

ANALYTICAL METHODS APPLIED TO AIR POLLUTION MEASUREMENTS

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PREFACE

This volume brings together the leading scientists pioneering in the development of improved techniques to measure the properties of particulate and gaseous air pollutant species.

Their work represents the latest technological advances in chemistry, physics, and electrical engineering in the development of instrumentation to characterize undesirable components in the atmosphere. These include the application of lasers and other electro-optical devices to measure pollutant concentrations across both open paths in the atmosphere and power plant smoke stacks *without physical sampling of the pollutant*.

The broad range of subjects includes thorough discussions of the rapidly advancing technique of gas-filter correlation spectroscopy, comparison of classical with newly developed X-ray fluorescent methods applied to the measurement of elemental composition of particles, and advances in techniques for extracting gaseous and particulate pollutants from power plant stacks. The topics further include the applications of chemiluminescent techniques to measure ambient concentrations of gaseous pollutants, and descriptions of two new techniques to measure sulfuric acid vapor at ambient concentrations.

Fourteen chapters are organized in three sections: Section I deals with methods to measure gaseous pollutants at ambient concentrations, Section II relates to procedures to characterize the properties of particulates in the atmosphere, and Section III describes instrumental methods for analysis of gaseous and particulate pollutants at source concentrations.

The total book is introduced by Dr. A. P. Altshuller, who also introduced the symposium at the 165th National Meeting of the American Chemical Society in Dallas, Texas, April 8-13, 1973, from which this

book emanated. We are fortunate to have his plenary lecture here, as it outlines the Environmental Protection Agency's requirements for air pollution monitoring in the 1970s and suggests various avenues that may be explored to meet these stringent requirements. This, in fact, sets the tone for the book.

It is felt that the reader will find this text useful as a review of the latest developments in air pollution measurement techniques, and that perhaps he may be inspired toward the development of other improved physical methods for characterizing the condition of our atmosphere.

The editors wish to express their appreciation to all who prepared manuscripts for this volume.

July 1974

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CONTENTS

Introduction	1
<i>A. P. Altshuller</i>	

SECTION I

TECHNIQUES TO MEASURE GASEOUS POLLUTANTS AT AMBIENT CONCENTRATIONS

1	Role of Gas Chromatography in Air Pollution Monitoring	17
	<i>R. Villalobos</i>	
2	Application of Chemiluminescence to the Measurement of Gaseous Pollutants	43
	<i>J. A. Hodgeson, W. A. McLennny, R. K. Stevens</i>	
3	Diode Lasers for Pollutant Monitoring	55
	<i>E. D. Hinkley and A. R. Calawa</i>	
4	A Chemiluminescent Approach to Measurement of Strong Acid Aerosols	71
	<i>T. G. Dzubay, H. L. Rook, R. K. Stevens</i>	
5	A New Technique to Measure Sulfuric Acid in the Atmosphere	85
	<i>P. S. Mudgett, L. W. Richards, J. R. Roehrig</i>	
6	A Comparative Review of Open-Path Absorption Methods for Ambient Air Pollutants	107
	<i>W. A. McLennny, W. F. Herget, R. K. Stevens</i>	

SECTION II

TECHNIQUES TO MEASURE CHEMICAL AND PHYSICAL PROPERTIES OF PARTICLES IN THE ATMOSPHERE

- 7 Application of X-Ray Fluorescence Techniques to Measure Elemental Composition of Particles in the Atmosphere 123
*J. M. Jaklevic, F. S. Goulding, B. V. Jarrett,
J. D. Meng*
- 8 An Instrument for Continuous Monitoring of Nitrate in Atmospheric Particulate 147
J. N. Driscoll and L. J. Forney
- 9 Application of an Oscillating Quartz Crystal to Measure the Mass of Suspended Particulate Matter . . 163
R. L. Chuan

SECTION III

TECHNIQUES TO MEASURE POLLUTANTS FROM STATIONARY AND MOBILE SOURCES

- 10 Cross-Stack Measurement of Pollutant Concentrations Using Gas-Cell Correlation Spectroscopy 193
D. E. Burch and D. A. Gryvnak
- 11 Absorption Spectroscopy Applied to Stationary Source Emissions Monitoring 233
H. C. Lord
- 12 Remote Sensing of SO₂ in Power Plant Plumes Using Ultraviolet Absorption and Infrared Emission Spectroscopy 245
H. M. Barnes, Jr., W. F. Herget, R. Rollins
- 13 A Review of Available Techniques for Coupling Continuous Gaseous Pollutant Monitors to Emission Sources 267
J. B. Homolya
- 14 Application of a Beta Gauge to the Measurement of Mass Emissions in a Coal-Fired Power Plant 285
J. W. Davis

INTRODUCTION

INSTRUMENTS FOR AIR POLLUTION MONITORING DURING THE 1970'S

A. P. Altshuller

INTRODUCTION

Progress in the development of new instruments for air pollution measurements has been much improved during recent years. I believe this progress can be attributed in good part to the resources made available by the Air Quality Act of 1970 to the Environmental Protection Agency.

The program has carried R/D from sensor development through field evaluation of prototype instruments. We have worked closely with instrument companies to encourage rapid commercialization and marketing of prototype instruments that performed satisfactorily. As a result, flame photometric, gas chromatographic and chemiluminescent analyzers have become available for sulfur dioxide, hydrogen sulfide, organic sulfur compounds, hydrocarbons, methane, carbon monoxide, ozone, nitric oxide and nitrogen dioxide. Research is in progress on instruments for particle mass, size and composition.

The obvious difficulty in attempting predictions is the inability to see beyond the horizon. Occasionally a method with little if any prior history of utility will burst forth as a highly versatile instrumental technique. A more satisfactory approach is to concentrate on future needs rather than attempt to estimate the details of progress on individual analytical techniques. Therefore, this chapter will concentrate mainly on research needs at present and in the immediate future. Several major areas have

been selected for discussion. No comprehensive listing of needs for specific instruments will be attempted.

PORTABLE AIR QUALITY DOSIMETERS

Community health studies, to be of the greatest effectiveness, should be accompanied by air quality measurement capabilities optimized to meet specific research needs. Past community health studies often have had to use the monitoring results from networks set up for other purposes. More recently monitoring sites have been set up to meet the requirement of specific health studies (CHESS).

Participants in health studies actually are exposed to a number of air quality environments, only one of which is the community atmosphere ordinarily monitored. The community air quality monitoring networks represent a number of compromises. Although a number of pollutants ordinarily are measured at each site, it does not follow that a site selected as appropriate for monitoring of carbon monoxide or sulfur dioxide can be equally appropriate for monitoring ozone or nitrogen dioxide. The practical limitation on number of sites often makes it difficult or impossible to construct concentration isopleths with sufficiently high resolution to satisfy particular needs. All of these problems are compounded if a monitoring network is expected to provide concurrently measurements for emergency episodes, trends in pollutant concentrations, health studies or transport and transformation of pollutants research. These difficulties again suggest the need to develop measurement techniques specifically tailored to health research requirements.

In health studies the integrated dosages to which participants are exposed are of great importance. These dosages are accumulated when individual participants are exposed not only to community atmospheres but also to the atmospheres in their homes, work and recreational environments and in movement between these various environments. The most practical approach to meeting these requirements is the development of personal air quality dosimeters or personal monitors.

Such dosimeters might be fountain pen or similar sized instruments carried on the person of individual participants. Such equipment is not presently available. Personal monitors the size and weight of

portable radios or attache cases are much closer to the present state-of-the-art in air quality instrumentation. A number of principles already successfully developed appear directly applicable to monitoring instruments in this size and weight range. Such monitors could be easily operated on line or battery power at a convenient location within home, office, shop, or motor vehicle. Two such analyzers might be provided per participant to provide for maintenance, calibration and other requirements.

Measurements for emergency episodes or transport research studies require rapid data handling justifying real time analyzers and signal processing. Health studies often do not require the same feed-back times. A simple magnetic tape system that permits mailing or periodic pickup might be satisfactory. Calibration systems can be built into analyzers in conventional monitoring sites. Unless such calibration systems can be readily miniaturized, an acceptable alternative could be periodic calibration at a central laboratory or mobile laboratory facility. Integrated measurement techniques with 1- to 24-hour integration times should be acceptable. A prime objective should be providing workable instruments in the shortest time possible so they can be utilized as soon as possible in community health studies.

Because individual health studies often are concerned with the impact of one or a few pollutants, multipollutant analyzer capability probably is not as pertinent as in other applications. Pollutants having high priority are sulfur dioxide, nitrogen dioxide and ozone. Measurement of particulate species probably is more practically approached by personal mini-samplers with subsequent laboratory analysis when 24-hour average or longer integration intervals are appropriate.

The above discussion is not meant to offer definitive criteria or guidelines for personal air quality monitors but rather to stimulate consideration of the best approaches to meeting these specialized needs.

PARTICLE MASS, SIZE AND COMPOSITION

Although a variety of real time air quality and emission measurement instruments exist, very few real time or even 1- to 2-hour average monitoring instruments exist for particles. About the only instrument now being placed in monitoring networks that responds

to a property of particles is the integrating nephelometer for measurement of visibility. Ordinarily sampling is done on a 24-hour average basis, with weighing to determine mass or laboratory analysis to determine chemical composition. By using x-ray fluorescence techniques 2-hour average samples often can be analyzed satisfactorily. Particle sizing can be done with various impactors requiring subsequent weighing and chemical analysis of the particles collected on the several stages. Electrical mobility and optical particle sizing equipment are available for sizing by particle number on a real time basis, but only research type instruments are available (Whitby Aerosol Analyzer, Rayco optical single particle counter) and these instruments plus an impactor are necessary to cover the 0.01-10 μg range.

Such research real time particle size analyzers do not provide particle mass directly nor permit chemical analyses. Therefore a group of various particle size analyzers, impactors, and filters must be used to accumulate all of the data needed for particle mass, size and composition in comprehensive field studies. In terms of monitoring needs for a control program the usual request is to simplify the measurements to one or two techniques that are simple and inexpensive in field use. Unfortunately such requests can be inconsistent with scientific requirements. Particles as they are emitted from sources and as they reside in the atmosphere undergo complex chemical and physical transformations. Gases emitted from sources are transformed to particle species in the atmosphere. Under these circumstances, the ability to relate air quality for particles to source emission control strategies can be resolved only by going progressively from the complex to the less complex measurement approach.

What I am suggesting is that comprehensive measurement programs are needed in order to determine exactly where simplifications can justifiably be made. Furthermore, even with these simplifications I believe it unlikely that the degree of simplification desired by control officials can be achieved. Whether this prediction is correct or not, it is important that the measurement techniques be developed and utilized as rapidly as possible to determine on the basis of sound experimental evidence the optimum approach to improved air quality of particulate pollutants.

The present experimental results indicate that a substantial fraction of the particle volume and

mass occurs in the particle size range around and below 1 μm . The particles in this range result from condensation of photochemically formed reaction products on very small nuclei followed by coagulation of very small particles particularly onto preexisting particles in the 0.1-1 μm range. Other small particles such as lead and bromine aerosols from vehicular exhaust also coagulate to form particles in this range. Particles larger than 1 or 2 μm appear to arise from primary emission sources or fugitive dusts. Silicates, aluminum, magnesium and much of the iron, and certain other metals in various forms are found in the particles above 1 or 2 μm . Certain other elements appear to be distributed more uniformly through the particle size ranges.

The significance of particle size has several aspects. Visibility reduction as measured by the integrating nephelometer and other techniques are closely related to particles between 0.1 and 1 μm . Laboratory studies on inhalation toxicity of sulfates indicate an increased effect in the range at or below 1 μm . However, the respirable range is often taken at 5 μm and below. The available size results for urban aerosols characteristic now indicate a maximum bimodal distribution with a maximum in the volume distribution below 1 μm and a minimum between 1 and 2 μm .

Most of the aerosol measured below 1 μm appears not to have originated as aerosol but to have formed by atmospheric reactions converting sulfur dioxide to sulfate, nitrogen dioxide to nitrate and organic vapors to organic aerosols. These species predominate over lead aerosols and other primary aerosol emissions in the <1 μm range. If so, it is essential to be able to associate quantitatively the air quality composition of these aerosol species with the control of emissions of the gaseous pollutant from which they are formed.

Since the control must be at the source and must be specific to chemical species, *i.e.*, sulfur dioxide, hydrocarbons, or lead, the relationships between degree of control and manifestation seem essential. For example, how much must atmospheric sulfates be reduced to achieve significant improvement in visibility through what degree of control of sulfur dioxide at emission sources?

It seems necessary to be able to measure mass in at least two preselected size ranges and to be able to determine chemical composition of the particles in these size ranges. Concurrently, visibility should be correlated with size and composition.

Since aerosol volume appears to be a function of relative humidity based on laboratory and field observations, a significant fraction of the mass of submicron liquids may be associated with condensed water at higher relative humidities. Other volatile species may be associated with the submicron particles. Volatile constituents can be lost on collection in filters on impactor surfaces. Therefore, *in situ* particle measurements may prove to give higher levels of submicron particles than do methods based on collection on surfaces.

At the present time organic aerosols are particularly poorly characterized. The only routine measurement made is of benzene-soluble material from glass fiber filters. In addition to possible losses of volatiles off filter surfaces, benzene will extract only a part of the organic aerosols. Polar organic aerosol materials are inefficiently extracted by benzene. Therefore, it appears that the available results significantly underestimate the mass of atmospheric organic aerosols. Another aspect of the problem associated with organic aerosols is the differing abilities of various organic vapors to participate in aerosol formation.

Work is underway to develop methods for determining sulfuric acid, sulfate and nitrate. Total sulfur can be determined by x-ray techniques, as can lead and some other species present in the submicron range. Since continuous gas analyzers are accepted as essential for gaseous pollutants, it would appear that continuous or semicontinuous analyzers for sulfur, nitrogen and organic particulates will come into demand. At present the emphasis continues to be directed toward improving the reliability of sampling in the field, with much of the analysis conducted at a central laboratory.

For particles with metastable characteristics, *in situ* sizing and chemical analysis would be ideal. *In situ* chemical analysis of individual particles should offer a real challenge to our analytical and instrumental ingenuity.

ELECTROOPTICAL MEASUREMENTS

Application of electrooptical techniques to measurement of air pollution is attractive for several reasons: (1) it avoids use of liquid or gaseous reagents, (2) it provides the potential for multi-pollutant analysis, (3) it provides *in situ* capabilities