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Chromatographic and Spectral Analysis of Polynuclear Aromatic Hydrocarbons—Quantitative Distribution in Air of Ontario Cities

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■ The separation and resolution of a number of polynuclear aromatic hydrocarbons (PAH's) were studied in samples of particulate matter collected from the urban atmosphere by methods involving thin-layer chromatography (TLC) and fluorescence spectroscopy, gas chromatography and mass spectroscopy (GC/MS). The concentration levels of 10 PAH's in particulate air samples from the Ontario cities of Toronto, Hamilton, Sarnia, and Sudbury were determined quantitatively by TLC–fluorescence methods over 3-month periods from April 1975 to March 1976. Among these cities, significant differences in concentrations, related to the predominant emission sources, were found for benzo(a)pyrene, benzo(e)-pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, naphtho(1,2,3,4-def)chrysene, and dibenzo(b,def)chrysene.

The sources, reactivity, metabolism, and carcinogenic properties of polynuclear aromatic hydrocarbons (PAH's) were reviewed in a 1972 monograph (*1*). These compounds occur in such diverse sources as fuel combustion products, motor vehicle exhaust, airborne particulate matter, cigarette smoke, sediments, high-boiling petroleum distillates, fumes from coke ovens, incineration of refuse, and processed foods. Resultant mixtures of PAH's from fuel combustion and other high-temperature processings of organic materials are extremely complex. Organic fractions of airborne particulate matter have been found to contain over 100 different PAH compounds (*2*). Some of these PAH compounds have been shown to be potent carcinogens in biological assays, but isomers of a specific aromatic group may differ greatly in their carcinogenicity. Thus, benzo(a)pyrene is a strong carcinogen, whereas the isomeric benzo(e)pyrene is noncarcinogenic, benzo(b)fluoranthene is carcinogenic, but benzo(k)fluoranthene is not. Similarly, benz(a)anthracene is positively carcinogenic, whereas chrysene has been reported as negatively or weakly carcinogenic. Such isomers are very difficult to separate by gas chromatography, even on high-efficiency gas chromatographic columns.

Pierce and Katz (*3*) have found that approximately 70–90% of the total PAH content of airborne particulates is associated with particles in the respirable size range of less than 5.0 μm in diameter. Such respirable particles may exert a significant influence on the inhalation health hazards associated with toxic airborne substances. It has been estimated that about 60% or more of all human cancers are due to environmental agents (*4*). Consequently, it is important to develop effective, quantitative separation techniques for the analysis of PAH compounds in air particulate samples, including the isolation of the individual components of isomeric groups that differ greatly in toxicity. Reported separation schemes employing thin-layer chromatography (*5–7*), adsorption chromatography and charge-transfer complexation (*8*), paper chromatography (*9*), and mass fragmentometry (*10*) have met with only limited or little success in the separation of isomers.

In this laboratory, procedures have been developed for the quantitative separation of PAH compounds from airborne particulate samples and for resolution of the individual members of each isomeric group by means of adsorption and partition thin-layer chromatography, followed by spectral analysis of individual compounds using fluorescence techniques (*3, 11–13*). This paper describes the application of these thin-layer chromatographic techniques, with certain improvements for the fluorescence analysis of 13 PAH compounds in a standard mixture and 10 PAH compounds in samples of airborne particulates collected in four cities of Ontario.

Experimental

Collection and Extraction of Organic Matter. Quarter sections of 100 fiberglass filters, containing suspended particulate matter collected by High Volume samplers at sampling sites in four cities of Ontario, were supplied by the Air Resources Branch of the Ontario Ministry of the Environment. The collection sites were as follows: (a) Toronto, Site 34007—this location is influenced mainly by exhaust emissions from heavy motor vehicle traffic. (b) Toronto, Site 33003—a suburban area that is subjected to occasional motor vehicle traffic, especially by motorists proceeding to work in the early morning and returning in late afternoon. (c) Hamilton, Site 29025—where the major source of particulates is derived from steel manufacturing and coke oven operations. (d) Sarnia, Site 14061—where the major source represents oil refinery and petrochemical operations. (e) Sudbury, Site 77016—the major source in this area consists of large nickel-copper smelting activities with emissions of particulates and large quantities of sulfur dioxide.

The particulate filters for each location were grouped into bundles representing seasonal, 3-month sampling periods over the 12-month period, April 1975 to March 1976, as follows: April–June, July–September, October–December, and January–March. Each filter bundle was installed in a glass extraction thimble, equipped with a sintered glass disc at one end, and the unit was inserted in a soxhlet extraction apparatus. The filter bundles were extracted with 250 mL of pure dichloromethane for 8–12 h.

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After the extraction, the extraction thimble was allowed to cool to room temperature, then was rinsed with 25 mL CH_2Cl_2, and all washings were collected in a receiving flask. The contents of each appropriate receiving flask were filtered through a clean, sintered glass filter funnel to remove any solid particles suspended in the solution. The receiving flask and sintered glass filter funnel were rinsed with 5–10 mL CH_2Cl_2 three times, and the entire extract was then reduced to about 2 mL in a 50-mL peak-shaped flask by means of a Buchler flash evaporator in a water bath. The water bath temperature was maintained between 30 and 35 °C.

The remaining solvent was evaporated under a stream of dry nitrogen until approximately 1 mL of the extract remained. The residue was transferred to a 1-dram vial. The pear-shaped flask was rinsed three times with 1-mL portions of CH_2Cl_2, and the washings were also transferred to the vial. The solution was then evaporated to dryness under dry N_2. The residue was weighed and stored in the dark at 0–3 °C in the refrigerator until thin-layer chromatographic resolutions and spectral analysis could be performed.

Chromatographic Isolation and Spectral Analysis. A study was made to determine the effectiveness of an analytical method based on thin-layer chromatography coupled with fluorescence spectrophotometry for the quantitative separation of individual compounds in a mixture of 13 pure PAH's, consisting of the compounds listed in Table I. The objective of this work was to determine the efficiency of recovery and precision of the method for the analysis of PAH's in organic extracts of samples of particulate matter.

Pure individual PAH's were dissolved in scintillation quality toluene to make a solution of approximately 0.1 mg/mL. This concentration was chosen for the various PAH's because it resulted in easy visual detection of the thin-layer spots, using a UV lamp. Toluene is not only a better solvent for the PAH's, it is also less volatile than other common solvents such as pentane and hexane, and thus has the effect of minimizing any errors in concentration caused by evaporation of the solvent. Preliminary adsorption thin-layer chromatography (TLC) was carried out on neutral aluminum oxide using pentane:ether (19:1 v/v) as the mobile phase. The aluminum oxide plates were purchased precoated from Brinkman of Canada Limited. Aliquots of the PAH standard mixture were added 1.5 cm from the bottom of the thin-layer plates with the aid of a clean, disposable capillary pipet of 2.0-μL capacity (0.5–1.0 μg of PAH per spot). After the solvent front was allowed to progress to a distance of 13–15 cm, the chromatogram was removed from the developing sandwich chamber and was then air-dried and examined under a nondestructive long-wavelength ultraviolet light source. The perimeters of the fluorescent areas of the PAH's were scribed, and their positions were recorded.

The above aluminum oxide–TLC procedure produced a separation of the mixture of 13 PAH's into four groups of arenes. The scribed, fluorescent areas were removed from the plates, and the PAH's eluted with 20–30 mL of hot spectrograde dichloromethane for 10–15 min. The solvent was then evaporated under a stream of dry nitrogen. The residue of each group was then dissolved in a specific volume of toluene.

Resolution of the individual arenes present in each isomeric group isolated by aluminum TLC was accomplished using thin-layer plates prepared from 40% acetylated cellulose with *n*-propanol:acetone:water (2:1:1 v/v/v) as the developing phase. Spotting, developing (2–3 h), and detection were carried out as before. The acetylated plates were prepared by producing a slurry of 15 g of 40% acetylated cellulose powder in 80 mL of absolute ethanol in a blender for 5 min. The resultant slurry was then spread to a thickness of 250 μm on five 20 × 20 cm glass plates by means of a Desaga spreader. The plates were air-dried for ½ h and then put in an oven at 40 °C for at least 6 h. The plates were then stored inside a desiccator at a constant relative humidity of 50 ± 2%.

Whereas dichloromethane was found to be an excellent solvent for removing organic compounds from such adsorbents as silica gel, alumina, or magnesium hydroxide, this solvent could not be used to elute isolated spots from cellulose or acetylated cellulose. Hence, each relevant spot appearing on a cellulose chromatogram was removed and replaced in a 50-mL weighing bottle that was equipped with a ground glass lid. To each weighing bottle was added 20–30 mL anhydrous diethyl ether. All slurries were kept in the dark at room temperature. After a specific time interval, the diethyl ether of each extract was evaporated under a stream of dry nitrogen at room temperature. The residues were then dissolved in spectrograde pentane, filtered to remove solid material, and transferred to fluorescence cells for spectrofluorometric examination. Samples of PAH's were efficiently degassed by displacing dissolved oxygen prior to luminescence analysis. Polycyclic compounds were spectrally identified and quantitated by comparison of fluorescence excitation and emission spectra of standard and unknown solutions.

The fluorescence excitation and emission spectra of each substance 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.

Table I. Comparative Resolution of PAH Standard Mixture on TLC Plates and Percentage Recovery[a]

Compound No.	PAH	Aluminum oxide TLC, R_{BaP}	40% Acetylated cellulose, R_{BaP}	Fluorescent color	% Recovery
I	Benzo(e)pyrene	0.98	6.61	Blue-green	87.4 ± 3.9
II	Benzo(a)pyrene	1.00	1.00	Blue	94.0 ± 4.5
III	Benzo(b)fluoranthene	0.99	1.51	Blue	85.3 ± 3.8
IV	Benzo(k)fluoranthene	0.00	3.07	Blue	90.7 ± 4.5
V	Perylene	0.94	4.52	Yellow	86.2 ± 4.2
VI	Dibenzo(def,mno)chrysene	0.87	1.36	Blue	94.2 ± 3.2
VII	Benzo(ghi)perylene	0.89	6.78	Blue	92.5 ± 5.1
VIII	Naphtho(1,2,3,4-def)chrysene	0.70	8.29	Yellow-green	86.5 ± 3.4
IX	Benzo(rst)pentaphene	0.61	1.61	Pink	93.7 ± 3.5
X	Dibenzo(b,def)chrysene	0.63	0.31	Green	87.9 ± 5.3
XI	3-Methylcholanthrene	1.06	5.13	Purple	81.1 ± 3.5
XII	Pyrene	1.18	6.40	Blue	85.0 ± 4.1
XIII	Dibenz(a,h)anthracene	0.78	4.53	Blue	89.7 ± 3.1

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

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

TLC Separation and Percentage Recovery of PAH Mixture of 13 Standards. The R_{BaP} values of the individual PAH's of the 13 components were determined for both the aluminum oxide and 40% acetylated cellulose plates. The R_{BaP} value is defined as the ratio of the distance traveled on a TLC plate by a compound to the distance traveled by benzo(a)pyrene. These values are shown in Table I.

The various PAH's can be separated into four major groups by TLC on aluminum oxide, followed by resolution into the component, individual PAH on 40% acetylated cellulose plates. Group I contains pyrene; Group II contains benzo(e)pyrene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, perylene and 3-methylcholanthrene; Group III contains dibenzo(def,mno)chrysene, benzo(ghi)perylene, and dibenz(a,h)anthracene; Group IV contains naphtho(1,2,3,4-def)chrysene, benzo(rst)pentaphene, and dibenzo(b,def)chrysene.

Eleven of the 13 PAH's were resolved effectively. However, perylene and 3-methylcholanthrene tend to overlap on each other. Efforts were made to separate the two compounds by changing the polarity of the developing phase in TLC, but without success. A study was made, therefore, of the fluorescent spectrum of each compound and of a mixture of the two compounds to determine the extent of interference, if any, at different excitation and emission wavelengths.

For the analysis of perylene and 3-methylcholanthrene, three solutions were prepared in pentane. The first solution contained pure perylene (0.28 μg/mL); the second contained only 3-methylcholanthrene (0.28 μg/mL). The fluorescence spectra were obtained for the solution of perylene at $\lambda_{ex} = 407$ nm and $\lambda_{em} = 438$ nm. A third solution containing a mixture of perylene (0.28 μg/mL) and 3-methylcholanthrene (0.28 μg/mL) exhibited the spectra for perylene, without any significant changes, at the above maximum excitation and emission wavelength. A similar result was obtained for the fluorescence spectra of 3-cholanthrene and that of the mixture with perylene at the above concentrations and maximum excitation and emission wavelengths of 295 and 395 nm, respectively. Consequently, perylene does not constitute an interference when mixed with 3-methylcholanthrene in analysis based on fluorescence at the appropriate maximum excitation and emission wavelengths.

Numerous procedures have been utilized (*14*) for the identification and/or quantification of organic components resolved by thin-layer chromatography. A TLC spot may be quantitated directly using a scanner or a densitometer (*15*). Because these measurements are made either through the plate or by reflection from the plate, the reproducibility of the procedure is difficult to control. To obtain a high degree of accuracy and precision, the spots must therefore be removed from the chromatogram and extracted. The eluate obtained from the extraction is then used for final quantitative analysis. Problems in the elution of the desired compounds separated by thin-layer chromatography may occur if the components become strongly bound to the adsorbent. The best eluting agent available is usually polar, volatile, and free from interfering agents.

Elution with 100 mL diethyl ether, in 2–3-mL quantities, has frequently been employed (*5, 16*) in the recovery of polycyclic compounds from adsorbents. The time required for elution ranged from 30 to 45 min at 50 °C, with reported recoveries of pure benzo(a)pyrene, varying between 30 (*5*) and 96% (*17*). However, peroxides have a tendency to form in anhydrous diethyl ether which is in contact with air (*18*). During the extraction process, peroxide formation in the eluant may destroy some of the PAH's being eluted. Spectrograde dichloromethane was found to be an excellent eluant for all polycyclic arenes and related structures. Only 20–25 mL CH_2Cl_2 need be used to elute the desired components at room temperature for 5–10 min from aluminum oxide TLC plates.

For the recovery of polycyclic isomeric arenes from acetylated cellulose thin layers, anhydrous diethyl ether was used as the eluting agent in place of dichloromethane, since the latter solvent dissolves cellulose. Other methods of elution and analysis of PAH's after separation on acetylated cellulose thin-layer plates have been attempted with recoveries of only 55% for benzo(a)pyrene (*5*). However, the elution method described in this paper, coupled with fluorescence analysis, yielded recoveries ranging from a minimum of 81.1 ± 2.5% for 3-methylcholanthrene to a maximum of 94.2 ± 3.2% for dibenzo(def,mno)chrysene and 94.0 ± 4.5% for benzo(a)pyrene, as shown in Table I. Elution times varying from 15 min to 72 h have produced quantitative recoveries. Peroxide degradation was probably of minimal importance because the extraction procedure allowed only a minimal amount of air to be brought into contact with the diethyl ether solution.

Because of the high vapor pressure of both dichloromethane and diethyl ether, the solvents were readily evaporated under a stream of dry nitrogen at room temperature, thereby reducing the probability of loss of the desired constituents by either evaporation or decomposition. The residues after evaporation could then be redissolved in the appropriate solvent for spectral analysis.

The majority of PAH structures possess extensive Π-conjugation; hence fluorescence spectral analysis lends itself well to the identification and quantification of these aromatic species. For the identification of a fluorescent species, two types of spectra were recorded—the fluorescence excitation spectrum obtained at a constant wavelength of fluorescence emission and the fluorescent emission spectra obtained by irradiating the compound at a wavelength of absorption. Since luminescence measurements are more sensitive than absorption spectral measurements by a factor of 10^2–10^3 (*19*), sensitivity to interfering agents is also greatly increased. For this reason, solvents of spectrograde quality were used throughout the analytical procedure. Luminescence analyses were prepared in a moderately dust-free atmosphere. Samples of PAH's require efficient degassing to remove oxygen before luminescence analysis since oxygen severely reduces fluorescence emission intensity, apparently through a diffusion-controlled quenching process. Dissolved oxygen was displaced in all samples by bubbling the solvent with dry nitrogen. The fluorescence excitation and emission spectra of the 13 PAH compounds analyzed in this study are shown in Table II. Results of this analysis have yielded better or comparable recoveries when compared to data of the literature.

Identification of Benzo(a)Pyrene Diones by MS. Benzo(a)pyrene (B(a)P) was oxidized on a TLC aluminum plate with 1 ppm ozone, by volume, under ultraviolet illumination, using the lamp described by Lane and Katz (*20*). The oxidized material was removed from the TLC plate and transferred to a flask containing chloroform. After solution and filtration, the liquid was concentrated down to a small volume at room temperature under a stream of N_2. The concentrated solution was spotted on a TLC plate of magnesium hydroxide, described by Pierce and Katz (*13*), and the chromatogram developed with chloroform as the mobile phase. The separated quinones were removed, and the spots were combined and dissolved in $CHCl_3$, filtered, concentrated and then subjected to MS analysis, using an electron impact of 70 eV and a DS-50 automatic data processing system. The background was subtracted, and the data normalized. The MS of the individual

Table II. Fluorescence Excitation and Emission Spectra of PAH's[a]

Compound no.	Fluorescence excitation spectra, wavelength, nm	Fluorescence emission spectra, wavelength, nm
I	274, 284, 300, 309, 324, $\underline{329}$, 349 358, 366	$\underline{389}$, 397, 410, 421
II	267, 286, 297, 333, 347, 365, 375 $\underline{381}$	$\underline{402}$, 407, 414, 424, 452
III	280, 293, $\underline{301}$, 340, 349, 368	404, $\underline{424}$, 446
IV	267, 294, $\underline{305}$, 323, 338, 350, 357 368, 377, 390	$\underline{402}$, 409, 418, 425, 435, 454
V	365, 384, $\underline{407}$	$\underline{438}$, 444, 465, 500
VI	263, 293, $\underline{302}$, 360, 377, 396, 402	$\underline{429}$, 436, 462, 466, 488
VII	288, 298, 329, 346, 362, $\underline{382}$	406, 415, $\underline{419}$, 429, 438, 444
VIII	274, 292, $\underline{304}$, 330, 340, 356, 374	$\underline{396}$, 402, 407, 419, 429, 455
IX	285, 297, 316, 332, 354, 373, $\underline{393}$	$\underline{432}$, 436, 447, 458, 492
X	299, $\underline{312}$, 378, 398, 421	$\underline{451}$, 480, 514
XI	265, 287, $\underline{295}$, 330, 345, 356, 378	$\underline{395}$, 418, 443
XII	262, 273, 306, 318, $\underline{332}$	370, 382, 289, $\underline{392}$
XIII	278, 290, $\underline{299}$, 321, 333, 348	$\underline{392}$, 402, 415, 442

[a] Most intense peak in each spectrum is underlined.

compounds served to identify B(a)P-6,12-quinone, B(a)P-1,6-quinone, and B(a)P-3,6-quinone. These quinones occur in the particulate matter of the urban atmosphere and have been identified in samples collected from the air of Toronto (*13*).

Quantitative Distribution of PAH's in Particulates of Four Ontario Cities. The concentrations of the particulates and the dichloromethane-soluble extracts (DSF) containing the PAH fractions at the above sites are presented in Table III. The higher mass concentrations of particulates and the DSF ($\mu g/m^3$) were found at the Hamilton and Toronto sites. The lowest concentration of particulates occurred at Sudbury, but the DSF concentration at Sudbury and Sarnia ($\mu g/m^3$) exhibited similar low levels.

Comparative concentration levels of 10 PAH compounds for 3-month periods from April 1975 to March 1976 in the four cities are presented in Tables IV–VIII in units of $\mu g/g$ of particulate matter (PM) and in nanograms (ng) per 1000 m^3 of air sample. The total concentrations of the 10 PAH's in the air of each city for the four seasons of the year are listed in Table IX. The relatively strong carcinogens, benzo(a)pyrene, benzo(b)fluoranthene, and dibenzo(b,def)chrysene are of special concern as potential health hazards. Benzo(ghi)perylene is listed as noncarcinogenic (*1*), although this compound and benzo(rst)pentaphene have been found to be mutagenic in bacterial assay studies by Salamone et al. (*21*). The carcinogenic activity, if any, of naphtho(1,2,3,4-def)chrysene is unknown. Of the remaining PAH's listed in Tables V–IX, benzo(e)pyrene, benzo(k)fluoranthene, perylene, and dibenzo(def,mno)chrysene (anthanthrene) are considered to have no carcinogenic potential.

The Hamilton site exhibited the highest concentration levels of PAH's in units of ng/1000 m^3 air, followed by the two Toronto sites. Comparative levels at Sarnia and Sudbury were much lower, with Sudbury exhibiting the lowest levels in three of the four seasons, on the basis of ng/1000 m^3 air. At three of the five sites (Toronto, at Bathurst and #401, Hamilton and Sarnia), the highest total concentration levels occurred during the period October–December. On the other hand, at the Toronto suburban site (Kennedy at Lawrence) and at the Sudbury site, the highest total concentrations were found during the winter period, January–March.

Table III. Mass Concentrations of Airborne Particulates and Dichloromethane-Soluble Fractions (DSF) of Collections at Various Sampling Sites

Period	No. of samples	Mean mass concn ($\mu g/m^3$)	DSF concn ($\mu g/m^3$)	DSF/ particulate × 100%
Toronto Site 34007 (Bathurst St. at Highway 401)				
Apr.–June 1975	5	91.0	10.8	11.9
Jul.–Sept. 1975	4	95.3	12.3	12.9
Oct.–Dec. 1975	6	82.8	12.8	15.4
Jan.–Mar. 1976	5	77.8	8.4	10.8
Toronto Site 33003 (Kennedy St. at Lawrence)				
Apr.–June 1975	6	76.6	6.8	8.9
Jul.–Sept. 1975	5	63.5	6.0	9.4
Oct.–Dec. 1975	5	60.7	7.1	11.7
Jan.–Mar. 1976	4	137.0	11.5	8.4
Hamilton Site 29025 (downtown)				
Apr.–June 1975	6	145.7	13.6	9.3
Jul.–Sept. 1975	5	138.8	15.9	11.4
Oct.–Dec. 1975	5	69.4	10.6	15.3
Jan.–Mar. 1976	4	83.6	7.5	9.0
Sarnia Site 14061 (near Mill Street refinery)				
Apr.–June 1975	4	61.8	3.0	4.8
Jul.–Sept. 1976	5	46.5	3.6	7.7
Oct.–Dec. 1975	5	52.3	6.0	11.5
Jan.–Mar. 1976	6	27.2	2.6	9.5
Sudbury Site 77016 (downtown)				
Apr.–June 1975	3	33.1	3.5	10.6
Jul.–Sept. 1975	6	43.0	5.3	12.3
Oct.–Dec. 1975	5	22.3	2.9	13.0
Jan.–Mar. 1976	6	23.4	3.6	15.4

The mutagen, benzo(ghi)perylene, occurred in relatively high concentrations at all of the sampling sites. Since the only common, large-scale activity that could result in similar emissions at all sites in these four cities is the exhaust gases from motor vehicle traffic, it is probable that this PAH is one of the principal products in the organic polycyclic fraction of the particulates discharged from motor vehicles.

It is assumed that the surprisingly low levels of particulate matter and PAH's in Sudbury air, notwithstanding the very large scale of nickel-copper smelting activity about 5 miles distant, are due to the high-efficiency performance of the

Table IV. Comparative Seasonal Concentration Levels of PAH's in Air of Ontario Cities April 1975–March 1976 [Location: Toronto (Bathurst at 401); Site No. 34007]

	Apr.–June 1975		Jul.–Sept. 1975		Oct.–Dec. 1975		Jan.–Mar. 1976	
	ng/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.
Benzo(a)pyrene	789	8.8	1047	11.0	1674	20.2	720	9.2
Benzo(e)pyrene	440	4.9	519	5.4	1294	15.6	781	10.0
Benzo(b)fluoranthene	866	9.7	798	8.4	1387	16.8	783	10.1
Benzo(k)fluoranthene	428	4.8	571	6.0	916	11.1	508	6.5
Perylene	102	1.1	123	1.3	193	2.3	108	1.4
Dibenz(def,mno)chrysene	46	0.5	44	0.5	234	2.8	34	0.4
Benzo(ghi)perylene	5849	65.3	7131	74.8	10 528	127.2	4413	56.7
Naptho(1,2,3,4,def)chrysene	270	3.0	362	3.8	538	6.5	228	2.9
Benzo(rst)pentaphene	58	0.7	60	0.6	150	1.8	67	0.9
Dibenzo(b,def)chrysene	313	3.6	183	1.9	446	5.4	213	2.7

Table V. Comparative Seasonal Concentration Levels of PAH's in Air of Ontario Cities April 1975–March 1976 [Location: Toronto (Kennedy at Lawrence); Site No. 33003]

	Apr.–June 1975		Jul.–Sept. 1975		Oct.–Dec. 1975		Jan.–Mar. 1976	
	ng/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.
Benzo(a)pyrene	657	8.7	408	6.2	729	11.7	814	5.9
Benzo(e)pyrene	478	6.3	375	5.7	400	6.6	791	5.8
Benzo(b)fluoranthene	890	11.8	693	10.6	1259	20.7	1829	13.4
Benzo(k)fluoranthene	328	4.3	285	4.4	597	9.8	519	3.8
Perylene	99	1.3	57	0.9	136	2.2	51	0.4
Dibenz(def,mno)chrysene	65	0.9	38	0.6	102	1.7	162	1.2
Benzo(ghi)perylene	5077	67.1	3303	50.5	4693	77.3	9814	71.6
Naptho(1,2,3,4,def)chrysene	410	5.4	201	3.1	300	4.9	2762	20.2
Benzo(rst)pentaphene	89	1.2	27	0.4	90	1.5	259	1.9
Dibenzo(b,def)chrysene	210	2.8	109	1.7	229	3.8	490	3.6

Table VI. Comparative Seasonal Concentration Levels of PAH's in Air of Ontario Cities April 1975–March 1976 [Location: Hamilton; Site No. 29025]

	Apr.–June 1975		Jul.–Sept. 1975		Oct.–Dec. 1975		Jan.–Mar. 1976	
	mg/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.
Benzo(a)pyrene	1404	9.6	2351	16.9	3498	50.6	1934	23.1
Benzo(e)pyrene	606	4.2	1407	10.1	3771	54.4	1607	19.2
Benzo(b)fluoranthene	813	5.6	2626	18.9	7841	113.1	2297	27.5
Benzo(k)fluoranthene	419	2.9	1425	10.3	5145	74.2	443	5.3
Perylene	141	1.0	283	2.0	403	5.8	347	4.2
Dibenz(def,mno)chrysene	70	0.5	128	0.9	369	5.3	150	1.8
Benzo(ghi)perylene	5809	39.9	7183	51.7	7532	108.7	6418	76.7
Naptho(1,2,3,4,def)chrysene	184	1.3	1017	7.3	2027	29.2	903	10.8
Benzo(rst)pentaphene	74	0.5	247	1.8	434	6.3	281	3.4
Dibenzo(b,def)chrysene	331	2.3	915	6.6	1132	16.3	704	8.4

Table VII. Comparative Seasonal Concentration Levels of PAH's in Air of Ontario Cities April 1975–March 1976 [Location: Southern Sarnia; Site No. 14061]

	Apr.–June 1975		Jul.–Sept. 1975		Oct.–Dec. 1975		Jan.–Mar. 1976	
	ng/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.	ng/1000 m^3 Air	µg/g p.m.
Benzo(a)pyrene	338	5.5	114	2.4	596	11.4	190	7.0
Benzo(e)pyrene	118	1.9	52	1.1	603	11.5	64	2.4
Benzo(b)fluoranthene	371	6.0	243	5.2	938	17.9	289	10.6
Benzo(k)fluoranthene	81	1.3	70	1.5	439	8.4	104	3.8
Perylene	27	0.4	13	0.3	87	1.7	19	0.7
Dibenz(def,mno)chrysene	23	0.4	8	0.2	44	0.8	7	0.3
Benzo(ghi)perylene	1038	16.8	1049	22.5	2700	51.7	1158	42.6
Naptho(1,2,3,4,def)chrysene	823	13.3	61	1.3	434	8.3	129	4.7
Benzo(rst)pentaphene	422	6.8	15	0.3	69	1.3	23	0.8
Dibenzo(b,def)chrysene	508	8.2	81	1.7	213	4.1	107	3.9

Table VIII. Comparative Seasonal Concentration Levels of PAH's in Air of Ontario Cities April 1975–March 1976 [Location: Sudbury; Site No. 77016]

	Apr.–June 1975		Jul.–Sept. 1975		Oct.–Dec. 1975		Jan.–Mar. 1976	
	ng/1000 m³ Air	μg/g p.m.	ng/1000 m³ Air	μg/g p.m.	ng/1000 m³ Air	μg/g p.m.	ng/1000 m³ Air	μg/g p.m.
Benzo(a)pyrene	175	5.4	111	2.6	342	15.3	444	19.0
Benzo(e)pyrene	23	0.7	45	1.1	255	11.4	317	13.6
Benzo(b)fluoranthene	255	7.8	173	4.1	417	18.7	650	27.8
Benzo(k)fluoranthene	57	1.7	74	1.8	197	8.8	271	11.6
Perylene	17	0.5	17	0.4	41	1.8	50	2.1
Dibenz(def,mno)chrysene	8	0.2	9	0.2	37	1.7	32	1.4
Benzo(ghi)perylene	779	23.9	1104	26.3	2321	104.0	3009	128.7
Naptho(1,2,3,4,def)chrysene	510	15.6	73	1.7	99	4.4	230	9.8
Benzo(rst)pentaphene	40	1.2	10	0.2	17	0.8	36	1.5
Dibenzo(b,def)chrysene	149	4.6	47	1.1	54	2.4	130	5.6

Table IX. Total Concentrations of 10 PAH's in Air of Ontario Cities April 1975–March 1976

	Toronto Site 34007		Toronto Site 33003		Hamilton Site 29025		Sarnia Site 14061		Sudbury Site 77016	
Season	ng/1000 m³ Air	μg/g p.m.	ng/1000 m³ Air	μg/g p.m.	ng/1000 m³ Air	μg/g p.m.	ng/1000 m³ Air	μg/g p.m.	ng/1000 m³ Air	μg/g p.m.
Apr.–June	9 161	102.4	8 303	109.8	9 851	67.8	3 749	60.6	2 013	61.6
Jul.–Sept.	9 838	113.7	5 496	84.1	17 582	126.5	1 706	36.5	1 663	39.5
Oct.–Dec.	17 360	209.7	8 535	140.2	32 152	463.9	6 123	117.1	3 780	169.3
Jan.–Mar.	7 855	100.8	17 491	127.8	15 084	180.4	2 090	76.8	5 169	221.1
Mean	11 053	131.6	9 956	115.5	18 667	209.6	3 417	72.7	3 156	122.9

Table X. Comparative Concentration Levels of PAH's in U.S. and Other Cities

PAH compound	New York City (*22*) ng/1000 m³ Air	Av U.S. urban (*23*) ng/1000 m³ Air	Antwerp (*24*) μg/g part.	Ghent (*10*) ng/1000 m³ Air	μg/g part.	Milan (*10*) μg/g part.
Benzo(a)pyrene	1150–1300	5700	51			
				5200	60	46
Benzo(e)pyrene	1400	5000	51			
Benzo(b)fluoranthene	800	2300–7400	83			
		(Detroit)		7700	90	68
Benzo(k)fluoranthene	600	500–2000	83			
Perylene	100–200	700	5	. . .	. . .	. . .
Benzo(ghi)perylene[a]	900	8000	12	. . .	. . .	. . .
Dibenzanthracenes	. . .	. . .	3	. . .	. . .	. . .

[a] Antwerp concentration includes anthanthrene.

electrostatic precipitators and the remarkable degree of dispersion of emissions from the 1250-ft-high smelter stack.

Published data containing concentration levels of some of these PAH compounds in the air of New York City (*22*), average of several U.S. cities (*23*), and in Antwerp (*24*), Ghent, and Milan (*10*) are presented in Table X. The Hamilton air levels of benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(ghi)perylene are considerably higher than the corresponding New York City concentrations.

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Fluidized-Bed Combustion of Coal with Lime Additives: Catalytic Sulfation of Lime with Iron Compounds and Coal Ash

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■ Iron oxide (Fe_2O_3) is catalytic to the sorption of SO_2 by CaO in a chemical environment similar to that in fluidized-bed combustion of coal. Four percent by weight of Fe_2O_3 physically mixed with CaO approximately doubles the sorption (sulfation) rate. The kinetic mechanisms of the catalytic reaction are discussed based on the view that SO_3 formation is the rate-limiting step. Coal ash also catalyzes the sulfation reaction, and Fe_2O_3 appears to be the active constituent in such catalytic effects. Other iron-containing compounds existent in coal and fluidized-bed combustion systems are oxidized rapidly in the combustion gases to form Fe_2O_3 and in turn catalyze the sulfation reaction.

In recent years, fluidized-bed combustion has been recognized as a promising and versatile technology for clean combustion of coal (*1–3*). One of the crucial factors in effecting this technology is a relatively high reactivity of the lime additive toward SO_2 to form calcium sulfate in the environment of the combustion gases. A significant amount of work has been done in the past to determine the effects of the reactivity of the variables under combustion conditions, such as temperature and concentration of SO_2 (*4, 5*), total pressure and rapidly changing atmospheres (*6, 7*), water vapor and oxygen partial pressures (*8, 9*), and the generic factor of the limestone (*10*).

Little attention has been paid to the effect, if any, of the solids in the fluidized bed on the reactivity. An exception is the effect of the added NaCl, which has been known as a catalyst (*11–14*). Coal ash generated in the combustion process is mostly of fine sizes and is entrained in the combustion gas. However, significant amounts of coal ash do remain in the fluidized bed at any instant. For example, in the pilot-scale fluidized-bed combustor at Argonne National Laboratory, about 5 wt % of the bed material was found to be coal ash (*13*). Moreover, the lime particles remaining in the bed contain significant amounts of Fe_2O_3 in the sulfated layer. For example, the work at Argonne showed that, based on electron microprobe analysis, the spent (recycled) lime sorbent contained up to 8% Fe in the sulfated layer (*14*). Consequently, the spent lime appeared reddish and brownish in color. Coal ash, which contained about 20% Fe_2O_3, was obviously the source of the iron contaminant. Being aware that Fe_2O_3 is a known high-temperature catalyst for the oxidation of SO_2 to SO_3 (*15*), we were prompted to examine the effects of Fe_2O_3 and the coal ash on the reactivity of lime with the combustion gases. It was also hoped that the results would shed light on the mechanism of the sulfation reaction of CaO as well as the sulfation kinetics in fluidized-bed combustion.

Experimental

A Du Pont thermoanalyzer Model 951 was used for the rate measurements. A small quartz boat with an area of about 0.6 cm^2 was used as the sample holder. The thermoanalyzer contained a time-derivative computer which took the derivative of the weight change with respect to time. The derivatives were used to calculate the rates of sulfation. A quartz tube packed with alumina chips and housed in a tubular furnace served as the preheater for the reactant gases. The steam in the reactant gas was generated by bubbling the inert carrier gas (N_2) through a water bath prior to entering the preheater. The bubbler was jacketed, and water was circulated in the jacket from a constant temperature water bath.

In a typical experiment, about 20 mg of calcium oxide sample was spread into a thin layer on the holder as the solid reactant. The preheated gas mixture flowed over the sample surface at a velocity of about 10 cm/s. This velocity was predetermined to be high enough to maximize the gas film diffusion rate. The initial rate, i.e., the rate in the initial 5 min, was employed to calculate all the kinetic parameters, because it was close to the intrinsic chemical rate. The calculation procedures were straightforward and were outlined previously (*8*).

All the solid samples were of reagent grades. The gases were supplied by Matheson Co. as custom-made premixed SO_2 in N_2 at various specified concentrations.

Results and Discussion

The rates of sulfation of the reagent-grade CaO were compared with those mixed with 4 wt % of Fe_2O_3. As shown in Figure 1, 4% of Fe_2O_3 almost doubled the rate. For a preliminary understanding of such catalytic effects, we compared the kinetic parameters of the reactions involved based on our experimental results as follows.

For the sulfation of CaO, regardless of the true mechanisms of the reaction, the valence of sulfur is changed from +4 to +6, or SO_2 is oxidized to SO_3. The following reactions can be written to represent the process:

$$\mathrm{CaO} + \mathrm{SO_2} + \tfrac{1}{2}\mathrm{O_2} \xrightarrow{r_a} \mathrm{CaO \cdot SO_3} \xrightarrow{r_b} \mathrm{CaSO_4} \qquad (1)$$

For the sulfation of CaO being catalyzed by Fe_2O_3, which is physically separated from the CaO, the following reactions may describe the sequences: