
ENVIRONMENTAL INSTRUMENTATION AND ANALYSIS HANDBOOK

RANDY D. DOWN

Forensic Analysis & Engineering Corp.

JAY H. LEHR

The Heartland Institute
Bennett and Williams, Inc.



WILEY-INTERSCIENCE

A JOHN WILEY & SONS, INC., PUBLICATION

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PREFACE

It has been two decades since environmental science, environmental engineering, and environmental consulting took root as major disciplines and professions throughout the developed world. The learning curve has been steep as it relates to the previously unrecognized physics of contaminant transport. Today those principles are usually well understood by a mature army of environmental professions.

An area that has lagged in full comprehension among the practitioners in these fields is an understanding and awareness of the hardware for measuring the physical and chemical characteristics of contaminated sites. The application of these instruments and methodologies to characterize the solid, liquid, and gaseous chemical content within a transport media are not well understood.

Professionals have long relied on personal experience, diverse journal articles, and manufacturer's advertisements and catalogs to choose efficient and accurate means of obtaining the necessary field data to characterize a site. This has resulted in too narrow a focus in the development of appropriate remediation programs and monitoring protocols.

More than three dozen talented environmental professionals who are experienced and adept at extracting the most telling and accurate data from the "field" have come together in this book to catalog nearly all the equipment and techniques that are available to modern scientists, engineers, and technicians.

This has been a fulfilling and rewarding effort: the gathering of the best and brightest professionals across many continents to share their expertise. We have asked them to describe the basic science, be it physics, chemistry, biology, hydrology, or computer data logging, that supports their field analysis followed by detailed explanations of the various hardware in use today. In most cases the authors offer descriptions of typical case studies in which the equipment was successfully utilized.

Of significant value are the pitfalls and foibles of the procedures and equipment that may not always measure up under less than ideal conditions. What may go wrong is often as valuable as what should correctly occur.

For ease of access, we have divided the description of field instruments and procedures into six basic categories: instrumentation and methodologies, water quality parameters, groundwater monitoring, wastewater monitoring, air monitoring, and flow monitoring. Some sections could have fit neatly in more than one category, but we trust the reader will have no trouble identifying the information being sought regardless of the category in which it is placed.

It is rare to have an opportunity to add a truly innovative package of information to the literature that has not been previously attempted. We are confident that this has been achieved through the cooperation and dedication of the many contributors to this book to whom we are eternally grateful.

We made no strong effort to confine the authors to a special format of presentation in length, depth, or breadth of their subject matter. We only asked that they enable the reader to fully understand the conditions under which field instruments and procedures were applicable and how to implement their use.

Some authors felt their specialty was in need of a comprehensive detailed expose not readily found in existing literature. They saw this book as an opportunity to supply just such a treatise. Other authors felt only a brief “how-to” manual approach was sufficient in their area of expertise. The reader will recognize these differences and likely benefit equally from both approaches.

Our profession has needed this handbook for the past decade. We hope it will fill the need for the next decade.

JAY H. LEHR

**INSTRUMENTATION
METHODOLOGIES**

INFLUENCE OF REGULATORY REQUIREMENTS ON INSTRUMENTATION DESIGN

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Forensic Analysis & Engineering Corp.
Raleigh, North Carolina

- 1.1 Introduction
- 1.2 Environmental Regulatory Requirements
- 1.3 Key Factors Influencing Development
- 1.4 Emerging Sensor Technology
- 1.5 Other Advancing Technologies
- 1.6 Regulatory Trends
- 1.7 MACT/BACT Analysis
- 1.8 Product Development
- 1.9 Networked Systems
- 1.10 Future Considerations
- 1.11 International Organization for Standardization
- 1.12 Conclusion
- 1.13 Additional Sources of Information

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1.1 INTRODUCTION

Federal, state, and local regulatory requirements have long played an important role in driving the advancement of new technologies for the measurement and control of environmental pollution. They will continue to do so. The same can be said for competitive advancements in measurement and control technology—that they drive the regulatory requirements. As this chapter will illustrate, regulations and competitive, technological development ultimately work hand in hand to influence the future of environmental instrumentation—thus the rapidly changing nature of environmental instrumentation and controls.

This handbook will serve as a valuable guide in the application of new and emerging environmental instrumentation and control technologies needed to meet current and future regulatory requirements.

1.2 ENVIRONMENTAL REGULATORY REQUIREMENTS

It was not intended that this handbook serve as a reference for environmental regulatory requirements. Regulatory requirements vary from state to state throughout the United States and abroad and are periodically updated and revised. Any information regarding regulatory requirements that pertains to your geographical location should be obtained directly from the appropriate local governing agencies. It is advisable to work with a local or regional environmental consultant or directly with the regulatory agency to determine which regulations apply to your specific application. Doing so will greatly reduce your risk of misapplying expensive instruments and potential incurring fines that may be imposed for failing to meet all regulatory requirements. Such fines can be very costly and embarrassing.

When involved in the development, specification, or selection and application of instrumentation, as it relates to environmental applications, this book will serve as a very useful technical resource. It will aid you in asking the right questions and avoiding some of the many potential pitfalls that can occur when trying to select and specify appropriate instrumentation for a measurement or control application.

1.3 KEY FACTORS INFLUENCING DEVELOPMENT

Two key factors drive the development of new technology as it applies to environmental measurement and control:

- Steps required to cost effectively meet compliance requirements dictated by federal and state regulatory agencies
- An opportunity to be highly profitable by being the first firm to develop and market a new, more cost-effective and reliable technology (sensor, transmitter, analyzer, telemetry device, and/or controller). Statistically, those companies that are first to market with a new technology tend to capture and retain 70%

or more of the total market share. Therefore, great emphasis is placed on being the first firm to market an innovative or more cost-effective, new product or technology.

New environmental measurement and control technology comes from many areas of science and industry. Government and private investments made in the development of new alloys and synthetic materials as well as smaller and lighter electromechanical components are one example. Sensor technology for the aerospace and auto industries is a good example of a major source of new technology and products. Spin-off applications, if applicable to industrial and commercial applications (and relatively cost effective), can have dramatic results in advancing control technology. Major aerospace and automobile manufacturers as well as government agencies often have greater resources with which to fund in-depth research and development.

1.4 EMERGING SENSOR TECHNOLOGY

Advancement of new sensor technology is by far the most influential factor in the evolution of regulatory requirements as well as instrumentation and control technologies. Keeping up with this technology is a major challenge for regulatory experts, scientists, and engineers who are tasked with providing clients and the general public with the optimal means of pollution measurement and abatement.

When establishing the minimum human exposure limit for known and suspected carcinogens, the regulatory minimum exposure level is often established by the minimum *measurable* concentration. The minimum measurement level established by the government must be achievable in terms of measurement accuracy and repeatability. Unattainable regulatory limits would be meaningless.

The ability of a measurement system to accurately monitor an environmental variable (such as humidity, temperature, pressure, flow and level) or to detect and analyze a specific chemical substance and its concentration over time is crucial if we are to successfully measure and control pollutants and preserve the health and safety of our environment.

Measurement, as discussed in greater depth later in this book, is a function of accuracy, precision, reliability, repeatability, sensitivity, and response time. As new sensor technology evolves, its value to the industry will be judged by its ability to meet these criteria and by its relative cost in relation to currently used technology.

1.5 OTHER ADVANCING TECHNOLOGIES

Closely following the rapidly advancing sensor technology and further influencing sensor development is the continuing development of solid-state electronics and large-scale integration of electronic circuitry into microcircuitry. Development of microminiature electronic components (such as resistors, diodes, capacitors, transistors, and integrated circuits) and “nanotechnology” (the development of

microminiature mechanical/electrical devices) has positively influenced the measurement and controls industry in multiple ways:

- Electronic and mechanical components are now physically much smaller.
- Being smaller, these devices require less electrical energy to function.
- Using less energy, they also produce less heat, allowing them to be housed in more compact, better sealed, and in some cases nonventilated enclosures.
- Allowing them to be tightly enclosed makes them better suited for use in harsh environments and means they are less likely to be influenced by variations in temperature, vibration, and humidity.
- manufacturing and assembly costs are significantly reduced.
- consumer prices are reduced.

If we look deeper, we find that other technological advances have allowed and supported the continued development of these microcircuits and components. A prime example is the advancement of clean-room technology. A dust particle, spore, strand of human hair, or chafe (particles of dry skin) will appear quite large under a microscope when examined alongside some modern-day miniaturized components and circuitry. Such environmental “contamination” can damage or impair the reliability and performance of these microminiature components.

Advancements in clean-room design and packaging technology have significantly reduced the risk of such contamination. This has largely been accomplished through the development of high-efficiency air filtration systems and better guidelines for proper “housekeeping,” such as

- wearing low-particulate-producing disposable suits, booties, and hair nets;
- providing pressurized gown-up areas, airlocks, and positively pressurized clean-room spaces (to prevent contaminated air from migrating into the cleaner space); and
- providing “sticky” mats at entering doorways to pick up any particulate that might otherwise be “tracked in” on the bottom of footwear.

Conversely, advancements in clean-room technology have largely occurred through improved accuracy in measuring and quantifying the presence of airborne contaminants.

Improved accuracy of particulate monitoring instrumentation is a good example of advancing sensor technology that is aiding the advancement in measuring and certifying clean-room quality, which in turn has aided advancements in sensor technology. This is a good example of different technologies that are ultimately working hand in hand to accelerate the advancement of environmental instrumentation technology.

Nanotechnology (the creation of functional materials, devices, and systems through control of matter on a length scale of 1–100 nm) may very well have the greatest impact of any technological advancement in measurement and control

technology over the next 10–15 years. The manipulation of physical properties (physical, chemical, biological, mechanical, electrical) occurs at a microminiature scale. To put it in perspective, 10 nm is approximately a thousand times smaller than the diameter of a human hair. A scientific and technical revolution is beginning based on the newfound ability to systematically organize and manipulate matter at the nanoscale.

1.6 REGULATORY TRENDS

Regulatory agencies tend to avoid direct specification of a technology to meet a regulatory requirement. They wisely prefer to define performance criteria (accuracy and reliability) that must be achieved in order to be in regulatory compliance. In so doing, regulatory agencies can avoid specifying a level of system performance that exceeds readily available technology. It also reduces the risk of specifying technologies that are available but are so cost prohibitive that they would create undue financial hardship for those companies found to be out of compliance.

Regulatory agencies must weigh the potentially high cost of available technology against the value derived by enforcing a cleaner environment and ultimately determine what is in the public's best interest. These decisions are often controversial and may be challenged in the courts. At risk are thousands of jobs, as companies are required to spend millions of dollars to significantly reduce their air emissions (or pretreat wastewater) and remain competitive with overseas companies. This burden on manufacturers must be weighed against the potential long-term (and perhaps yet-unknown) impact of the exposure of people and the environment to human-generated contaminants.

An effective approach to working with industry to continuously improve our nation's air and water quality while not financially crippling U.S. companies (which in some cases compete with overseas firms facing fewer environmental restrictions) is to employ a MACT (maximum achievable control technology) or BACT (best available control technology) analysis and gradually increase restrictions on certain pollutants over a period of several years.

Graduated environmental restrictions allow several things to occur that aid industry: They allow industrial firms time to determine and budget for the cost of compliance, schedule downtime (if necessary), and investigate methods of changing their internal production processes to lower the level of emitted pollutants requiring control. They also allow system developers and pollution control system manufacturers additional time to develop methods to meet compliance requirements that are more cost effective than current technology may allow.

1.7 MACT/BACT ANALYSIS

Addressing the issue of abatement costs versus the benefits to the environment requires a methodology that will establish the best approach based on present-day

technology. Typically, the approach that has been adopted by many state regulatory agencies is either a BACT or MACT study and report.

In a MACT or BACT analysis, the feasible alternatives for pollution control are examined and compared in a matrix, weighing factors such as pollutant removal efficiency, capital costs, operating costs, life expectancy, reliability, and complexity. Ultimately, a *cost per unit volume of pollutant removed*, usually expressed in *dollars per ton*, is established for each viable option. The option having the best projected cost per volume of removed pollutant is usually selected unless there are extenuating reasons not to (such as a lack of available fuel, insufficient space for the equipment, or a lack of trained or skilled support staff needed to operate or maintain the system).

As an example, a BACT or MACT analysis for abatement of pollutant air emissions will often include evaluation of such technologies as carbon recovery systems, thermal oxidizers, scrubbers, dust collectors, and flares.

Evaluating these various technology options requires a detailed determination of their cost of construction, operation, maintenance, waste disposal, and salvage. Typically, an environmental consultant is contracted to perform an independent BACT or MACT analysis. This helps avoid potential public concerns over a perceived conflict of interest if the analysis were performed in-house.

Pollution abatement system costs often range well into the thousands, in some cases millions, of dollars. Cost of abatement systems is largely dependent upon:

- Type and controllability of substances to be abated
- Supplemental fuel costs
- Disposal of the removed pollutant (if any)
- Quantity (volumetric flow rate) of the pollutant

Some pollutants, such as mercury, are much more difficult to remove than others, such as volatile organic compounds (VOCs). They may also need to be handled and disposed of differently (further driving up the total cost of abatement).

As a general rule, the larger the volume of pollutants generated, the physically larger the equipment needed to handle it, and perhaps the more equipment is needed to control it. All of these characteristics serve to drive up the cost of abatement.

Various pollution abatement systems are described in greater depth later in this book.

1.8 PRODUCT DEVELOPMENT

As mentioned earlier, many factors influence the development of pollution control technology and environmental instrumentation. Among the major factors influencing instrumentation development are:

- Increasingly stringent regulatory requirements
- Continuing advancements in microelectronics

- Advancing clean-room technology
- Sensor development for the aerospace and automotive industries (“spin-offs”)
- Emerging networking technologies (Internet, Ethernet, Fieldbus, wireless telemetry)
- A globally competitive market for instrumentation and controls

Manufacturers of sensors used in environmental control applications and pollution abatement technologies will continue to develop and market new sensor technology, with no apparent end in sight. As the technology advances, allowing more cost-effective measurement of pollutants, more stringent environmental limits will be imposed until the general public is satisfied that sufficient pollution control strategies have been established to reverse the concerns over a clean environment.

1.9 NETWORKED SYSTEMS

The current trend in the instrumentation industry as a whole is to network what are referred to as “intelligent” transmitters and analyzers that contain their own microprocessors. Typically, they have a unique device address on a daisy-chained, twisted/shielded pair of wires. The transmitter or analyzer onboard microprocessor has the ability to run self-diagnostics and identify hardware problems (e.g., sensor failure). This ability to diagnose a transmitter or sensor problem from a remote location (using the workstation PC, a laptop, or a hand-held diagnostic tool) has particular value when the transmitters are mounted in such difficult-to-access locations as the top of a high exhaust stack without the use of special equipment.

Smart transmitters are also capable of transmitting output data at a much faster “digital” speed than an analog signal that requires a longer scanning period for a computer or processor to determine and update its output value. This gives them a faster system reaction time (or scan time). Typically, such networked “intelligent” transmitters are connected to a DCS (distributed control system) by a single network cable (typically a single twisted and shielded pair of wires). In such a system, the central processor at the front end of the system (also referred to as operator workstations) communicates over a daisy-chained serial connection (twisted pair of wires) directly with each field device. Large systems can have hundreds of such field devices. As mentioned earlier, each smart device is assigned a unique address for identification.

Portable instruments have also advanced a great deal in the last 20 years. This is largely due to the advancements in microelectronics and batteries. Battery technology has allowed battery size, weight, and cost to be reduced. This further enhances the performance of portable instruments, which will be discussed in much greater depth later in this handbook. Portable instruments offer many advantages as well as some disadvantages when compared to stationary instruments.

1.10 FUTURE CONSIDERATIONS

Looking into our future (albeit without the aid of a crystal ball), it would seem that the greatest advances in environmental instrumentation development over the next 10 years will likely center around advanced technology and cost reductions in the areas of:

- Faster data processing
- More intelligent field devices
- Lower cost analyzers
- Microminiature electromechanical applications using nanotechnology
- Extensive use of wireless telemetry
- Faster sensor response times (greater sensitivity, quicker response to changes in the measured variable)

An improved ability to detect and measure concentrations of airborne pollutants and reduced costs for these instruments will likely lead to more stringent clean-air requirements. An analogy is the introduction and development of electric and combination gas-and-electric cars (cleaner fuel-burning transportation), which will continue to drive clean-air technology as well as slow down the depletion of our finite supply of fossil fuels.

Another potential change in our near future will be greater efforts by pollution control system manufacturers to market packaged abatement systems, with instrumentation and controls a pretested part of the overall system package.

1.11 INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

With significant advances in science and technology and a greater sharing of technologies in large part due to the end of the Cold War and creation of a worldwide web, the engineering community worldwide has grown much closer. It has thus become apparent that international quality standards are needed in order to provide a consistent level of quality engineering and management standards worldwide. The International Organization for Standardization (ISO) develops standards for this purpose. Its standards are being adopted by many international firms and professional organizations. These quality standards may someday be adopted by regulatory agencies as a minimum level of quality that must be attained. This will influence the development and quality of instrumentation worldwide in a very positive way.

An example of these standards, ISO 9001, specifies requirements for a quality management system for any organization that needs to demonstrate its ability to consistently provide product that meets customer and applicable regulatory requirements and aims to enhance customer satisfaction. Standard ISO 9001:2000 has been organized in a user-friendly format with terms that are easily recognized by all

business sectors. The standard is used for certification/registration and contractual purposes by organizations seeking recognition of their quality management system.

The greatest value is obtained when the entire family of standards is used in an integrated manner. This enables companies to relate them to other management systems (e.g., environmental) and many sector-specific requirements (such as ISO/TS/16949 in the automotive industry) and will assist in gaining recognition through national award programs.

1.12 CONCLUSION

Keeping up with technological advancements in environmental instrumentation and control systems is a daunting task for scientists, engineers, and technicians. There is no end to this process. Aside from the laws of physics, we can anticipate a continuation of major technological advances in the years ahead.

The good news is that the cost of the technology will likely continue to decline while sensitivity and capability of the instruments will continue to rise. Much in the way that PC technology has evolved in recent years, advancing technologies will drive capability up and at the same time, through healthy competition, drive costs down.

Environmental instrumentation will continue to play a vital role in monitoring and protecting our health and in our very existence. The better we understand how to correctly apply it, the better our opportunity to understand and manage the impact on our environment.

1.13 ADDITIONAL SOURCES OF INFORMATION

Information contained in this handbook will aid you in understanding the various applications and solutions most often encountered in this field. It would not be possible to provide all of the answers in a single volume.

Supplemental information can be found by reading technical articles in trade journals and through lectures and conferences conducted by organizations such as the Instrumentation, Systems and Automation Society (ISA), formerly known as the Instrument Society of America.

Equipment suppliers and system houses, although somewhat biased toward their own supplier's line of instruments and components (because that is how they generate the most revenue), are often a good source of information, particularly regarding availability and cost. They tend to be more knowledgeable than consultants about the technical aspects of their specific product lines. They often are involved with the installation, programming, and servicing of the equipment, not just the performance and specification aspects, as are many consultants.

Independent engineering consultants offering expertise in environmental *and* instrumentation-and-control applications are another good resource. Good consultants offer an advantage (over system houses) of not being biased toward a

particular manufacturer's equipment. They tend to act more on the client's behalf because they do not stand to profit by convincing the client to use a particular manufacturer's product line. They can also help establish budgetary costs and scheduling requirements for the design, purchase, and installation of the instruments and controls.

Another source of useful information is the technical library. Most public libraries are virtually devoid of any helpful or current literature on environmental instrumentation and controls. University libraries are much more likely to retain the technical of books and other literature that can be useful.

Helpful guidance in selecting instrumentation for an environmental application can be found on the Internet using one of many very good search engines. The Internet can be used to find useful information on:

- New technological innovations
- New product releases
- Equipment pricing and specifications
- Available literature and catalogs
- Consultants
- Manufacturers

In conclusion, seek out the information that you will need in order to obtain the proper instrumentation for your application *before* making a substantial investment. In the long run, it will save a great deal of time and help avoid costly and sometimes embarrassing rework.

IN SITU VERSUS EXTRACTIVE MEASUREMENT TECHNIQUES

Gerald McGowan
Teledyne Monitor Labs, Inc.
Englewood, Colorado

- 2.1 Extractive Measurement Techniques
 - 2.1.1 Conventional Extractive Systems
 - 2.1.2 Hot, Wet Extractive Systems
 - 2.1.3 Dilution Extractive Systems
 - 2.1.4 Special Systems
- 2.2 In Situ Measurement Techniques
 - 2.2.1 Across-the-Stack Systems
 - 2.2.2 Probe-Type Systems
- 2.3 Key Application Differences
 - 2.3.1 Conventional Extractive Systems
 - 2.3.2 Hot, Wet Extractive Systems
 - 2.3.3 Dilution Extractive Systems
 - 2.3.4 Across-the-Stack Systems
 - 2.3.5 Probe-Type In Situ Systems
- 2.4 General Precautions
- References

Environmental Instrumentation and Analysis Handbook, by Randy D. Down and Jay H. Lehr
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Both extractive and in situ gas analysis systems have been used successfully in a wide variety of applications. Similarly, they have both been misapplied, which often results in poor performance coupled with maintenance and reliability problems. It is the intent of this chapter to provide sufficient information that potential users can better understand the system capabilities and limitations and avoid the problem installations. Extractive systems are characterized by a sample extraction and transport system in addition to the gas conditioning systems and analyzers required for the actual measurement. In situ systems are characterized by their ability to measure the gas of interest in place, or where it normally exists, without any sample extraction or transport systems. To be useful in today's environmental and process monitoring environment, such measurement systems must be augmented with automated calibration and diagnostic systems that enhance the accuracy and reliability of such systems. Calibration systems must provide a complete check of the normal measurement system to ensure the integrity and accuracy of resulting measurements. Specifications for such systems often require the ability to calibrate with known (certified) calibration gases or, alternately, a gas cell or similar device of repeatable concentration indication. Gas samples of particular interest for this application typically originate in a combustion process that dictates much of the sample extraction, transport, and conditioning systems. The typical applications of interest are those associated with U.S. Environmental Protection Agency (EPA) continuous emission monitoring system (CEMS) requirements, and such regulatory compliance is assumed as a basis of comparison for these systems of interest. The EPA requires that the performance of each CEMS be individually certified in the actual installation. The performance certification requirements are described in US 40 CFR 60, Appendix B, and 40 CFR 75, Appendix A. In Europe, a type approval for a given CEMS and application are often required for use in government-regulated applications.

(Note: Some of the suppliers of the various components discussed herein have been identified in those sections. For a complete list of suppliers, please search the Internet using one of the search engines or consult web pages with industry information, such as www.awma.org, www.isadirectory.org, www.thomasregister.com, www.manufacturing.net, www.industry.net, and www.pollutiononline.com. EPA emission measurement and regulatory information is available at www.epa.gov/ttn/emc, www.epa.gov/acidrain, www.epa.gov/acidrain/otc/otcmain.html, www.access.gpo.gov, and <http://ttnwww.rtpnc.epa.gov/html/emticwww/index.htm>.)

2.1 EXTRACTIVE MEASUREMENT TECHNIQUES

Extractive measurement systems have been widely used for many years to allow gas analyzers to be located remote from the sampling point. Sampling points are often in hostile environments such as duct, pipes, and smoke stacks, which are exposed to the weather and where it is difficult to maintain good analyzer performance. By extracting a sample from the containment structure of interest, cleaning it up to the degree necessary to transport it, transporting it for tens or hundreds of

meters to an analyzer cabinet, further conditioning the sample as needed for the analyzers, and feeding it to an analyzer in an analyzer-friendly environment, it is much easier to achieve the desired degree of measurement accuracy and reliability. This section will address the critical issues involved in extractive systems. Conventional extractive systems are herein defined as those using a gas cooler/drier to reduce acid gas and water dewpoints in the sample of interest, thereby providing dry-basis concentration measurements. They do not necessarily remove all water content, but they reduce it to a level of about 1% v/v or less. Other extractive systems include hot, wet extractive systems where the gas sample is maintained in a hot, wet state from the point of extraction through the point where it is discharged from the analyzer and dilution extractive systems where the extracted gas sample is diluted with a clean air supply prior to measurement. Both of the latter systems provide wet-basis concentration measurements.

GASES OF INTEREST. Air pollutants of most common regulatory interest include SO₂ (sulfur dioxide), NO_x (oxides of nitrogen to include NO and NO₂), and CO (carbon monoxide). The EPA has established primary ambient air quality standards for these gases as well as for particulate, ozone, and lead. Other pollutant, hazardous, or toxic gases of interest include TRS (total reduced sulfur), HCl (hydrogen chloride), NH₃ (ammonia), and THCs (total hydrocarbons). In addition to the above pollutants, a diluent measurement is usually required that may be either O₂ (oxygen) or CO₂ (carbon dioxide). The diluent measurement allows the pollutant measurement to be compensated or corrected for the dilution or reduction of pollutant concentration that occurs when excess air is applied to the burners or otherwise added to the exhaust stream of a monitored process. Of this group of gases, it is important to recognize that HCl and NH₃ cannot be accurately measured in a system that cools/dries the sample gas in the presence of water condensate since these gases are water soluble and are removed with the water. The THC measurements are also affected by moisture removal as only the light hydrocarbons may pass through the system without substantial degradation. It should be further noted that O₂ cannot be measured in a dilution system if the dilution air supply contains O₂, as with instrument air. In such cases O₂ is measured by a separate sensor or probe installed at the stack where the O₂ is measured in the undiluted gas stream. Stack gas velocity or flow measurements are often used in conjunction with SO₂, NO_x, and CO₂ in order to determine emissions in pounds per hour or tons per year; however, such gas flow measurement devices will not be described herein.

ANALYZERS/SENSORS. Sulfur dioxide is typically measured with UV (ultraviolet) absorption, UV fluorescence, or IR (infrared) absorption. Infrared absorption analyzers, often called NDIR (nondispersive infrared) analyzers (meaning without a spectrally dispersive element such as a grating), are often enhanced with GFC (gas filter correlation), which reduces their sensitivity to interference from H₂O and other gases. Gas filter correlation is most effective in reducing interferences when the gas of interest exhibits sufficient fine structure in the spectral region of

interest. In general, GFC provides high specificity for diatomic molecules but may not be as effective in measuring triatomic molecules, which have more broadband absorption characteristics and less fine structure. Because of the very broad absorption characteristics of H_2O and CO_2 in much of the IR region, they are common interferents for many NDIR-measuring instruments. Special care is often required to ensure that either virtually all the H_2O is removed from the sample or a very specific detection technique is used, such as GFC, in order to provide the required measurement accuracy. The UV-measuring instruments are largely immune from this problem since H_2O does not absorb in the UV spectral region. Ultraviolet fluorescence-based SO_2 instruments have been developed for ambient air monitoring at low levels (<20 ppm) and with minimum detectable levels of less than 1 ppb. Such analyzers are based on illuminating the sample gas with a UV light source, which excites the SO_2 molecules, and monitoring the resulting fluorescence (emission of UV energy at longer wavelengths than the excitation wavelength), which is produced when the molecule relaxes to its normal state. Proper selection of excitation and detection wavelengths is required to minimize interference due to quenching agents such as CO_2 , O_2 , and H_2O and other coexisting gases. For most applications, a hydrocarbon removal device (permeable membrane) is used to minimize the potential interference from such gases.

Oxides of nitrogen are defined as the sum of NO and NO_2 as measured by a reference method (EPA 40 CFR 53) that incorporates an O_3 -based chemiluminescent method and an NO_2 -to-NO converter. With this method, O_3 and the unknown sample gas are mixed in a reaction cell attached to the front of a photomultiplier tube where the $\text{NO} + \text{O}_3$ reaction produces an excited NO_2 molecule. When this excited molecule relaxes, it emits light that is detected by the photomultiplier tube and provides a signal from which the concentration of NO is calculated. Thus the instrument basically measures NO, but with the NO_2 -to-NO converter (molybdenum catalyst heated to about 600°F), it also measures NO_x . The NO_2 is calculated as the difference between the raw sample measurement of NO and the converter-processed sample, which provides a measure of NO_x . For most combustion sources NO_x consists of 95–99% NO with the remainder being NO_2 . Thus, in many applications, it is possible to measure NO and report it as NO_x . The EPA requires lb/mmBtu and lb/h of NO_x to be reported as if it were in the form of NO_2 since that is the final oxidized state of NO after it is discharged into the atmosphere and subjected to atmospheric chemical reactions. The predominance of NO in many applications is significant since NO is best measured in the UV or with chemiluminescence and NO_2 is a weak absorber in both the UV and in the IR. The NO_2 also absorbs in the visible light spectra and is one of the few gases visible to the human observer, but the measurement of NO_2 using visible light has proven difficult. Chemiluminescent analyzers that depend on the reaction of ozone and NO have been developed for ambient air quality measurements and have excellent low-level (<0.1–20-ppm) measurement capability. Minimum detectable levels for such analyzers are less than 1 ppb. They can be ranged for higher concentrations by reducing the sample flow rate into the reaction cell. In the application of chemiluminescent analyzers to CEMS applications, care must be exercised to ensure that the analyzer

interference rejection characteristics are suitable for the major stack gas constituents of interest. The O_2 and CO_2 in the sample stream can cause quenching of the chemiluminescent reaction, the effect of which is dependent on specific analyzer design details. In combustion applications the concentrations of O_2 are lower, and CO_2 is much higher, than in the typical ambient air monitoring applications. Special CEMS configurations of NO_x analyzers have been developed to minimize the CO_2 quenching effect by increasing the sample dilution with the ozone carrier gas. Calibration gases may need to contain the typical level of CO_2 observed in the sample in order to maximize the accuracy of the system. Further, if substantial NO_2 is present in NO_x , one must ensure that the converter included in the NO_x analyzer can handle such high NO_2 concentrations. The IR measurement of NO and/or NO_2 is particularly difficult because their primary spectral absorption signatures are overlaid by H_2O absorption. Thus GFC or dispersive techniques are usually required to obtain reasonable H_2O interference rejection. The UV absorption measurement of NO is much more specific with respect to water interference and provides good sensitivity, but not down to ambient levels without special techniques.

Carbon monoxide and CO_2 are usually measured in the IR using a combination of NDIR and GFC measurement techniques. This technique has been perfected for use in CO ambient air quality analyzers and has been extended to higher ranges as well as to CO_2 measurement. The optical measurement path length is the primary variable to scale analyzer measurement ranges, with near 5 m path length used for ambient CO measurements down to 0.1 ppm or less and progressively shorter path lengths associated with higher concentration measurements. Multipass cells are used to reduce the physical size and volume associated with such long path lengths. With proper design, such instruments can be made relatively insensitive to typical levels of H_2O in dry-sample systems. However, CO is affected by CO_2 since they spectrally overlap each other, but proper selection of the measurement band and the use of GFC reduces this effect to near negligible proportions.

Note: If other gases cause substantial interference with the measurement of the gas of interest, the interference can generally be reduced by either of three techniques: (1) physically removing it from the sample by using a specific filter targeted at the interfering species; (2) measuring the interfering gas and mathematically subtracting its contribution from the measurement of the gas of interest; and (3) calibrating it out by using a calibration gas(es) which includes the known interferent so that its effect is taken into account during the calibration of the instrument. The latter only works well if the concentration of the interfering gas is reasonably stable in time.

Oxygen is measured either by a solid-state electrolyte (zirconium oxide) sensor technique or with paramagnetic techniques in most CEMS applications. The solid-state electrolyte technique, also known as the fuel cell technique, has been perfected over many years as both an in situ analyzer and a conventional bench/rack extractive-type analyzer. It is extremely rugged and reliable and easily meets CEMS performance requirements. It has no known interferences, although care must be exercised in some applications since it provides a measurement of net

O₂, that is, the O₂ left over after the coexisting combustibles have been combusted. The zirconium cell is operated at near 1500°F, which causes the combustibles in the gas stream to combust on the surface of the cell and leaves the residual O₂ to be measured by the cell. This is not normally of any significance since combustibles are on the order of tens or hundreds of ppm, and O₂ is on the order of several percent (tens of thousands of ppm) of the gas. Paramagnetic techniques are also very well developed and do not have the complication of a hot measurement cell associated with the zirconium oxide approach. They can exhibit some NO interference and must be applied properly for reliable operation. Electrochemical cells are also used for O₂ measurements. Their lifetime is limited, necessitating periodic replacement.

Electrochemical cells can also be used to measure SO₂ and NO_x as well as other gases of interest. Current technology has produced cells that reduce the potential poisoning and interference effects of older designs and are quite robust. When properly used, they can provide accurate and reliable measurements over short-(hours) to medium-term (days) time periods. They do require periodic ambient air refresh cycles so that measurements must be interrupted from time to time, or dual cells can be used that alternate between the refresh and measurement cycles. They have been used very successfully in hand-held and portable test instruments but have never gained significant market acceptance in U.S. CEMS applications.

The catalytic sensor is another gas detection technique that has been used extensively for combustion control applications and, with further refinements, has been recently applied to continuous emission monitoring. Historically, catalytic sensors were used for CO and combustible monitoring where it was relatively easy to provide a heated catalyst that when exposed to combustible gases would facilitate combustion and a rise in temperature of the catalyst. This temperature rise was then correlated with the concentration of the combustible. Such sensors were also subject to poisoning of the catalyst and were not highly specific. A prepackaged sensor-based system has been marketed that uses advanced catalytic techniques to measure CO and NO_x (both NO and NO₂) with a zirconium oxide sensor for O₂. Such catalytic sensors are inherently simple to operate and eliminate much of the complexity associated with traditional optical-based analyzers, but they must be carefully configured for the specific application.

KEY CONCERNS. In any extractive gas measurement system, there are two key concerns: sample integrity and minimizing maintenance of the sample train. Sample integrity is typically maintained by ensuring that the sample is kept in a hot, wet condition up until the point that it is either diluted or where the water is deliberately removed. If water is removed, one must consider the potential degradation of some of the acid gases and hydrocarbons. As the temperature of the gas stream is reduced, condensables are removed along with the liquid water. Further, the water-soluble gases in the sample will be reduced by virtue of their interaction with water on the walls of the cooler. Verifying that the sample train is leak free is, of course, basic to the operation of an extractive system. For parts of the sample train under vacuum, this is of particular concern. Sample train temperature is also