ENVIRONMENTAL POLLUTION INSTRUMENTATION

Edited by
R. L. Chapman

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Selected Papers from Symposia Presented
Under the Auspices of
The Analysis Instrumentation Division
INSTRUMENT SOCIETY OF AMERICA

Edited By
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FOREWORD

One of the charter functions of the Instrument Society is to provide essential forums for exchange of information and uninhibited discussion between those who use instruments and those who contrive them. This collection of papers was selected from recent Analysis Instrumentation Division Symposia. It includes presentations by both users and manufacturers of air and water pollution instruments as well as one paper on the most recently recognized pollutant - noise. The papers are arranged topically with air first, then water and finally noise. Subject and author indexes are provided at the end.

Three years ago, the Air Pollution Instrumentation Committee of the Analysis Instrumentation Division published a similar monograph, edited by Donald F. Adams of Washington State University. That book was well accepted and apparently filled a need. It is hoped that this new monograph also serves a useful purpose and will, in effect, broaden the influence of the original forum from which the material came.

The editor recognizes the contributions of the Air Pollution Instrumentation Committee Chairman, John W. Scales of Union Carbide Corporation, his assistant, Gordon Ortman of the U.S. Public Health Service, and the several other Analysis Instrumentation Division session developers who initiated the programs from which these papers were selected. Appreciation is also expressed for the labor and support of Mr. Glenn F. Harvey, Manager, ISA Publication Services, and his staff; and for the help and encouragement of Dr. Lewis Fowler, Coordinator of Technical Publications of the Analysis Instrumentation Division.

The contributions of the authors, of course, are what made the publication possible and are duly acknowledged.

Robert L. Chapman, Editor
Associate Director
Analysis Instrumentation Division
Instrument Society of America

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INSTRUMENTATION FOR MONITORING AIR POLLUTANTS*

A. P. ALTSHULLER**

INTRODUCTION

The increased interest and concern about control of air pollution at all levels of government has significantly increased the need for reliable instrumentation for measurement of pollutants both in the atmosphere and in emissions from automobiles and stationary sources. Public Law 90-148, referred to as the "Air Quality Act of 1967," specifically mentions instrument needs. Section 104(b) entitled, "Research Related to Fuels and Vehicles," contains the following statement: "In carrying out the provisions of this section the Secretary may (1) conduct and accelerate research and development of low-cost instrumentation techniques to facilitate determination of quantity and quality of air pollutant emissions." Furthermore, Section 306 of this law cites, among the reports required by the Congress, a report on "the development of quantitative and qualitative instrumentation to monitor emissions and air quality."

ORGANIZATIONAL STRUCTURE

The Secretary of Health, Education, and Welfare is responsible for implementing provisions of this law. The organization within the Department of Health, Education, and Welfare responsible for conducting the operational aspects of air pollution activities is the National Air Pollution Control Administration (NAPCA). The Division of Chemistry and Physics of this Administration has as one of its responsibilities, conducting instrument research and development both in-house and by contract.

At present we are carrying out a modest in-house and contract program on instrument development. A small number of instrument research projects are supported by research grants from the

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**U.S. Department of Health, Education, and Welfare; Consumer Protection and Environmental Health Service; National Air Pollution Control Administration, Division of Chemistry and Physics; Cincinnati, Ohio.

National Air Pollution Control Administration (NAPCA). In a joint research effort by the automotive and petroleum industries and NAPCA, a few of the projects are concerned with instrumentation. The Edison Electric Institute and NAPCA are concerned with development of improved LIDAR equipment. Despite these efforts, requirements for improved instrumentation, especially as air pollution efforts are conducted increasingly at the local level, are so great that we are far from meeting the varied needs.

General criteria for improved instrumentation are as follows:

1. Simplicity of construction and operation;
2. Reliability and reproducibility of operation over long time intervals;
3. Adequate sensitivity to meet requirements of specific applications; and
4. Specific response to pollutant or pollutants of interest.

Additional criteria apply to continuous air monitoring operations:

1. Unattended operation;
2. Real-time data output;
3. Systems capable of monitoring two or more pollutants concurrently by the same measuring technique;
4. Ability to monitor an increasingly wide range of pollutants; and
5. Capability for direct input to computers.

Unfortunately, few of the currently available instruments for atmospheric or emission analysis meet all or even most of these criteria.

One way of outlining instrument needs by areas of application is given below with examples.

I. Emission Analysis
  A. Vehicular
    1. Automotive
      a. Research and development
        -aldehyde and organic oxygenate instrumentation
      b. Certification and surveillance
        -simplified FID, gas chromatographic, and nitrogen oxides instruments
      c. Inspection equipment
        -low-cost, simple operation for total hydrocarbons and carbon monoxide, and potentially for nitrogen oxides (unless visual inspection is used)
    2. Diesel
      a. Improved smoke meters
      b. FID equipment directly applicable to diesel emissions

      - c. Odor instruments to replace odor panels
  - B. Stationary Sources
    - 1. In-stack
      - a. Particulate monitoring
      - b. Sulfur dioxide and nitric oxide
    - 2. Remote Stack Monitoring
      - a. Particulates - LIDAR
      - b. Sulfur dioxide - IR emission or UV absorption
      - c. Nitric oxide - Raman or IR
- II. Atmospheric Analysis
  - A. Area Monitoring
    - 1. Point Sampling Analyzers
      - a. Single component - ozone or nitric oxide
      - b. Multicomponent systems
    - 2. Long-path Spectrophotometric Analyzers
  - B. Personal Monitoring Instruments
    - Very small, lightweight dosage equipment

The concentration ranges of interest are wide. Carbon monoxide in automobile exhaust is in the one percent range; hydrocarbon and nitrogen oxides in automobile exhaust, and sulfur dioxide and nitrogen oxides in stack emissions are in the 0.01 to 1.0 percent range; carbon monoxide in the atmosphere is in the 0.1 to 100 ppm range; and other atmospheric pollutants range from 0.001 to 1 ppm. Thus, the range of concentrations spans more than seven factors of ten. In some instances, individual instruments with at least thousandfold ranges are needed for convenient monitoring operations.

The present instrumentation for monitoring of emissions particularly emphasizes the non-dispersive infrared principle. For atmospheric analysis, conductiometric, coulometric or galvanic, colorimetric, flame ionization, and non-dispersive infrared are all used or compete for application to individual pollutants. It is impractical to consider the limitations of each existing instrument and the potential or limitation of various alternative instrumental approaches; therefore, a selection of examples will be used to illustrate some possibilities and problems in future instrument development.

AIR QUALITY INSTRUMENTATION

Our present air quality instrumentation represents the instrument technology of ten or fifteen years ago. As a result, we now face the following problems:

1. The oxidant instruments do not measure ozone specifically. The chemiluminescent type, ozone instrument which presently is a laboratory type analyzer with respect to its operation and reliability is being modified to provide an acceptable air moni-

toring instrument.

2. The carbon monoxide instrument is not only specific for carbon monoxide but also responds to water vapor and carbon dioxide, either introduced inadvertently into the cell or included in the atmospheric sample. Its sensitivity and reliability are completely inadequate below five ppm and probably marginal between five and ten ppm. But most of the carbon monoxide concentration values are below ten ppm and more will be so as control proceeds. Based on our past work, we have developed a successful gas chromatographic analyzer that can replace both the carbon monoxide and methane analyzers.

3. Nitric oxide is analyzed with an oxidation step followed by colorimetric reaction. Because the oxidation step has always been incomplete, we may consistently underestimate ambient nitric oxide levels. We have hopes of developing a direct method of analysis of nitric oxide by a flame emission or gas chromatographic technique.

4. Nitric oxide and nitrogen dioxide are both presently analyzed colorimetrically by a procedure due to Saltzman. However, the stoichiometric factor involved has been under constant debate, with Stratman maintaining 1.0 and Saltzman 0.7. Obviously, absolute quantitative determinations cannot be obtained until either this difference is resolved or a new instrument is developed.

Many substances of interest are not monitored in our present CAMP systems; these include hydrogen sulfide, formaldehyde and other oxygenated hydrocarbons, ethylene and other individual hydrocarbons, and ammonia. We have a number of approaches available for analysis of these substances either by extension of present procedures or by development of new instruments.

Although I wholeheartedly support the concept of multicomponent analyzers, I should point out the following limitations of several approaches:

1. Gas Chromatography - Excellent for carbon monoxide, carbon dioxide, hydrocarbons, and peroxyacyl nitrates. Recent work indicates potential for sulfur dioxide and hydrogen sulfide. Substrate and detector sensitivity limitations make it very difficult to presently measure nitrogen oxides, ozone and ammonia at atmospheric concentrations of interest; however, monitoring gas chromatographs are practical for a considerable number of the pollutant gases of interest.

2. Ultraviolet Spectroscopy (correlation technique) - Satisfactory for sulfur dioxide and nitrogen dioxide, and ozone is

a possibility. Nitric oxide and ammonia are other possibilities, but their ultraviolet bands are near the oxygen absorption region and quantitation for nitric oxide appears questionable, because of peculiar band characteristics.

3. Infrared Spectroscopy - Promising for ozone, sulfur dioxide, carbon monoxide, and peroxyacyl nitrates; poor for nitric oxide and nitrogen dioxide; possibly acceptable sensitivity for ethylene, acetylene and ammonia. However, the use of newly developed lasers may avoid interference difficulties for some molecules of interest such as nitric oxide.

4. Raman Spectroscopy - Sensitivity limited; only carbon monoxide looks like a possibility in atmospheric analysis.

5. Electron Impact Spectroscopy - No great advantage over other spectroscopic techniques except in vacuum ultraviolet region. Demonstration of marginal capability for atmospheric carbon monoxide which is in a window region. Water vapor, oxygen and nitrogen are severe interferences in this region.

6. Microwave Spectroscopy - High potential specificity, but sensitivity may be a limiting factor for many pollutants of interest. The practical ability to carry out quantitative analysis of gases by microwave spectroscopy remains to be demonstrated.

7. Mass Spectroscopy - Complex; sensitivity limited below one ppm; cannot analyze for carbon monoxide or ethylene in the presence of ethane or formaldehyde at atmospheric concentrations with medium resolution instruments. Nitrogen dioxide is difficult to do at all without extensive condition of inlet system. While photoionization mass spectrometers offer improved specificity, their limited sensitivity imposes constraints for practical usage in air pollution.

CONCLUSIONS

These comments should suggest that no single "black box" can be developed to replace single-component analyzers. We are more likely to need two and even three multicomponent instruments to cover six to ten pollutants of interest. It is also possible that no multicomponent instrument will ever be as satisfactory for certain pollutants as a specially developed, single-component instrument. In a number of instrument packages, selective adsorption or pretreatment may increase versatility.

We have no capability in terms of real-time analysis of any particulate material such as lead, sulfate, fluoride, or polynuclear aromatic hydrocarbons. If we need such instrumentation to provide measurements for criteria development, we should start the automation of laboratory procedures based on atomic absorption, flame emission, or other high sensitivity techniques.

A number of the instruments developed for ground-based air quality determinations should be capable of being made sufficiently compact and lightweight for determination of concentrations aloft by aircraft measurements.

It has never been shown that point source instruments are optimum for the measurement of air quality. Open-path instruments may possibly provide more representative results. We hope to develop open-path instruments for sulfur dioxide, nitrogen and ozone. Measurements using these instruments would be compared with present CAMP instrumentation. As an example, such equipment could be used for determination of nitrogen dioxide concentrations on and off freeways and also to prove whether the brown coloration in pollution layers can be attributed quantitatively to nitrogen dioxide.

Finally, there is a need to determine dosages of pollutants experienced by individuals in varying environmental situations through the development of very small and lightweight dosage instruments to be carried by volunteers in health studies.

METEOROLOGICAL INSTRUMENTATION FOR AIR POLLUTION APPLICATIONS*

HARRISON E. CRAMER**

ABSTRACT

Requirements for meteorological information in air pollution studies and control programs are outlined and basic components of meteorological data systems for industrial as well as urban applications are described. Examples of current measurement techniques are provided and areas in which these techniques appear to be deficient are specified.

INTRODUCTION

Meteorological measurements are an essential part of air pollution studies and air pollution control programs, because the transport and disposal of airborne waste products are primarily effected by the wind. Quantitative estimates of the capacity of the atmosphere for transporting and diluting waste products are thus critically dependent upon a satisfactory knowledge of the structure of the wind field within large volumes of air. The size of the volume varies from one to many hundreds of cubic miles, depending on whether one is concerned with the air pollution problems of a large urban complex or megalopolis or with the pollution from a single source such as a factory stack.

All meteorological variables exhibit large variations in both space and time. The energy spectrum of the wind speed is shown schematically in Figure 1. An approximate space frequency scale in cycles/km is shown at the top of the figure. Major energy inputs are associated with the various scales of atmospheric motion extending from the planetary waves of the general circulation through the large migratory pressure systems of the synoptic scale to the local wind systems of the mesoscale and microscale. The highest-frequency energy input to the spectrum

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arises from airflow over surface roughness elements such as uneven terrain, trees, and buildings. The input due to convection shown in Figure 1 signifies the contribution of large convective cells that typically develop over land surfaces in fair weather during the middle of the day. At night, the convection input is replaced by a slightly lower frequency input from gravity waves or inertial oscillations. Local wind circulations refer to thermally-driven airflows such as land-sea breezes and mountain-valley winds.

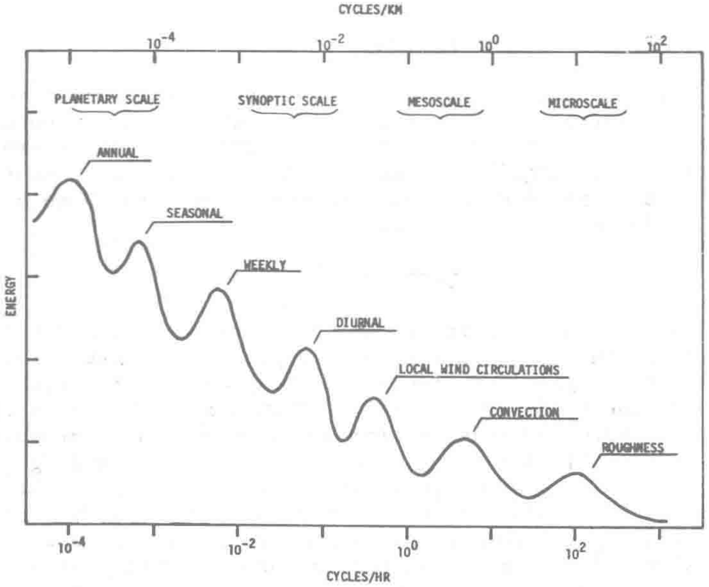

Figure 1. Wind energy spectrum for various scales of atmospheric motion.

Because of the broad time and space variability inherent in meteorological quantities and because of the large air volumes involved, the specification of meteorological measurements for air pollution studies and control programs poses numerous problems. The purpose of this paper is to describe the various types of meteorological information required in these applications, to provide examples of the data systems needed to satisfy these requirements, and to point out areas in which existing meteorological measurement techniques are deficient.

REQUIREMENTS FOR METEOROLOGICAL INFORMATION

Specification of the requirements for meteorological information in air pollution applications begins with a consideration of the generalized mathematical models used to predict the concentration fields downwind from various types of sources. The ground-level concentration downwind from a continuous point or volume source, for time periods of the order of one hour, is given by a mass continuity equation of the general form[1,2]:

$$\chi\{x,y,z=0;\ h,H,\tau\} = \frac{Q}{\pi\,\bar{u}\,\sigma_y\,\sigma_z}\left\{\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\right\}\left\{\exp\left[-\frac{1}{2}\left(\frac{h}{\sigma_z}\right)^2\right] + \sum_{n=1}^{\infty}\left[\exp\left[-\frac{1}{2}\left(\frac{2n\,H_m-h}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{2n\,H_m+h}{\sigma_z}\right)^2\right]\right]\right\} \quad (1)$$

where χ is the volumetric concentration; x,y,z refer to a Cartesian coordinate system centered at ground level at the source in which x is along the mean wind direction, y is along the crosswind direction, and z is directed vertically; h is the effective height of the source above ground level; H_m is the maximum depth of the layer through which the effluent is dispersed; τ is the time interval over which concentration estimates are required; Q is the source strength expressed in terms of the weight of material released per unit time; $\bar{u}$ is the mean wind speed; and σ_y, σ_z are, respectively, the standard deviations of the crosswind and vertical concentration distributions.

Meteorological quantities in addition to the mean wind speed $\bar{u}$ and the maximum depth of the mixing layer H_m mentioned above are implicit in the crosswind and vertical terms of Equation (1). The standard deviations of the crosswind concentration σ_y and the vertical concentration σ_z are defined by simple power laws of the form:

$$\sigma_y\{x\} \propto \frac{\sigma_v}{\bar{u}}\,(x)^{\alpha} \propto \sigma_{A'}(x)^{\alpha} \quad (2)$$

and

$$\sigma_z\{x\} \propto \frac{\sigma_w}{\bar{u}}\,(x)^{\beta} \propto \sigma_{E'}(x)^{\beta} \quad (3)$$

where $\frac{\sigma_v}{\bar{u}}$ is the lateral intensity of turbulence; $\sigma_{A'}$ is the standard deviation of azimuth wind direction in radians; $\frac{\sigma_v}{\bar{u}}$ is the vertical intensity of turbulence; $\sigma_{E'}$ is the standard deviation of elevation angle in radians; and α, β are empirical constants of the order of unity.

In estimating concentration patterns for time periods considerably longer than one hour, and especiallly for seasonal and annual patterns the lateral spread of the effluent is given by the frequency distribution of azimuth wind direction. Following Meade and Pasquill,[3] the appropriate model equation is of the form:

$$\chi\{r,\theta,z=0;\ h,H_m,\tau\} = \frac{2Qf\{\theta_i\}}{\sqrt{2\pi}\ \overline{u}\ \theta_i\ r\ \sigma_z}\left\{\exp\left[-\frac{1}{2}\left(\frac{h}{\sigma_z}\right)^2\right] + \sum_{n=1}^{\infty}\left[\exp\left[-\frac{1}{2}\left(\frac{2n\ H_m-h}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{2n\ H_m+h}{\sigma_z}\right)^2\right]\right]\right\} \quad (4)$$

where r is the radial distance from the source; θ_i is an angular sector in radians in which the relative frequency of the wind direction over the time period τ is $f\{\theta_i\}$, as defined by the seasonal or annual wind rose.

Some of the basic concepts mentioned above are represented schematically in Figure 2 which shows the dilution and transport of pollutants emitted from a single tall stack. The material within the plume is transported downwind in the direction of the x coordinate and spreads in both the lateral or y direction and the vertical or z direction. The vertical spreading stops when the top of the plume intersects the top of the mixing layer at height H_m. The lateral spreading continues along the downwind plume trajectory unless restricted by topographical barriers such as the sides of a valley. As shown in the figure, the plume width is given by the quantity 4.30 σ_y when the form of the crosswind concentration distribution is approximately Gaussian. The dimensions of the reference volume are thus fixed by the height of the top of the mixing layer, the maximum downwind distance of interest, and by the crosswind angular sector within which the plume is found. The angular width of the plume at any given instant is usually only a few degrees, but, within a period of ten minutes to one hour, variations in azimuth wind direction produce a meandering of the plume within an angular sector that is 50 to 100 degrees in extent.

As mentioned in the introduction, meteorological variables are highly space and time dependent. Also, the meteorological predictors used in the mathematical models for estimating concentration fields must be representative of the airflow within the reference volume over the time period for which concentration estimates are desired. This requirement is in practice very difficult to satisfy because of the large dimensions of the refer-