429, 436, 462, 466, 488
VII	288, 298, 329, 346, 362, <i>382</i>	406, 415, <i>419</i> , 429, 438, 444
VIII	274, 292, <i>304</i> , 330, 340, 356, 374	396, 402, 407, 419, 429, 445
IX	285, 297, 316, 332, 354, 373, <i>393</i>	432, 436, 447, 458, 492
X	299, <i>312</i> , 378, 398, 421	451, 480, 514
XI	294, 317, <i>332</i> , 383, 404, 427	457, 483, 523
XII	275, 292, 300, 316, 330, 380, <i>401</i>	466, 473, <i>502</i>

^a Most intense peak in each spectrum is italicized.

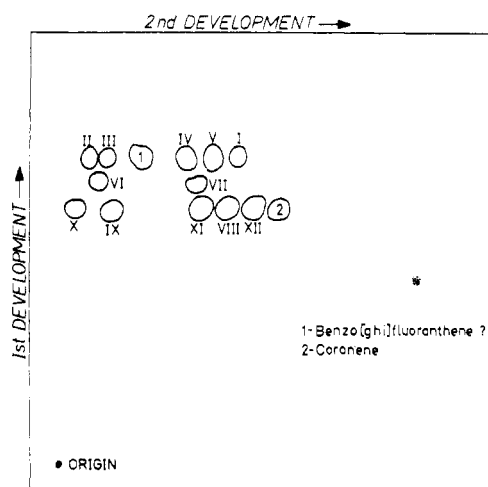


Figure 3. Two-dimensional TLC chromatogram of BSF showing resolution of the individual pentacyclic and hexacyclic arenes

high PAH content. Regardless of the initial degree of elution, the majority of PAH content will be removed after 8 hours of soxhlet extraction using spectrograde benzene as the eluant.

Chromatographic Isolation and Spectral Analysis. Resolution of the individual members of each isomeric group was achieved through a two-step TLC process of initial adsorption and final partition thin-layer chromatography. The R_B values of the PAHs obtained with each of the above systems appear in Table II [R_B value is defined as the ratio of the distance travelled by a specific compound to that of benzo[*a*]pyrene (5)]. For all twelve PAHs, the R_B values on aluminum oxide ranged from 0.76 to 1.02 while the R_B values for the individual members of each isomeric group were quite similar. Quantitative separation of each isomeric arene was achieved on acetylated cellulose with R_B values ranging from 0.40 to 7.99. As the degree of adsorbent acetylation increased, the resolution of the individual arenes also increased. Two-dimensional thin-layer chromatography using a composite aluminum oxide:40% acetylated cellulose plate also proved satisfactory for the resolution of the above polycyclics. A representative chromatogram of the pentacyclic and hexacyclic arenes present in a BSF appears in Figure 3. Fluorescence spectral analysis confirmed the presence of all the above polycyclic arenes in the BSF except dibenzo[*def,p*]chrysene. Coronene, a heptacyclic arene, was identified in the same extract. In addition, benzo[*ghi*]fluoranthene, a pentacyclic arene, was tentatively

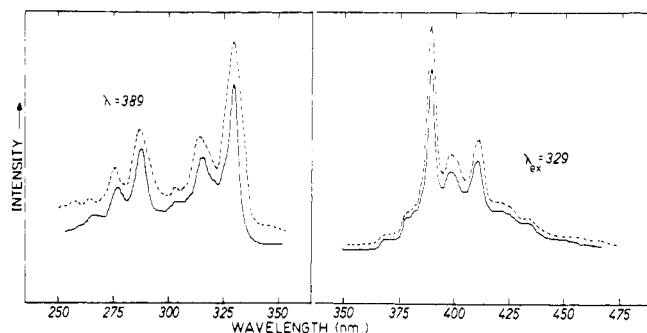


Figure 4. Fluorescence excitation and emission spectrum of benzo[*e*]pyrene. (—) Model compound, (---) extract from BSF

identified. Although two-dimensional TLC proved effective for identification purposes, quantitative data recorded with this type of system should be viewed with caution as no internal standards may be applied to the same plate. As a result, the two-step TLC process described above was used for all quantitative estimation of PAH content in airborne particulate matter. Total recoveries for the above two-step separation process ranged from $84 \pm 6\%$ for dibenzo[*def,p*]chrysene to $92 \pm 4\%$ for benzo[*k*]fluoranthene (Table I). All quantitative data have been corrected for the losses reported.

Since all the aforementioned PAHs possess extensive π conjugation, fluorescence spectral analysis is a useful aid in the identification and quantification of these polycyclic hydrocarbons. Fluorescence spectral band positions of the model compounds are given in Table III. The most intense peak in the fluorescence excitation and emission spectra is indicated. The uncorrected spectra of three polycyclic arenes, benzo[*e*]pyrene, benzo[*ghi*]perylene, and naphtho[1,2,3,4-*def*]chrysene, representative of pentacyclic, C_{22} hexacyclic, and C_{24} hexacyclic groups, are reproduced in Figures 4, 5 and 6, respectively. In each spectrum, the solid line represents the model compound, whereas the dashed line represents the TLC fraction having the same R_B value and fluorescent color as does the model compound. The spectra of the standard PAHs were recorded at a lower sensitivity as an aid in the comparison of the individual spectral characteristics. In most samples, the two superimposed spectra were significantly similar. Fluorescence spectral analysis of any one of the above compounds in a mixture of polycyclic arenes from the same isomeric group would yield a distorted spectrum in which the fluorescence excitation and emission peaks would be obliterated or at least distort-

Table IV. PAH Content of Ambient Aerosols Collected at York Sampling Site

Compound No.	16/06/72-21/06/72		5/08/72-14/08/72		14/11/72-9/12/72		13/03/73-19/03/73	
	$\mu\text{g/g part}$	$\text{ng}/1000 \text{ m}^3$	$\mu\text{g/g part}$	$\text{ng}/1000 \text{ m}^3$	$\mu\text{g/g part}$	$\text{ng}/1000 \text{ m}^3$	$\mu\text{g/g part}$	$\text{ng}/1000 \text{ m}^3$
I	8.3	314.4	2.6	169.4	1.1	77.9	2.2	119.1
II	12.5	471.6	3.2	206.5	2.6	186.3	3.0	162.6
III	10.7	401.7	3.0	195.4	2.0	142.0	2.1	113.5
IV	10.2	384.3	2.8	183.7	1.9	132.1	2.0	108.6
V	3.6	135.4	1.3	84.6	0.4	26.7	1.1	59.6
VI	3.4	126.6	2.0	130.3	0.2	14.2	0.3	16.1
VII	5.4	205.2	2.2	143.2	0.3	21.2	1.4	75.7
VIII	2.5	96.1	1.1	71.9	0.2	14.1	0.3	16.1
IX	4.5	170.3	1.0	65.1	0.1	6.9	0.3	16.1
X	4.4	165.9	0.8	27.4
XI	5.1	192.1	1.9	123.3

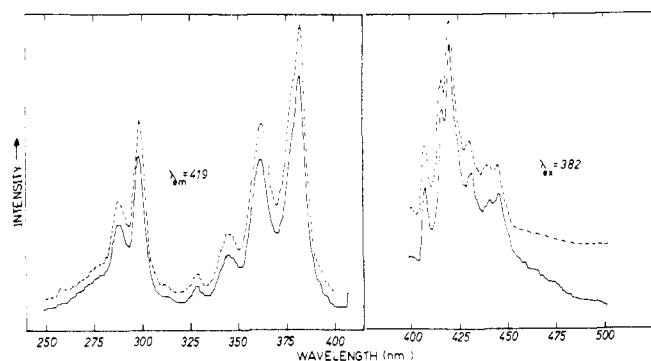


Figure 5. Fluorescence excitation and emission spectrum of benzo[ghi]perylene. (—) Model compound, (---) extract from BSF

ed. In cases where the major fluorescence excitation and emission spectral peaks are distorted, errors in the estimation of PAH content computed by comparison of peak height of unknown PAH fraction and the model compound would ensue. These errors were especially pronounced when analyzing compounds possessing low fluorescence quantum yields.

In sufficiently dilute solutions and in the absence of interfering substances, fluorescence emission intensity is a linear function of concentration. Beer's law was obeyed for PAH concentrations below 10^{-5} mol/l. Solutions of PAHs were efficiently degassed by displacing dissolved oxygen with dry nitrogen prior to luminescence analysis.

Quantitative estimations of the PAHs identifiable in the BSF appear in Table IV for the four sampling periods specified. The concentration of the pentacyclic arenes was usually higher than the concentration of the hexacyclic arenes with the exception of perylene. Benzo[ghi]fluoranthene, another pentacyclic arene, was identified but since no model compound was available, quantitative estimates could not be secured. Dibenz[def,p]chrysene could not be identified in the BSF. However, this result may be due to the fact that this polycyclic arene exhibits a relatively weak fluorescence intensity and a lack of significantly sharp maximal peaks in the excitation or emission spectra. As a result, identification and quantification in atmospheric aerosols is made difficult. The above data indicate that although the PAH concentration is relatively low at this sampling site, there appears to be a definite seasonal trend with lower PAH content occurring in the midsummer season and higher PAH content occurring in the winter season. The lower PAH content during summer periods may be due to a greater photochemical destruction of the atmospheric arenes during this time period (17). However, the above consideration is complicated by the fact that during

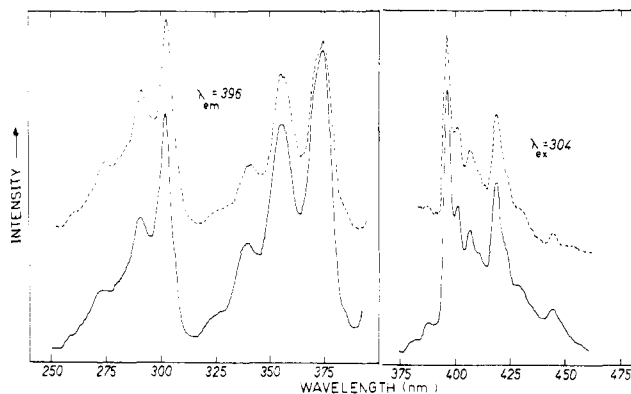


Figure 6. Fluorescence excitation and emission spectrum of naphtho[1,2,3,4-def]chrysene. (—) Model compound, (---) extract from BSF

different seasons, different fuels and fuel burning practices may lead to different types and/or amounts of arene emissions.

CONCLUSIONS

A chromatographic procedure involving the relatively simple and rapid isolation of pentacyclic and hexacyclic isomeric arenes on aluminum oxide and acetylated cellulose thin-layer plates has been described. A total of twelve polycyclic arenes: five pentacyclic, two C_{22} hexacyclic, and five C_{24} hexacyclic arenes, were quantitatively resolved by the above TLC technique and analyzed by fluorescence spectrophotometry. Combination TLC-fluorescence analysis was employed in the quantitative estimation of these isomeric arenes in suspended particulate matter.

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Utilization of Ultrasonic Nebulization in Atomic Absorption Spectrometry: Trace Metal Analysis in Samples of High Salt Content

Haleem J. Issaq^{1,2} and Lawrence P. Morgenthaler³

Department of Chemistry, Georgetown University, Washington, D.C. 20007

The possibility of applying ultrasonic nebulization to trace metal analysis in samples of high solid (salt) content was explored. The system used consisted of an "Ultramist" nebulizer connected to a temperature controlled heater in series with a condenser and burner head. No memory effects were detected after continuous nebulization for ten minutes of aqueous solution of metal chlorides corresponding to 1000 $\mu\text{g/ml}$ copper, calcium, and magnesium, and to 500 $\mu\text{g/ml}$ lead. The system tolerance for solutions of high salt content (1–3% by weight) was very good: no burner slot clogging and no deposits inside the system were observed over 10–20 minute nebulization periods. Continuous nebulization of 1% to 3% sample up to 20 minutes gave very little memory, corresponding to less than 1 $\mu\text{g/ml}$. Also, quantitative results for the analysis of copper in a solution of synthetic ocean water and in 4 w/w% NaCl solution, both without dilution, were obtained.

Since its introduction as an analytical tool, atomic absorption has found a wide variety of applications in many different fields; biological, clinical, oceanographic, and others. These fields require not only a sensitive technique, but one which can handle samples with high solid content, i.e., 2 w/w% or greater. In most cases, the laminar flow burner cannot tolerate concentrated salt solution and the sample has to be diluted in dilution factors of 50 or greater, depending on the concentration of the salt in solution and time of nebulization. The dilution is necessary in a laminar flow burner, because when a droplet of solution containing a large amount of salt hits the hot slot of the burner, the water (solvent) vaporizes, leaving behind the solid salt particles which collect more solid particles with time, leading to clogging of the slot of the burner head.

Hell and Ramirez-Munoz (1) developed a new burner, the Autolam Burner, for trace analysis in samples of high salt content; with this burner, a dilution of biological samples was necessary. For blood serum, the dilution is 1:25.

Venghiattis (2) used a heated chamber-condenser system for 200 $\mu\text{g/ml}$ lead, but reported a memory at these levels. Morgenthaler (3) reported memory effects with a commercial heated chamber burner system.

The system under investigation will be tested with high salt content solutions for memory effects, high solid tolerance, and quantitative measurements.

EXPERIMENTAL

Apparatus. The apparatus used was described earlier (4).

Reagents. All stock solutions were prepared from Baker analytical grade reagents in deionized water and acidified (0.1–1.0N) with hydrochloric acid.

Procedure. Samples of High Salt Content. Memory: The present system was tested for memory effects using solutions of Mg, Ca, Pb, and Cu. The procedure followed is outlined below.

The conditions used are: heating chamber temperature, 350 °C; sample aspiration rate, 0.75 ml/min.

A solution of 200 $\mu\text{g/ml}$ of the element to be analyzed was nebulized for five or ten minutes. Nebulization was stopped and the sample compartment only, was washed with deionized water. Then deionized water was nebulized to see if there was any absorption; if no absorption was observed, a higher concentration was used, usually up to 1000 $\mu\text{g/ml}$ or more; while, if absorption was observed, lower concentrations were used.

Ten percent absorption was considered as negligible memory, because it would correspond, in most cases, to less than 1 $\mu\text{g/ml}$ of the analyte. This is justified considering the high concentration of the samples used.

Tolerance to Samples of High Salt Content. The procedure followed is the same as in the previous section. A stock solution of 5 w/w% MgCl_2 in 1N HCl was prepared, then diluted to the required concentration. The conditions used are 1 ml/min sample aspiration rate, 350 °C chamber temperature, lean air-acetylene flame, and 12 mA lamp current. A multi-element hollow cathode lamp was used containing calcium and aluminum.

When the previous experiment was repeated, with 5 w/w% MgCl_2 solution, under the same conditions but with the temperature of the chamber increased to 650 °C, the flame extinguished after 2 to 3 minutes. This is believed to be due to deposits of salt particles on the spikes in the mixing area, thus blocking the passage of air and acetylene, and will be discussed in greater detail later. When the temperature was decreased to 150 °C and the sample nebulized for ten minutes, no deposits in the slots or in the mixing area were formed. There were some deposits around the slot on the burner head. When water was aspirated, 20% absorption was obtained. The temperature was increased again to 200 °C and the sample was aspirated for ten minutes; no deposits were observed in the mixing area or inside the slot, but there was slight memory.

¹ Author to whom correspondence should be addressed.

² Present address, Litton Bionetics, Frederick Cancer Research Center, P.O. Box B, Frederick, Md. 21701.

³ Present address, Fisher Scientific, Waltham, Mass. 02154.