

# ANALYSIS OF AIR POLLUTANTS

PETER O. WARNER

A VOLUME IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY:  
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Edited by

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AIR POLLUTION CONTROL DIVISION

A WILEY-INTERSCIENCE PUBLICATION

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# SERIES PREFACE

## Environmental Science and Technology

The Environmental Science and Technology Series of Monographs, Textbooks, and Advances is devoted to the study of the quality of the environment and to the technology of its conservation. Environmental science therefore relates to the chemical, physical, and biological changes in the environment through contamination or modification, to the physical nature and biological behavior of air, water, soil, food, and waste as they are affected by man's agricultural, industrial, and social activities, and to the application of science and technology to the control and improvement of environmental quality.

The deterioration of environmental quality, which began when man first collected into villages and utilized fire, has existed as a serious problem under the ever-increasing impacts of exponentially increasing population and of industrializing society, environmental contamination of air, water, soil, and food has become a threat to the continued existence of many plant and animal communities of the ecosystem and may ultimately threaten the very survival of the human race.

It seems clear that if we are to preserve for future generations some semblance of the biological order of the world of the past and hope to improve on the deteriorating standards of urban public health environmental science and technology must quickly come to play a dominant role in designing our social and industrial structure for tomorrow. Scientifically rigorous criteria of environmental quality must be developed. Based in part on these criteria, realistic standards must be established and our technological progress must be tailored to meet them. It is obvious that civilization will continue to require increasing amounts of fuel, transportation, industrial chemicals, fertilizers, pesticides, and countless other products and that it will continue to produce waste products of all descriptions. What is urgently needed is a total systems approach to modern civilization through which the pooled talents of scientists and engineers, in cooperation with social scientists and the medical profession, can be focused on the development of order and equilibrium to the presently disparate *segments of the*

human environment. Most of the skills and tools that are needed are already in existence. Surely a technology that has created such manifold environment problems is also capable of solving them. It is our hope that this Series in Environmental Sciences and Technology will not only serve to make this challenge more explicit to the established professional but that it also will help to stimulate the student toward the career opportunities in this vital area.

*Robert L. Metcalf*

*James N. Pitts, Jr.*

*Werner Stumm*

# PREFACE

In the recent past, much of the data that have characterized the environmental deterioration of our atmosphere have suffered from limitations inherent in applying, without adaptation, classical chemical methodology to the chemical analysis of air pollutants. Only recently, through the efforts of the U.S. Environmental Protection Agency, together with other municipal agencies both here and abroad, have the necessary skills been consolidated to arrive at analytical methods to determine trace but nonetheless hazardous quantities of pollutants in air.

This text has been assembled in response to the need to present this information in an organized form, and is addressed to undergraduate science majors and beginning graduate students as both a program of study and a reference manual in collecting and analyzing air samples, primarily in the urban environment. Some discussion is devoted to the origin and properties of common and some less-common air contaminants. At the beginning, considerable emphasis is placed on methods for the identification of dust-particulates, since these form the largest, most visually obvious class of air contaminants.

Organic compounds, which find their way into the urban industrial atmosphere, are treated from the point of view that physical separation must be adapted to the sampling method if a specific compound is to be determined selectively. Alternatively, advantages are presented for the determination of organic compound families such as total aldehydes, or the index of total aromatics, since these chemically relatable groups are often traceable to a common community source.

Later, in the treatment of gaseous air contaminants, the air chemistry of the individual gases is discussed in some detail, especially when this knowledge is helpful in understanding the principle as well as the application of a given method of analysis. Occasionally, for example, in the case of monitoring ambient hydrocarbons, the object of a given air quality measurement may be the control of some other pollutant, in this case, total oxidant, whose presence is ultimately related to the air chemistry of the nonmethane portion of hydrocarbons.

Since the result of the chemical analysis is only as reliable as the collection

method used to obtain the air sample, a great deal of attention has been devoted to methods of air sampling. Here I have encouraged the reader to select the best method of air sampling by weighing advantages and disadvantages of a number of sampling approaches in various situations. I emphasize not only the mechanics of separating the contaminant sample from the body of air, but also the need for accuracy in the measurement of the body of air itself, so that actual concentration of pollutant in amount per unit air volume can be analytically significant.

A growing awareness of the need for reliable measurements of community odor has prompted an extensive review of up-to-date methodology in sensory-response analysis. The theoretical basis for these measurements is presented together with detailed procedures and equipment needed to arrive at meaningful reproducible odor intensities.

Many such step-by-step procedures are included together with simplified directions designed to enable the beginning environmentalist with a background in laboratory science to set up sampling equipment and collect useful data. On the other hand, more sophisticated approaches such as spectrofluorescence and x-ray diffraction are described in some detail to encourage the use of these instrumental methods, which furnish almost invaluable aid to the air pollution chemist in specifically identifying urban-industrial pollutants, such as polynuclear aromatic hydrocarbons, and minerals, such as silica and cermets, which recent medical research indicates are related to human health.

PETER O. WARNER

*Detroit, Michigan*  
*July 1975*

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P.O.W.



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# ORIGIN AND IDENTIFICATION OF PARTICULATE AIR POLLUTANTS

## INTRODUCTION

The solution to many problems encountered in the identification of airborne particulate matter lies in the synthesis of a considerable amount of knowledge gathered from chemistry, physics, microscopy, crystallography, and ultimately experience.

It is estimated that up to 15% of the total settleable dust and perhaps as much as 25% of suspended particulate is of natural origin. Thus pollution itself is by no means pure pollution. Its composition is governed not only by the makeup of the industry that causes it, but also by the makeup of the land on which the industry stands. The Western states are noted for siliceous air, which is made up of fine particles whose settleable air loading varies from 3 to 5 tons of sand per square mile per month. Air masses in the arctic are noted for "ice fogs," which form at temperatures below 45°F as a result of humidity rising from both natural sources and population centers scattered throughout the icy wasteland. And marine and coast atmospheres contain suspended salt nuclei. Because of these symbiotic conditions in natural air, it is well to consider the earth's natural atmosphere before exploring its sometimes less natural contaminants. Among the natural contaminants that make up a portion of any collected pollutant samples are suspended dust from volcanoes, soil from air erosion of farmland, hydrocarbons from coniferous vegetation, pollen, and particulate carbon smoke of natural origin.

If we assume an air loading of 100  $\mu\text{g}/\text{m}^3$ —as exists in many urban atmospheres—it is surprising to find 45% silica, 13%  $\text{Fe}_2\text{O}_3$ , 6%  $\text{Al}_2\text{O}_3$ , 24% carbon, 1% lime, 1% alkali sulfates, and 3% limestone, and the balance a mixture of such materials as vanadium, magnesium, alkali carbonates and chlorides, titanium, zincite, and a number of light and heavy metal sulfates together with organics and fibers.

### COMMON AIR CONTAMINANT PARTICULATES

Probably more time, effort, and money have been spent on the study of fuel combustion products as air contaminants than on any other source in industrial technology. The introduction of the automobile added only one new class of particulates to the queue of classes awaiting their turn as potential hazards to human health and as a source of consternation to the laboratory chemist working at their separation and identification. Particles such as lime, limestone, and cement dust from kilning operations, coke dust and polycyclic aromatics from coking operations, iron oxides from the various ore smelting procedures, and fluorides from nonferrous metallurgy have joined with asphalts, solvents, synthetic monomers, butyl rubber, and carbon black from the construction and heavy polymer industries. All these emissions are homogenized with such proprietary air species as fly ash from electrical power plants and windblown slag from storage piles in the vicinity of blast furnaces and the road construction material process plants, to which the iron and steel industries address this marketable by-product. Blown insulation is still another example of a proprietary air contaminant.

Home space heating is perhaps the least major source of carbonaceous particulate, although such urban materials as windblown salt from winter treatment of roads have recently appeared as rather substantial causes of extensive local particulate pollution. Further examples of such local pollution are the following:

1. Particles of copper, copper oxides, boron and silicon carbides, iron and iron oxide, aluminum, magnesium, and silica from grinding and milling operations.
2. Carbon black and kish (graphitic carbon) graphite from steel and rubber processing.

Of the major particulate pollutants probably the most prevalent and very often the most difficult to separate from road dust and natural pollutants is common fly ash. The discussion that follows should help to delineate the classification of types of fly ash contaminant and aid in its separation and identification in a typical sample of industrial particulate.

#### Coal and Coal Fly Ash

The most common sampling techniques for particulates (as described in Chapter 5) involve dustfall and high-volume sampling. These produce sample weight in excess of 1 g and particles in the overall range of 0.1 to 100  $\mu$  in diameter. This is a good sample analytically, since most analytical methods

involving the determination of metals, for example, begin with samples of particle size similar to that of settleable dust. In this case, the samples are already rather finely divided and require little sample preparation except for the high-volume filtered dust that must itself be removed from the filter medium before analysis. This is usually accomplished by dissolution in dilute nitric or hydrochloric acid or by ultrasonic peptization if such instrumentation is available.

The chemistry used in separating the collected particles depends on the nature of the sample. Combustion is a very complex process, so that fly ash may proceed through a number of mechanisms, giving particles of various types. Typical fly ash (Figure 1) looks like a mixture of geometrically amorphous, but surprisingly characteristic, particles whose approximate shape, particle diameter, and relative degree of agglomeration permit quite reliable optical identification.

When coal burns, the heat generated may vaporize material that can subsequently condense to produce the fine particles that are called soot. These range in size from less than  $0.1$  to  $10.0 \mu$  in diameter. Depending on the volume of air present and the temperatures involved, the burning of carbon fuel may yield particles as small as  $50 \text{ \AA}$ —a class with properties similar to those of the pyrophoric powders of refractory metals, or the more familiar face talc.

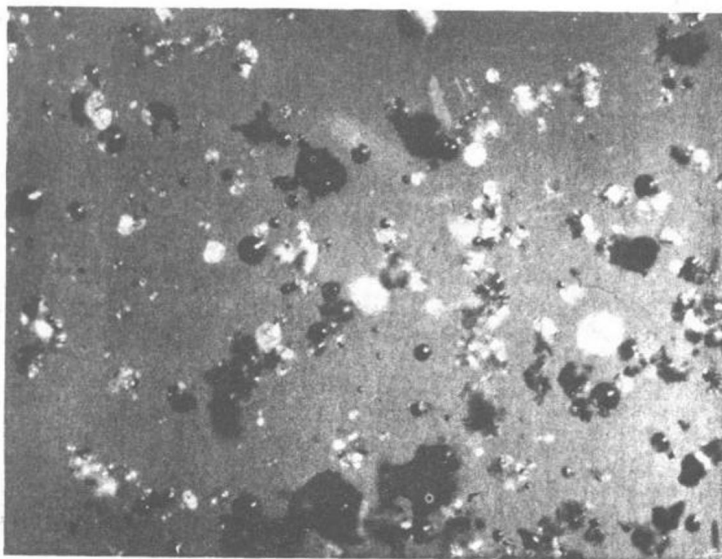


Figure 1. Typical coal fly ash. (Magnification  $100\times$ .)

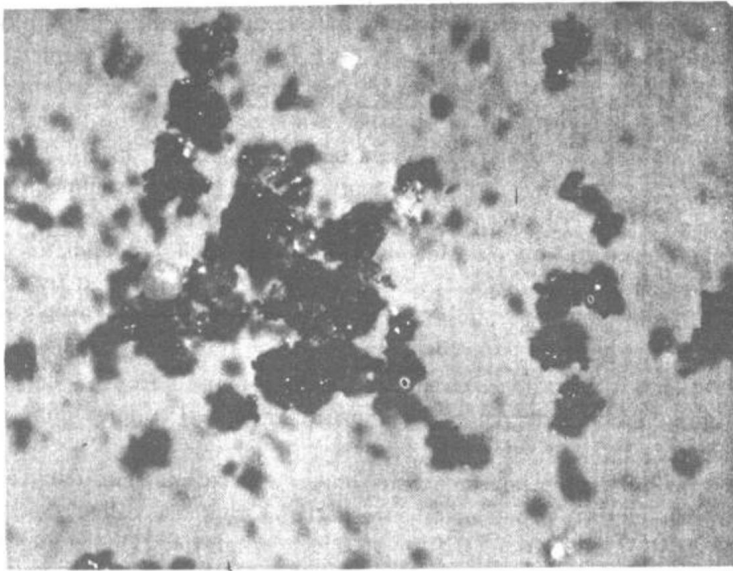


Figure 2. Coal, fly ash mixed with fine carbon black. (Magnification 100 $\times$ .)

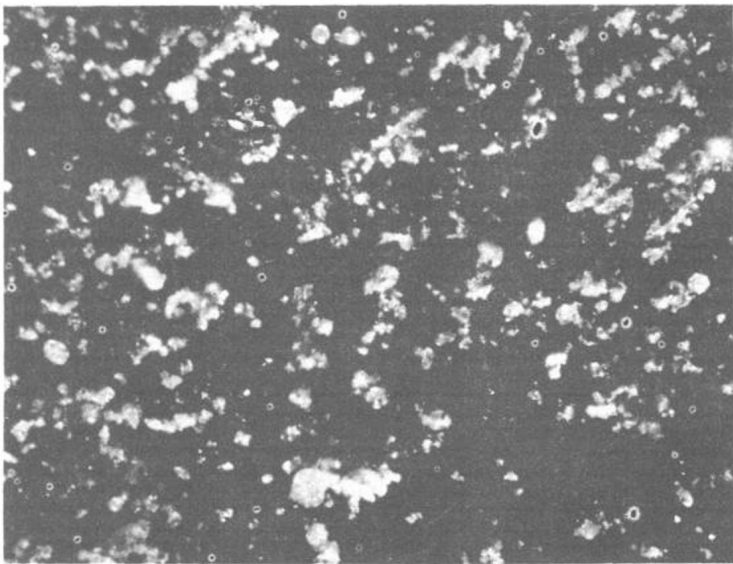


Figure 3. Pulverized coal fly ash. (Magnification 100 $\times$ .)



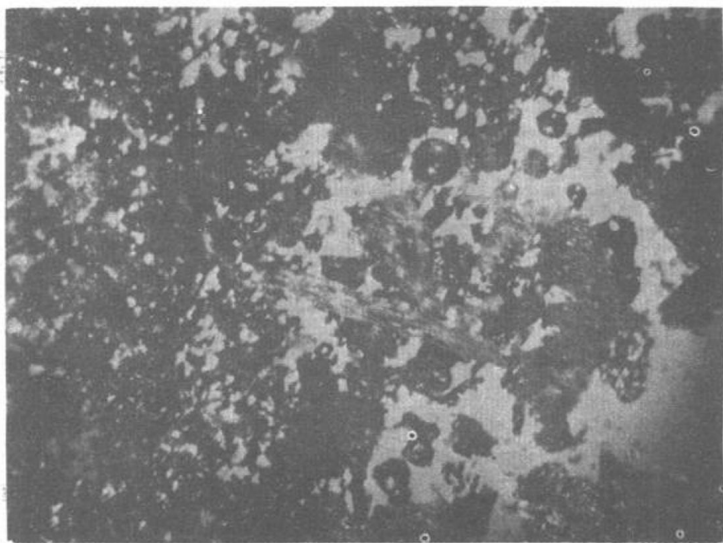
Figure 4. Windblown coal particulate. (Magnification 40 $\times$ .)

Such particles of carbon are, as one might imagine, highly surface-active and rather graphitic in appearance under microscopic examination.

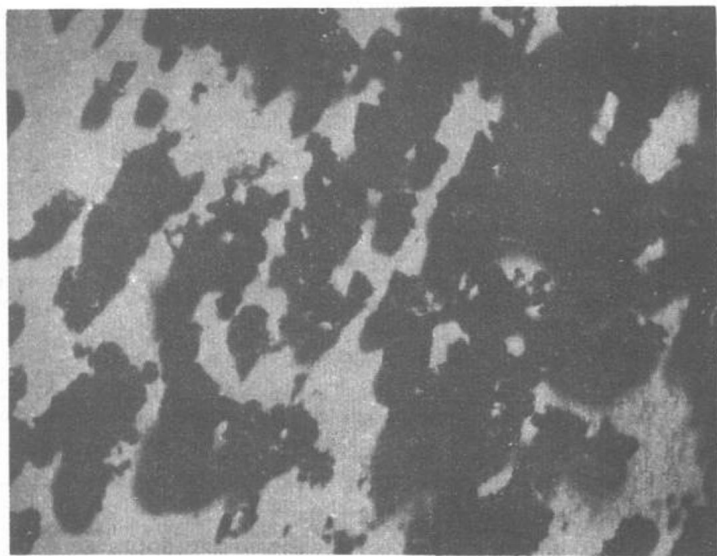
Ordinarily, very small particles ( $< 0.1 \mu$ ) are quite unstable under the gross combustion conditions usually associated with space heating and industrial power plant operations. Hence they are less common in the average urban particulate. One important exception is the submicron carbon black that escapes from automobile tires through ordinary road wear. This "dry grinding" often results in the unzipping of the butadiene-styrene polymer system with substantial formation of monomer, together with carbon black, which is thought to be quite long-lived in the atmosphere. Figure 2 illustrates this particulate and shows its relative size when mixed in equal portions with a sample of ordinary fly ash.

If the fuel itself is particulate, such as fuel designed for pulverized coal-fired boilers, the resulting particulate looks as shown in Figure 3. Here, it is noteworthy that the carbonaceous dust is reduced to practically the size of table salt. This salt is merely the concentrated, mixed alkalis and heavy metal compounds present in the original fuel that have been converted to carbonates, sulfates, and halides in the combustion process.

Nearly all coal combustion produces fly ash of the appearance shown in Figures 1 and 3. Since coal is usually stored near its combustion site, the fly ash found in the immediate to proximate vicinity of coal-burning facilities is very



**Figure 5.** Stoker-coal fly ash particulate. (Magnification 40x.)



**Figure 6.** Oil fly ash. (Magnification 40x.)

often mixed with coal particles (Figure 4). These are rather easily recognized by their generally smoother surface, which may in some cases appear dull but oily. Such windblown coal dust seriously increases local air pollution but is often overlooked because of the more obvious emission of carbon as a smoke plume. The particulate produced by stoker coal (Figure 5) is cusped, probably because of the preferential downward direction of burning in the stoker-fired furnace or boiler.

Oil burning produces a characteristic field of particles somewhat smaller than those produced by coal burning. These particles (Figure 6) are remarkably uniform in size distribution—a property that remains seemingly independent of the type of burner used, except when a malfunctioning burner produces a large volume of carbon soot from which very small particles aggregate to form chain or brush-heap-like, low density clumps. Careful probing with a filament may reveal such properties and aid in the identification of coal or oil soot.

### **Coke and Coke Fly Ash**

The burning of coke produces particulate as shown in Figure 7, whereas coke itself (Figure 8) looks glossy and appears, under microscopic examination, to be made up of the following:

1. Coke balls: shiny spheres, especially prominent in petroleum coke.
2. Coke char: flat flakes irregular in shape.
3. Coke glance: shiny flat surfaces in which some cell structure is visible.

A very common mixture is that of particulate coke and coal that arises from air streams over a common storage area such as supply yards or from coking operations that use coal as starting material. Here the degassed coke appears much shinier than does coal, whose surface is coated with amorphous tars. It should be noted that a method exists for separating coke and coal microscopically, based on the specific reflectance of a large population of particles.<sup>1</sup> Such solid fuel samples also lend themselves to separation by x-ray diffraction, described later in this chapter.

### **Other Combustion-Related Particulates**

Since many power plants have already been converted to the combustion of natural gas, with marked subsequent improvement in the quality of community air, it is interesting that even this advance in technology may be an occasional source of a product called gas soot, which is unlike most previously discussed



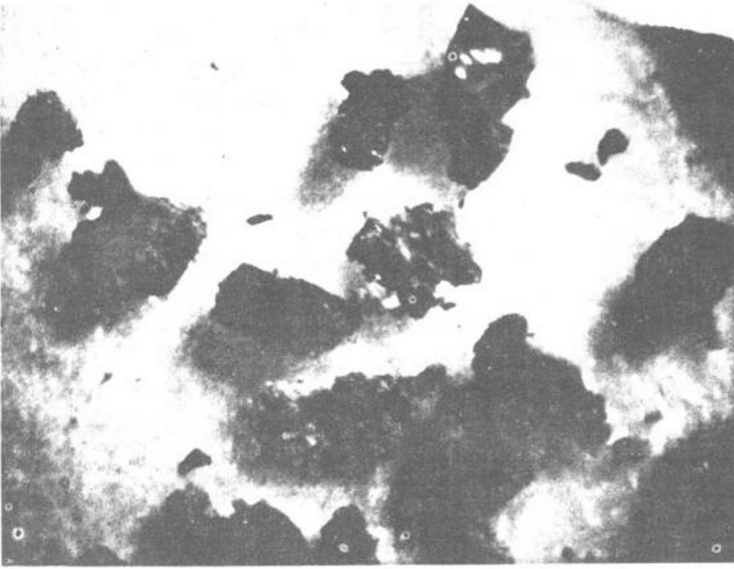


Figure 7. Coke fly ash particulate. (Magnification 40x.)

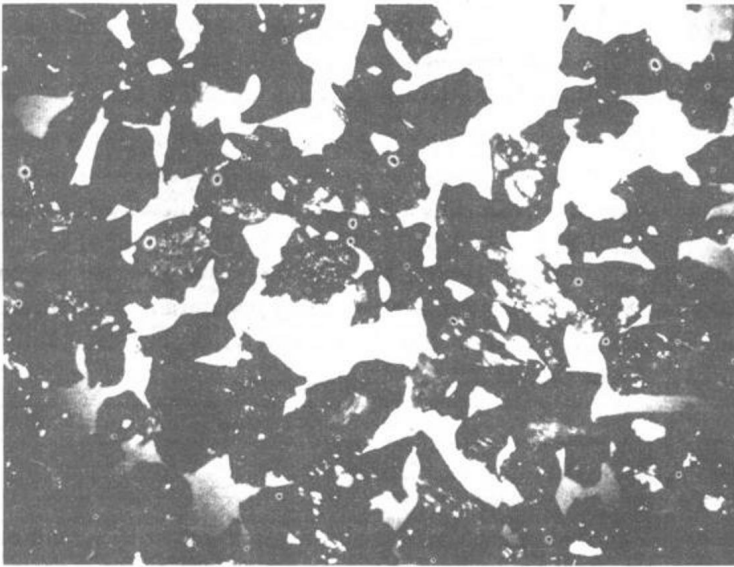


Figure 8. Coke particulate. (Magnification 40x.)