PB-204 877

INSTRUMENTATION FOR THE DETERMINATION OF NITROGEN OXIDES
CONTENT OF STATIONARY SOURCE EMISSIONS   VOLUME 1

Leo P. Parts, et al

Monsanto Research Corporation
Dayton, Ohio

October 1971

Volume   PB 204 877

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OF NITROGEN OXIDES CONTENT

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By

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DAYTON
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DAYTON, OHIO 45407

APTD-0847

MRC-DA-307

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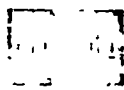Leo P. Parts
Paul L. Sherman
Arthur D Snyder

Contract No EHSD 71–30

For

Environmental Protection Agency
Office of Research and Monitoring
Durham, North Carolina

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY

DAYTON
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NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va 22151

75

BIBLIOGRAPHIC DATA SHEET	1. Report No APTD-0847	2.	3. Recipient's Accession No.

4. Title and Subtitle
INSTRUMENTATION FOR THE DETERMINATION OF NITROGEN OXIDES CONTENT OF STATIONARY SOURCE EMISSIONS

5. Report Date
October 1971

6.

7. Author(s)
Leo P. Parts, Paul L. Sherman, Arthur D. Snyder

8. Performing Organization Rept No MRC-DA-307

9. Performing Organization Name and Address
Monsanto Research Corporation
Dayton Laboratory
Dayton, Ohio 45407

10. Project/Task/Work Unit No

11. Contract/Grant No
EHSD 71-30

12. Sponsoring Organization Name and Address
Environmental Protection Agency
Office of Research and Monitoring
Durham, N C.

13. Type of Report & Period Covered

14.

15. Supplementary Notes DISCLAIMER: This report was furnished to the Office of Air Programs by Monsanto Research Corporation, Dayton Laboratory, Dayton, Ohio 45407 in fulfillment of Contract EHSD-71-30

16. Abstracts
Information regarding the state-of-the-art of NO_x (x = 1 to 2) monitoring instrumentation has been assembled and evaluated The evaluation was based on the present and projected requirements in stationary source emissions monitoring, the operational characteristics and performance capabilities of the instruments, and on the cost/performance criteria. Commercially available and prototype instruments, and laboratory-stage instrumental methods are covered. Instruments based upon wet chemical methods were excluded. The design and operational features of seven instruments which are undergoing laboratory and on-site evaluation at a fossil fuel burning installation are described Sixteen other NO_x analysis concepts were also evaluated. Chemiluminescence, correlation spectrometry, mass spectrometry and selective photoionization have been identified as the preferred analysis methods upon which new NO_x emissions monitoring instruments can be based, using currently available technology, to meet the performance requirements. Novel and potentially useful monitoring techniques, based on the evolving laser technology, were identified. Materials, devices, and information needed to establish the practical usefulness of these techniques in source monitoring are discussed

17. Key Words and Document Analysis 17a. Descriptors

Nitrogen oxides
Air pollution
Measuring instruments
Exhaust gases
Monitors
Infrared equipment
Ultraviolet equipment
Electrochemistry
Luminescence
Gas chromatography

Nucleation
Lasers
Mass spectrometry
Photoionization
Fluorescence

17b. Identifiers Open-Ended Terms

17c. COSATI Field/Group 13B, 14B

18. Availability Statement

19. Security Class (This Report) UNCLASSIFIED	21. No of Pages 76
20. Security Class (This Page) UNCLASSIFIED	22. Price

USCOMM DC 40310-P71

INSTRUMENTATION FOR THE DETERMINATION
OF NITROGEN OXIDES CONTENT
OF STATIONARY SOURCE EMISSIONS

Volume I

October 1971

By

Leo P. Parts
Paul L. Sherman
Arthur D. Snyder

To

Environmental Protection Agency
Office of Research and Monitoring
Durham, North Carolina

Contract No. EHSD 71-30

MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
Dayton, Ohio 45407

In December of 1970, the Environmental Protection Agency contracted with Monsanto Research Corporation to conduct a laboratory and field evaluation of commercially available continuous monitors for nitrogen oxides emitted from stationary sources.

This report, Volume I, details the survey of instrumentation and techniques capable of measuring NO_x emissions which preceded the start of laboratory and field testing of the commercially available units.

The literature search conducted for this report encompassed the following journals and Government abstracting publications:

Chemical Abstracts (1906-1970)
Chemical Titles (last two years)
Analytical Abstracts (1969-1970)
Analytical Chemistry (April issues from odd-numbered years)
Environmental Science and Technology (1967-1970)
Journal of Air Pollution Control Association (1958-1970)
NAPCA Abstract Bulletin (1970)
Technical Abstract Bulletin (1964-1970)
Scientific and Technical Aerospace Reports (1963-1970)
U.S. Government Research and Development Reports (1968-1970)

Approximately 300 abstracts and papers were identified as those most relevant for establishing the methods which have been developed, proposed, or which appear applicable for continuous monitoring of nitrogen oxides.

Information regarding commercial instruments was obtained from the manufacturers in the form of technical sales brochures and operating manuals. The information collected by Stevenson, Jordan and Harrison, Management Consultants, Inc., in interviews of manufacturers was also used.

A computer-search of information pertaining to nitrogen oxides measurement and measurement methods was conducted by the Air Pollution Technical Information Center. This search has been supplemented by monthly updates through June 1971, abstracted primarily from recent acquisitions

Volume II, which will contain the results of the laboratory and field tests, will be available on or about 1 February 1972.

This report is based on work accomplished under Contract EHSD 71-30, with the Environmental Protection Agency, Division of Chemistry and Physics, Durham, N.C.

Frederic C. Jaye
Project Officer
Stationary Sources Emission Measurement Methods Section

ABSTRACT

Information regarding the state-of-the art of NO_x
(x = 1 to 2) monitoring instrumentation has been assembled
and evaluated. The evaluation was based on the present
and projected requirements in stationary source emissions
monitoring, the operational characteristics and performance
capabilities of the instruments, and on the cost/performance
criteria

The report encompasses commercially available and proto-
type instruments, and laboratory-stage instrumental methods are
Instruments based upon wet chemical methods were excluded from
consideration.

Four commercial instruments based on the measurement
of nondispersed infrared radiation absorption, one instrument
based on visible radiation absorption, and two instruments
based on voltammetric principles are undergoing laboratory
and on-site evaluation at a fossil fuel-burning installation
in the present program. The design and operational features
of these instruments are described.

The evaluation encompassed sixteen other NO_x analysis
concepts. Chemiluminescence, correlation spectrometry, mass
spectrometry and selective photoionization have been identified
as the preferred analysis methods upon which new NO_x emissions
monitoring instruments can be based, using currently available
technology, to meet the performance requirements.

Novel and potentially useful monitoring techniques,
based on the evolving laser technology, were identified
Materials, devices, and information needed to establish the
practical usefulness of these techniques in source monitoring
are discussed.

1. INTRODUCTION

The purpose of the effort summarized in this report was to assemble and evaluate information regarding the state-of-the-art of continuous NO$_x$ (x = 1 to 2) monitoring instrumentation. Reliable instrumentation will be required for the development of effective air pollution control technology. The present report encompasses commercially available instruments, prototypes, and laboratory-stage instrumental methods. The instruments and methods have been evaluated for their present or potential applicability to the monitoring of NO$_x$ emissions which emanate from stationary installations.

Most of the presently used source monitoring instruments represent adaptations of laboratory and process control instrumentation. The instruments most widely used for NO$_x$ monitoring are based on the absorption of nondispersed infrared radiation (ref. 1,2), on the oxidation of NO to NO$_2$ and subsequent measurement of absorption in the visible spectral range (ref. 3), and on electrochemical principles (ref. 4,5).

The need for pollution monitoring instruments of improved specificity and sensitivity has been discussed in recent publications (ref. 6-11). To reduce the maintenance requirements and complexity of instruments, it is highly desirable that the NO$_x$ monitoring instruments would be based on direct measurement of some physical property of the nitrogen oxides in the gaseous test sample. Alternatively, physical phenomena associated with specific gas phase reactions of pollutants with some reactive species (e.g., luminescent emission) lend themselves readily to optoelectronic monitoring.

Wet chemical methods that entail preparation, metering and continuous consumption of aqueous reagents (i e , photometric measurement of light-absorbing product formation, conductometric analysis) are not considered to be among the preferred methods for continuous monitoring of NO$_x$ emissions. Therefore, such methods are not discussed in this report.

The following are some target criteria of demonstrated or projected performance that would be desirable in emission monitoring instruments

Selective response to NO and/or NO$_2$ attainable.

Range of 0-2000 ppm for immediate applications, 0-200 ppm range for controlled emission monitoring applications

Attainable accuracy and repeatability ±2% of maximum
range during seven days of continuous operation.

Minimal interference by water vapor, carbon dioxide,
carbon monoxide, and sulfur dioxide.

Response time less than 2 minutes.

Capability for multifunctional operation (NO,
NO_2, SO_2, CO, and O_2).

Sufficiently rugged to require minimal repair while
used in fuel-burning industrial installations.

Simplicity of design and operation

Minimal sample conditioning required.

Low cost.

The sources of information, upon which the present evalua-
tion and report are based, are listed in the Foreword. In
Section 2 of this report, three categories of NO_x monitoring
methods are discussed. Those which are applied in the presently
available commercial instruments are described in Section 2.1.
Five methods of demonstrated feasibility, that could be used
as the basis of new source monitoring instruments, are described
in Section 2.2. Three additional methods of potential utility,
which are based on recent technology and require further
development and evaluation to establish their practical utility,
are discussed in Section 2.3.

Abstract descriptions of NO_x monitoring methods of the
above-listed three categories with relevant references are pre-
sented in Section 3. This section contains also the abstract
descriptions of eight additional NO_x analysis methods that have
been described in the literature. The latter are not believed
to represent the basis for reliable, economically competitive
monitoring instruments.

2. DISCUSSION

2.1 Methods Applied in Commercially Available Instruments

The instruments for the monitoring of NO_x emissions from
all types of stationary sources, that were commercially available
at the time when work on this program was initiated, are based
on three detection concepts

Absorption of nondispersed infrared radiation

Photometric measurement of visible and ultraviolet
radiation absorption in selected wavelength ranges.

Voltammetric measurement.

Nondispersive infrared radiation measurement instruments utilize
a broad-spectrum emission source in conjunction with a spectro-
phonic detector. This detector is responsive only to radiation
at the NO absorption wavelength. Since emission gases other
than NO (e.g., H_2O) absorb to some extent at this wavelength,
the nondispersive infrared instruments are subject to inter-
ference. To eliminate or minimize interference, auxiliary
absorption cells or optical filters are incorporated that remove
most of the radiation at wavelengths at which the interfering
substances absorb. The presently available nondispersive infra-
red instruments do not monitor the NO_2 component of NO_x which
constitutes approximately 5% of the total nitrogen oxides.

The commercially available photometric analyzer for NO_x
represents an adaptation of a multipurpose instrument, based
on dual-wavelength monitoring, to pollution control applications.
Monitoring for NO_x is based on the measurement of light trans-
mission at a wavelength (4360 Å) in the visible spectral region
at which NO_2 absorbs radiation. No other gaseous component,
emitted by fossil fuel burning installations, absorbs at this
wavelength. Therefore, no interference would be caused by
other emission gas components.

Since NO_2 is a minor nitrogen oxide component in emission
gases, the gas sample is oxidized with oxygen at 5 atmospheres
pressure. The 10-minute analysis cycle, necessary for complet-
ing the oxidation, introduces a time delay into the analytical
data acquisition process

The voltammetric instruments have been developed within
the past five years. Their design entails new concepts, combin-
ing diffusion of gaseous pollutants through a permeable membrane
into an electrolyte with electrochemical oxidation or reduction.
The diffusion is the rate-controlling process. The current
generated in the electrochemical oxidation at a fixed potential

is proportional to the concentration of the electro-reactive species in the gas. It appears that the attainment of selective oxidation, alteration of electrode surfaces, temperature-sensitivity of output, and evaporation of water from the sensor compartment may represent problem areas that will require investigation and remedial measures. It should also be noted that the voltammetric instruments are very compact and therefore convenient to use for noncontinuous multi-site monitoring at a fuel-burning installation.

The following monitors which were commercially available in January 1971 are being evaluated in our laboratory and field test program.

Nondispersive infrared instruments

> Model 315 Infrared Analyzer by Beckman Instruments, Inc.
>
> UNOR-2 by the Bendix Corporation
>
> Uras-2 by Intertech Corporation
>
> LIRA Model 200 by the Mine Safety Appliances Company

Photometric analyzer

> Model 461 Photometric Analyzer by the duPont Company

Voltammetric instruments.

> Air Pollution Monitor Model NX 130 by the Dynasciences Corporation
>
> Series NS-200A Monitor with Type N76H2 Faristor sensor by EnviroMetrics, Inc.

A third instrument, based on the voltammetric technique, has recently become available from Theta Sources, Inc (ref 12)

Section 3 of this report provides specific information regarding each of the instruments that is undergoing testing in the present program The selection was based on a preliminary user survey, conducted under a subcontract by Stevenson, Jordan, and Harrison, Management Consultants, Inc., in which the currently more widely used instruments were established

The following novel types of instruments have either very recently been introduced on the market, or they are known to be under development in industry

An on-stack optical absorption measurement instrument of proprietary design, offered by the Enviromental Data Corporation (ref. 13).

An emission spectrophotometer for multicomponent analysis (NO_x, SO_2, CO) of sampled stack gases was recently introduced by Monitor Labs, Inc. (ref. 14).

A second-derivative ultraviolet spectrometer, developed by Spectrometrics of Florida, has been used for ambient air monitoring. A modified instrument, based on the same principle, is soon to be tested for the monitoring of NO_x emissions from combustion sources (ref. 15).

An instrument that measures the absorption of fluorescent radiation, generated by a mixture of isotopically differing species, is under development for stack emissions measurement by Arkon Scientific Laboratories (ref. 16).

Since many operational features of the last-listed four instruments are believed to be of proprietary nature, they cannot be discussed in detail at the present.

2.2 NO_x Monitoring Methods Used in Prototype Systems

A number of approaches have been explored in the search for reliable instrumental methods of NO_x analysis. Some of these approaches have been based on well-established technology. However, more frequently, the reported exploratory investigations represent attempts to utilize newly evolved technology for the solution of existing analytical problems.

The search of the literature has revealed that the applicability of the following methods has been investigated for NO_x analysis

1 Chemiluminescence ($NO + O$)
2. Chemiluminescence ($NO + O_3$)
3 Gas chromatograpny
4 Condensation nucleation
5 Correlation spectrometry
6. Dielectric constant measurement
7 Electron-excitation
8 Gas phase ionic conductance
9 Inverse radioactive tracing
10 Interference spectrometry
11. Laser radiation absorption
12 Laser Raman scattering
13. Mass spectrometry

14. Paramagnetism measurement
15. Photoionization
16. Vibrational fluorescence

Abstract descriptions of the principles involved in the utilization of each listed method are presented in Section 3. References to pertinent publications, comments regarding the operational principles and features, and information regarding the commercial developmental status can also be found in that section of the report

Eight methods merit further consideration. The following five are at the developmental stage at which prototype source monitoring instruments can be designed, constructed and evaluated.

  Chemiluminescence   (NO_x + O)
  Chemiluminescence   (NO_x + converter + O_3)
  Correlation spectrometry
  Mass spectrometry
  Selective photoionization

Three additional methods may prove to be of practical utility at some time within the next ten years·

  Laser radiation absorption
  Laser Raman scattering
  Vibrational fluorescence

The latter three approaches to NO_x monitoring are based on the evolving laser technology. Conceptual feasibility has been demonstrated. However, exploratory research, laser materials development, and equipment design are required before these methods can be reliably evaluated for their practical utility in monitoring NO_x emissions in plant environment.

It should be noted that two of the methods that are recommended for immediate consideration (chemiluminescent emission from the reaction with atomic oxygen and correlation spectrometry) are applicable for simultaneous NO_x, SO_2, and CO monitoring. Mass spectrometry can be applied for simultaneous monitoring of NO_x, SO_2, and O_2. All eight methods are based on the measurement of some specific structure-related property of the pollutants contained in the emission gases

2 3   Brief Discussion of Potential New Approaches to the Monitoring of NO_x Emissions

It has recently been demonstrated that the measurement of *chemiluminescent emission* can be utilized for the monitoring of atmospheric NO content at concentrations ranging to the low value of 5 ppb (ref. 17). This method is based upon the measurement of chemiluminescent emission intensity associated with the reaction of nitric oxide with atomic oxygen

$$NO + O \rightarrow NO_2^* \tag{1}$$

$$NO_2^* \rightarrow NO_2 + h\nu \tag{2}$$
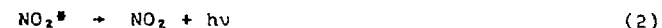
The method is applicable for the monitoring of total nitrogen oxides, since the NO_2 present in the gaseous sample yields NO upon reaction with atomic oxygen·

$$NO_2 + O \rightarrow NO + O_2 \tag{3}$$

Nitric oxide formed from NO_2 by reaction (3) is reoxidized by atomic oxygen, with concomitant emission of radiation around 6300 Å

The system developed for nitric oxide monitoring in ambient atmosphere has been demonstrated to be even more sensitive in the monitoring of SO_2 *via* the chemiluminescent reactions

$$SO_2 + O \rightarrow SO_3^* \tag{4}$$

$$SO_3^* \rightarrow SO_2 + h\nu \ (\lambda \sim 3500 \text{ Å}) \tag{5}$$
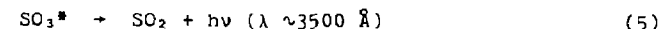
The reaction of carbon monoxide with atomic oxygen is also accompanied by chemiluminescence However, a relatively smaller fraction of the evolved energy appears as emitted radiation in the visible spectral range ($\lambda \sim 4350$Å) and the present detection limit for carbon monoxide is 100 ppm. It is believed that the chemiluminescence ($\lambda \sim 3890$Å) quantum efficiency for the reaction of CO with atomic nitrogen, that produces CN, is sufficiently high to utilize that reaction for CO monitoring at low concentrations.

It is visualized that a source monitoring system based on chemiluminescent reactions with atomic oxygen and atomic nitrogen (for CO) can readily be developed. This will entail lowering the sensitivity of the chemiluminescent ambient atmospheric NO_x detector It appears possible to develop a multifunctional system for simultaneous continuous monitoring of NO_x, SO_2 and CO in emission gases. This development will also require the

design of an optical detection system for simultaneous measurement of luminescence in three spectral ranges, characteristic for each of the three major pollutants present in emission gases.

Nitric oxide reacts readily with ozone

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad (6)$$
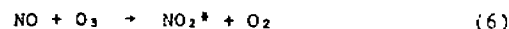
The measurement of chemiluminescent radiation emission [see reaction (2)] associated with this reaction (ref. 18) has been applied for nitric oxide monitoring in ambient air and in automobile emissions (ref. 19-21). The reaction rates of ozone with NO_2, SO_2, and CO are much lower than the corresponding rate for the reaction with NO. Therefore, the monitoring of the chemiluminescence intensity arising from the introduction of gaseous ozone at low concentrations into emission gases is directly applicable only for the monitoring of their NO content (ref 19).

The total NO_x content of emission gases could be determined by using a converter in which NO_2 is quantitatively reduced to NO. Need has been indicated for the development of a reliable converter that will allow the use of the $NO_x + O_3$ chemiluminescence monitor on all types of emission sources.

Correlation spectrometry (ref. 22-27) entails the matching of absorption maxima of the material being analyzed with the reference spectrum (correlation mask) contained in the monitoring instrument The intensity of radiation transmitted through the mask is detected photoelectrically, it is related to the concentration of the analyzed substance

Correlation spectrometry has been employed most extensively and successfully for remote (frequently aerial) monitoring of atmospheric pollutants (NO_2, SO_2). This method has also been used for SO_2 monitoring in stack emission gases The optical system of the sensor has been inserted into the stack for the latter purpose. To detect nitrogen oxides in stack emission gases at the required low concentrations, it may be essential to utilize a multiple-reflection optical system Monitoring emissions external to the stack, subsequent to removal of particulate matter, would considerably simplify problems associated with the protection of the optical components of the spectrometer. The usefulness of a correlation spectrometer would be significantly enhanced in the present application through the incorporation of multi-component pollutant detection capability

New mass spectrometric instruments have evolved during the recent years which provide somewhat reduced resolution and range capabilities, when compared with conventional laboratory systems,

for very significant reduction of complexity, weight, and cost. Omegatrons (ref. 28-30), quadrupole (ref. 31,32), ion storage (ref. 33), and single-focusing mass spectrometers have been developed. These have been used primarily for residual gas analysis, space cabin atmosphere monitoring, and process control instrumentation. With the exception of NO_2^{16} and $CO^{16}O^{18}$, CO and N_2, these mass spectrometers offer sufficient resolution to separate the peaks associated with the major pollutants in emissions emanating from fossil fuel-burning installations.

The natural abundance of the O^{18} isotope in oxygen is 0.2%. The parent peaks of NO_2^{16} and $CO^{16}O^{18}$ coincide in low-resolution mass spectrometric measurements. Should it be necessary to determine NO_2, in addition to NO in emission gases, it will be essential to incorporate a logic sub-system in the instrument that will automatically subtract the $CO^{16}O^{18}$ contribution from the m/e = 46 peak intensity

To enhance the sensitivity of mass spectrometers, the signal-to-noise ratio can be improved by modulated beam operation For this purpose, the sample ion beam is periodically interrupted, the background contribution is measured, and a correction is applied to the monitored m/e peaks The low-resolution mass spectrometers will certainly provide sufficient sensitivity, when operated in the modulated beam mode, for emissions monitoring even in the low ppm range

Gas phase ionization can be induced with vacuum ultraviolet radiation Nitric oxide and nitrogen dioxide have lower ionization potentials (9.26 eV and 9.83 eV, respectively, ref. 34-40) than other gases commonly encountered in emission gases. The ionization potentials of SO_2, CO and CO_2 are 12.34, 14 01, and 13.79 eV, respectively Thus, it is feasible to effect selective photoionization of nitrogen oxides in emission gases (at $\lambda = 1050$ to 1350 Å) and to monitor their concentrations by conductivity measurement. Instruments designed for high-altitude atmospheric NO detection and monitoring have demonstrated the applicability of this method even for low-concentration measurements.

The ionization potentials of most emission gas components (major pollutants other than NO_x, combustion products, and atmospheric gases) are in the range of 12-14 eV. Therefore, the selective photoionization technique does not appear to be applicable for multifunctional monitoring of pollutants emitted by the major types of emission sources.

The discovery and development of lasers has opened new avenues to pollution monitoring. These novel energy sources provide collimated, monochromatic radiation in the infrared,

visible, and ultraviolet spectral ranges. The main advantages of laser energy sources – the very narrow wavelength range, the intensity, and the collimation of emitted radiation – must be evaluated with reference to advantages that can be gained through these characteristics, the reliability and stability of operation, and the cost.

It is well to appreciate that laser technology is still in infancy, significant discoveries that affect technological developments occur with a high frequency. The versatility, operational capabilities and reliability of lasers are continuously improving, their cost is diminishing.

Because of the inherent or attainable frequency coincidence of some laser emission lines with absorption bands or vibrational-rotational lines of pollutants, *laser radiation absorption* has been utilized for pollutant monitoring (ref. 41-50). Long-path detection systems have been used for atmospheric monitoring (ref 41,42). A laser spectrophone has been demonstrated to be applicable for the analysis of NO in collected gaseous samples at concentrations below 1 ppb (ref. 47-49).

Nitric oxide can be monitored by absorption measurement with iodine (ref. 41,42), carbon monoxide (ref. 44,50), and InSb spin flip Raman (ref. 47-49) lasers. All three approaches entail the use of gas lasers. Carbon monoxide lasers, when operated at liquid nitrogen temperatures, emit by vibrational-rotational transitions in the broad spectral range extending from 1216 to 2013 cm^{-1}. The emitted spectrum consists of approximately 200 pressure-broadened lines of ~ 0.05 cm^{-1} half-width (ref. 51,52). The frequencies of some CO laser emission lines correspond to absorption frequencies of NO, NO_2, and SO_2 (ref. 50). The CO laser, when operated at the liquid nitrogen temperature, could in principle be used for multifunctional pollutant monitoring. When operated at room temperature, the spectral range of radiation emitted by the CO laser is much narrower (ref. 53) and it does not encompass the fundamental vibrational frequencies of NO_2 and SO_2.

Precise tuning to the desired frequency, in the range of 5 to 6 µm, has been attained by inducing spin flip stimulated Raman emission from InSb by CO laser excitation (ref 47,54,55) Thus, collimated radiation of very narrow spectral range can be generated at frequencies that correspond to the centers of NO absorption lines. Furthermore, monitoring can be conducted at frequencies at which the atmospheric water causes no interference. The spin flip Raman laser has very recently been used to determine NO concentrations below 1 ppb (ref 49). Strong magnetic fields and cryogenic temperatures are required for the attainment of spin flip Raman laser emission. Those requirements

are presently a distinct handicap in continuous source monitoring. However, this novel technique is of definite interest as a laboratory method applicable with very low NO concentrations.

The application of semiconductor lasers has been proposed for pollution monitoring (ref. 46). Emission at the desired frequencies is attained by controlling the composition and operating temperature of these lasers. The emission line width attained with $Pb_{1-x}Sn_xTe$ is very narrow ($< 3.3 \times 10^{-6}$ cm^{-1}). The thermal tuning range, attained through the control of diode current is ~ 40 cm^{-1}. Emission ranging from 6.5 to 32 µm has been attained with $Pb_{1-x}Sn_xTe$ lasers through compositional variation (ref. 46). It is visualized that $PbSn_{1-x}Se_x$ can be induced to emit at shorter wavelengths, which would encompass NO (5.50 µm) and CO (4.86 µm) absorption ranges (ref. 46).

Semiconductor lasers are generally less complex in design, and physically more compact and rugged than gas discharge and spin flip Raman lasers. Detection capability in the fractional ppm range is visualized with the former. Semiconductor laser radiation absorption measurement is a technique that merits thorough feasibility and utility evaluation for the monitoring of emissions from stationary sources.

Extensive *laser Raman scattering* measurements have been conducted with solid and liquid materials. To date, the lasers have found little use in Raman scattering measurements with gaseous compositions. Some interesting demonstrations of the latter type of applications have entailed the measurement of Raman-scattered laser radiation by pollutants in the atmosphere (ref. 56).

Conventional gas Raman spectrometer systems contain a cylindrical gas sample cell that is positioned concentrically with respect to linear- or spiral-shaped continuous discharge-type excitation sources (ref. 57,58). The Raman-scattered radiation is transmitted through an optical window that is mounted onto one end of the cylindrical sample cell. To enhance the scattered radiation collection efficiency, and to focus the scattered radiation onto the entrance slit of the spectrometer, the gas sample cell is equipped with alignable mirrors in both ends.

A laser Raman gas cell with internal reflecting optics has been described very recently by Welsh (ref 59). The exciting radiation is directed into the cell through the same slit that is used for the collection of scattered radiation Multiple traverses of exciting radiation through the cell enhance the scattered radiation intensity.

It would be of interest to explore the usefulness of laser-excited Raman emission measurement for the monitoring of gaseous pollutants. In contrast to conventional Raman-scattering measurements with gases, it appears advisable to use pulsed exciting radiation in conjunction with time-gating techniques for Raman-scattered radiation detection Since the Raman-scattering efficiency is proportional to the fourth power of exciting radiation frequency, it would be desirable to utilize an intense, ultraviolet laser source (e.g., the nitrogen laser, emitting at 3371 Å).

To prevent oxidation of the mirrors in the Raman cell, protective coatings are essential. A conventional high-resolution optical and time-gating photosensor system could be utilized, monitoring the radiation intensity at frequencies characteristic for the specific pollutants. To attain further enhancement of the signal-to-noise ratio, the correlation mask detection method could be employed for the measurement of scattered radiation intensity.

A preliminary evaluation of the practicality could be attained by calculations based on: (1) incident radiation intensity, (2) optical system configuration, (3) Raman-scattering cross sections of NO, NO_2, and other pollutants, and (4) detector sensitivity.

Sources of pulsed, coherent infrared radiation have made it feasible to investigate vibrational energy transfer and relaxation processes. A part of the evolved energy is emitted through *vibrational fluorescence* at frequencies that are characteristic for the molecules. The measurement of the vibrational fluorescence intensity is therefore potentially applicable for gas analysis. Some preliminary results, apparently affected by the indirect thermal excitation of the samples, have been reported.

It appears desirable to evaluate critically the applicability of vibrational fluorescence for the analysis of nitric oxide and other pollutant gases at low concentrations. This will require the design of a gas sample holder, equipped with optical windows, that will minimize the indirect thermal excitation contribution to fluorescence emission. It will also be essential to investigate intramolecular energy transfer processes to and from the pollutant species, to establish the effects of gas composition and pressure on the efficiency of fluorescent radiation emission. Furthermore, optimized detector system design, usefulness of the correlation mask technique, and the application of signal-integrating techniques merit evaluation

The utilization of the vibrational fluorescence technique presents several options in the types of excitation sources that could be used. These sources must be evaluated in conjunction with appropriate detection methods. Similarly to other methods involving the use of lasers, which have been recommended for further evaluation, vibrational fluorescence measurement lends itself to simultaneous multiple pollutant monitoring.

METHODS APPLIED IN COMMERCIAL INFRARED INSTRUMENTS

Beckman Instruments, Inc., Model 315 Infrared Analyzer

Principle of Operation

Optically, the Beckman Model 315 Infrared Analyzer and Intertech Corporation's instrument Uras-2 (see the description on p. 18) are quite similar.
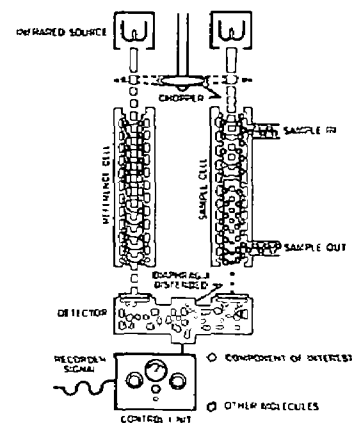
The diaphragm of the Model 315 Infrared Analyzer is part of a capacitance-type detection system of the sensor. The capacitance changes, caused by cyclic pressure differences in the two halves of the sensor when NO is present in the sample cell, modulate a radio-frequency signal from an oscillator. This signal is subsequently demodulated, amplified, and used as input to an indicating meter or to a recorder.

The Beckman Infrared Analyzer can be equipped with either filter cells or optical filters to attain complete absorption in the spectral range in which interfering substances would cause partial absorption.

Performance Specifications Indicated by the Manufacturer

Response time	90% electronic response in 0.5 sec. Instrument response depends on sample cell size and gas flow rate.
Measuring ranges	from parts per million to 100% NO
Zero drift	≤1% for 8-hour period
Span drift	≤1% full scale for 24-hour period
Reproducibility	normally within ±1% full-scale

Reference –

Bulletin 4055D, Beckman Instruments, Inc.

NONDISPERSIVE INFRARED

The Bendix Corporation, UNOR 2

Principle of Operation

The operation of the UNOR 2 instrument is based on the detection of radiation absorption in the sample compartment by means of a tandem two-component sensor unit that contains the gas which is being monitored. The sensor geometries and gas pressures are established to maintain equal pressure in the two compartments when the beam is not attenuated upon traversing the sample compartment.

The spectral distribution of transmitted energy (i.e., the intensity as a function of frequency) is dependent on NO concentration in the sample compartment. Because of the structure of the vibrational-rotational bands, the heating of gases in the two-sensor compartments is affected by the spectral distribution of incident energy. Thus, when absorption occurs in the sample compartment, the microphone-type capacitor (13) responds to the pressure difference between the two sensor compartments which contain the absorbing gas. The sensor capacitance change is converted by an amplifier to a direct current signal which is amplified and subsequently either indicated or recorded by the instrument.

1 Radiation source
2 Synchronous motor
3 Rotating chopper
4 Sample cell
5 Reference cell
6 Analysis chamber
7 Beam combiner
8 Detection chamber
9 Front measuring chamber
10 Rear measuring chamber
11 Connecting channel
12 Connecting channel
13 Diaphragm of capacitor
14 Measuring amplifier
15 Output meter
16 Recorder
17 Gas pump
18 Automatic interference indicator
19 Safety filter in the gas inlet
20 Safety filter in the gas outlet

Performance Specifications Indicated by the Manufacturer

Response time   3 sec for 90% response
Measuring range   300 ppm to 50% NO
Zero drift   ·   <1% of full-scale
Reproducibility .   within ±1% of full-scale

References -

"UNOR-2 Einstrahl-Ultrarot-Gasanalysator," Bulletin No. 1557, H. Maihak AG, Hamburg, Germany.

Bulletin SB342-1069, Bendix Process Instruments Division.

NONDISPERSIVE INFRARED

Intertech Corporation, Uras-2

Principle of Operation

The operation of Uras-2 is based on the absorption of infrared radiation from a broad-spectrum source by the sample and subsequent measurement of radiation intensities of the monitoring and reference beams. The sample gas is transported through the sample cell (4, top), whereas the reference cell contains nitrogen. The two sections of the sensor (5), separated by a thin metal membrane, are filled with the gas which is being monitored.

The radiation transmitted through the sample and the reference cell is absorbed by the sensor in the spectral range at which the substance being monitored has absorption bands. The absorption of radiation causes expansion of gas in the sensor. The difference in beam intensities, resulting from absorption of radiation by the gas in the sample cell, causes unequal expansion of the two sections of the sensor. This is measured by the capacitance-type detector that transmits the signal to an amplifier and to a meter or to a recorder.
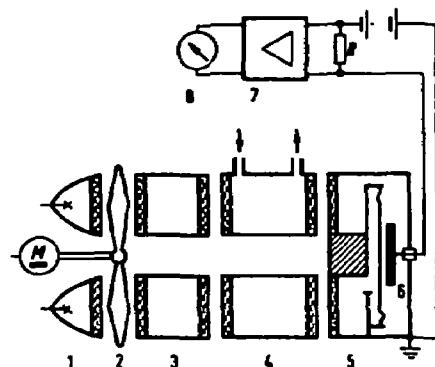
1 Radiation emitter
2 Mechanical chopper
3 Filter
4 Measuring gas cells (top· sample cell, bottom: reference cell)
5 Sensor
6 Capacitance-type detector
7 Amplifier
8 Meter or recorder

Filter cells are incorporated in the instrument to eliminate interference by substances whose infrared absorption bands overlap with those of the substance being monitored. The interfering substance is introduced into the filter cells in both beams. Thereby, radiation in the spectral range at which interference exists is completely absorbed from both beams

References -

Technical Data Sheet CG 4.3e, Intertech Corporation, September 1966.

Bulletin CG 100, Intertech Corporation, May 1969.

Catalog 8, "Analysers and Detectors for Gases and Liquids, Hartmann and Braun, G.m.b.H., April 1968.

NONDISPERSIVE INFRARED

Mine Safety Appliances Company, LIRA Model 200

Principle of Operation

The absorption of infrared radiation, emitted by Nichrome fila-
ments, is monitored in the NO absorption spectral range.

LIRA OPTICAL SYSTEM
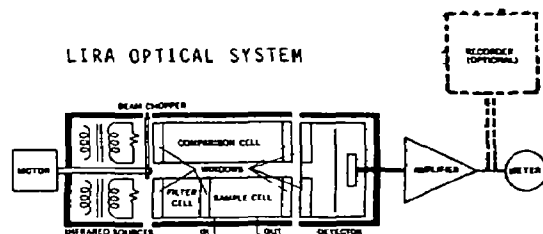
The two nondispersed infrared beams, which are periodically
interrupted by the semicircular chopper, traverse the sample
and the reference cell, respectively. The transmitted radia-
tion is directed into the sensor compartment. This compartment
contains the gaseous compound(s) whose concentration is being
monitored in the gas sample. Incorporated in the sensor is a
microphone that is equipped with a membrane which responds to
pressure fluctuations in the sensor gas compartment. The
capacitance change of the microphone during the pressure fluc-
tuations is converted to an analog electrical signal that is
amplified and subsequently fed to a meter or recorded.

The detector and recorder systems are electronically balanced
when no radiation is absorbed from the beam that traverses the
sample compartment. Absorption of radiation in the sample cell
causes unequal gas expansion in the sensor during the two con-
secutive beam-chopper half-cycles This results in different
capacitance values, the difference is recorded in terms of NO
concentration.

To prevent interference by compounds which absorb in the spectral
range of NO absorption, a filter cell is incorporated in tandem
with the sample cell. The filter causes total absorption in the
range in which the interfering compound would cause partial and
variable absorption

Performance Specifications Indicated by the Manufacturer

Response time   : 90% of final reading in 5 sec (or 0.4 sec
                     as an added option).

Measuring ranges. From 0 to 100 ppm up to 0 to 100% full-scale
                     by using cells of different lengths.

Zero drift   . <1% of full scale in 24 hr.

Reproducibility : within ±1% of full scale.

Ambient temperature range. -1° to +49°C

Selectivity   . results affected <1% by background varia-
                     tions during most analyses.

Reference -

Bulletin No. 0705-12, Mine Safety Appliances Company, Instrument
Division.

NONDISPERSIVE VISIBLE AND ULTRAVIOLET

duPont Company, Model 461 Photometric Analyzer

Principle of Operation

The monitoring with the duPont photometric analyzer is based on
the measurement of the difference in absorption by the sample
at two separate wavelengths. The radiation from a light source
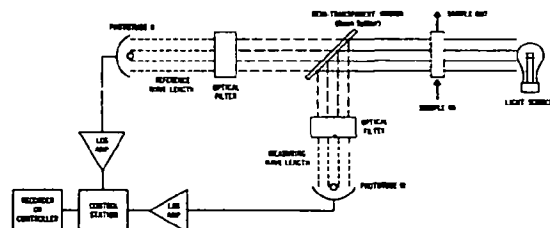
traverses a sample. The transmitted radiation is subsequently
split into two beams. An optical filter that transmits radiation
at the wavelength at which the sample absorbs strongly (measuring
wavelength), and that absorbs radiation essentially completely
in the remaining portion of the spectrum, is positioned between
the sample and the phototube M. A second filter, which transmits
only at a reference wavelength, at which the substance that is
being monitored does not absorb, is placed in the second part of
the split beam

The current from the phototubes, which is related to the incident
radiation intensity, is amplified. The output from the amplifiers
is corrected for the logarithmic relationship between the inten-
sity and concentration. The differential output from the two
amplifiers is proportional to the concentration of the monitored
compound.

The Model 461 Photometric Analyzer is equipped with a sampling
system for quantitative oxidation of NO_x to NO_2. When the system
is operated in this mode, the 4360 Å mercury line is used for the
sample analysis beam, and the 5460 Å mercury line serves as the
reference beam. When the nitrogen oxides are oxidized and deter-
mined as NO_2, an eight-minute sample residence time is required
to complete the oxidation.

Performance Specifications Indicated by the Manufacturer

Response time	1 sec standard, down to 0.001 sec available
Measuring ranges	0.05 to 4.0 absorbance units
Zero drift	<1% full-scale in 24 hrs
Reproducibility	~1/4% (usually limited by recorder)
Accuracy	in % of analyzer reading = (% accuracy of calibration standard) + (±1% of analyzer reading) + (±1/4% of full-scale range).

Allowable temperature range: 0° to 100°C.

References

DuPont 400 Split Beam Photometric Analyzer Instruction Manual,
Instrument Products Division, E. I. duPont de Nemours &
Co. (Inc.).

DuPont 461 Nitrogen Oxides Analyzer System, Instrument Products
Division, E. I. duPont de Nemours & Co. (Inc.).

400 Photometric Analyzer, Instrument Products Division, E. I.
duPont de Nemours & Co. (Inc.).

ELECTROCHEMICAL

Dynasciences Corporation, Air Pollution Monitor Model NX 130

Principle of Operation

The sensor operates on the voltammetric principle. The electrodes and the electrolyte are enclosed in the sensor that is equipped with a semipermeable membrane. The nitrogen oxides diffuse through the membrane and they are oxidized at the anode. The rate of diffusion is proportional to the concentration of nitrogen oxides in the atmosphere to which the membrane is exposed.
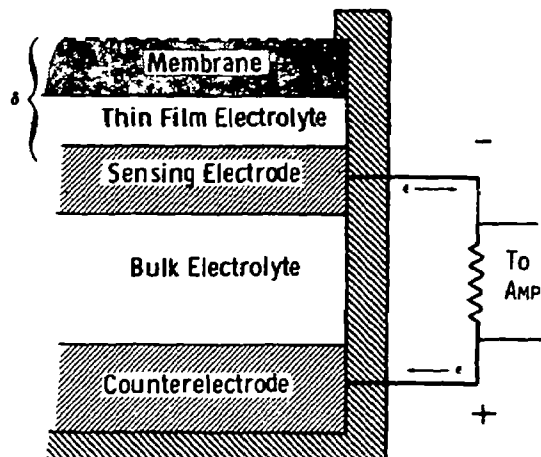
Since the diffused NO_x is subsequently quantitatively oxidized to the nitrate ion, the current is directly proportional to the NO_x concentration in the gas to which the membrane is exposed. The current measured with the potentiostat is amplified and displayed in terms of NO_x concentration on the meter.

The selectivity of the voltammetric sensor is attained through the appropriate combination of electrodes, electrolyte and membrane. Information regarding the identity of materials used in commercial instruments has not been disclosed.

The sensor operating life may vary from 3 to 9 months. It is apparently frequently limited by the vaporization of the solvent through the membrane. The sensor part of this electrochemical system is readily replaceable.

Performance Specifications Indicated by the Manufacturer

Response time   : 90% of full-scale in 18 sec.

Measuring ranges: 0 to 500, 0 to 1500, and 0 to 5000 ppm

Span drift   : <1% of full-scale in 24 hrs

Reproducibility · within ±2% of full-scale by using the integral meter. Within ±1% of full-scale by use of external potentiometric recorder.

Ambient temperature range: +5° to 49°C

Specificity   . no response to N_2, O_2, CO, CO_2, hydrocarbons, and water vapor

Reference

Operating Instructions for Dynasciences Air Pollution Monitor, Instrument Systems Division, Dynasciences Corporation, Subsidiary of Whittaker Corporation.

ELECTROCHEMICAL

EnviroMetrics, Inc., Series NS-200A
With Type S64H2 and Type N76H2 Sensors

Principle of Operation

The principle of operation of this instrument, equipped with interchangeable Faristor^{TM} sensors, has not been fully disclosed by the manufacturer. The Faristor^{TM} sensors are reported to be liquid-state devices that contain surfaces onto which the pollutants are adsorbed. The adsorption is followed by electron transfer either to or from the adsorbate. The current flow is determined mainly by the rate at which the gas molecules reach the catalytically active surface and by the valence change which the adsorbed species undergo at this surface.

It is believed that the EnviroMetrics sensors operate on the voltammetric principle. Presumably the catalytically active electrodes and the electrolyte are enclosed in the sensor that is equipped on one surface with a semipermeable membrane. The membrane is exposed to the atmosphere being monitored. The current generation by the sensor is permeation-controlled by the transport of the pollutant gas through the membrane. The rate of permeation is proportional to the pollutant concentration in the atmosphere.

The selectivity of the sensor is attained through the appropriate combination of catalytically active electrodes and electrolyte. Faristor-type sensor N76H2 is generally used for total NO_x monitoring in combustion source emissions. A type S64H2 sensor is available for SO_2 monitoring.

Performance Specifications Indicated by the Manufacturer

Response time	90% of full scale in 5 to 10 seconds
Measuring ranges	continuously variable from 0-50 ppm to 0-10,000 ppm full scale. Linear response in the 0-5,000 ppm range as a minimum.
Reproducibility	within ±2% of full scale.
Ambient temperature range:	-1° to +65°C.
Specificity :	type N76H2 Faristor^{TM} sensor is specific to the total NO_x. When the NO_2 content in NO_x is less than 10%, the total error in NO_x is less than 2%. This error increases to 10% when NO_2 content is 50% of the total NO_x. The manufacturer recommends Series N-122 analyzer for NO_x monitoring in gases that contain a high percentage of NO_2 in NO_x.
Reference	*The Faristor Plug-in Module*, by EnviroMetrics, Inc.

NO$_x$ MONITORING METHODS
CURRENTLY APPLIED IN PROTOTYPE SYSTEMS

CHEMILUMINESCENCE (USING ATOMIC OXYGEN)

Principle of Operation

Electronically excited nitrogen dioxide is produced upon the reaction of nitric oxide with atomic oxygen

$$NO + O \rightarrow NO_2^* \qquad (1)$$

The deactivation of NO_2^* is accompanied by light emission

$$NO_2^* \rightarrow NO_2 + h\nu \quad (\lambda_{max} \simeq 6300 \text{ Å}) \qquad (2)$$

Nitrogen dioxide reacts with atomic oxygen without light emission and at a faster rate than nitric oxide

$$NO_2 + O \rightarrow NO + O_2 \qquad (3)$$

The NO formed in reaction (3) will subsequently undergo chemiluminescent oxidation via reaction (1). Thus, the total nitrogen oxides (NO_x) content can be determined by reaction with atomic oxygen.

Prototype instruments have been developed for the monitoring of NO_x in ambient air, based on reactions 1-3. The sample and oxidant gas streams are combined in a spherical or in a tubular reactor The atomic oxygen in the oxidant gas is generated by microwave or by electrical discharge prior to the entry into the reactor. Light emission is monitored with a photomultiplier detector. The photocurrent has been found to be a linear function of NO concentration over the concentration range from 4 ppb to at least 100 ppm.

SO_2 and CO react also with atomic oxygen by chemiluminescent mechanism. Maximum detection sensitivities of 1 ppb and 150 ppm, respectively, have been attained with these gases individually. The emission wavelength maxima of the NO-O, SO_2-O, and CO-O reactions (6300 Å, 3500 Å, and 4350 Å) are sufficiently separated for simultaneous monitoring of these three pollutants with one instrument.

Commercial Equipment

None marketed at the present. Prototype instruments have been built by Monsanto Research Corporation.

References

a   Principle of operation. 17, 60, 61

b.   Applications   17

c.   Data   17

d.   Specific instrument description· 17

Discussion

Advantages

a   Based on gas phase chemical reactions. Does not require wet chemicals.

b.   Can be used for simultaneous monitoring of NO_x, CO, and SO_2.

c.   Rapid response (<1 sec.).

d.   High reliability expected.

e.   Utilizes inexpensive optics.

Disadvantages

a.   The flow reactor requires continuous evacuation to maintain P ∿ 1-5 torr.

Conclusions

A potentially inexpensive multifunctional instrument that could be used for the monitoring of the major gaseous pollutants emanating from stationary fossil fuel-burning emission sources. Further development required to utilize this instrument for multifunctional monitoring at concentrations encountered in source emissions.

CHEMILUMINESCENCE (USING OZONE)

Principle of Operation

The reaction of nitric oxide with ozone produces electronically excited nitrogen dioxide molecules·

$$NO + O_3 \rightarrow NO_2^* + O_2$$

The transition of NO_2^* to the electronic ground state

$$NO_2^* \rightarrow NO_2 + h\nu$$

is accompanied by light emission in the 6000 to 8750 Å region

Nitric oxide detectors have been developed that are based on the measurement of light emission emanating from its reaction with ozone. Nitric oxide- and ozone-containing gas streams are combined at subatmospheric pressure in a spherical flow reactor that is equipped with an optical window. Light emission is measured with a photomultiplier tube. A linear response is obtained at NO concentrations ranging from 1 ppb to 1%.

NO_2 reacts only slowly with ozone, producing NO_3, (ref. 62), this reaction is not accompanied by chemiluminescent emission at 6000 to 8750 Å Therefore, the described method is directly applicable only for the monitoring of NO in gases which also contain NO_2. It is very probably suitable for stationary source monitoring if the instrument is equipped with a converter in which the NO_2 is quantitatively reduced to NO.

The above-described technique is being developed for ambient air and mobile source emissions monitoring.

Commercial Equipment

Available from AeroChem Research Laboratories, Inc The instrument can be purchased with an optional accessory for converting NO_2 to NO prior to admission of the gas into the reactor.

References

a   Principle of operation   18, 19

b.   Applications   6, 19, 20

c.   Data   19-21

d   Specific instrument descriptions·   19, 21

Discussion

Advantages

a.   CO and SO_2 cause no interference.

b.   Rapid response (<1 sec).

c.   High reliability expected.

d.   Utilizes inexpensive optics.

e.   System is also applicable for ozone monitoring

Disadvantages

a.   The chemiluminescent reaction of $NO + O_3$ can be used directly to measure the NO content of the gas. The determination of the total NO_x content requires the reduction of NO_2 to NO.

b.   The flow reactor requires continuous evacuation to maintain P < 1 torr.

Conclusions

A useful instrument for the monitoring of NO over a very broad concentration range.

Recommendations

Disseminate the results of prototype instrument evaluation, conducted by APCO, on ambient air and mobile source monitoring. Ascertain reliable performance or develop a converter for rapid, quantitative reduction of NO_2 to NO. Conduct verification of the combined system (converter and analyzer) in actual source monitoring.

GAS CHROMATOGRAPHY

Principle of Operation

Gas sample components are separated in a chromatographic column and their quantities are determined with various detectors (e.g., thermoconductivity or flame ionization measurement devices) upon elution.

The gas sample is transported in the column by an inert carrier gas (e.g., helium, argon). The separation of gas components is based on the molecular weight-dependent differences of gas phase diffusion rates, the interaction with solid adsorbents contained in the column, and the rate of diffusion and the solubility in the stationary phase. Since these are temperature-dependent phenomena, the efficiency of separation in a column is affected by the temperature.

Nitrogen oxides are reactive gases. The residence time of a sample in a chromatographic column is long ($\sim$2 to 15 minutes). Therefore, columns are used which are constructed of materials inert to NO_x and packed with support and stationary phase materials that do not react with NO_x. Reactive chromatographic systems (ref. 63), in which the analyzed substances are caused to undergo reactions prior to detection do not need to be inert toward NO_x.

Numerous references (ref. 64-88 represent those considered most relevant as background information) pertain to the analysis of NO_x by chromatographic techniques. It appears that only the following column materials have been applied successfully for the separation and quantitative determination of NO_2 and NO Fluoropak 80 packing with SF-96 (a methyl silicone oil) as the stationary phase (ref. 70, 76), silanized glass beads (ref. 71), firebrick support with fluorinated paraffin oil (ref. 74), and Porapak R and Q (ref 82).

Commercial Equipment

Although a variety of chromatographic instruments are produced by a number of manufacturers, none appears to have been specifically designed for continuous monitoring of emission sources.

References

a. Principle of Operation   64-88

b. Applications   71-73, 79, 80, 82-84

c. Data: 63, 65, 67-72, 76-82, 86-88

d. Specific Instrument Descriptions·   63, 67-69, 71, 76-78, 80-88.

Discussion

Advantages

a. High sensitivity at low concentrations with sensitive detectors.

b. High selectivity attainable.

Disadvantages

a. Lack of real-time analysis capability. Minimum analysis time approximately two minutes.

b. Column pretreatment required prior to NO_x analysis. Some column packing materials require prolonged pretreatment.

c. The separation characteristics of chromatographic columns in NO_x separation frequently change upon exposure to reactive gases and even upon admission of air.

Conclusions

The susceptibility of chromatographic columns used for NO_x analysis to the alteration of operational characteristics necessitates frequent recalibration and militates against their use in continuous monitoring systems for source emissions.

CONDENSATION NUCLEATION

Principle of Operation

Liquid or solid particles, 0.001 to 0.1 micron in diameter, function as nucleation sites for water droplets in an atmosphere supersaturated with water vapor. If the material that is to be analyzed is gaseous, it is usually converted into finely divided liquid or solid form (by various chemical means) prior to contacting with saturated water vapor and subsequent expansion. The scattering of light by the aerosol, that is rapidly ($\sim$10 msec) formed under controlled, reproducible conditions, is related to the concentration of the nucleating substance. The lower detection limits with various substances have been found to range from 1 ppb (for Hg, SO_2) to 5 ppm (CO_2, C_2H_5OH). The reported detection limit for NO_2 is 0.5 ppm.

Commercial Equipment

None currently marketed for NO_x monitoring. Prototype models have been developed by the General Engineering Laboratory and the Advanced Technology Laboratories of the General Electric Company. Monitors based on condensation nuclei formation are marketed for SO_2, Hg, NH_3 and CO analysis by the Environment/One Corporation of Schenectady, N. Y.

References

a. Principle of operation   89, 90

b. Applications.   89

c. Data: 89

d. Specific instrument description·   89, 90

Discussion

Advantages

a. A simple and potentially low-cost instrument.

b. Rapid response (1-2 sec).

c. Portable

d. Can be developed into an instrument for the monitoring of NO and/or NO_2.

Disadvantages

a. This instrument requires very reproducible removal of particulate matter, down to the sub-micron level, from the sample gas stream.

b. Can be subject to interferences when applied to multicomponent samples of varying composition.

c. In the simplest design form the condensation nucleation instrument could be calibrated in terms of the NO_2 content of the emission gases. This concentration is a function of the NO/NO_2 ratio and of the partial pressure of constituent gases. To determine the total NO_x content, NO in the gas sample must be oxidized.

Conclusions

Because of the above-cited disadvantages, the condensation nucleation technique does not appear useful for NO_x monitoring in source emissions.

CORRELATION SPECTROMETRY

Principle of Operation

Correlation spectrometry is based on the matching of the absorption maxima of the material being analyzed with the reference spectrum (correlation mask) contained within the monitoring instrument. Spectral regions of maximum absorbance by the compound being analyzed appear as regions of maximum transmittance on the correlation mask, which is incorporated in the exit aperture of the instrument.

The correlation spectrometer used for source monitoring utilizes a built-in light source that emits strongly in the spectral region of interest. The sample cell (or a flow-through unit) is positioned between the light source and the dispersive element. The latter is either a grating or a diffraction prism. The dispersed spectrum is directed onto the correlation mask. The wavelengths of the dispersed beam and the corresponding positions of the correlation mask are brought into coincidence with a desired frequency. This is achieved by either sweeping the dispersed spectrum across the correlation mask, or by traversing this mask through the dispersed light beam.

The light intensity transmitted through the correlation mask is detected with a photomultiplier tube. The intensity of transmitted light or its time derivative is related to the concentration of the substance being analyzed.

Commercial Equipment

Correlation spectrometers for the monitoring of NO_2 in ambient atmosphere have been developed by Barringer Research, Ltd., Rexdale, Ontario, Canada. Source monitors for SO_2 have been developed by the same firm. Similar monitors for NO_x are reportedly under development by Barringer Research, Ltd. (ref. 91). The correlation spectrometer type source monitors are available in the United States from Combustion Engineering Associates.

References

    a. Principle of operation   22-27

    b. Applications   25, 27, 92-94

    c. Data: 25, 27

    d. Specific instrument description   24, 25, 27

Discussion

Advantages

a. Multifunctional operational capability attainable through the use of more than one correlation mask.

b. Could be used for the monitoring of NO_2 and/or NO in the multifunctional mode.

c. Interference by compounds known to be present can be eliminated through the use of only the non-coinciding absorption bands in the mask, or by monitoring with more than one correlation mask.

d. A high signal-to-noise ratio is attained through simultaneous measurement of absorbance by the sample in several spectral ranges in which the major absorption bands appear.

e. Rapid response (<1 sec).

f. The lower detection limit with a 1-meter optical path length through the sample is believed to be less than 1 ppm (ref. 27).

Disadvantages

a. The optical system of the self-contained source monitoring system is subject to damage when the supply of air for the optics-protective air curtain becomes discontinued.

b. When the instrument is used directly in the stack, the varying particulate matter content would affect the accuracy of results.

Conclusions

A novel and potentially useful technique that can very probably be developed to meet the required performance criteria for source monitoring. To protect the optical components of the instrument in source monitoring, it would be advantageous to filter the gas stream. Filtration could be effected either in or external to the stack.

DIELECTRIC CONSTANT MEASUREMENT

Principle of Operation

The design is based on the effect of the dielectric properties of the gaseous sample, introduced into the capacitor of a Clapp oscillator, on the resonance frequency of the oscillator. The output of this oscillator is beat against that of a reference oscillator that contains only carrier gas in the capacitor. The difference frequency between the two oscillator circuits is a linear function of the polarizable additive content in the carrier gas that traverses the sample compartment. The lower detection limit for NO_2 has been reported as 200 ppb.

Commercial Equipment

None available.

References

a.   Principle of operation: 95

b.   Applications: 95, 96

c.   Data   96

d.   Specific instrument description: 95, 96

Discussion

Advantages

a.   An inexpensive instrument

b.   Portable

c   Rapid response

Disadvantages

a.   Nonspecific for compositions that contain more than one polarizable component. Stack emissions contain a number of polarizable compounds (i.e., CO_2, H_2O, SO_2, NO, NO_2, CO, and other compounds in smaller amounts).

Conclusions

The dielectric constant measurement instrument would be applicable for emissions measurement only as one of a multi-instrument complement. Although these instruments may not respond selectively or specifically to the components being analyzed, a mathematical analysis of the responses of these instruments would provide the compositional information

ELECTRON-EXCITATION

Principle of Operation

A gas sample is exposed to electron beam irradiation. A fraction of the kinetic energy of electrons is transferred to the gas molecules. A portion of this transferred energy appears as fluorescent radiation of wavelengths that are characteristic for the energy acceptor. The fluorescent radiation intensity is related to the acceptor concentration (ref. 97).

The electron beam excitation technique has been used in aerodynamic studies for gas density measurement, flow visualization, temperature measurement, and also for gas composition analysis (ref. 98).

Commercial Equipment

Electron beam instruments have not been developed commercially for gas analysis.

References

a.   Principle of operation   97

b.   Applications: 98

c.   Data: 99, 100

d.   Specific instrument description·   99, 100

Discussion

Advantages

a.   Sample removal from gas stream is not necessarily required

Disadvantages

a.   Intensity of radiation emitted by NO upon exposure to electron beam irradiation is low.

b.   Nitric oxide emission bands overlap with the intense emission bands of nitrogen.

c.   Emission by nitric oxide occurs from a resonance level, the emitted radiation is subject to self-absorption.

d.   High equipment cost

Conclusions

It does not appear probable that electron beam excitation of light emission by nitric oxide can be developed to a method of required sensitivity for NO_x stack emissions monitoring.

GAS PHASE IONIC CONDUCTANCE
(INVOLVING CHARGE TRANSFER AND RECOMBINATION)

Principle of Operation

Some approaches to the utilization of gas phase ionization measurement for NO_x detection entail the determination of the effect of its addition on the electrical conductivity of a carrier gas. The recombination of ionized species in argon (ref. 101) and in argon-ethylene mixtures (ref. 102) is enhanced in the presence of NO and NO_2. Detection of 10^{-8} to 10^{-10} mole is feasible (ref. 101). Since the effect of NO_x on the conductivity of ionized argon is not specifically limited to these oxides, the method has been used only in chromatographic eluant detector devices.

The conductivity of a gaseous medium is reduced very rapidly and significantly when finely divided particulate matter is injected into an ionized gas. The solid particles serve as catalytic recombination sites for the charged particles. Detectors have been developed in which nitrogen dioxide is allowed to react with ammonia. The aerosolized ammonium nitrate that is formed is introduced into a chamber in which gas phase ionization is caused by an incorporated radioactive (alpha) source. The reduction of ionic conductance in the chamber is related to the NO_2 content of the introduced gas sample (ref. 102, 103).

Commercial Equipment

An ionization monitor, based on the last of the above-described operational principles is marketed by the Mine Safety Applicance Company, Pittsburgh, Pa., under the name M-S-A Billionaire.

References

    a.   Principle of operation· 101-104

    b.   Application· 103, 104

    c.   Data   101-103

    d.   Specific Instrument Description· 101-104

Discussion

Advantages

a. High sensitivity

b. Rapid response

c. Portable instrument

Disadvantages

a. Lack of specificity.

b. Conductance measurements that entail particulate solid formation require oxidation of NO.

Conclusions

Because of the lack of specificity for NO_x detection with emissions from stationary sources, the above-described methods would only be of interest in conjunction with a gas-separative technique.

INVERSE RADIOACTIVE TRACING

Principle of Operation

The inverse radioactive tracing method entails the reaction of nitrogen dioxide with the Kr^{85}-hydroquinone clathrate. The reaction of hydroquinone in the clathrate with NO_2 is accompanied by the release of radioactive Kr^{85} (β-emitter, having a half-life of 10.3 yrs) which is monitored by radioactive counting techniques. The rate of release of Kr^{85} in a flow-through sensor unit is proportional to NO_2 concentration in the analyzed gas.

The minimum detected NO_2 concentration is 2 ppm. NO does not react with hydroquinone, nor does it displace Kr in the clathrate.

Commercial Equipment

One or two instruments were built by Tracerlab, formerly a division of the Laboratory for Electronics, Inc. (ref. 105, 106). More recently, a prototype instrument has been built by Panametrics, Inc. to investigate the feasibility of automobile exhaust monitoring by the inverse radioactive technique (ref. 107).

References

a. Principle of operation: 106-108

b Applications 106-108

c Data 107

d. Specific instrument descriptions 106, 107

Discussion

Advantages

a. A very simple and potentially low-cost instrument.

b. Portable instrument.

c. Rapid response (<5 sec).

Disadvantages

a Requires an auxiliary oxidation unit for NO.

b. Water destroys the clathrates at relative humidities above 90%

c. SO_2 and SO_3 interfere.

d The Kr^{85} clathrate is consumed and requires replacement at periodic intervals (~3-6 months).

Conclusions

Sufficient information has not been reported to definitively evaluate the applicability of the inverse radioactive tracing method for the present purpose. The effect of temperature on the rate of release of Kr^{85}, the extent of interference by SO_2, the effect of water at relative humidities below 90% on the reaction rate, and the effect of air flow rate need to be known to evaluate the performance of this instrument.

Principle of Operation

An interferometer contains the following major components: a broad-spectrum radiation source, a beam splitter, and a radiation detector. The energy beam is divided with a partially transparent beam splitter. One of the beam components is reflected from a mirror, which is traversed at a constant speed, and the two beams are subsequently recombined before entering the sample compartment. Subsequent to transmission through the sample, the radiation is focused onto a detector.

Recombination of the two beam components causes constructive and destructive interference. The recombined beam intensity at a given wavelength is a function of sample absorbance at this wavelength, and of the optical path lengths of the two beam components.

The interferometers utilize portions of the electromagnetic spectrum in a nondispersed form. The detector output is recorded as a function of time (i.e., optical path lengths of the two beam components). Computerized data reduction is used to analyze the interferometer signal output and to convert it to a conventional spectrum.

Commercial Equipment

Commercial instruments are available from the Block Engineering Company, Cambridge, Mass.; Digilab, Inc., Cambridge, Mass.; Idealab, Inc., Franklin, Mass.; and Beckman Instruments, Inc., Fullerton Calif. Instruments offered by Beckman Instruments, Inc., cover mainly the far infrared spectral range (500 to 3 cm^{-1}).

References

a.   Principle of operation: 109-113

b.   Applications   112, 114

c.   Data: 109, 114, 115

d.   Specific instrument description   109, 110, 113, 114, 116

Discussion

Advantages

a. The utilization of nondispersive optical systems enhances the signal-to-noise ratio of interference spectrometers, in comparison with corresponding instruments that contain dispersive optical systems. High ultimate sensitivity can be expected through further development of the infrared interferometric technique.

b. Applicable for simultaneous monitoring of NO_x, CO, and SO_2.

Disadvantages

a. Instrumental malfunctions affect greatly the reliability of results because of the data analysis technique employed with this method.

b. The systems are presently still in an early evolutionary phase and they are therefore quite costly.

Conclusions

The development of interference spectrometric techniques has greatly accelerated during recent years because of the availability of high-speed computer equipment required for data reduction with this method. Interference spectrometry, in conjunction with data storage (for multiple scan analysis) represents a potentially very useful technique for the analysis of gas components at low concentrations. The utilization of this method for NO_x monitoring in plant environment would require the development of ruggedized instruments whose operation would not be affected by temperature fluctuation and other changes of the environment.

LASER RADIATION ABSORPTION

Principle of Operation

Certain laser emission lines coincide with the absorption ranges of common air pollutants (ref. 41-47, 50). Thus, the attenuation of emitted laser radiation intensity upon transmission through gaseous samples can serve as the basis for monitoring the concentrations of pollutants. The measurement of the absorption of laser radiation has been considered primarily for ambient atmospheric monitoring. However, it is equally applicable for source monitoring. Enhanced sensitivity can be attained by using folded-path sample cells. The sensitivity of laser spectroscopic measurements can also be increased with spectrophone-type (optoacoustic) detectors (ref. 45, 117).

The third-strongest emission line of the iodine laser at 1818.74 cm^{-1} coincides with the strongest absorption band of NO (ref. 41, 42). Some carbon monoxide laser emission lines coincide with the absorption lines of NO at 1780 to 1940 cm^{-1}, the v_1 band of NO_2 at $\sim$1620 cm^{-1}, and the v_3 band of SO_2 at $\sim$1360 cm^{-1} (ref. 44,50).

To attain CO laser emission at the NO_2 and SO_2 fundamental frequencies, and thus multifunctional monitoring capability, the laser must be operated at liquid nitrogen temperature (ref. 51).

Frequency-tuning over $\sim$400 cm^{-1} spectral range, at wavelengths longer than those of the laser emission, has been attained by the spin flip Raman technique (ref. 54,55,118,119). Tuning is attained by applying strong magnetic fields to the semiconductor stimulated Raman scattering emitter. Stimulated Raman emission from InSb has been induced by CO and CO_2 laser irradiation. The emitter must be maintained at cryogenic temperatures [presently up to 77°K, conceivably to 190°K at some later date (ref. 120)], and a trade-off exists between the refrigeration and magnetic field strength requirements. The spin flip Raman technique offers presently the capability for NO monitoring at very low concentrations (<1 ppb), which is of primary interest in ambient atmosphere monitoring

The feasibility of using solid-state junction lasers for pollutant monitoring has been demonstrated (ref. 46). Control of emission frequency is attained by varying the Pb-to-Sn ratio and the operating temperature. Using $Pb_{1-x}Sn_xTe$, emission was attained through the range of 6.5 to 32 µm, which does not encompass the absorption bands corresponding to the fundamental stretching frequency of NO and CO. It is believed (ref 46)

that semiconductor materials with the required emission charac-
teristics can be developed for absorption measurement at 5.33
and 4.66 µm.

Commercial Equipment

None available.

References

a. Principle of operation. 41-43, 45-47

b. Applications: 41-47, 50

c. Data: 41-47, 50

d. Specific instrument description: 43, 45, 47, 54,
    55, 117

Discussion

Advantages

a. Spectroscopic technique of very high sensitivity
    because of the narrow spectral range of the light
    source.

b. The narrow spectral range of laser emission also
    assists in minimizing interferences.

c. Multifunctional operating capability with certain
    laser light sources.

d. Very low (<1 ppb) minimum detection limit.

Disadvantages

a. Developmental status and relatively high cost of the
    required laser radiation sources at the present time.

b. Complexity of systems, that is a contributing factor
    to the high cost.

Conclusions

Present gas laser systems applicable for NO_x monitoring are
costly and they are not very rugged. It would be desirable to
develop solid-state junction lasers which would. (1) emit at
the absorption maxima of NO, (2) be physically compact and
rugged, and (3) be amenable to low-cost production.

LASER RAMAN SCATTERING

Principle of Operation

The interaction of electromagnetic radiation with polariz-
able molecules leads to scattering of radiation by these
molecules. Most of the scattered radiation is of longer wave-
lengths (Stokes lines) than the incident radiation. A small
fraction of scattered light is of shorter wavelengths (anti-
Stokes lines) than the incident radiation   The energy differ-
ence between the incident and scattered radiation corresponds
to the molecular vibrational frequencies.

Only a small fraction of incident energy is scattered as
Raman radiation. The scattering efficiency of molecules is
related to their polarizability.

The feasibility of utilizing lasers for remote monitoring
of pollutant gas emission from stationary sources has been
investigated (ref. 121-123). A multiple-reflection cell for
Raman scattering measurements with gaseous samples, designed
specifically for use with laser excitation sources, has recently
been described (ref. 59).

Commercial Equipment

Laboratory Raman spectrometers utilizing lasers as radia-
tion sources are commercially available.

References

a. Principle of operation· 121-123

b. Applications: 122, 123

c. Data: 122

d. Specific instrument description. 57-59, 122

Discussion

Advantages

a. Potentially applicable for simultaneous monitoring
    of NO_x, CO, and SO_2.

b. Rapid response (<1 sec).

Disadvantages

a. Intense laser light sources are still at an evolu-
    tionary stage and their cost is presently high.

Conclusions

It would be desirable to establish the low-concentration analysis capabilities of the laser Raman scattering technique with gaseous materials, such as NO_x, SO_2 and CO. The nitrogen laser, emitting in the ultraviolet spectral range (3371 Å) is a preferred light source. To enhance the signal-to-noise ratio, a preferred light source. To enhance the signal-to-noise ratio, the detector should be time-gated to the pulsed emissions from the laser.

MASS SPECTROMETRY

Principle of Operation

In analyzing gases by mass spectrometric methods, the molecules are subjected to bombardment by electrons which are released by a thermoionic emission source. The electron-molecule interaction results in ionization and/or dissociation in a pattern that is characteristic for the molecule. When the ionization is conducted in a low-pressure environment, immediate recombination of the charged particles can be prevented. The ions are accelerated in an electric field and the monoenergetic ion beam is introduced into the magnetic field. Traveling in a circular path, the radius of curvature is proportional to the square root of the mass for singly-charged particles. Electrometer-type detectors, positioned to intercept the circular path of the charged ionic fragments, are used to measure the relative concentrations of the species with different m/e ratios (ref 124).

The time-of-flight mass spectrometer utilizes a similar ionization source. The ions are accelerated into a linear drift tube. The time required by the ions to travel from the entrance port of the drift tube to the collector plate increases with the m/e ratio of the species. An outstanding feature of the time-of-flight mass spectrometer is the high speed at which samples are analyzed (<0.1 msec) (ref. 124).

Omegatron is a mass spectrometer that is based on the cyclotron resonance principle (ref. 28-30), it has high sensitivity but only moderate resolution. Because of these characteristics, its small size, and bakeout capability, the omegatron is used for residual gas analysis in vacuum systems.

The quadrupole mass spectrometers utilize an electrical quadrupole field to effect ion separation (ref. 31,32) This field is created by applying rf and dc voltages to four parallel-positioned metal rods. Opposite rods are connected in pairs and adjacent rods are of different polarity. The ion trajectories depend on their m/e ratios and on the quadrupole field parameters. With selected field parameters, only ions of specific m/e ratio impinge upon the detector, other ions are neutralized on the charged rods.

The quadrupole mass spectrometers have a high sensitivity because of their large acceptance angle. Their design does not entail the use of magnets. Complete mass ranges are scanned in less than 0.25 sec.

An ion storage mass spectrometer has been recently reported (ref 33). The separation of ions is effected in a three-dimensional quadrupole electric field. The ions are stored on wire mesh electrodes, from which they are freed upon pulsing for detection by an electron multiplier The ion storage mass spectrometer is a very small device, it has good resolution at low (<100) m/e values.

Commercial Equipment

Numerous manufacturers market mass spectrometers (ref. 125). Some companies listed in the cited reference market moderately-priced instruments of sufficient resolution which have the required sensitivity for NO_x stack emissions measurement

References

a   Principle of operation   28-33, 124

b   Applications   126-131

c   Data   126-131

d   Specific instrument description·   28-31

Discussion

Advantages

a.   Rapid response (<1 sec).

b.   Multifunctional operational capability attainable

c.   The lower detection limit is ≈1 ppm.

d   Temperature fluctuations are not expected to affect instrument response greatly

Disadvantages

a.   Automated correction for the contribution of minor gas components (HCHO, C_2H_6) to the major m/e peak of NO may be required.

b.   Continuous evacuation required.

c.   Conditioning of mass spectrometers by exposure to nitrogen oxides may be required

d   Need for interface accessories for sampling transfer that will not remove the oxides of nitrogen from the sample.

Conclusions

Significant advances have been made during recent years in the development of moderate-cost mass spectrometers. In view of the advantages that these instruments (i.e., omegatrons, quadrupole and ion storage mass spectrometers) offer, it appears advisable to evaluate their utility in stationary source emissions measurements.

PARAMAGNETISM

Principle of Operation

Magnetic susceptibility of nitric oxide ($+1.461 \times 10^{-3}$ in cgs units per mole at 293°K) and of nitrogen dioxide ($+0.150 \times 10^{-3}$) has been used as the basis for their determination in gas mixtures. The gas mixture is passed through a magnetic field that deflects paramagnetic molecules. Two electrically heated wires are mounted in the sensor assembly. The latter is positioned in the magnetic field in such a manner that the paramagnetic molecules are deflected from one of the heated wires in the direction of the other. This causes one of the wires to be cooled and the adjacent wire to be warmed. For given paramagnetic molecules, the temperature differential between the two wires is related to the concentration of these molecules.

Commercial Equipment

None known to be marketed.

Reference

Ref. 132

Discussion

Advantages

a. Rapid response.

b. A simple and potentially low-cost instrument.

c. Portable.

d. CO and SO_2 cause no interference.

Disadvantages

a. It would be desirable to reduce NO in the gas to NO_2 that has high magnetic susceptibility, for the attainment of maximum signal strength. Conversion of the mixed oxides of nitrogen to either NO or NO_2 is essential because both species are paramagnetic.

b. Oxygen has a magnetic susceptibility of 3.449×10^{-3} in cgs units per mole at 293°K. The concentration of oxygen in emission gases is high ($\sim 3\%$) and it does not remain constant. Oxygen would therefore strongly interfere with NO_x determination.

Conclusions

Because of the above-cited serious disadvantages, the paramagnetism measurement is not a useful method for NO_x analysis in gas mixtures that contain oxygen.

PHOTOIONIZATION

Principle of Operation

Nitric oxide has an ionization potential of 9.26 eV (ref. 34-37). The corresponding value for NO_2 is 9.83 eV (ref. 37-39) The ionization potentials of other stationary source emission gas components have values above 12 eV (ref. 34 and 133). Thus, it is feasible to monitor the NO_x content in emission gases by selective photoionization with ultraviolet radiation having wavelengths in the 1050 to 1350 Å range.

Selective photoionization in an ion chamber, in conjunction with ion collection current determination, has been applied for the measurement of NO concentration in the earth's atmosphere (ref. 134 and 135). This method was found to provide a very high detection sensitivity ($<<1$ ppb).

Commercial Equipment

A prototype commercial instrument for NO analysis, based on photoionization measurement, is at an advanced development stage. Commercialization is projected by Walden Research Corporation for the spring or summer of 1972 (ref. 136).

References

a. Principle of operation: 34, 36, 37, 40, 134, 137

b. Application: 135

c. Data: 134

d. Specific instrument description: 40, 134

Discussion

Advantages

a. With emission gases, response specific to NO_x.

b. High sensitivity.

c. Rapid response.

d. Portable instrument.

Disadvantages

a. Interference by aromatic hydrocarbons, which may be encountered in some emission source.

Conclusions

The selective photoionization method, involving the measurement of gas phase ionization induced by short-wavelength ultraviolet radiation (1050-1350 Å) merits further experimental development and evaluation.

Limitation of applicability with sources that emit pollutants of low ionization potential (e.g., benzene, IP = 9.25 ev), should be established.

VIBRATIONAL FLUORESCENCE

Principle of Operation

Subsequent to the absorption of infrared radiation of a given wavelength by molecules in the gas phase, thermal equilibrium is re-established by emission of radiation and by collisional energy transfer.

A requirement for absorption of radiation is the correspondence of the quantum energy of incident radiation to the energy requirement for a quantum-mechanically allowed vibrational-rotational transition. The radiation emitted by molecules is of equal or longer wavelength than the incident radiation. Emission of radiation that occurs subsequent to vibrational excitation is known as vibrational fluorescence. The wavelengths of vibrational fluorescence emission correspond to those known from absorption spectra.

Commercial Equipment

None available.

References

    a.   Principle of operation: 138-140

    b.   Applications· 141-145

    c.   Data: 141-143, 145

    d.   Specific instrument description   138, 141-143

Discussion

Advantages

    a.   Enhanced specificity of detection may be attained by vibrational fluorescence measurement with compounds that have coinciding absorption regions. Compounds which absorb radiation in the same spectral region frequently exhibit fluorescence in non-overlapping spectral ranges.

    b.   Rapid response.

Disadvantages

    a.   Compensation or correction for indirect (thermal) excitation will be required for quantitative analytical measurements

Conclusions

Vibrational fluorescence measurement has become practically feasible through the development of intense monochromatic emission sources, the lasers. Such measurements have recently been applied in interesting and significant studies pertaining to intra- and intermolecular energy transfer processes (ref. 138, 139).

Attempts have been made to apply vibrational fluorescence measurements for analytical purposes (ref. 141-143). The reported data (relatively intense emission at quantum energies higher than the quantum energy of exciting radiation) suggest that a sizeable fraction of the measured effect arose from indirect excitation.

Vibrational fluorescence measurement represents a new and potentially very useful gas analysis technique. It appears highly advisable to conduct studies with the objective of defining the potential of this technique for analytical applications, specifically for NO_x monitoring in the present case. Such studies must be conducted with full cognizance of energy transfer processes that affect the emission characteristics of specific components in gas mixtures of variable compositions. Means for minimizing or compensating for the contributions to emission which result from energy transfer between the gas and its containing walls must also be investigated.

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