Analytical Chemistry of Aerosols

ANALYTICAL CHEMISTRY OF AEROSOLS

Edited by

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ANALYTICAL CHEMISTRY OF AEROSOLS

The Editor

Professor Dr. Kvetoslav Rudolf Spurny was Head of the Department of Aerosol Chemistry at the Fraunhofer Institute for Environmental Chemistry and Ecotoxicology in Germany from 1972 to 1988. He has retired but is still working as an aerosol chemist. Prior to 1972, he was an environmental chemist at the Institute for Occupational Hygiene in Prague (1952 to 1956) and Head of the Department of Aerosol Sciences at the Czechoslovak Academy of Sciences in Prague (1957 to 1972). He was a visiting scientist at the National Center for Atmospheric Research, Boulder, CO, U.S.A. (1966 to 1967) and visiting scientist at the Nuclear Research Center, Fontenay aux Roses, France, in 1969.

Dr. Spurny obtained his Diplomate in Physics and Chemistry from Charles University, Prague, in 1948; a Ph.D. in chemistry at the same university in 1952; and a C.Sc. as a Candidate of Chemical Sciences at the Czechoslovak Academy of Sciences in Prague in 1964.

Professor Spurny is a member of the American Chemical Society, American Association for the Advancement of Science, American Association of Aerosol Research, British Occupational Hygiene Society, the New York Academy of Sciences; and was president of the Association for Aerosol Research from 1983 to 1984. He has written six books on aerosols and over 150 original publications in aerosol physics and chemistry. He was recipient of the David Sinclair Award in Aerosol Sciences in 1989.

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Acknowledgments

The editor is extremely grateful to all the contributors to this book. Their reviews build a mosaic together that illustrates the state of art in the methods for chemical analysis of aerosols at the end of the 20th century.

He would also like to thank the publishers, who have, with great perseverance, enthusiasm, and patience, brought this book to fruition. In doing so, they have contributed to the development of atmospheric environmental science.

What Is an Aerosol?

An assembly of liquid or solid particles suspended in a gaseous medium long enough to be observed and measured; generally about 0.001 to 100 μm in size (K. Willeke and P. A. Baron in *Aerosol Measurement*, Van Nostrand, Reinhold, New York, 1993).

The designation *aerosol* was coined by F. G. Donnan in about 1918 and introduced in the meteorological literature in 1920 by A. Schmauss (The chemistry of fog, clouds, and rain. *Umschau* 24: 61–63, 1920).

Introduction

During the "classical" period of aerosol science, i.e., before the 1960s, only physical properties of aerodispersed systems were of interest and only physical parameters of particle clouds and of single particles were measured. Only later, mainly since the 1980s, has interest in physicochemical and chemical properties of aerosols increased.

There were several reasons for this development. In the fields of environmental hygiene, medicine, and toxicology, the importance of the chemical composition and chemical properties and interactions of inhaled "bad" aerosols had been recognized. In the various fields of high-technology, which use aerosol systems and their reactivities to produce important materials, the importance of aerosol chemistry and chemical aerosol analysis has been discovered.

Furthermore, the chemistry and chemical composition of aerosols are of great, and often basic, importance in several other fields. The chemistry of atmospheric aerosols is involved in cloud physics processes, such as condensation, evaporation, ice crystal formation, etc. Modern clean-room technologies require almost "aerosol-free" atmospheres. Even very low concentrations of very small particles are "dangerous" for production processes. The knowledge of the chemical composition of these particulate air contaminants is helpful in estimating and finding air contamination sources.

Other fields in which chemical composition of aerosols plays an important role are the applications of medical aerosols and basic research in animal inhalation toxicology. Basic as well as applied research and control strategies in indoor and outdoor atmospheric environments could not progress without well developed and effective methods for chemical aerosol analysis.

The great progress in chemical aerosol analysis was enabled by a fast, intensive, and successful development and improvement of analytical chemistry. Modern physical, physicochemical, biochemical, and biophysical analytical procedures have made it possible to analyze ppm, ppb, ppt, and even smaller amounts of substances in aerosol samples, and even single aerosol analysis has become realistic and useful.

Generally speaking, there exists only one analytical discipline — analytical chemistry. Its application is very broad, and for several applications, smaller or greater methodological sampling and other modifications are necessary. For this reason, it seems reasonable to use the term *chemical analysis of aerosols* and/or *analytical chemistry of aerosols*.

Methods of chemical analysis of aerosols are continuously developing and improving. This is probably why it is difficult to compile a handbook or a textbook dealing with the analytical chemistry of aerosols. Nevertheless, it is worth mentioning some of the important monographs in this field, such as the book by Malissa and Robinson, *Analysis of Aerosol Particles by Physical Methods*, published by CRC Press in 1978, the monograph by Spurny, *Physical and Chemical Characterization of Individual Airborne Particles*, published by Ellis Horwood, Chichester, in 1986, and the important book by J. P. Lodge, *Methods of Air Sampling and Analysis*, published in 1988 by CRC Press.

I have tried in this book to encourage several well-known colleagues from the field of aerosol analysis to contribute their work. Our task was to show the existing procedures and trends in the measurement and analysis of atmospheric aerosols. We hope our aim has been at least partially fulfilled and that we have also presented some new or experimental methods for chemical aerosol analysis. The fact that the authors are from different continents, demonstrates that modern analytical techniques are now available for aerosol analysis in all technically well-developed countries.

Kvetoslav R. Spurny
Schmallenberg Germany
November 1998

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Kvetoslav R. Spurny

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1.1 INTRODUCTION

The period of classical aerosol physics (Spurny, 1993) was characterized by the use and exploitation of measurement and experimental techniques common during that time. In my opinion, the classical period of aerosol science research lasted approximately until the middle of the 20th century, ending with the publication of the *Mechanics of Aerosols* (Fuchs 1955, 1964). No lasers, no computers, and no spectroscopic analytical tools were available during this period.

1.2 THE EARLY DAYS

The existence of unpleasant and harmful particles in the outdoor and indoor atmosphere was referred to in very early literature. For example, the Romans complained of the foul air in ancient Rome. Serious particulate air pollution led to the prohibition of coal burning in London in 1273, followed

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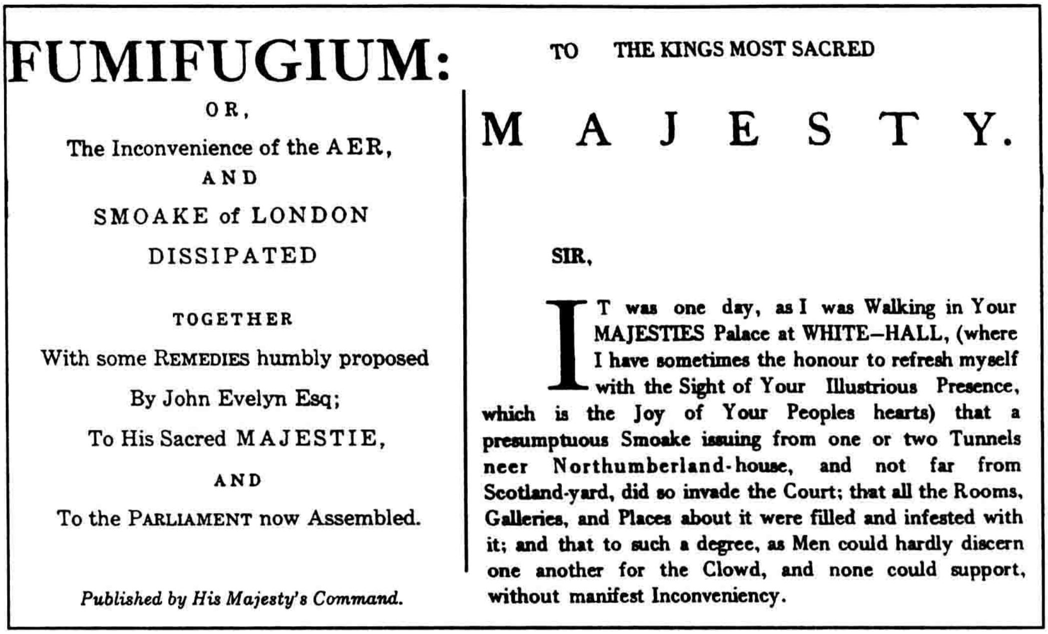

FUMIFUGIUM:

OR,

The Inconvenience of the AER,

AND

SMOAKE of LONDON

DISSIPATED

TOGETHER

With some REMEDIES humbly proposed

By John Evelyn Esq;

To His Sacred MAJESTIE,

AND

To the PARLIAMENT now Assembled.

Published by His Majesty's Command.

TO THE KINGS MOST SACRED

MAJESTY.

SIR,

IT was one day, as I was Walking in Your MAJESTIES Palace at WHITE-HALL, (where I have sometimes the honour to refresh myself with the Sight of Your Illustrious Presence, which is the Joy of Your Peoples hearts) that a presumptuous Smoake issuing from one or two Tunnels neer Northumberland-house, and not far from Scotland-yard, did so invade the Court; that all the Rooms, Galleries, and Places about it were filled and infested with it; and that to such a degree, as Men could hardly discern one another for the Clowd, and none could support, without manifest Inconveniency.

FIGURE 1.1 The title page of John Evelyn's *Fumifugium.*

by a Royal Proclamation by Edward I in 1306. In 1661, the first major tract regarding particulate air pollution was submitted to Charles II by John Evelyn (Lodge, 1969). His *Fumifugium...* (Figure 1.1) contained a graphic description of pollution in London. However, the very birth of aerosol science and aerosol measurement did not occur until the second half of the 19th century. It was closely combined with initial developments in colloid chemistry. During this period, the first observations and simple measurement of fine particles in the atmosphere occurred (Podzimek, 1985, 1989).

Following Podzimek's review (1985) H. Becquerel hypothesized about the existence of fine particles in the air, the *condensation nuclei*, in 1847. Their existence was confirmed about 30 years later by the experiments of Coulier (Coulier, 1875). Between 1880 and 1890, John Aitken made several observations that demonstrated the fundamental role of dust particles in the formation of clouds and fog. He evaluated Coulier's experiments on condensation phenomena and his condensation nuclei hypothesis and recognized Coulier as the first to show the important part played by nuclei in the cloudy condensation of water (Aitken, 1880, 1881, 1888, 1889). Aitken developed the first expansion-type dust chamber, and in 1887 also developed the first out-of-pocket condensation nuclei counter. J. Aitken (Figure 1.2), who was born in Falkirk, Scotland in 1839 and died in 1919, built this instrument himself. It is interesting that the next generation of Aitken instruments were not produced and commonly used until the 1930s in Germany (Scholz, 1931).

Of equal importance in the middle of the 19th century were the observations and simple measurements performed by John Tyndall, who was born in 1820 in Ireland and died in 1893 in England. Tyndall studied in Marburg, Germany with W. Bunsen, and later worked with Michael Faraday, eventually becoming his successor. His observation, that dust and smoke in a room are easily detectable from scattered light when a beam of sunlight enters the room, was used in 1856 by Faraday to indicate the presence of colloidal particles in liquids. A decade later, Tyndall extended the method to detect aerosols and first applied it to the detection of the particulate pollution in London air (Tyndall, 1871; Gentry, 1996). Tyndall was not only the father of tyndallometers and nephelometers, of ultramicroscopes and optical particle counters, but also the indirect inventor of thermal precipitators. In 1870 he reported the observation of a narrow region above a heated body

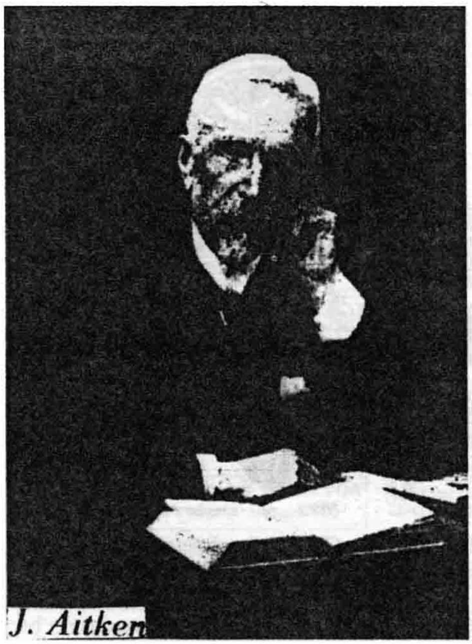

FIGURE 1.2 John Aitken (1839–1919). The founder of atmospheric aerosol science and aerosol measurement techniques.

in a dusty atmosphere. Several years later Lord Rayleigh (1882), Lodge (1883), Lodge and Clark (1894), as well as J. Aitken (1894) observed that a dark space completely surrounded a heated body. This was the discovery of the thermophoretic effect (see also Fuchs, 1971).

Some early measurements exist, prior to the 1900s, of microbiological aerosol particles in room air (Singerson, 1870–1874; Preining, 1996). However, the broader development of aerosol measurement methods and equipment is dated after 1900 and primarily after 1920. During this period the negative health effects of industrial aerosols and dusts were recognized (Sinclair, 1950; Davies, 1954; Drinker and Hatch, 1954). The measurement of aerosols in general, and specifically industrial dust, can be made while particles are airborne, or particles can be collected on a surface and measured physically or chemically. In the early 1920s, as well as during the entire period before the 1960s, these were the preferred collection methods in the industrial hygiene field.

1.3 THE MEASUREMENT PHILOSOPHY

I began my aerosol measurement work at the end of the 1940s and can remember very well the philosophy of dust measurement at that time. The most important reason for dust measurement in the workplace was the high incidence of silicosis in industry and in the mines. An important observation of the high mortality of hard-rock miners, accredited to Agricola (George Bauer, *De Re Metalica*), first appeared in 16th century literature (Drinker and Hatch, 1954). The recognition that silica (quartz dust) produces the characteristic pulmonary diseases of pneumoconiosis and silicosis dates to the latter 1920s (Collis, 1926).

A broad need for the measurement of industrial dust in the workplace was recognized before, but primarily after, the Second World War. What kinds of physical methods for dust sampling and for sample evaluation were available at that time? Generally speaking, knowledge of inertia particle separation, filtration, thermophoresis, and, somewhat later, particle separation in electrostatic fields already existed. However, very few sample evaluation methods existed, even though light microscopy methods that could be used for particle counting and sizing were available. Therefore, the