Air Pollution Monitors – A Survey

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Abstract

In recent years, ambient air quality monitoring has become an essential part of most industrial establishments in order to satisfy the requirements of the National Environmental Policy Act. This has made air quality surveys even more complex, requiring adequate planning to assure that prescribed objectives can be attained in the shortest possible time and at the least cost. Air quality is usually monitored in order to characterize air quality in urban areas, near large sources of pollution, or where there are sensitive environmental receptors. Therefore, a criterion for selecting air pollution monitors is required because monitoring is expensive, time consuming, and requires skilled personnel and sophisticated analytical equipment.

The most common and probably preferred way of classifying and selecting monitors is based on their operating principles, the most common of which are: electromagnetic radiation, chemical affinity or reactivity, electrical or magnetic fields, thermal or mechanical excitation, and other combinations or variations of these.

Practically, the final selection is based on several factors and the initial cost is always important. In addition, familiarity with one specific type of technique may influence the selection (favorably or unfavorably). Accuracy, reproducibility, and speed of response are as important as cost, particularly in control installations. Proper selection of the best analyzer for a given measurement requires a complete knowledge of the monitoring process variables such as compositions, temperatures, and pressures. Selection is then based on a sound understanding of the principles of operation and an equally sound understanding of the chemistry and operation of the processes.

This paper represents a survey that will aid in the selection and understanding of air pollution monitors and their basic operating principles. The main focus will be on gas pollutants. It is a summary of the author's research project completed in part for the partial fulfillment of the Masters Degree in Safety at Department of Engineering Technology and Industrial Studies, Middle Tennessee State University.

I. Introduction

Air quality is a dynamic and complex environmental phenomenon having large temporal and spatial variation. The temporal and spatial variations in atmospheric levels of pollution, which is the essence of air quality, are caused by: changes in the source emission rates and in the meteorological and topographic conditions, which contribute to the dilution of the material, provide chemical reactions in the atmosphere, and control the removal of various pollutants.

Monitoring air quality can become complex since it requires large amount of data collection that provide an overview of the dynamic nature of air quality in terms of temporal and spatial variations. Collecting and analyzing the samples of ambient air in order to evaluate air quality requires the application of advanced technology in the areas of analytical chemistry; operation and calibration of electrochemical and meteorological instruments; and data recording, collecting, and processing. Source strength information is required if a meaningful data interpretation and valid prediction of future air quality is required. Furthermore, air quality concentrations will be relatively high near sources but will become diluted and undergo transformation with distance. Thus, a wide range of values that requires measurement and analytical methods must be sensitive enough to measure highly diluted material.

In recent years, ambient air monitoring has become an important part in order to satisfy the requirements of the National Environmental Policy Act. This has made air quality surveys even more complex, requiring adequate planning to assure that prescribed objectives can be attained in the shortest possible time and at the least cost.

II. Objectives of Air Monitoring

Air quality monitoring is usually undertaken to characterize air quality in urban areas, near large point or line sources of pollution, or where there are sensitive environmental receptors. The ability to assess the air quality of an area depends on accurate data collection that details existing conditions and building models that can be used to predict future pollution levels.

Historically the practice of air monitoring has been limited to industrial hygiene and air pollution measurements except for a few other very specific applications, such as radiation. A myriad of different instruments, techniques, and methods, operating by means of a variety of chemical and physical principles, are now available to perform proper data collection and monitoring.

Many changes are occurring in the field of environmental and occupational sampling to identify and quantify exposures to polluting agents. Sampling can measure the amount of a contaminant present in the air, especially in a worker's breathing zone, or on a surface. Sampling can characterize what might be present in a bulk sample. Urine, blood, or breath samples might also be collected in order to determine how much of a chemical or other agent an individual actually has absorbed. However, the most appropriate characterization of exposure may involve integrating some or all of these areas of sampling, as well as adapting the sampling strategy to reflect the toxic effects of a material. Reliable measurements of airborne contaminants are useful for selecting personal protective equipment, identifying sources of contaminants, determining whether and which engineering controls can reduce exposures, assessing the potential health effects of exposure, and determining the need for specific medical monitoring.

III. Equipment Classification and Selection

The main focus of this paper is placed on the detection and measurements of gas-phase pollutants. Gas analyzers are usually classified according to one or more of the following:

Selective or non-selective: An analyzer will be selective in analyzing a gas stream if it responds only to one specific component of the gas stream rather than detecting a physical property of the stream. An infrared analyzer is usually applied to monitor a single component in a process stream and within the restraints placed on its applications. It should do so regardless of variations of other components in the same gas stream. However, a thermal conductivity analyzer measures the thermal conductivity of the total gas stream and is therefore non-selective since the thermal conductivity will vary as components in the gas stream vary.

Continuous or semi-continuous: Many analyzers provide a continuously recorded data or an overall picture of the pollutant concentration against time. Others, however, are time-dependent analyzers. The gas chromatograph is an example of a semi-continuous analyzer where column elution time of less than one to ten minutes is required before a recorded peak is complete. A paper-tape monitor for hydrogen sulfide is another example of a semi-continuous analyzer. In this case, a time of 1 to 4 hours is required to determine the concentration of a sample. Other analyzers using thermal conductivity or non-dispersed infrared detectors are practically instantaneous on readout and are therefore classified as continuous.

By operating principles: The most common and probably preferred way of classifying process analyzers is on the basis of their operating principles. These include the following properties: electromagnetic radiation, chemical affinity or reactivity, electrical or magnetic fields, thermal or mechanical energy, and combinations or variations of these.

In practical applications, the final selection is based on several factors. Initial cost is always important. The familiarity of personnel with one type may influence the selection (favorably or unfavorably). Accuracy, reproducibility, and speed of response are as important as cost, particularly in process control installations. Proper selection of the best analyzer for a given measurement requires a complete knowledge of the process variables such as compositions, temperatures, and pressures. Selection is then based on a sound understanding of the principle of operations of different methods, and an equally sound understanding of the chemistry and operation of the processes. The most common air pollution monitors are:

1. Gas Chromatograph: Probably the most popular and widely used process analyzer today is the gas chromatograph. It is highly sensitive, extremely flexible to applications, and quite reliable especially with the recent advances that include solid-state components. The gas chromatograph consists essentially of a six-part system: carrier gas, sample injection, chromatograph column, detector, electronics, and recorder.

A means of injecting a fixed-volume of sample into the flowing carrier is usually done by using linear or rotary valves that trap the sample in a void or tubing length and place it in the flowing carrier stream. The heart of the chromatograph is the chromatographic column. Its function is to separate the sample components and thus permit the carrier gas to elute the component of interest to the detector as a binary, mixed with the carrier gas. The detector then monitors the gas discharged from the column. The most common detector system is of the thermal conductivity type. Flame ionization detectors also find increasing use in chromatographs because of the extreme sensitivity and some degree of selectivity. Thermal conductivity and flame ionization detectors are probably used in 96 to 98 percent of the process units in service today.

Common gas analysis applications include those mentioned previously plus many more. Ranges vary from a few ppm up to 5000 ppm (V/V). Some manufacturers are: Beckman, Phillips Electronics, and Honeywell.

2. Infrared: Next to the gas chromatograph this is perhaps the most versatile and popular type of analyzers. Its operating principle is based on the unique absorption of electromagnetic radiation (infrared spectrum) for specific gases. The amount of absorption is proportional to the quantitative concentration of the gas. The electronic circuitry and detection components are somewhat complex in this case. In basic terms, however, the reference gas is sealed in a membrane and the absorption of radiation by the reference gas is compared to the sampling gas stream. Common applications include: CO, CO_2, SO_2, CH_4, NH_3, and some hydrocarbons. Exceptions include O_2, H_2, N_2, and most diatomic gases, and the rare gases. Ranges vary from 0-10 ppm (V/V) up to 1000 ppm. Major suppliers include: Beckman, Leeds & Northrup, Mine Safety Appliances, and Teledyne.

3. Ultraviolet: Another widely used radiant energy analyzer is the ultraviolet unit that operates in the electromagnetic spectrum from 100 to 400 milli-microns. Its operating principle is similar to that of the infrared analyzers. Common applications include: NO_2, NO_X. Ranges vary from 0-10 ppm (V/V) up to 500 ppm. Famous manufacturers include: Beckman, DuPont, and Teledyne.

4. Colorimetric: This wet chemical method is a reference for SO_2 analysis. In this method a specific absorbent is used to form a stable nonvolatile complex with the gas to be analyzed and a subsequent reaction with an acid bleached compound gives a sensitive, specific, and temperature independent color reaction. The color reaction is identified by a dual beam visible light source with separate photocells. Other gas interferences such as SO_3, NH_3, CO are eliminated by the addition of a specific acid. Several applications include: SO_2, NO_2, H_2S, NO_x, HCHO, and total oxidants. Ranges vary from 0.1 ppm up to 0-10 ppm (V/V) and higher. There are numerous manufacturers some of which are: Technicon, Beckman, DuPont, and Scientific Industries.

5. Thermal Conductivity: This is one of the simplest methods for measuring high concentrations of binary gases. Its principle of operation is based on the fact that each elemental gas has a characteristic ability to conduct heat at a different rate. A reference gas, usually the major constituent of the binary mixture, envelops one leg of a reference filament of a Wheatstone bridge. Another filament of the bridge circuitry detects changes in heat dissipation rate of the sample gas as a function of the bridge resistance. The degree of unbalance between the reference and the sampling filaments is converted to a quantitative percentage of the gas concentration. Common applications include the measurements of: CO_2 in air, SO_2 in air, H_2 in air, H_2 in N_2, H_2 in O_2, O_2 in H_2, H_2 in Cl_2 and Cl_2 in air. Standard -measurement ranges vary between 0 to 5 percent (V/V) and up to 100 percent (V/V). Major manufacturers include: Beckman, Leeds & Northrup, Mine Safety Appliances, and Teledyne.

6. Chemiluminescent: The chemiluminescent reaction of NO with ozone and subsequent optical detection has added new expectations. No reactant gas or wet chemicals are required, yet sensitivity in the ppm range makes this a pro-mixing instrument for stationary-source monitoring. Common gas analysis: NO, NO_X. Ranges: 0-5 ppm (V/V) up to 1000 ppm (V/V). Manufacturers include: Aerochem, and Combustion.

7. Coulometric: Coulometry is based on the principle of electrically generating a selected ion in a titration cell. The amount of current required to generate sufficient ions to maintain a zero reference value is directly proportional to the reduction of ions caused by the readable gas (SO_2, H_2S, etc.). Applications include: SO_2, H_2S, CH_3SH, $(CH_3)S$, $(CH_3)_2S_2$. Ranges vary from a few ppm to 1000 ppm.

8. Flame Ionization: This method is primarily used to determine the concentrations of hydrocarbons present in a gas stream or ambient air. The flame formed when hydrogen burns in air contains a negligible number of ions. The introduction of traces of hydrocarbons into the flame results in a complex ionization, producing a large number of ions. A polarizing voltage applied between the burner jet and the collector produces an electrostatic field in the vicinity of the flame. This field is measurable with an amplifier circuit and is directly proportional to the hydrocarbon concentration. Major applications are hydrocarbons, inert gases, CH_3, primarily compounds with C-H bonds. Sensitivity range varies between 0-5 ppm and up to 0-25 ppm. Some suppliers are: Beckman and MSA.

9. Spectrophotometer: A complex series of lenses and filters transmit radiant energy of specific wavelength (visible, ultraviolet, infrared) to a gas sample where the absorption of radiant energy causes an imbalance between sample and reference beams which gives rise to an AC electrical signal from the detector. This signal is amplified to power a sensitive servomotor that drives a precision optical attenuator into the reference beam until the beams are of equal intensity. The recorder pen is directly coupled to the attenuator and thus directly records the sample absorption on a linear transmittance scale. Applications include SO_2, NH_3, and many derivates of phenols, alkenes, ketones. Range ability from 1-ppm scale up to a factor of 10 ppm (V/V). Manufacturers include: Beckman and Phillips Electronics.

10. Paramagnetic: Oxygen is paramagnetic; that is, it is attracted by a magnetic field. This paramagnetic property of oxygen, caused by its atomic and molecular structure, is inversely proportional to its absolute temperature. When oxygen is heated, it loses its paramagnetic property and becomes diamagnetic (repelled by a magnetic field). Successive heating and then cooling of a precision resistor of a Wheatstone bridge provides a current signal proportional to oxygen content of the gas. Primary use of this technique is for measuring the concentration of O_2 in the range 0-0.5 percent and up to 100 percent. Manufacturers include: Bailey Meter, Beckman, L & N, and MSA.

11. Electrochemical Membrane-Type Polarographic Sensor: These small, inexpensive cartridge sensors have an excellent potential. The operating principle is a liquid-state nonohmic variable resistor in which a pollutant-selective activating surface ruptures the gas molecular bonds, releasing energy as a voltage signal proportional to the pollutant concentration. With sensitivities of 10-15 ppb, full-scale ranges from 0.1 ppm to 0-10,000 ppm are available. Major applications include: NO_X, NO_2, SO_2, H_2S, and total sulfur. One manufacturer is Envirometrics.

12. Electrochemical Transducer: The sensor consists of an electrochemical cell, which is covered with a membrane having a high permeability for SO_2. As SO_2 diffuses through the cell, an electrochemical reaction takes place, which produces an electric current directly proportional to its concentration. The cell is impermeable for ions and large molecules. The cell does not

respond to gases such as O_2, CO_2, CO, NO_2, O_3, or C_{12}. Recent applications are: SO_2, NO_X, NO_2, C_{12}. Range varies from 0-5 ppm (V/V) up to 5000 ppm. Major suppliers are: Dynasciences, and Theta-Sensors.

13. Paper-Tape: When lead acetate-impregnated tape is exposed to H_2S, a reaction occurs causing the tape to turn black. The density of the black spot is measured in a transmission photometer. This measurement gives the average H_2S concentration for the sample period. Major applications include: H_2S, fluorides. Sensitivity varies between 0-1 ppm up to 0-20 ppm (V/V). Major suppliers include: Research Appliance Company.

IV. Air Monitoring System Development

The proper development of a cost effective air quality survey involves not only air quality monitoring, but also meteorological monitoring, calibration, and data acquisition systems. Failure to recognize this fact results in a design that is based on many compromises, which may fail to meet the sampling objectives. A cost effective system should reflect both the realities of current air quality monitoring system technology and the ultimate application for which the measurement system is intended. It is especially important to develop a systematic plan for the implementation of the system in advance of choosing specific pieces of hardware.

Air quality monitoring systems require the determination of air quality in both the microscale and the mesoscale and characterization of both primary (directly emitted) and secondary (formed in the environment) pollutants. Sufficient temporal and spatial resolution of air quality must be obtained to meet the specific objectives of the monitoring system within the broad objectives of characterization of air quality in urban areas, near sources and where there are sensitive receptors.

1. Setting the Objectives: The starting point of any air quality study is defining the objectives of the air monitoring system. Abstract objectives, like obtaining background levels or validating mathematical models, must be translated into clear meaningful statements in terms of the desired sampling results. These include the quantity of data needed, what air pollutants should be measured, the season of the year in which the sampling should be undertaken, and where and how many sampling sites should be chosen.

2. Choosing Parameters to Be Measured: Once the objectives are clearly defined, the next step is to determine the physical parameters to be measured. If the objective is to obtain background concentrations of pollution, then only the ambient levels of specific material need to be measured. If the objective is to validate a mesoscale model so as to predict background concentrations, then meteorological conditions (i.e., wind speed and direction and mixing depth) must be monitored in addition to the ambient levels of pollution. If the objective is to validate or calibrate a microscale model or develop an empirical model to predict pollutant concentrations, then real-time measurements of air pollution concentrations, meteorological conditions, and source strength conditions must be taken into consideration. The topographic and demographic features of the study area should also be determined and taken into consideration in the design of the field experiment.

3. Selecting a Sampling Site: In choosing a technically suitable location for an air quality-monitoring site, one must consider the representativeness of the site in terms of its exposure to air pollutants and prevailing meteorological conditions. Site exposure is heavily dependent on the relative location of pollutant sources and the effects of terrain on meteorological conditions. Specific station objectives should consider where the maximum background concentrations are expected to occur and where the maximum source contribution to air pollution is expected to occur. The location of human receptors should be taken into account. It should be recognized that site selection is a very critical element in the monitoring system design. If the wrong site is picked, or if a critical site is missed, no amount of accurate collection of data will allow the objectives of the study to be fully realized.

The number of monitoring sites that should be used in the study will depend on the diversity of the land use patterns, meteorological regimes, source design configurations, and the sensitivity of the receptors. This number will be limited by: the number of technically suitable sites available, the constraints of money and manpower available, and the level of statistical significance or confidence desired in the results.

4. Setting a Sampling Schedule: The duration of the project and sampling schedules that are consistent with the objectives of the overall study must be defined. Air sampling schedules can be designed on a random or a systematic basis for both long- and short-term studies. In general, studies that are designed to validate simulation models are of a shorter duration than studies designed to document the extent of an existing pollution problem. In the case of photochemical oxidants, sampling only during the summer may be all that is needed. The availability of a historical air quality record within the urban area may allow another season to be utilized with data correlation providing the worst-case conditions. If the objective is to collect data to validate a microscale pollution dispersion model, then conducting a very extensive monitoring investigation but having duration of only one week might accomplish this task.

5. Choosing an Air Sampling Method: In choosing an air sampling method, one may consider a continuous air monitoring, integrated grab sampling, intermittent sequential sampling, or a combination of these. The air sampling method chosen depends on the air pollutant to be measured, the available utilities at the monitoring site, the frequency of sampling at the site, the number of sites, the distance between sites, and the duration of monitoring required. In addition, the air sampling method must be compatible with the requirements of sample size, rate of sampling, and the response rate of the analyzer to be used.

6. Selecting Equipment: In selecting equipment, an analytical method for measuring air pollutant concentrations must be chosen, a suitable instrument is identified, and then the equipment is purchased. Air sampling and instrument calibration equipment must also be available. Air sampling shelters must be designed and fabricated.

7. Setting Calibration Procedures: Analyzers must be calibrated to insure accurate measurements. The calibration of an air pollution analyzer involves the preparation of gas mixtures of known air pollutant concentrations. These are injected into the analyzers and the instrument response is adjusted to match the known pollutant concentration. There are basically two levels of sophistication in air monitoring instrument calibration. A primary instrument calibration

requires that reference methods (generally wet chemical methods) of measurement be conducted in operation side-by-side with the analyzer being calibrated. A primary calibration will include a check of the instrument response at several different pollutant concentration levels (i.e., 20%, 40%, 60% and 80% of full scale) so that the instrument linearity can be checked. In general, however, a primary calibration is difficult to perform under field conditions requiring wet laboratory facilities. For this reason, primary calibrations are usually performed periodically (every 90 days) and supplemented by secondary calibrations. Secondary calibrations depend on the generation of gas mixtures of known pollutant concentrations, which can be used to check the analyzer response at a single upscale point. The output of the analyzer can then be compared for accuracy with the known gas concentration. In this way the instrument can be checked frequently to see if it is operating correctly. Gas mixtures of known pollutant concentration can be purchased in pressurized steel cylinders, or can be generated using permeation tubes. The frequency of calibration must be determined after observing the operating characteristics of the instrument under field conditions. Very stable instruments may need secondary calibration only several times each week, while unstable instruments may require secondary calibration several times per day.

8. Choosing a Data Recording Method: The recording methods available include (a) continuous strip chart recorders, (b) scanning analog or digital electronic data loggers, and (c) manual data recording by the instrument operator. The data recording method used depends primarily on the type of air sampling method employed. When using continuous analyzers, strip chart recorders or scanning data loggers are usually used. When using the intermittent sequential sampling method, or when analyzing grab samples, manual recording of the data on specially prepared data forms is frequently the most efficient and least expensive method. The engineer must also choose between on-site data recording and use of a telemetry system.

The important concern in data recording is that each air quality measurement be correctly time-referenced. When monitoring is conducted at several locations simultaneously, the data recorders used at each station must be carefully synchronized, so that a correct time reference can be assigned to each measurement when the data are analyzed. In general, it is a good practice to analyze and record all measurements in the chronological order in which they are taken and to record instrument calibration data along with the air sample measurements.

9. Analyzing Data: Air quality studies inherently involve the taking of a limited number of samples from a very variable and uncontrolled population (the environment). For this reason, air quality data is analyzed using statistical methods. Special methods are available for the analysis of air quality data, which predict the behavior of the total population based on a limited number of samples. Limited field measurements may not record the maximum concentrations, but statistical analysis can be used to determine these values.

Analyses that are very useful in air quality assessment include (a) concentration frequency distribution, (b) averaging time analysis, (c) spatial distributions of pollutants, (d) regression analysis, and (e) determination of compliance.

The type of analyzer used, the method and frequency of calibration, and the competence of the field personnel govern the magnitude of the error due to the sampling procedure. The statistical

significance of the results is strongly dependent on the sampling frequency and the duration of the study.

10. Reporting Results: The final step is determining how results should be reported. Results of the monitoring can be presented in the form of graphs, histograms, pollution roses and isopleth maps. The method chosen should be the one that best illustrates the relationship of an observed pollutant concentration with some other variable. Graphs of pollution concentration versus time are perhaps the best way to illustrate diurnal, daily and seasonal trends in pollution level. The frequency of occurrence of various pollution levels can best be illustrated by plotting the cumulative frequency distribution of pollution concentrations on log probability graph paper. When the pollution concentration is dependent on the wind direction, pollution roses can be used to illustrate the relationship. In most cases, the observed pollution concentrations vary at different geographical locations. In this case, isopleth maps showing the average pollution concentrations at different locations represent a good method for displaying the results of the air quality study.

V. Instruments Used to Measure Most the Common Gases

Table 1 below lists various instruments frequently used in measuring the concentrations of the most common pollutants.

Table 1. Common Pollutants and the Instruments to Detect Them

Ammonia	Carbon Dioxide	Carbon Monoxide	Chlorine
Catalytic	Electrochemical	Electrochemical	Calorimetric
Colorimetric	Infrared Absorption	Infrared Absorption	Dry reaction
Conductivity	Ionizing Cell	Catalytic	Electrochemical
Dry Reaction Substrate	Thermal Conductivity	Photoconductive	Electroconductivity
Electrochemical		Solid State Electrolytic	Solid State
Infrared Absorption		Thermochemical	UV Absorpition
Photoionization			
UV Absorption			

Ethylene Oxide	Hydrogen	Methane	Nitrogen Oxides
Infrared Absorption	Colorimetric	Chromatographic	Chemiluminescent
Photoionization	Dry Reaction	Electrochemical	Colorimetric
Nucleation & Crystal Growth	Electrolytic	Flame Safety Lamp	Electroconductivity
	Infrared Absorption	Infrared	Solid State Electrolytic
	Solid State Electrolytic		Infrared Absorption

Oxygen	Ozone	Phosphine	Sulfur Dioxide
Paramagnetic Cell	Chemiluminescent	Dry Reaction	Calorimetric
Chemical Absorption	Coulometer	Photoionization	Dry Reaction
Electrolytic	Ionization		Electrochemical
	Ultraviolet Absorption		IR&UV Absorption
			Solid State Electrolytic

VI. Summary

This paper represents a survey that will aid in the selection and understanding of air pollution monitors and their basic operating principles. The main focus was on gas pollutants. The paper also represents a compilation of the most common pollutants and possible instruments used to detect them. It is hoped that this paper will help individuals working in the field to minimize air pollution.

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