

Handbook of
POLYCYCLIC
AROMATIC
HYDROCARBONS
Volume 2

Emission Sources and
Recent Progress in
Analytical Chemistry

edited by

Alf Bjørseth

Thomas Ramdahl

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Emission Sources and Recent
Progress in Analytical Chemistry

Edited by

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Preface

The historical evolution of knowledge about chemical carcinogens and environmentally induced carcinogenesis is strongly linked to characterization of polycyclic aromatic hydrocarbons (PAH). The environmental importance of this class of compounds is as high today as ever.

Environmental and biochemical studies of PAH form a large and comprehensive area of research. Very few people have the ability and the opportunity to engage actively in all aspects of such research. We have seen the need for an extensive and systematic treatise describing our present knowledge of PAH in areas relevant to researchers and educators, as well as industrial hygienists and representatives of environmental agencies.

Three years ago the first volume of this handbook was published, reviewing the state of the art for important topics such as sampling of PAH, analytical methods, and occurrence in important environmental matrices. However, the research in this subject is developing so fast that we found it necessary to update some important areas, and to add new information on selected topics. The present volume of the handbook therefore concerns sources of PAH, their emission factors, and relative importance. Further, it deals with exposure, uptake, metabolism, and detection of PAH in the human body. Finally, the handbook contains an update of information in selected research areas.

In recent years, many studies have been devoted to derivatives of PAH, such as nitrogen-, sulfur- and oxygen-containing compounds. This is reflected also in some chapters in this volume. The term polycyclic aromatic compounds (PAC) has been introduced to cover all these derivatives, including PAH, and this will also be used throughout the book where appropriate.

It is our hope that the readers will find this book a good contribution to their knowledge about PAH and a useful supplement to the information given in Vol. 1.

We would like to express our sincere thanks to all the contributors to this handbook, for their cooperation, their hard work, and their patience while their manuscripts were being prepared for press. We are also indebted to our colleagues at the Central Institute for Industrial Research, in Oslo, Norway, for their valuable advice and encouragement.

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1

Sources and Emissions of PAH

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I. INTRODUCTION

Since the British surgeon Sir Percival Pott in 1775 reported [1] that chimney sweeps in Britain often developed cancer of the scrotum, there has been an awareness of the harmful effects of soot, tar, and pitch. However, more than 150 years passed until carcinogenic constituents in pitch [2] were identified as polycyclic aromatic hydrocarbons (PAH). By 1976 more than 30 PAH compounds and several hundred derivatives of PAH were reported to have carcinogenic effects [3,4], making PAH the largest single class of chemical carcinogens known today.

Potential hazards from the occurrence of PAH in the environment have been noted in the drinking water standards set forth by the World Health Organization's Committee on the Prevention of Cancer [5], as well as by several national agencies concerned with PAH in food, working atmospheres, and effluents from industries and mobile sources [6,7].

It was also fairly recently that chemical characterization of sources to PAH emissions was initiated. Reliable analysis of PAH emissions requires instrumentation which has been available only for the last 30-40 years, and even today the quantitative information about PAH emissions from anthropogenic as well as natural sources is limited. In this chapter we review, briefly the formation mechanisms and sources of PAH, estimate emission factors for known anthropogenic sources of PAH, and establish their relative importance.

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II. FORMATION OF PAH

PAH can be formed by thermal decomposition of any organic material containing carbon and hydrogen. Formation is based on two major mechanisms:

1. Pyrolysis or incomplete combustion
2. Carbonization processes

A pioneering contribution to their understanding has been made by Badger and coworkers [8,9]. The chemical reactions in flames proceed by free-radical paths, and a synthetic route based on this concept has also been postulated for the formation of PAH. Based on the results of a series of pyrolysis experiments, Badger suggested a stepwise synthesis of PAH from C_2 species during hydrocarbon pyrolysis. These pyrolysis studies were conducted by passing the hydrocarbon vapor in nitrogen through a silica tube at 700°C . Badger's data have been supported by Boubel and Ripperton [10], who found that benzo[a]pyrene (BaP) is also produced during combustion at high percentages of excess air, although the amount of BaP is larger at lower percentages of excess air.

Badger and Spotswood [11] also pyrolyzed toluene, ethylbenzene, propylbenzene, and butylbenzene and obtained high yields of BaP with butylbenzene, a potential intermediate in Badger's reaction scheme. Obviously, it is not necessary to completely break down the starting material to a two-carbon radical in order to form BaP. Any component of the combustion reaction that can contribute intermediate pyrolysis products of the structure required for BaP synthesis would also be expected to lead to increased yields of BaP.

Other and more recent studies of the PAH formation models also tend to confirm most of the mechanisms proposed by Badger. Crittenden and Long [12] determined the chemical species formed in rich oxyacetylene and oxyethylene flames. Compounds identified suggest that the C_2 species react to form C_4 , C_6 , and C_8 species, and that reactions involving styrene and phenylacetylene are probably important in the formation of PAH. Also, a $C_{10}H_{10}$ species was detected in the gases of both flames which corresponds to the C_4 -substituted benzene postulated by Badger.

In spite of the tremendous number of different PAH that might be formed during the primary reactions, only a limited number of PAH enter the environment. Many of the PAH formed by primary reactions will have short half-lives under pyrolysis conditions, and will stabilize in subsequent reactions. At high temperatures the thermodynamically most stable compounds will be formed in corresponding quantitative ratios. These are mainly the unsubstituted parent PAH. Irrespective of the type of material to be burned, surprisingly similar ratios of PAH are formed at a defined temperature. For example, thermal decomposition of pit coal, cellulose, tobacco, and of polyethylene and polyvinyl chloride carried out at 1000°C yields very similar PAH profiles [13]. Consequently, PAH profiles seem to depend more on the combustion conditions than on the type of organic material burned.

The absolute amount of PAH formed under defined pyrolysis conditions depends, however, on the reaction temperature as well as the material. The amount of BaP formed by pyrolysis of various substances at 840°C in a nitrogen stream is shown in Table 1. The table demonstrates the relative unimportance of the oxygen-containing carbohydrates in the generation of BaP compared to the C_{32} paraffin or β -sitosterol, a common plant sterol. Furthermore, the absolute amount of PAH formed during incomplete combustion is dependent on temperature, as shown in Table 2. Under comparable conditions, 1 g of tobacco yields 44 ng of BaP at 400°C and 183,500 ng of BaP at 1000°C [15].

Table 1. Levels of Benzo[a]pyrene Produced on Pyrolysis (840°C, N₂)

Substance pyrolyzed	μg BaP/g pyrolyzed
Glucose	47.5
Fructose	98.4
Cellulose	288.8
Stearic acid	1200
Dotriacontane	3130
β-Sitosterol	3750

Source: Ref. 14. Reprinted with permission of Raven Press, New York.

At temperatures below approximately 700°C, the pyrolysis products contain, in addition to the parent PAH, larger amounts of alkyl-substituted PAH, mainly methyl derivatives. A typical example is tobacco smoke, which yields soot quite abundant in alkyl-substituted PAH [16]. Figure 1 shows schematically the relative abundance of PAH as a function of the number of alkyl carbons at different formation temperatures as given by Blumer [17]. As indicated by the figure, the number of alkyl carbons present as side chains on PAH correlates closely with the temperature at which the compounds are formed.

Table 2. Formation of Benzo[a]pyrene and Benzo[e]pyrene from Blend Tobacco (100 g) as a Function of Temperature (1000 ml N₂/min)

Temperature (°C)	BaP (μg)	BeP (μg)
400	4.4	3.2
500	12.9	8.4
600	32.0	19.0
700	56.0	29.4
700 ^a	88.6	45.2
800	270.0	155.0
900	1,820.0	824.0
900 ^a	4,725.0	2,015.0
1000 ^a	18,350.0	6,710.0

^aAt 1500 ml/min to avoid a back reaction of the condensate.

Source: Ref. 13.

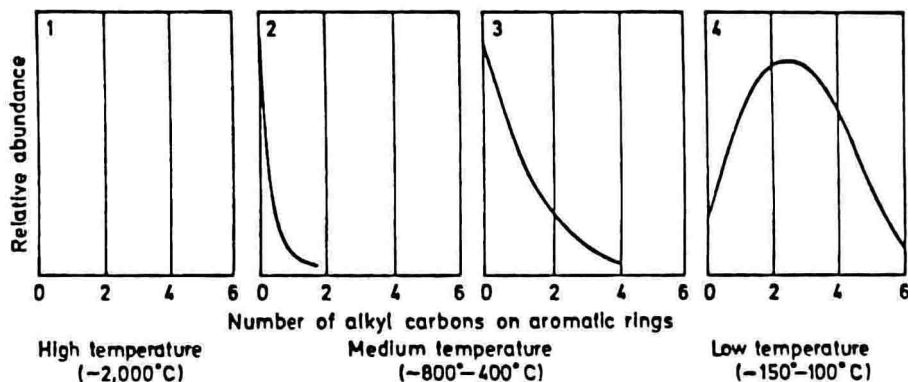


Figure 1. The relative abundance of polycyclic aromatic hydrocarbons as a function of the number of alkyl carbons at different formation temperatures. From Polycyclic aromatic compounds in Nature, Max Blumer [17]. (Copyright © 1976 by Scientific American, Inc. All rights reserved.)

PAH is not formed solely by high temperature and open flames. Various processes of carbonization that occur (e.g., during the generation of mineral oil and coal) lead to the formation of PAH from decaying biological material at low temperatures (below 200°C) and high pressure over a period of millions of years. The transformation resembles pyrolysis, but the reactions are exceedingly slow because of the modest temperatures involved.

III. SOURCES OF PAH

Although it is recognized that there are natural sources of PAH [17,18] (i.e., volcanic activity and biosynthesis), the anthropogenic sources are predominant and by far the most important to air pollution [13]. This chapter therefore deals mainly with anthropogenic sources.

Table 3 lists the main sources, divided into two categories: stationary and mobile sources. The stationary sources include industrial sources, power and heat generation, residential heating, incineration, and open fires. The second category is that of the mobile sources, which include gasoline-engine automobiles, diesel-engine automobiles, trucks, airplanes, and sea traffic. In all the processes listed, organic material is burned or strongly heated, and will in most cases result in emissions of PAH.

IV. EMISSION FACTORS

A. General

The amount of PAH released from any process is largely dependent on raw materials and the combustion technology. Therefore, a given process with a fixed set of process parameters may produce a specific and invariable amount of PAH. The amount can be correlated to the process parameters, and thus a relative emission factor for the process can be established. Emissions from industrial sources are determined primarily by the production level of the plants emitting PAH. The emission factor can be expressed as weight of PAH per ton of product. In the case of mobile sources, the consumption of fuel could be chosen as the emission-determining unit, giving an emission factor expressed as micrograms of PAH per kilogram of fuel consumed.

Table 3. Sources of PAH

Stationary sources

1. Residential heating	3. Power and heat generation
Furnaces, fireplaces, and stoves (wood and coal)	Coal- and oil-fired power plants
Gas burners	Wood- and peat-fired power plants
	Industrial and commercial boilers
2. Industry	4. Incineration and open fires
Coke production	Municipal and industrial incinerators
Carbon black production	Refuse burning
Petroleum catalytic cracking	Forest fires
Asphalt production	Structural fires
Aluminum smelting	Agricultural burning
Iron and steel sintering	
Ferroalloy industry	

Mobile sources

5. Gasoline-engine automobiles
- Diesel-engine automobiles
- Rubber tire wear
- Airplanes
- Sea traffic

Although numerous publications deal with PAH, very few studies link the emission to any process parameter. These studies are therefore not suited for emission factor development, as such. Another problem is the inconsistency of reported PAH compounds. For different reasons BaP has been measured more frequently than any other PAH. In these cases, BaP can help in judging how a given source contributes to the total PAH emission by comparing it to values of BaP emission from other sources. However, BaP is only a minor component, usually less than 5% of the total amount of PAH. In studies where more PAH than BaP are measured, the number of PAH analyzed may vary, depending on the analytical technique employed. Hangebrauck et al. [19] analyzed 10 different PAH in emission samples by column chromatography and ultraviolet-visible spectrophotometry, whereas modern glass capillary gas chromatography can separate and quantify more than 40 PAH in comparable samples [20]. The term "total PAH emissions" therefore depends strongly on the number of compounds determined. Because measurements of the same source often give large differences, the emission factors

presented consist of a minimum, a maximum, and an intermediate value when possible. *The emission of bicyclic aromatic compounds is not included in the calculation of PAH emission factors.*

Emission factors for PAH are available in only a few reports. However, the U.S. Environmental Protection Agency has published a comprehensive report [21]. Most of the emission factors in this report were developed from data reported by Hangebrauck et al. in their relatively comprehensive 1967 study [19]. A literature search conducted by EPA to update this information resulted in very few additional data. The emission factors discussed below have been updated wherever new results were available.

B. Emission Factors for Specific Sources

1. Residential Heating

Wood- and coal-burning stoves and wood-burning fireplaces are frequently used for residential heating. The combustion of wood and coal is often incomplete, due to slow, low-temperature burning with insufficient access to air at the burning surface. This results in the formation of large amounts of PAH, which may be released directly to the atmosphere.

Two Scandinavian studies of wood stoves yielded emission values between 1 and 36 mg of PAH (22-26 individual PAH compounds determined) per kilogram of dry fuel [22, 23] while an American study [24] measured 270 mg/kg (26 compounds). These differences may reflect variations in design, sampling methodologies, test cycles, and so on, and illustrate the difficulty of calculating a single emission factor for a given source. In Table 4 the emission factor is given, with an intermediate value of 40 mg PAH/kg dry wood.

Residential coal firing gives an emission factor of 60 mg/kg [19,25]. However, this factor can vary over five orders of magnitude with respect to the type of coal used [26]. Emissions from residential heating with oil vary with the size of the burner. A 100,00 Btu/hr (30 kW) burner has been found to emit 150 μ g/kg oil [19], whereas a smaller, 25,000 Btu/hr (7.5 kW) unit has been found to emit 10 mg/kg oil [27]. Further measurements are needed to establish good emission factors for residential oil heating.

2. Aluminum Production

Production of primary aluminum is based on two different technologies, using Söderberg or prebaked anodes. PAH may be emitted from the carbon electrodes containing tar and pitch as binder [28]. The emissions from the prebaked electrodes are usually 1-10% of that of the Söderberg electrodes. To the best of our knowledge, only one plant have been studied to determine the total PAH emission from the production of aluminum [29]. The PAH emission to air was determined to approximately 35 metric tons of PAH at a plant with an annual production of 83,500 tons of aluminum using the Söderberg process. The PAH in this study represent the sum of some 25 compounds.

Assuming that the Söderberg and the prebaked process each cover 50% of the worldwide production, and that the prebaked process emits 5% of that of the Söderberg process, an emission factor of 235 g/ton aluminum produced is established for aluminum production, as shown in Table 5. It should be stressed, however, that the data base is limited to one technology and one aluminum plant. The emission factors calculated here therefore reflect considerable uncertainty.

Table 4. Emission Factors for Residential Heating

Source	Benzo[a]pyrene		PAH		References
	Range ($\mu\text{g}/\text{kg}$)	Typical ($\mu\text{g}/\text{kg}$)	Range (mg/kg)	Typical (mg/kg)	
Wood stoves	1-10,000	500	1-370	40	22-24
Fireplaces		700		29	24
Coal furnaces		1500	1-1200	60	19,25
Oil (30 kW)	2.0-4.4	2.2	0.006-0.75	0.15	19
Oil (7.5 kW)			0.9-21.6	10	27