# EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux

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# EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux

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# *Forward*

Optical Remote Sensing (ORS) technologies have been available since the late 1980s. In the early days of this technology, there were many who saw the potential of these new instruments for environmental measurements and how this technology could be integrated into emissions and ambient air monitoring for the measurement of flux. However, the monitoring community did not embrace ORS as quickly as anticipated. Several factors contributing to delayed ORS use were:

- **Cost:** The cost of these instruments made it prohibitive to purchase, operate and maintain.
- **Utility:** Since these instruments were in essence perceived as "black boxes." Many instrument specialists were wary of how they worked and how the instruments generated the values.
- **Ease of use:** Many of the early instruments required a well-trained spectroscopist who would have to spend a large amount of time to setup, operate, collect, validate and verify the data.
- **Data Utilization:** Results from path integrated units were different from point source data which presented challenges for data use and interpretation.

Over the years, the air monitoring community has come to accept both the challenges and overall utility of ORS technologies and applications. The emissions monitoring community and monitored sources have been employing ORS for a number of years and are using these technologies to answer questions that traditional instrumentation could not address. In addition, ORS technology has been applied to ambient and fenceline monitoring, including near-roadway monitoring. Therefore, application of ORS technology has an expanding place with other air measurement tools.

The EPA staff and other scientists and engineers in the monitoring community recognized that a compilation of ORS material was needed to encourage wider use and understanding of ORS. Questions on how instruments generate data and how an agency or source validates and verifies data are universal, whether the instrument is optically remote or an extractive instrument on site or within the stack. With this in mind, the EPA developed this Handbook to assist the "non-spectroscopist" in understanding and using data and information generated by ORS. This Handbook is divided into five sections:

- **Section 1:** Discusses what ORS means and how this technology can be used. It also has a number of tables that have a "crosswalk" between the different technologies and their use (i.e., techniques).
- **Section 2:** describes the different technologies or "hardware" that are currently available that are considered "optically remote."
- **Section 3:** Explains how to use the "hardware" with different techniques and how to calculate emission flux.
- **Section 4:** Discusses the "other" data that needs to be collected to understand and better validate and verify the ORS data.

- **Section 5:** Provides a very brief overview of how to validate and verify this data once it is collected.

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## *List of Acronyms*

| **Acronym** | **Description** |
|---|---|
| µg/m$^3$ | micrograms per cubic meter |
| Mm | micrometer |
| 2-D | two dimensional |
| 3-D | three dimensional |
| ANSI | American National Standards Institute |
| AOM | acousto-optic modulator |
| ASQC | American Society for Quality |
| bLS | Backward Lagrangian Stochastic |
| BTX | benzene, toluene, elemental mercury and p-xylene |
| C2H2 | acetylene |
| CCD | charge-coupled device |
| CEA | cavity-enhanced absorption |
| CEMs | continuous emissions monitors |
| CFCs | chlorofluorocarbons |
| CH4 | methane |
| CO | carbon monoxide |
| CO2 | carbon dioxide |
| COSPEC | correlation spectrometer |
| CRDS | cavity ring-down spectroscopy |
| CRLAS | cavity ring-down laser absorption spectroscopy |
| CW | continuous wave |
| DGPS | differential global positioning system |
| DIAL | Differential absorption LIDAR |
| DIAL/LIDAR | differential absorption light detection and ranging |
| DOAS | differential optical absorption |
| DQI | data quality indicators |
| DQO | data quality objective |
| EPA | Environmental Protection Agency |
| ETV | environmental technology verification |
| FID | flame ionization detectors |
| FTIR | Fourier transform infrared |
| g/s | grams per second |
| GPS | global positioning system |
| HAP | hazardous air pollutants |
| HITRAN | high-resolution transmission molecular absorption database |
| HRPM | horizontal RPM |
| ICOS | integrated cavity output spectroscopy |
| IR | infrared |
| LASER | light amplification by stimulated emission of radiation |

## *List of Acronyms*

| **Acronym** | **Description** |
|---|---|
| LDAR | leak detection and repair |
| LOD | levels of detection |
| MAX-DOAS | Multi-axis Differential Absorption Spectroscopy |
| MCT | mercury-cadmium-telluride |
| MOST | Monin–Obukhov similarity theory |
| MQOs | measurement quality objectives |
| N2O | nitrous oxide |
| NO | nitric oxide |
| NO2 | nitrogen dioxide |
| NOx | nitrogen oxides |
| NUC | non-uniformity correction |
| NWIR | Northwest Infrared |
| NWS | National Weather Service |
| O3 | ozone |
| OA-CEA | off-axis cavity enhanced absorption |
| OAICOS | off-axis integrated cavity output spectroscopy |
| OP | open-path |
| OP-TDL | open-path tunable diode laser |
| ORS | optical remote sensing |
| OTM10 | Other Test Method 10 |
| PDCs | path-determining components |
| PIC | path integrated concentration |
| PID | photo-ionization detectors |
| PMT | photo multiplier tube |
| ppb | parts per billion |
| ppm | parts per million |
| ppmm | ppm for one meter of path length |
| PRF | pulse repetition frequency |
| PZT | piezoelectric transducer |
| QA | quality assurance |
| QAPP | quality assurance project plan |
| QC | quality control |
| QC-Laser | Quantum Cascade Laser |
| QMP | quality management plan |
| QP | quality program |
| QS | quality system |
| RADAR | radio detection and ranging |
| RDT | ring-down time |
| RH | relative humidity |
| RPM | radial plume mapping |

## *List of Acronyms*

| **Acronym** | **Description** |
|---|---|
| SBFM | smooth basis function minimization |
| SF6 | sulfur hexafluoride |
| SO2 | sulfur dioxide |
| SOF | Solar Occultation Flux |
| SOx | sulfur oxides |
| SSE | sum of squared errors |
| TDC | tracer dilution correlation |
| TDL | tunable diode laser |
| TDLAS | tunable diode laser absorption spectroscopy |
| UV | ultraviolet |
| VOCs | volatile organic compounds |
| VRPM | vertical radial plume mapping |
| µs | microseconds |

# 1.0 Introduction

This document is intended as a Handbook for those planning to use or review remote emissions measurement and monitoring approaches for stationary sources or for data users building their expertise about current information concerning the technologies and application in these types of measurements. For the purposes of this Handbook, “remote measurement” is defined as any measurement of air emissions conducted away from the point or area where the pollutant is released. This definition includes optical remote sensing (ORS), as well as other approaches such as those coupling point measurements with a mobile measurement platform. As our air quality management programs evolve, we need more measurements of non-point or unvented sources, often referred to as fugitive sources or fugitive emissions. Remote measurement technologies offer approaches that have been otherwise unavailable to measure emissions from these challenging sources.

The information presented in this document is written to be accurate and informative, as well as more “user friendly” than technical papers or review articles found in the open literature (i.e., peer reviewed literature and articles in periodicals that are available on the Internet). Practical information is provided for those who need to understand the principles behind the use of spectroscopy or other remote measurement technologies, but who may not be trained in these technologies and their applications. This document is intended to aid readers in understanding the uses and limitations of data generated by remote measurement approaches. In this document, you will find discussion of the practical uses and operation of remote sensing equipment and applications of these and other technologies to produce emissions data. Some of the complex technical information has been provided in summary form with illustrations.

## 1.1 Purpose of the Handbook

The purpose of this Handbook is to describe the primary remote measurement technologies and current approaches to use these technologies. This Handbook also describes how potential users can assess the applicability of remote measurements and the resulting data to their emissions measurement needs. We designed this Handbook for EPA, state, local, and tribal measurement project leads; measurement contractors; industry managers planning measurements to create emission factors; and those reviewing test plans and test reports. When the term “measurement” is used in this Handbook, it is referring to short-term studies (e.g., emission fluxes assessment); the term monitoring is used for long-term studies (i.e. spatial and temporal trend assessment).

Optical remote measurement techniques are most typically designed and used to measure concentrations and, when paired with meteorological data, allow for calculation of mass fluxes of pollutants downwind of fugitive and non-point emission sources. Optical remote techniques provide opportunities to measure sources that are not conducive to measurement using more traditional stack testing or single point ambient techniques. Actual application, however, needs to be determined on a case-by-case basis.

This Handbook describes the more prevalent and technologically demonstrated open-path, cell-based, and point measurement technologies used to make remote measurements This Handbook provides a background for the application of remote measurement techniques for emissions measurements. Viable applications for qualitative and quantitative measurements of constituents in air are also described as examples of different ways remote measurement technologies can be applied to meet measurement and monitoring requirements. Quantitative emissions data from remote measurements may then be used for multiple purposes including development of emission factors, evaluation of exposure levels, compliance with ambient regulatory limits, and identification of sources of air pollution. Examples of several pollutant detection and quantification methods are provided to show the focus of current monitoring applications.

Applications of ORS are relatively new, but maturing rapidly. For example, Differential Optical Absorption (DOAS) and Fourier Transform Infrared (FTIR) systems have been commercially available since the early 1990s. These earlier instruments, although designed for both background ambient and higher stationary source emission-related monitoring applications, have mostly been employed to measure stationary and fugitive source emissions.

This document is intended to be “user friendly” — it will have as much practical information for those not trained in these technologies and approaches as those who are. This Handbook will discuss the practical uses and operation of the instruments used to make remote measurements and the data generated. Some of the more technical information have been simplified, and illustrations have been updated and clarified to make them more understandable. Internet links and references have been added throughout the document to allow the reader to research quickly more detailed information.

### 1.1.1 Stationary Sources and Emissions Points

Stationary sources are one of the major contributors of pollution to the atmosphere. They are non-moving, fixed-site producers of air pollution such as power plants, chemical plants, oil refineries, manufacturing facilities, and other industrial facilities. Air pollution from stationary sources is produced by two primary activities: (1) stationary combustion of fuel such as coal, oil, wood, or natural gas, and (2) pollutant losses from industrial processes. Industrial processes include petroleum wells, refineries, chemical manufacturing facilities, and smelters.

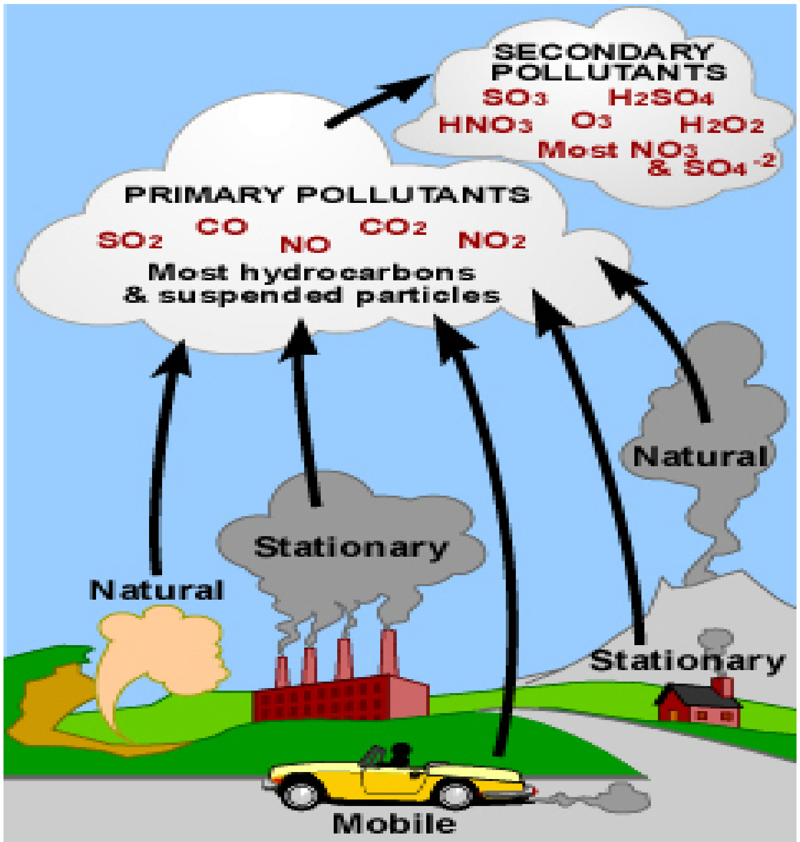

**Figure 1-1. Types and sources of air pollutants**

EPA defines emission points from stationary sources vary between EPA programs. An emission point is the specific place or piece of equipment from which a pollutant is emitted. Stationary sources, such as a facility or factory may have many possible emission points. Air pollutants can be emitted from smokestacks, storage tanks, equipment leaks, process wastewater handling/treatment areas, loading and unloading facilities, and process vents. These sources emit various types of pollutants which are discussed in Section 1.2.1.

### Ducted or Vented Emissions

A process vent is basically an opening where substances (mostly in gaseous form) are “vented” into the atmosphere. Common process vents in a chemical plant are distillation columns and oxidation vents, for example.

**Figure 1-2. Stationary sources**

Historically, ducted or vented stationary source emissions have been measured in the ducts or stacks before release into the atmosphere. These sources were often referred to as point sources because the final release of emissions can be traced to a single or multiple defined duct or stack exhaust. Ducted sources permit emission stream parameters, such as flow rates, temperature, pressure, and other physical characteristics, to be recorded within the accuracy requirements for end data use because they are confined under relatively steady conditions.

### Area or Fugitive Emissions Sources

Those stationary facilities or activities whose individual air emissions do not qualify them as point sources are called area sources. Area and fugitive sources are often collections of a multitude of minor sources with individually small emissions that are impractical to consider as separate point sources. Area sources, including fugitive emissions, are those emissions that could not reasonably pass through a stack, chimney, vent, or other ducted line that could easily be characterized with conventional point source or stack sampling methods. Measurement of emissions from these sources traditionally requires total enclosure techniques, or a combination of point measurements and modeling using upwind-downwind or exposure-profiling methods.

Area sources represent numerous facilities and activities, including various unintended or irregular emissions. Fugitive and area sources may release small amounts of a given pollutant individually, but collectively can release significant amounts of a pollutant. For example, dry cleaners, vehicle refinishing, animal feeding operations, gasoline dispensing facilities, and residential heating do not typically qualify as point sources, but collectively, the various emissions from these sources are classified as area sources.[2]

Fugitive emissions from storage tanks are due to pollutants that can leak through the roofs and through tank openings when liquids expand or cool because of outdoor temperature changes. In addition, air pollutants can escape during the filling and emptying of a storage tank. Air pollution is also produced when wastewater containing volatile chemicals comes in contact with the air.

Both stationary point source and area source emissions measurements have traditionally been performed using single point sampling that accumulates and integrates sampled gas for a set period of time followed by analysis for target components. Continuous point source instrumental methods have also been applied to stationary source emissions and area source measurements. Instrumental methods collect samples from a single point and provide information on the concentration of a target component of interest over relatively small increments of time. A critical issue with traditional air measurements is collection and reporting of data from a single point that is assumed to be representative of the air or emission being monitored. This assumption is verifiable when ducts or stacks are sampled but much less certain for area source and ambient measurements.

## 1.2 Why Remote Measurement?

Fugitive emissions are emissions not contained or caught by a capture system and are often caused by equipment leaks, evaporative processes, and windblown disturbances. These emissions may occur from breaks or small cracks in seals, tubing, valves, or pipelines, as well as when lids or caps on equipment or tanks have not been properly closed or tightened. For example, when natural gas escapes via fugitive emissions, methane, volatile organic compounds (VOCs), and any other contaminants in the gas (e.g., hydrogen sulfide) are released to the atmosphere. Other examples of area sources with significant fugitive emissions include landfills or waste lagoons.[3]

**Figure 1-3. Potential Fugitive Sources**

Kantamaneni, R., MUSCAT 10-11 May 2010 Regional forum, Methane to Markets Partnership: An Overview of Opportunites

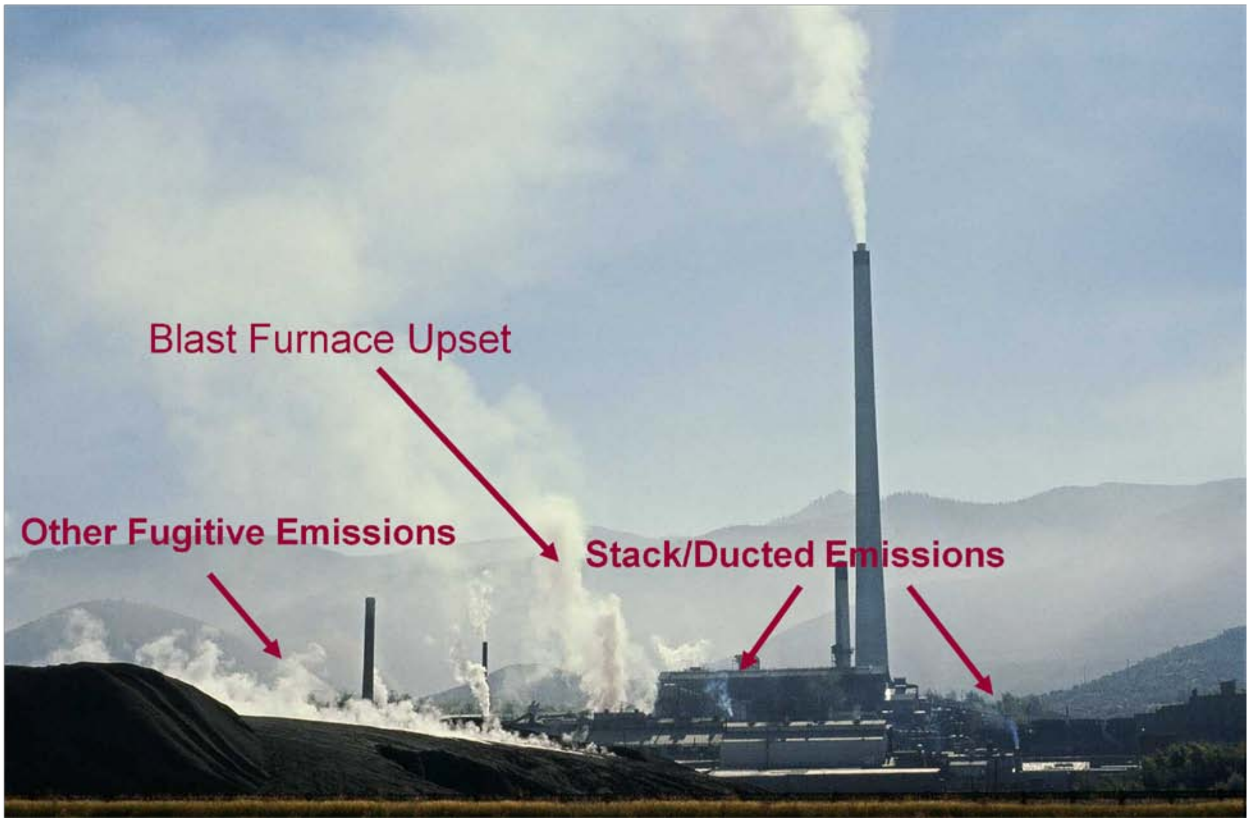

**Figure 1-3. (cont). Potential Fugitive Sources**

Area and fugitive emissions sources are especially challenging to monitor because the pollutants of interest are not contained within a duct or stack before release. The development of emission factors for area sources is equally difficult due to the measurement challenges. In contrast, stationary stack measurements and their related emission factors' determination are well-established and documented. Over the past 20 years, remote measurement approaches, including ORS methods, have been progressing technologically and gaining greater use as an emissions estimation tool, especially for stationary area sources and some on-road/near-road mobile sources. A significant number of remote measurement activities have been performed for open area sources such as landfills, wastewater treatment plant ponds, agricultural waste, wastewater lagoons, oil and gas field production sites, waste ponds for mining operations, and ambient fenceline concentrations surrounding large chemical and refinery facilities. These types of sources are prime candidates for the application of remote measurement techniques because the ORS technology and techniques are small, mobile, do not take lengthy setup time and can return data quickly to the staff collecting the data and to the operators of the facilities.

### 1.2.1 Pollutant Focus: Criteria Pollutants, HAPs, Greenhouse Gases, and Ozone Depleting Substances

The remote measurement technologies and approaches addressed in this Handbook are focused on four groups of pollutants currently regulated or on the regulatory horizon under the Clean Air Act. These four groups are:

- criteria pollutants,
- hazardous air pollutants or HAP,
- greenhouse gases, and
- ozone-depleting substances.

**Gaseous Criteria pollutants** are those inorganic pollutants (e.g., carbon monoxide, sulfur oxides, nitrogen oxides and ozone) that are common and found all over the United States. The EPA uses these “criteria pollutants” as indicators of air quality. Each of the criteria pollutants are discussed in detail below.[4]

> ***Carbon monoxide (CO)*** is a colorless, odorless gas formed when carbon in fuel is not burned completely. Motor vehicle exhaust contributes about 60 percent of all CO emissions nationwide.[4] Other sources of CO emissions include industrial processes (such as metals processing and chemical manufacturing), residential wood burning, and natural sources such as forest fires.
>
> ***Sulfur oxides ($SO_x$)*** are colorless gases formed when fuel containing sulfur, such as coal and oil, is burned and when gasoline is extracted from oil or metals are extracted from ore. Sulfur dioxide ($SO_2$) is the criteria pollutant that is the indicator of $SO_x$ concentrations in the ambient air. Other sources of $SO_2$ are industrial facilities that derive their products from raw materials like metallic ore, coal, and crude oil, or that burn coal or oil to produce process heat. Examples are petroleum refineries, cement manufacturing, sulfuric acid

plants and metal processing facilities. Also, locomotives, large ships, and some non-road diesel equipment currently burn high sulfur fuel and release $SO_2$ emissions into the air in large quantities.

***Nitrogen oxides ($NO_x$)***, is the generic term used to describe the sum of nitric oxide (NO), nitrogen dioxide ($NO_2$), which is a criteria pollutant, and other oxides of nitrogen. $NO_x$ is a group of highly reactive gases that play a major role in the formation of ozone. $NO_x$ form when fuel is burned at high temperatures, as in a combustion process. The primary sources of $NO_x$ are motor vehicles, electric utilities, and other industrial, commercial, and residential sources that burn fuels.

***Ozone ($O_3$)*** is a gas composed of three oxygen atoms. It is a unique criteria pollutant in that it is exclusively a secondary pollutant. It is not usually emitted directly into the air, but at ground level is created by a chemical reaction between $NO_x$ and VOCs in the presence of heat and sunlight. $O_3$ has the same chemical structure whether it occurs miles above the earth or at ground level and can be “useful” or “damaging” to the environment depending on its location in the atmosphere. Useful $O_3$ occurs naturally in the stratosphere and forms a layer that protects life on earth from the sun’s harmful rays or ultraviolet radiation. In the earth’s lower atmosphere, or troposphere, ground-level $O_3$ is considered damaging or destructive. $O_3$ is the most prevalent chemical found in photochemical air pollution, or smog. [4]

**HAPs or air toxics** are those pollutants that are known or suspected to cause cancer, respiratory problems or other serious health effects, or are thought to have adverse environmental or ecological effects. The presence of HAPs in the air can be more localized than criteria pollutants and the highest levels are usually found close to the emission sources. Examples of air toxics include benzene, found in gasoline; mercury from coal combustion; perchloroethylene from some dry cleaning facilities; and methylene chloride used as a solvent by a number of industries. Most air toxics originate from man-made sources including mobile sources (e.g., cars, trucks, construction equipment), stationary sources (e.g., factories, refineries, power plants), and indoor sources (e.g., some buildings materials and cleaning solvents).[5]

**Greenhouse gases** are those compounds that enhance the retention of the sun's heating of the earth. Clouds and a natural layer of atmospheric gases absorb a portion of earth's heat and prevent it from escaping into space. This keeps our planet warm enough for life and is known as the natural "greenhouse effect." Scientific evidence shows that the greenhouse warming effect is being increased by the release of certain gases into the atmosphere that cause the earth's temperature to rise. This rise in temperature caused by greenhouse gases is called "global warming" and contributes to climate change on the planet. Carbon dioxide ($CO_2$), methane, particulate matter (especially black carbon or soot), $NO_x$, fluorinated compounds, and $O_3$ are some of the compounds contributing to global warming. $CO_2$ emissions account for about 81 percent of greenhouse gases released in the United States and are largely due to the combustion of fossil fuels in electric power generation, motor vehicles, and industries. Methane emissions, which result from agricultural activities, landfills, and other sources, are the next largest contributors to greenhouse gas emissions in the United States and worldwide.[6]

**Ozone-depleting substances are** compounds such as chlorofluorocarbons (CFCs), halons, carbon tetrachloride, methyl bromide, and methyl chloroform. The stratosphere contains a layer of $O_3$ gas that protects living organisms from harmful ultraviolet-B radiation from the sun which has been linked to many harmful effects, including various types of skin cancer, cataracts, and harm to crops, materials, and marine life.[7]

### 1.2.2 Increased Knowledge and Advancement of Remote Sensing to Emissions Measurement

There are four major optical sensing approaches that will be described in more detail in later sections of this Handbook. They include the following:

- **Active.** Open-path ORS techniques typically use optical telescopes to transmit and receive energy beams, such as ultraviolet (UV), infrared (IR), or visible wavelength range.

- **Passive.** Open-path ORS techniques receive light energy from pollutants activated by an external uncontrolled source such as combustion gases (e.g., Passive FTIR radiation) or the sun (e.g., Solar Occultation and mobile DOAS).

- **Backscatter.** ORS techniques use energy reflected from pollutants after activation from a controlled source of light energy (e.g., Differential Absorption Light Detection and Ranging (DIAL/LIDAR) systems).

- **Mobile.** Measurement methods do not have to be optically based. However, optical technologies have been engineered to be rugged enough to allow stable operation from a moving vehicle. Typically these optical techniques sample the gas into a confined cell while moving along a path to be measured (e.g., cavity ringdown, white cell and FTIR tracer release systems).

**Active**. ORS techniques use the light generated under controlled conditions from one of many sources including heated glow bars for IR light, quartz lamps filled with deuterium or xenon gas, or laser light. The light energy is broadcast over relatively long distances (up to 1,000 meters) in an open-air setting. A simplified schematic of an open-path ORS technique to measure emissions from an open source is provided in Figure 1-4. In general, open-path ORS test methods involve the transmission of an energy beam across a path (straight line or two-dimensional plane) located downwind of the emission source to be measured (e.g., wastewater lagoon). The pollutant concentration along the line or plane is determined by evaluating certain qualities of the energy beam (e.g., the amount of light absorbed) after it has passed through the sample path and is captured by a receiver. Chemical compound reference spectra and computational algorithms are used to translate the instrument signal into a pollutant path-integrated concentration (e.g., parts per billion (ppb) benzene per meter). Additionally, a mathematical calculation routine, combined with meteorological data (wind speed, wind direction) collected during the sampling event, is needed to convert the ORS instrument output (e.g., a path-integrated concentration or a flux measurement) to an emission flux rate (e.g., milligrams per second). Open-path ORS methods can be designed and applied in several different ways to capture area source emissions in both vertical and horizontal planes. The predominant measurement applications that use ORS technologies in the open-path mode include line of sight monitoring, Radial Plume Mapping[8] (RPM), and Backward Lagrangian Stochastic (bLS) Modeling.

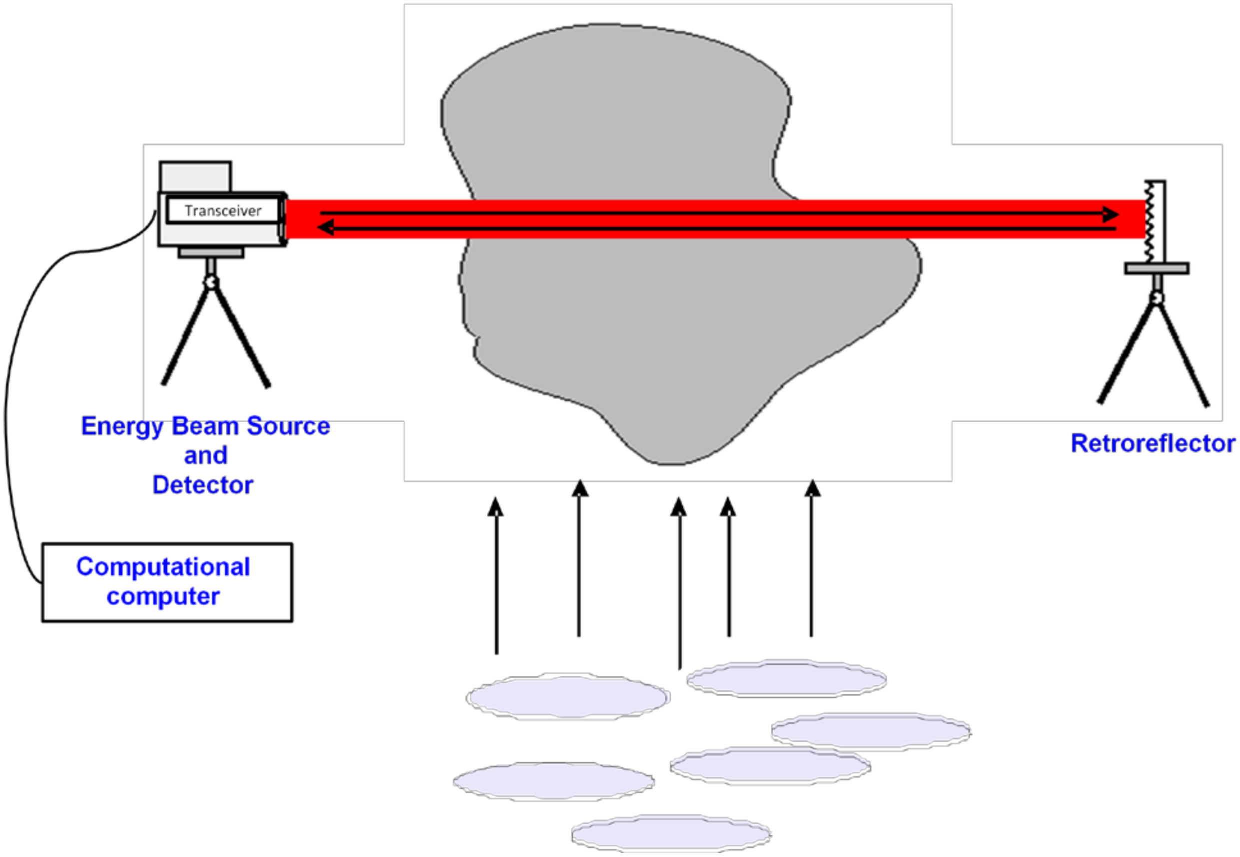

**Figure 1-4. Diagram for Monostatic Optical Remote Sensing**

**Passive.** Open-path techniques use the same technology as active without the need for a controlled source of energy. The PFTIR technique is an example of this technology. PFTIR can be used to measure infrared spectra in air at elevated temperatures because hot gases emit radiation with the same infrared signature as their absorption spectrum. Hot gases above the flame zone in an industrial flare contain combustion products such as $CO_2$, CO, and vapor phase organic material resulting from products of incomplete combustion. For example, hot gases emitted by the flare can be identified and quantified using the radiant FTIR absorption measurements.

The primary difference that must be taken into account between optical remote infrared absorption (e.g., FTIR) and hot gas radiance measurements using PFTIR is the temperature dependence of the FTIR spectral measurements. The results of PFTIR are both temperature and concentration dependent. Knowing the source temperature at the location where the gas concentrations are measured is necessary to quantify the compounds of interest.

**Backscatter.** Open-path optical measurement approaches used in this Handbook refer to the use of Light LIDAR technology. DIAL is an application of LIDAR using powerful lasers directed into the atmosphere to measure reflected light energy from aerosols, dust, and gases. The DIAL measurement is achieved by the direct impingement of the laser beam on these materials and its subsequent reflection and scattering. Because the target substances vary in concentration along the axis (optical path) of the transmitted beam, the receiving telescope equipment analyzes the strength of the returning (reflected) beam continually during its reception.[9] The reflected beam strength is reduced from the original transmission strength by a measureable amount that is proportional to the concentration of the target matter.

**Mobile.** Optical monitoring approaches use optical techniques to measure gas samples pumped into measurement cells where pressure and temperature are controlled. Unlike stationary monitoring techniques, mobile optical techniques allow the user to move along and between the emission plumes generated by area or fugitive sources. A tracer ratio application of mobile monitoring can be used to simulate emissions from a source through the release of a tracer gas at or near the center of the area source with subsequent measurement of the tracer and emission compound(s) concentrations downwind of the source. Measurements must be conducted at a distance from the source that is sufficient for the plume (e.g., from a landfill or wastewater lagoon) and tracer gas to be well mixed and close enough that emission plume is measurable well above background concentrations. These distances can range from 1 to 5 km to achieve proper mixing.[10]

### 1.2.3 Advantages Over Closed Path Techniques

Although open-path ORS techniques have been used for 20 years and are well-established, they are constantly improving and gaining use to characterize and quantify pollutant emissions from sources that are not conducive to traditional point source testing methods, such as large area sources. Improvements often include changes to technologies that improve detection limits or the types of compounds detected. For large area sources, ORS methods have distinct advantages when compared with traditional single point measurement techniques, such as photo-ionization detectors (PID), PID/flame ionization detectors (FID), Summa canisters, various sorbent methods, and flux boxes. Specific advantages and disadvantages of the ORS measurement technologies and applications are addressed in Chapters 2 and 3 of this Handbook. The advantages of ORS applications should be determined on a case-by case-basis tailored to specific measurement goals and objectives. Some of the general ORS advantages are as follows:

- More likely to identify emissions “hot spots” because measurements are collected over a large area,
- Achieve better spatial and temporal emissions resolution,
- No sample shipping costs,
- Perform direct, measurement-based emission calculations, and
- Represent personal exposure better than fixed point monitoring.

Some general issues that require consideration when ORS methods are used include the following:

- More costly initial sampling instrumentation investment,
- Experienced manpower and higher site preparation cost more to deploy,
- Dependent on weather conditions (e.g., heavy rain, fog, dust), and
- Dependent on chemical interferences (e.g., water, oxygen, $O_3$ and $CO_2$).

As the use of open-path ORS technologies to quantify emissions from area sources has advanced, the desire to use ORS data in the development of atmospheric models and to support air quality standards has increased. However, use of remote sensing presents some challenging issues. Classical point measurement technologies and their associated results are typically based on the size of the stack or leak, flow data, moisture, bulk gas molecular weight and stack pollutants to be measured. Performance tests for emission masses are usually snapshots of short duration and not continuous. Using ORS data, unlike point sources wherein emissions measurements are typically straightforward, a more critical evaluation of the ORS method application, the emission mechanism of the source, and the source activity is needed of the emissions developer to ensure that the resulting data provides an accurate representation of average emissions from the source. While developing emission factors from optical remote technology applications is beyond the scope of this document, it is the aim of the Handbook to provide the technology background, application examples, and quality information for optical remote measurements that can assist all data users to develop emission results comparable to those routinely generated by traditional point source testing methods.

## 1.3 Contents and Overview of the Handbook

### 1.3.1 Contents

Remote sensing emissions data are often collected through an un-ducted or uncontained air parcel or emission plume. Results are reported in terms of “path-integrated” values. One issue in using these data is how comparable the remote sensing techniques are to short term stack or point source testing. Other potential issues include how representative remote sensing measurement techniques are for fugitive and area sources and if they adequately characterize temporal and spatial variability. It is possible that properly planned ORS measurement activities conducted over multiple weeks provide cost-effective, accurate, temporal, and spatial data from an emissions source enabling annualized emissions mass flux to be determined. This Handbook provides information that can be used by remote sensing data generators and users to answer questions regarding ORS monitoring data use. The Handbook is organized with the following sections:

- Section 2.0 focuses on ORS Technologies that form the backbone of the applications that generate emissions data.
- Section 3.0 describes the approaches and applications of the technologies described in Section 2.0 as they relate to fenceline and open-path measurements.
- Section 4.0 addresses ancillary data that needs to be collected in conjunction with the ORS measurements.

- Section 5.0 discusses data validation and verification.

### 1.3.2 Overview of Handbook Sections

This Handbook discusses remote measurement technologies, applications of those technologies, ancillary data necessary to use the remote measurement data, potential issues with using remote measurement data for emission factors development, models, and other atmospheric process needs. The discussions of remote measurements used to make the emissions measurement are in two separate sections. The first focuses only on the technologies including the specific hardware, scientific principles involved, how the pollutant concentrations are measured, pollutant and performance capabilities, and general strengths and limitations. The second section addresses how the technologies can and are being used to measure and monitor stationary source emissions including measuring mass emissions flux, monitoring emissions concentrations, and detecting fugitive emissions leaks. The Handbook also includes examples of remote measurement projects and readily available test reports.

Section 1.0 provides an introduction to the Handbook including background information that is necessary to understand the more detailed sections to follow. In this section you will also find a description of the EPA Quality System (QS) and how it can be used to create a data collection system that gathers data of sufficient quality for its intended use. The Measurement Quality Objectives (MQOs) in Section 1.4.2 will be useful to organizations planning remote measurement programs. The tables will help users to quickly review the requirements of a particular program. If an agency is required to perform a particular type of monitoring, such as those listed in Tables 1.1 through 1.5, this Handbook clearly lists all of the MQOs and calibration and accuracy criteria so that the agency can make the right choices when purchasing or upgrading its equipment for a specific program.

Section 2.0 provides an overview of the remote measurement detection technologies that are currently available for remotely measuring pollutant emissions concentrations. Included in this overview are discussions of FTIR, Tunable Diode Laser (TDL), UV-DOAS, and LIDAR spectroscopy technologies. In addition, qualitative ORS technologies including Thermal Infrared Imaging are described. Each of these technology descriptions includes information on the basic principles of operation, the pollutants that can be monitored, typical quality control (QC) and quality assurance (QA) for the technology, strengths, limitations, example vendors, and applications.

Section 3.0 describes the predominant remote measurement applications used to deploy the detection technologies addressed on Section 2.0 and to quantify emissions concentrations and flux measurements. This section also describes how the different technologies are applied to measurement methods, which is an extremely important section in this Handbook. The application descriptions briefly summarize the activity and explains how the application is verified or validated in field tests, and details typical QA/QC associated with the application. Section 3.0 also describes siting considerations or information. Each application in Section 3.0 includes a table of strengths and limitations that must be taken into account during the planning, implementation, and interpretation of field study results. Applications covered in Section 3.0 include RPM using EPA Other Test Method 10 (OTM-10), Differential Absorption LIDAR (DIAL), Tracer Dilution Correlation (TDC), Solar Occultation Flux (SOF), and bLS emissions modeling. Section 3.0 provides examples of how these applications are used in fugitive emissions and area source emissions flux and concentration measurement, site remediation, plant fenceline monitoring, fugitive leak detection, and ambient air measurement.

Section 4.0 presents the ancillary measurements and data that may be needed for each ORS application. Ancillary data may include meteorological measurements, industrial process information and source activity necessary to translate ORS results generated from the detection technique and measurement application combinations described in Sections 2.0 and 3.0, respectively, into emission data that meet project specific data quality objectives.

Section 5.0 addresses various methods to validate and verify remote measurement data.

## 1.4 General Discussion of the EPA Quality System

The EPA recently issued new guidance on its Quality Program (QP) policy. The document, "EPA Quality Program Policy"[11] states that this policy:

- Recognizes existing policies and procedures as the foundation of an Agency-wide Quality Program**,**
- Establishes an approach for identifying and addressing Agency quality issues,
- Provides a structure and procedures to ensure and enhance the effectiveness of the Quality Program and its application to Agency products and services.

Systematic planning is a key project-level component of the EPA QPs and is a component of the QS as shown in Figure 1.5.

The EPA policy is based on the national consensus standard, ANSI/ASQC E4-1994, Specifications and Guidelines for Environmental Data Collection and Environmental Technology Programs, developed by the American National Standards Institute and the American Society for Quality (ANSI/ASQC).[12] The ANSI/ASQC E4-1994 specification is consistent with the international standard ISO 17025. The ANSI document describes the necessary management and technical elements for developing and implementing a QS by using a tiered approach. The standard recommends documenting: (1) each organization-wide QS in a Quality Management Plan (QMP) or Quality Manual (to address requirements of Part A: Management Systems of the standard) and (2) the applicability of the QS to technical activity-specific efforts in a Quality Assurance Project Plan (QAPP) or similar document (to address the requirements of Part B: Collection and Evaluation of Environmental Data of the standard). The EPA has adopted this tiered approach for its mandatory agency-wide QS. This document addresses Part B requirements of the standard for systematic planning for environmental data operations.

In accordance with EPA Order 2106.0[11], the EPA requires that environmental programs performed for or by the Agency must be supported by data of the type and quality appropriate to their expected use. The EPA defines environmental data as information collected directly from measurements, produced from models, or compiled from other sources such as databases or literature.

### 1.4.1 Data Quality Objectives

EPA Order 2106.0 requires that all EPA organizations (and organizations with extramural agreements with EPA) follow a systematic planning process to develop acceptance or performance criteria for the collection, evaluation, or use of environmental data. A systematic planning process is the first component in the *planning phase* of the project tier (see the bottom tier of Figure 1.5), while the actual data collection activities take place in the *implementation phase*.

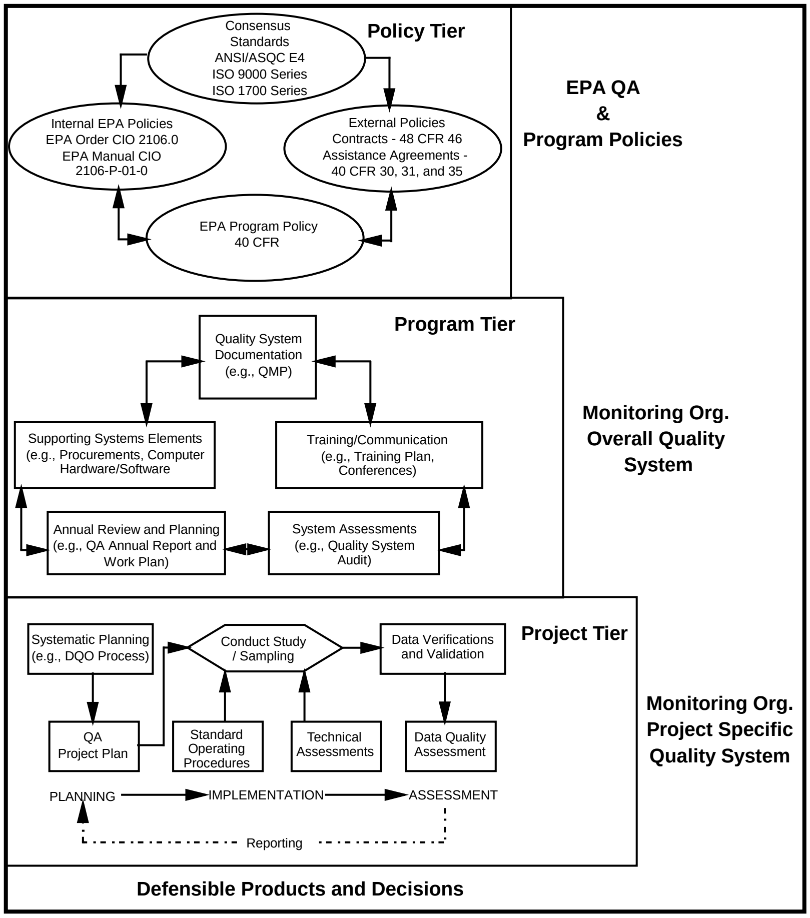

**Figure 1-5. The EPA Quality System**

Systematic planning is a planning process based on the scientific method and includes concepts such as objectivity of approach and acceptability of results. Systematic planning is a common-sense, graded approach to ensure that the level of detail in planning is commensurate with the importance and intended use of the work and available resources. This framework promotes communication among all organizations and individuals involved in an environmental program. Through a systematic planning process, a team can develop acceptance or performance criteria for the quality of the data collected and for the quality of the decision. When these data are being used in decision-making by selecting between two clear alternative conditions (e.g., compliance/non-compliance with a standard), the EPA's recommended systematic planning tool is called the Data Quality Objective (DQO) Process.

The DQO Process is a seven-step planning approach to develop sampling designs for data collection activities that support decision-making. This process uses systematic planning and statistical hypothesis testing to differentiate between two or more clearly defined alternatives.

Step 1. Define the problem.

Step 2. Identify the problem and the associated decision(s).

Step 3. Identify information needed for the decision.

Step 4. Define the boundaries of the study.

Step 5. Develop a decision rule.

Step 6. Specify limits on decision errors.

Step 7. Optimize the design for obtaining data.

The DQO Process is iterative and allows the planning team to incorporate new information and modify outputs from previous steps as inputs for a subsequent step. Although the principles of systematic planning and the DQO Process are applicable to all scientific studies, the DQO Process is particularly designed to address problems that require making a decision between two clear alternatives. The final outcome of the DQO Process is a design for collecting data (e.g., the number of samples to collect and when, where, and how to collect samples).

The development and implementation of a QS should be based on a "graded approach," that is, the components and tools of a QS (Figure 1.5) apply according to the scope and nature of an organization, program, or project and the intended use of its products or services. This approach recognizes that a "one size fits all" approach to quality management is not appropriate and that the QS of different organizations and programs should (and will) vary according to the specific needs of the organization. For example, the quality expectations of a research program are different from those of a regulatory compliance program because the intended use of the products differs. The same applies to remote sensing data. Monitoring agencies that use this Handbook are strongly encouraged to understand their data objectives, perform the DQO Process if needed, and use the MQOs described in Section 1.4.2 if they are applicable to an agency's program. Additional explanation and details on the DQO Process can be found in EPA's *Guidance on Systematic Planning Using the Data Quality Objectives Process*.[12]

When an agency or entity is monitoring for non-regulatory purposes (e.g., background concentrations, modeling applications, or exposure), these MQOs are recommended information. Meeting MQOs for non-regulatory meteorological monitoring is strongly advised.

### 1.4.2 Measurement Quality Objectives

Once DQOs are designated for a program or project, measurement indicators must be determined to understand if the DQOs are being met. Most state/local/tribal agencies that collect data do so to support programs that are federally mandated or that need to meet federal requirements. However, other non-regulatory applications exist, such as modeling applications, state implementation plan development, and forecasting. These programs require different MQOs because the application is different (i.e., different DQOs). The following prescribed objectives should be decided and discussed within the QS.

- **Measurement.** Type of measurements and/or the parameter needed to be collected.

- **Method.** The method is different from the measurement in that a particular instrument can be utilized in different methods. The method will dictate the precision, bias, and representativeness of the sampling data.

- **Reporting Units.** Reporting units must be decided before the program begins. If it is a regulatory program, then ppb or micrograms per cubic meter (µg/m$^3$) would be the appropriate units. However, if it is a modeling exercise, then grams per second (g/s) may be the appropriate unit.

- **Detection Limits.** It is very critical to state the levels of detection (LOD) for a particular program. The LOD can be very difficult to quantify until the ORS is actually in the field of operation. It should also be noted that LODs can be defined in different ways. It is best to define and state LOD in the quality documents developed for a particular program.

- **Minimum Sample Frequency.** This objective is required to define how often data must be collected to meet the end user's requirements for precision and representativeness. Measurements must be taken often enough to meet model or modeling input criteria.

- **Completeness.** For most programs/projects, there is a minimum amount of data required to allow the data users to make decisions concerning the environment. A rule of thumb is 75 to 85 percent data completeness.

- **Precision.** Precision is the measure of agreement among repeated measurements of the same property under identical conditions. This can be very difficult to measure using ORS.

- **Bias.** Bias is the systematic or persistent distortion of a measurement process that causes errors in one direction. Bias, like precision, can be very difficult to determine with ORS. The project or program must be able identify and determine the magnitude of its measurement bias.

- **Representativeness.** Representativeness is collection of the measurement location, frequency, duration, and other factors that demonstrate the results correspond to the emission characterization required by the data users.

## 1.5 Selecting the Right Tool: Technology/Application Cross-Table References

This section outlines the possible “cross-over” of different technologies (i.e., instruments) with the applications (i.e., methods) described in this Handbook. Tables 1-1 and 1-2 are not meant to be the final word on how these technologies and applications can be utilized, but serve as a reference for those seeking a match between the technologies and applications. As applications and technologies expand and new technologies and applications are developed, it is foreseen that these tables will expand as well.

**Table 1-1. Technology vs. Application Cross-Table**

| | Emission-Rate Estimation Methods | | | | | | |
|---|---|---|---|---|---|---|---|
| **Active ORS Technology** | **Point Source** | **Area Source** | **Stationary and Mobile Tracer Correlation** | **Vertical Radial Plume (VRPM)** | **Solar Occultation Flux (SOF)** | **Plane Concentration Flux*** | **Back Lagrangian Stochastic (bLS)** |
| Fourier Transform Infrared (FTIR) | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Ultraviolet (UV) and UV-DOAS | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Tunable Diode Laser (TDL ) | ✓ | ✓ | ✓ | ✓ | | ✓ | ✓ |
| Differential Lidar (DIAL) | ✓ | ✓ | | ✓ | | ✓ | ✓ |
| Cavity Ring down Spectroscopy (CRDS) | ✓ | ✓ | ✓ | | | ✓ | ✓ |

## 1.6 Strengths and Limitations

Tables 1-2 and 1-3 provide summaries of each technology and each application's strengths and limitations, respectively. More detail is provided for each in the sections specific to the technology or application being investigated.

**Table 1-2. Technology Strengths and Limitations**

| Strengths | Limitations |
|---|---|
| **Fourier Transform Infrared Spectroscopy – 2.1** | |
| Relatively low instrument cost (about $80,000 - $125,000) | Gas-phase water spectral interference as well as CO and $CO_2$ interference[5,14,15] |
| FTIR equipment is fairly rugged and portable | Typical set-up time can range from several minutes to several hours and a minimum of two people |
| There are a large number of compounds that are infrared active (absorb IR light) | Weak IR absorption features for many inorganic molecules such as sulfur dioxide and nitrogen oxides[6] |
| Large number of compounds can be analyzed simultaneously | Infrared beam has a limited range and may not be sensitive enough to meet ambient data quality objectives. Maximum path length is on the order of 400–500 meters. |
| No gas calibration standards necessary (uses standard reference spectral library) | Multiple vertical or horizontal path measurements necessary to calculate plume flux, can require significant time and cost to set up and implement |
| FTIR can be used to locate discrete emissions hotspots at a facility/area source. Some instruments are electrically cooled and sensitive | Typical infrared detectors require cryogenic cooling to operate. Liquid nitrogen used for detector cooling must be refilled and maintained regularly (weekly). |
| Multi-compound coverage makes FTIR ideal for leak detection or source location where the facility being monitored has multiple compounds present | Not applicable to homonuclear diatomic gases such as chlorine, oxygen, and nitrogen[1,2,3] |
| Equipment can be allowed to run unattended for extended periods with remote access to check instrument operation and recover data | Single beam open-path method measures concentration along a path. The path must capture most if not all of an analyte plume to provide accurate measure of emissions. |
| No sample collection, handling, or preparation is necessary | Field implementation and data collection requires highly experienced personnel |
| **Tunable Diode Laser – 2.2** | |
| Field units are light weight, typically under 75 Kg, and relatively easy to transport and setup | Detects only one compound per laser. |
| Less expensive than alternative technologies | Fewer measurable compounds and limited sensitivity. |
| Wide linear response resulting in measurements from 0.1 to 1,000 ppm for many target compounds. | Quantitation limited to compounds with overtone absorbencies in the near- and mid-IR range |

**Table 1-2. Technology Strengths and Limitations (continued)**

| Strengths | Limitations |
|---|---|
| **Tunable Diode Laser – 2.2 (continued)** | |
| The ability to measure longer path lengths (1 km compared to other ORS technologies) | With all open path optical measurements, blocked beams result in no measurements |
| Robust field use with low maintenance, minimal consumables to operate | |
| Rapid response – typically 1 second | |
| Unattended measurements collection | |
| Minimizes interference from other gases resulting in high compound specificity | |
| Lower equipment cost per measurement, ability to multiplex signals | |
| **UV-DOAS – 2.3** | |
| 24/7 remote monitoring | Set up of remote receiving optics or reflectors can be difficult |
| Low cost long term deployment | Fixed observation area. Long term deployment depends on constant wind direction. |
| Monitoring of three criteria pollutants and trace species simultaneously as per 40 CFR 58. | A number of species do not have appropriate UV-visible absorption structures making them undetectable by UV-DOAS |
| Absolute measurement system – off line or laboratory gas calibrations can be performed | Accurate reference spectra needed – reference spectra can be a source of error |
| Typical path length is 500 m, Longer measurement path length possible – up to 10 km. | Long path lengths can cause complications when analyzing results |
| Non-contact measurements can detect unstable atmospheric species. | Affected by poor visibility conditions |
| Can provide near real time data. | Retro reflector or remote optics do not allow collection of vertical plume evolution data |
| Portable. Can be used in mobile applications | |
| **LIDAR – 2.4** | |
| In contrast to PIC measurements taken by other instrumentation system, DIAL relay concentration data as a function of distance along the beam path | Measureable species are limited to those with unique absorption bands. Chemical species with common absorption characteristics can only be measured as classes of compounds |
| Reported path lengths up to 3000 meters | The absorption wavelengths of species are temperature and pressure dependent. It is necessary to check the applicability of wavelengths selected for measurement based on temperature and pressure variation in target absorption. |
| Collects backscattered light without the use retro-reflectors | Sufficient aerosol or molecular material must be in the atmosphere to create sufficient backscatter |

**Table 1-2. Technology Strengths and Limitations (continued)**

| Strengths | Limitations |
|---|---|
| **LIDAR – 2.4 (continued)** | |
| Scan along measurement plane requires 10 to 15 minutes | Rapidly changing wind speed or direction may cause measurements to change rapidly and may affect mixing ratios of measured surrogates to compounds of interest. |
| Instrumentation is moved around measurement site obtaining multiple plume scans from various locations increasing accuracy of plume characterization | Small number of vendors providing DIAL systems and services |
| Instrumentation can also be mounted on airborne platform for increased mobility and expanded applications | High cost has limited the number of commercial DIAL studies in the United States |
| Real time data allows for leak identification and inputs to process change decisions | Beam path is limited by the geographical constraints of the measurement location |
| Allows for simultaneous concentration measurements of multiple species and classes of species | Only two wavelengths are used operationally, this makes it difficult to post process data and investigate spectral artifacts |
| **IR Camera – 2.5** | |
| Fast screening speed compared to conventional leak detection methods | Cannot quantify the concentration of a leak without additional technology. |
| Leak assessment can be done without interruption to plant operations. | Camera use requires individuals with specific training. Some models are easier to use than others. |
| Cost-effective compared to traditional leak detection methods. | Cannot be used during rain or fog and is not as effective during overcast skies. |
| Accurately assess the size of each leak. | The camera has a specified nominal operating range for ambient temperature. |
| Better able to isolate the exact source of a leak despite close proximity to other leaking sources in real time and record in a video format. | Operation is not intrinsically safe and use is limited in hazardous areas. |
| Wide field of view: More likely to identify leaking components in unconventional places. | |
| Exposure risk minor because leaking components can be viewed at a distance. | |
| **Cavity Ring Down Spectroscopy – 2.6** | |
| Minimal maintenance required and no consumables are needed. Turnkey operation with the potential for remote access and control. “User friendly”. | May need to apply sample filtering components to avoid interferences. |
| Ability to measure very small changes in short time frames. Can rapidly scan spectra continuously for high temporal resolution and real-time results. | Limits the method to the laser spectral ranges available. |
| Greatly increases sensitivity with much longer effective pathlengths. Insensitive to vibrations during measurements. | Are only able to reflect over a small wavelength range (about ± 15%) relative to the center wavelength. Multiple species detection difficult. |

**Table 1-2. Technology Strengths and Limitations (continued)**

| Strengths | Limitations |
|---|---|
| **Cavity Ring Down Spectroscopy – 2.6 (continued)** | |
| Allows for extended wavelength range scanning, increasing sensitivity by probing multiple absorption lines while also eliminating other interferences. | Key components that typically drive up the cost of the instrumentation, depending on application. |
| Minimal-to-no drift making frequent calibration unnecessary. Enhanced accuracy and system stability. | |
| Renders the method immune to ambient changes (such as relative humidity and temperature) and laser intensity fluctuations. Also produces a large linear dynamic range. | |
| Little-to-no sample pre-conditioning or treatment required before analysis. | |
| Easy field deployment and installation. Quick sample exchange in a smaller volume cavity with moderate flow rates. Advances in components allow for a fairly rugged portable system. | |
| Logistically simpler for field use to eliminate the need for a large power source. | |

**Table 1-3. Application Strengths and Limitations**

| Strengths | Limitations |
|---|---|
| **OTM 10 Radial Plume Mapping - 3.1** | |
| Measures high temporal and spatial emission data. | Reliant upon ideal meteorological conditions. |
| Directly calculates emission rates. | Difficulties in characterizing emissions from side-sloping areas. |
| Captures the distribution of all major emissions in an area and isolates emissions from specific measurement areas. | Larger uncertainty associated with capturing emissions from sources far away from the VRPM configuration. |
| Can provide real-time PIC data for multiple compounds simultaneously. | Compounds can create interference depending on the technology used. This can be avoided by using to systems, but this is very expensive. |
| **DIAL – 3.2** | |
| See strengths and limitations listed in the technology table. | |

**Table 1-3. Application Strengths and Limitations (continued)**

| Strengths | Limitations |
|---|---|
| **Solar Occultation Flux – 3.3** | |
| Increases measurement accuracy by reducing uncertainty. | System requires vibration reduction platform and a smooth mobile path. |
| Decreases instrumental complexity for field operations and reduces amount of scattering errors in the UV. | Calculations based on wind speed measurements inherently add uncertainty due to the stochastic, uncontrollable, and highly variable nature of wind speed. |
| Multiple species detection over a wide range of wavelengths. | Uncertainty of plume height increases measurement error from wind speed term. |
| More suitable for frequent field application. | Inappropriate to make measurements in the presence of clouds. |
| Decreased cost and easier field application. | Difficulty in separating emissions sources that are close together. |
| Higher specificity and better signal-to-noise (relative to DIAL). | |
| Corresponds to unstable meteorological conditions where wind gradients due to convection are smoothed out. | |
| **Tracer Correlation – 3.4** | |
| Provides the ability to determine if varying meteorological conditions affect the calculation of emission rates | Logistical challenges such as the availability of roads and location. |
| Ability to calculate emission rates within 15-30% precision. | Tracer gas cylinders are expensive and more difficult to transport. |
| | Changing weather conditions affect the calculation of emission rates. |
| **Backward Lagrangian Stochastic – 3.5** | |
| Requires only a single concentration measurement – as opposed to many concentration measurements made in the vertical or horizontal plane of the plume | Assumes ideal atmospheric conditions. Uncertainty of emission height can cause errors in predictions |
| Substantial freedom to choose convenient measurement locations | Placement of atmospheric sensors relative to source can have a major effect on the quality of the predictions generated by the model |
| An economical alternative for determining emissions | When multiple unknown sources are present the calculations are very sensitive to sensor placement |
| Handles complex source shapes and sizes with relative ease | Rapid atmospheric changes or extreme stability invalidate MOST and cause $Q_{\mathrm{bLS}}$ estimates to be inaccurate |
| Free downloadable software available online | Very experienced personnel required to generate high-quality data from the bLS model |

**Table 1-3. Application Strengths and Limitations (continued)**

| Strengths | Limitations |
|---|---|
| **Backward Lagrangian Stochastic – 3.5 (continued)** | |
| Meteorological data can be directly entered into the model based on field measurements or the model can estimate them using data variables developed from standard empirical relationships | Where flow obstacles such as buildings or fences are present, measurements are often better made further downwind of the source, well away from the obstacles. |
| Can be used in locations with wind disturbances | Short to long computational time |
| **Cavity Ring Downs Spectroscopy – 3.6** | |
| See strengths and limitations listed in the technology table. | |

Table 1-4 summarizes the quantitation range for each of the optical technologies, as well as the expected sensitivity, accuracy, and precision. Where possible, quantitative values verified by the EPA's Environmental Technology Verification (ETV) Program were used. This table is a general comparison between the different types of optical technologies. The parameters listed are dependent upon factors such as the chemical properties of the analyte measured, path length and signal strength, and may be better or worse for each specific site specific application depending on these conditions. It is also valuable to note that quantitative limits of each technology establish the limit for application in which they are used (i.e., the sensitivity of vertical radial plume mapping (VRPM) is limited by the FTIR or TDL technology used to collect the measurements).

**Table 1-4. Quantitative Summary of ORS Technologies**

| TECHNOLOGY | TYPICAL RANGE OF APPLICATION | SENSITIVITY (DETECTION LIMITS) | ACCURACY | PRECISION (RSD) |
|---|---|---|---|---|
| **FTIR**[14] | 0-50 ppm | < 1.0 ppmm | 0-30% | < 1.0% |
| **TDL**[15,16] | 0-800 ppm | < 15.0 ppmm | 0-40% | < 5.0% |
| **UV-DOAS**[17,18] | 0-1000 ppb | < 0.10 ppbm | 0-20% | < 5.0% |
| **LIDAR** | 0-120 ppb | low-ppb Range | 0-15% | < 1.5% |
| **IR Camera** | N/A | N/A | Qualitative Only | Qualitative Only |

## 1.7 Future Evolution and Updates of this Handbook

The EPA will periodically update and correct this Handbook. Updates will include the addition of new information as well as feedback from stakeholders. This document will be updated, at the discretion of the EPA, depending on the availability of resources.

This document does not contain EPA policy information; it is strictly an information document. It is envisioned that in later editions, new ORS technologies and techniques will be described in this document.

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# 2.0 Optical Remote Sensing Technologies

ORS technologies measure the concentration of chemicals in an open air path or in contained air samples collected from discreet sampling points. They do this by measuring the interaction of electromagnetic energy (i.e., different wavelengths of light) with the air's components. Open-path technologies measure the concentrations of chemicals or particulates across an open path of air. They do this by emitting a concentrated beam of electromagnetic energy into the air and measuring its interactions with the air's components. Open-path technologies provide an average concentration over a line of sight. Point-source applications of these technologies measure the concentration of a confined sample of air drawn into the apparatus from a point or points in air.

Some technologies (e.g., TDL) are capable of simultaneously measuring one or two compounds. Other technologies (e.g., UV-DOAS) are capable of measuring several compounds simultaneously, while others (e.g., FTIR) can measure a large number of compounds simultaneously. ORS technologies are used to measure the average chemical concentrations over a set distance or at a stationary point. The path average over a set distance has an advantage over point-source measurements that may miss high-concentration plumes running between sampling devices. Both open-path and point-source applications of these technologies have been used to detect hotspots in area sources and to obtain path integrated averages. Each of the technologies has advantages and disadvantages for these applications. The technologies described in Chapter 2 can be used alone or in combination to provide three major types of data: plume characterization, short term flux measurements and long term monitoring studies. In Chapter 2, we discuss how each of several prominent ORS technologies operates.

# 2.1 Fourier Transform Infrared Spectroscopy

FTIR spectroscopy is an optical spectroscopy technology adapted to perform real-time monitoring of gaseous and volatile organic compounds in air. The technique is capable of detecting and quantifying multiple compounds simultaneously, even in harsh industrial environments, using the characteristic spectral features of the individual compounds.[1]

FTIR spectrometers are well-suited to remote sensing applications because they are durable, portable, and do not require daily routine calibration. The technology, however, is not simple to operate and requires experienced staff to ensure correct operation and valid results. Both extractive and open-path (OP-FTIR) environmental applications of the technology have been demonstrated. The EPA test methods have been written for both open-path (OTM10, TO-16r) and extractive (Method 318, Method 320 and ASTM D6328-03) measurement by FTIR. In open-path mode, the IR radiation beam can be directed over distances of up to 400 to 500 meters to measure selected compounds in emission plumes or dispersed air parcels. Alternatively, in extractive mode, gas can be drawn into a closed cell with a folded path length of 10 to 100 meters. Optical remote spectroscopy applications focus on open-path mode. Mobile tracer applications focus on extractive mode.

Compound-specific concentration is determined using standard IR spectra of known concentration. The onboard computer software and spectra library allow real time determination of concentration for preset compounds. Post-test processing of IR spectra allow other compounds in air samples to be determined. Every measurement uses calibrated reference spectra taken at conditions similar to the unknown field samples to determine compound concentrations therein.

## 2.1.1 Basic Operation

The FTIR instrument sends an IR beam of light through a region (closed-cell or open-path) containing the compounds of interest and captures the resulting IR spectra from the sample. Figure 2-1 illustrates the basic components of an open-path FTIR spectrometer. Infrared light generated by an IR emitting source is guided through an interferometer. The interferometer consists of an IR source, beam-splitter, mirrors, a laser, and a detector. The IR energy goes from the source to the beam-splitter, which splits the beam into two parts. One part is transmitted to a moving mirror and one part is reflected to a fixed mirror. The moving mirror oscillates back and forth at a constant velocity. This velocity is timed according to the very precise laser wavelength in the system, which also acts as an internal wavelength calibration. The beam reflected from the moving mirror and the beam reflected from the fixed mirror have traveled different distances since being generated by the source and are recombined at the beam-splitter.[1,2]

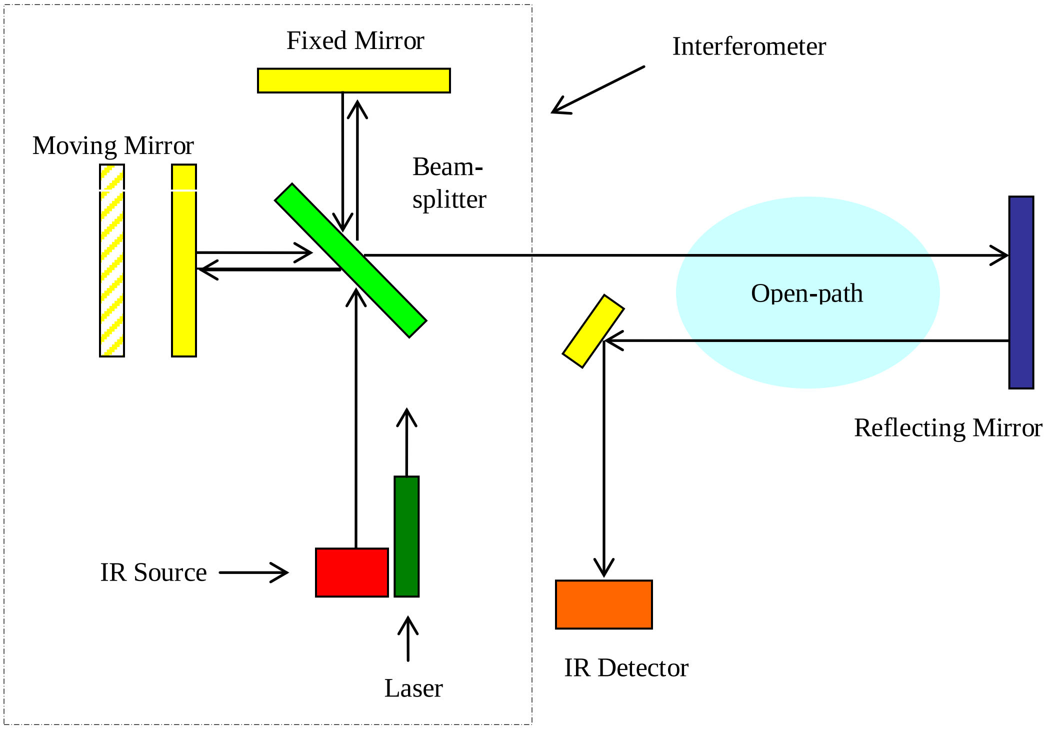


**Figure 2-1. Diagram Showing the Beam Path and Major Components of an OP-FTIR**

When the beams are recombined, some of the wavelengths recombine constructively and some destructively, which creates an interference pattern. This interference pattern is called an interferogram. The recombined IR beam then passes from the beam-splitter into the open-path where a portion of the IR energy is absorbed by the gaseous compounds to be measured. The resulting IR beam reaches the IR detector where the interference pattern is detected, digitized, and transformed mathematically into a standard single beam infrared frequency spectrum using an algorithm known as a Fourier transform. A reference or background single beam spectrum is also collected without a sample and the ratio of the two single beam spectra is computed to produce a background corrected transmittance spectrum. This transmittance spectrum can be converted to absorbance by taking the negative $\log_{10}$ of the data points.[2]

The vibrational frequencies of all the infrared absorbing molecules in the IR beam path are captured in the IR spectrum. When a molecule absorbs light, the energy of the molecule is increased and the molecule is promoted from its lowest energy state (ground state) to an excited state. Light energy in the infrared region of the electromagnetic spectrum stimulates molecular vibrations. Molecular species display their own characteristic vibrational structure when stimulated by IR radiation.[3] Figure 2-2 shows the IR absorption spectra for nitrous oxide, $CO_2$, CO, NO, $NO_2$, and ammonia. The units of vibrational frequency are wave number. Wave number and vibrational structure are used to identify a particular molecule.

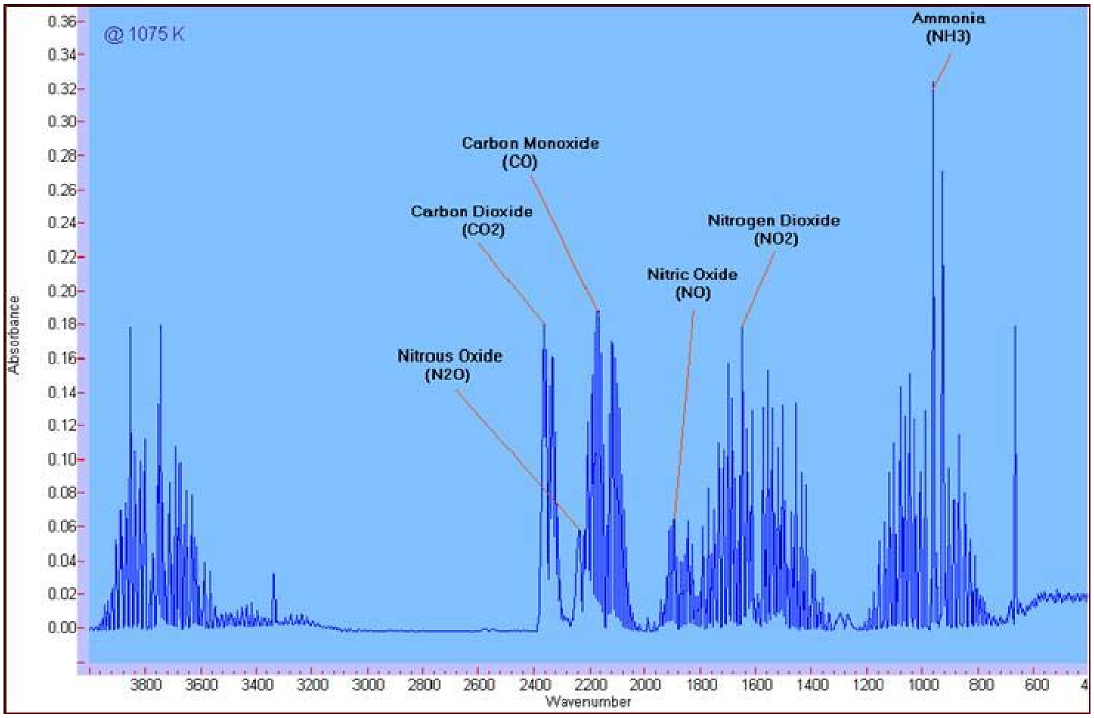


**Figure 2-2. FTIR Absorption Spectrum Recorded at 1075° K**

Once a compound has been identified, its spectrum can also be used to measure the compound's concentration because the amount of IR radiation absorbed from the IR beam is proportional to the concentration of the compound in the sample or open path. According to the Beer-Lambert law, there is a linear relationship between absorbance and concentration as shown in Equation 1.[1,2,3]

$$A = \varepsilon c l \qquad \textbf{Eq. 1}$$

Where: $A$ = absorbance intensity
$\varepsilon$ = absorption coefficient
c = sample concentration
l = sample path length

FTIR systems typically operate in two modes: extractive cell or open-path. Extractive cell measurements can be conducted either from a single location or from a mobile measurement platform.[4] In the field, OP-FTIR systems can operate with telescopes transmitting and receiving the IR beam so monitoring of long outdoor paths is possible. The pollutants normally measured in this process are at ambient temperature and usually in the low ppb concentration range.[5] Typical applications of open-path monitoring include fence-line monitoring of industrial sites, landfill sites, waste lagoons, urban air monitoring in metropolitan areas, accidental release detection/identification, and detection of agents or surrogates important to homeland security monitoring applications.[6,7] It should be noted that moisture due to fog or high humidity will cause spectral interferences, which can limit the use of this technique to pollutants that do not have overlapping absorption features with gas-phase water.[5]

### Extractive (Closed) Cell Measurement Applications

For extractive or closed-cell FTIR measurements, the beam is sent through a cell that is mounted in the instrument itself. As shown in Figure 2-1, the IR beam passes through the cell and is focused onto the detector. Gas-phase samples are pumped into a sealed, constant temperature cell and analyzed. Sample cell path lengths can vary from 10 cm to 150 m folded-path cells. The longer the path length the more sensitive the measurement becomes because the IR beam has a greater chance of interacting with the absorbing compounds. The pollutants measured in this type of arrangement are usually at higher concentrations than those found in open-path FTIR measurements. Typical applications of extractive FTIR monitoring include stack testing of flue gases and vehicle exhaust.[6,7] Figure 2-3 shows a photo of an FTIR unit used for extractive monitoring of stack gas. This unit is equipped with a 32 m folded path length cell that extends from the end of the instrument.

**Figure 2-3. FTIR Closed Cell Unit Used to Monitor Stack Gas**

## Open-Path Measurement Applications

There are a number of instrumental configurations for open-path (OP) instruments. The simplest OP systems are bistatic configurations. This configuration derives its name from the fact that both the transmitter and receiver must be fixed in a static position and precisely aimed at each other. The OP-FTIR equipment projects the IR light beam directly along a path to a detector/receiver. Bistatic configurations in general have the requirement of supplying power at both the receiver and transmitter, which can be a disadvantage in some locations. Additionally, there is a requirement for alignment at both receiver and transmitter, which can be time-consuming for mobile systems.[8]

Monostatic configurations were developed to address issues raised with bistatic designs. In a monostatic configuration, all of the optical components of the transmitter and receiver are in the same location, and a retro-reflector is used to return the light from the transmitter to the receiver. This configuration derives its name from the fact that only the transceiver portion of the instrument needs to be precisely pointed as the retro-reflector returns light to its source regardless of orientation. A diagram of a typical monostatic configuration is shown in Figure 2-4.

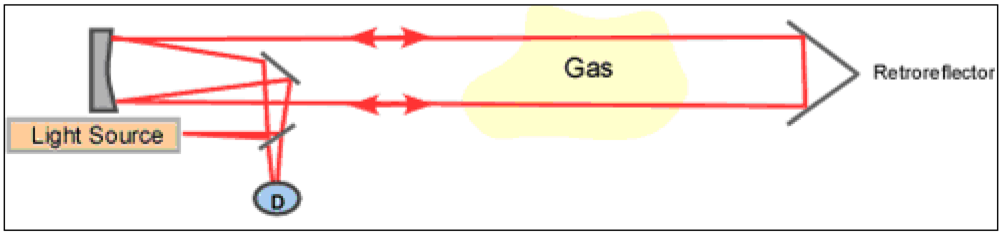
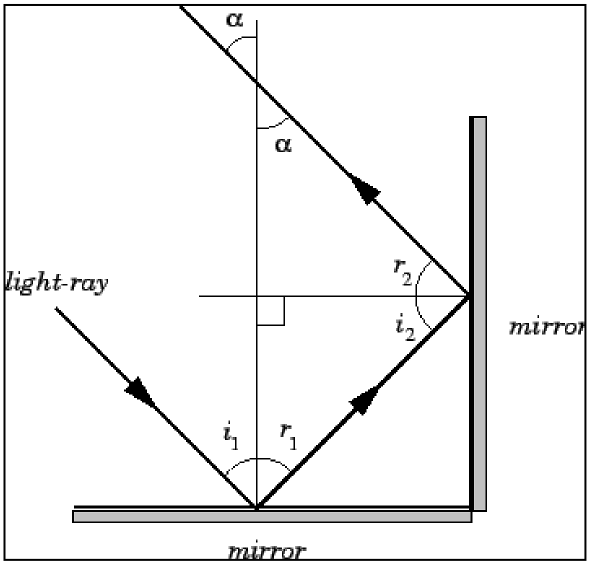


**Figure 2-4. Basic Setup Used to Make Monostatic Open-path FTIR Measurements**

Retro-reflecting mirrors, as they are called, are configured with three perpendicular reflective surfaces in the shape of a corner. A combination of three mutually perpendicular mirrors reflects light incident from any direction through 180° as shown in Figure 2-5. Such a combination of mirrors is called a corner-cube reflector. Corner-cube reflectors beam FTIR light back to its exact point of origin. This property reduces the divergence of the beam on its return path back to the detector compared to divergence that would result from a flat mirror. Also, the retro-reflector array can be very large to capture and return essentially the entire divergent signal from the telescope.



(http://farside.ph.utexas.edu/teaching/316/lectures/node133.html)

**Figure 2-5. The Corner-cube Reflector**

In the monostatic mode, the IR laser beam is split twice, once leaving the OP-FTIR and once on its return. This design requires a beam splitter in the optical path that removes 50 percent of the light from the outgoing beam and 50 percent of the light from the return beam for an overall loss of 75 percent of the total light intensity.

The dual-telescope monostatic configuration has lower detection limits because it does not utilize a beam splitter in the optical path. A translating retro-reflector, which is essentially a portion of a very large cube, is used to return the light beam offset to align with the receiving telescope. This single, large retro-reflector does not have the divergence reversal properties of the corner-cube array. The second telescope adds cost and complexity to the system.[8] However, when compared with monostatic mode, bistatic systems are harder to align and maintain because any shift in the transmitter or detector can result in system misalignment.[7,9] Both operating modes measure only the compounds that are in the beam path. Emissions outside the beam path are not measured. In these situations, measurements have been conducted along multiple beam paths to more accurately characterize the emission plume.

Figure 2-6 shows a telescopic FTIR transmitting and detection unit, which would be used for open-path field monitoring applications. Figure 2-7 shows a typical retro-reflecting mirror. The retro mirrors are surface coated with a reflective material to reduce extraneous glare from outside stray light. Retro-reflecting mirrors are often contained in a protective housing, which is closed when the unit is not in use to protect the sensitive reflecting surfaces from exposure to inclement weather conditions.

**Figur2-6. Typical Telescopic FTIR Transmitting and Detection Unit**

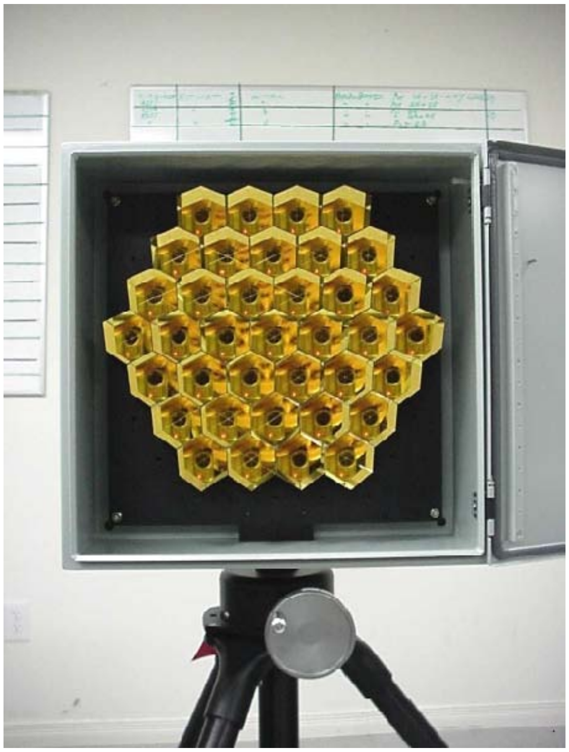


**Figure 2-7. Retro Reflecting Mirror Used to Reflect the IR Beam Back to Detection Unit**

### 2.1.2 Pollutants and Relative Levels That Can Be Measured

Table 2-1 provides an example list of compounds that have been measured using OP-FTIR spectroscopy.[6,7] This list is not all-inclusive, but shows that many compounds can be measured via OP-FTIR. Another feature of OP-FTIR is that many compounds can be monitored simultaneously as opposed to other beam technologies that can monitor only single compounds. As with other optical sensing systems, OP-FTIR produces a path integrated concentration (PIC) in units of parts per million (ppm) or ppb times length, i.e., ppb (meters).[6] Dividing the final ppb (meters) result by the total optical path length gives the path integrated gas concentration in ppb.

**Table 2-1. Example List of Compounds Measured by FTIR Open-path Systems**

| Species | | |
|---|---|---|
| **acetaldehyde** | 1,4-dimethyl piperazine | methyl mercaptan |
| acetic acid | **1,4-dioxane** | **methyl methacrylate** |
| acetone | ethane | 2-methyl propene |
| **acetonitrile** | ethanol | morphaline |
| acetylene | ethyl acetate | nitric acid |
| **acrolein** | ethylamine | nitric oxide |
| **acrylic acid** | **ethylbenzene** | nitrogen dioxide |
| **acrylonitrile** | ethylene | nitrous acid |
| **ammonia** | **ethylene oxide** | ozone |
| **benzene** | ethyl mercaptan | pentane |
| **1,3-butadiene** | **formaldehyde** | **phosgene** |
| butane | formic acid | **phosphine** |
| butanol | furan | propane |
| 1-butene | halocarb-11 (CCl3F) | propanol |
| cis-2-butene | halocarb-12 (CCl2F2) | **propionaldehyde** |
| trans-2-butene | halocarb-22 (CHClF2) | propylene |
| butyl acetate | halocarb-113 (CFCl2CF2Cl) | **propylene dichloride** |
| **carbon disulfide** | hexafluoropropene | **propylene oxide** |
| **carbon monoxide** | hydrocarbon continuum | pyridine |
| **carbon tetrachloride** | **hydrogen chloride** | silane |
| **carbonyl sulfide** | **hydrogen cyanide** | **styrene** |
| **chlorobenzene** | hydrogen sulfide | **sulfur dioxide** |
| **chloroethane** | isobutene | sulfur hexafluoride |
| **chloroform** | isobutanol | 1,1,1,2-tetrachloroethane |
| **m-cresol** | isobutyl acetate | **1,1,2,2-tetrachloroethane** |
| **o-cresol** | isobutylene | **tetrachloroethylene** |
| **p-cresol** | isoprene | **toluene** |
| cyclohexane | isopropanol | **1,1,1-trichloroethane** |
| **1,2-dibromoethane** | isopropyl ether | **1,1,2-trichloroethane** |
| m-dichlorobenzene | **methanol** | **trichloroethylene** |
| o-dichlorobenzene | methylamine | **trimethylamine** |
| **p-dichlorobenzene** | methyl benzoate | 1,2,4-trimethylbenzene |
| **1,1-dichloroethane** | **methyl chloride** | **vinyl chloride** |
| **1,2-dichloroethane** | **methylene chloride** | **m-xylene** |
| **1,1-dichloroethylene** | methyl ether | **o-xylene** |
| dimethylamine | **methyl ethyl ketone** | **p-xylene** |
| dimethyl disulfide | **methyl isobutyl ketone** | |

Compounds in **bold** are EPA Hazardous Air Pollutants (HAPs) CAA -112Title 42, Chapter 85, Subchapter I, Part a U.S. Code 7412 (b)

Detection limits can vary widely from compound to compound depending on a number of factors such as instrument configuration, the condition of retro-reflecting mirrors, humidity, beam path length and the absorbance strength of the target compound(s) at the wavelength chosen for analysis. Detection limits are typically reported in ppm for one meter of path length (ppmm). They can be determined empirically using cell based measurements or estimated by solving equation 1 for an absorbance that is three times the mean signal noise if the absorbance coefficient and noise are known at the wavelength used to measure the compound(s) of interest. Detection limits for specific sampling episodes are calculated by dividing ppmm by the actual meters of path length during field sampling. Typically, FTIR manufacturers report detection limits for commonly monitored pollutants as part of the literature for their instrumentation. In general, open-path FTIR detection limits in the single digit ppb levels can be achieved for a number of strong IR absorbing compounds.[7,10] Extractive FTIR detection limits for a 10 meter folded path length are typically on the order of 1 to 10 ppm. Some compounds such as benzene have detection limits in the 30-50 ppb range because gas-phase water interferes with this measurement.[7] Other compounds, such as hydrogen sulfide, are weakly IR absorbing molecules and have detection limits in the 300-800 ppb range.[7]

### 2.1.3 Typical QA/QC

To ensure measurement accuracy and data verification, instrumentation response should be verified annually (detector and IR source) using a known concentration of a standard gas mixture. Certificates of calibration should be kept on file and available for review. Maintenance records should be kept in bound notebooks for any equipment adjustments or repairs that could affect measurement performance. Maintenance notebooks should include the date and description of maintenance performed. Calibration checks should be performed after major service and regularly during analysis.[11,12] QA and QC procedures for the measurement of gaseous compounds by extractive FTIR are discussed in great detail in EPA Test Method 320 or ASTM D6328-03. These procedures for OP-FTIR are discussed in more detail below.

## Calibration Spectra

A gas-phase FTIR reference spectrum is collected at a known temperature and pressure in a fixed path length enclosed cell for the compound of interest from a sample of known concentration. A series of measurements can be made at different concentrations and a calibration curve that relates the measured absorbance and the gas concentration can be developed to confirm a linear response of signal with concentration. These calibration spectra are stored in a spectral reference library used by the computer during real-time sample processing. Several national databases exist of IR spectra collected under different conditions that can be used for sample analysis. Because Beer’s law is theoretically linear, often only a single point calibration is necessary to determine sample concentration. Spectra collected over a range of concentrations allow instrumental nonlinearity to be evaluated. Use of spectra at or near the concentration measured in the field reduces bias caused by nonlinearity. Unknown sample concentrations can be determined by comparing sample absorption intensities to absorption intensities in the standard reference spectra. The higher the concentration of compound being measured, the more IR radiation characteristic of that compound is absorbed. Complex mixtures of IR sensitive compounds can be determined for a single spectrum by solving a multiple linear regression matrix using characteristic wavelengths of compounds and the relative intensities of sample IR spectral features compared to calibration spectral features.

Tables of absorbance coefficients are available, and standard reference spectra for numerous compounds can be purchased. Suppliers of reference spectra include Pacific Northwest National Laboratory, which continues to develop the Northwest Infrared (NWIR) spectral library of quantitative infrared absorption spectra[13] and the high-resolution transmission molecular absorption database (HITRAN) compiled by Harvard University.[14]

Figure 2-8 shows an example of a typical single point calibration curve where the sample absorbance is plotted against concentration. Interpolation of the curve at a given absorbance measurement gives the concentration of the molecular species being analyzed.

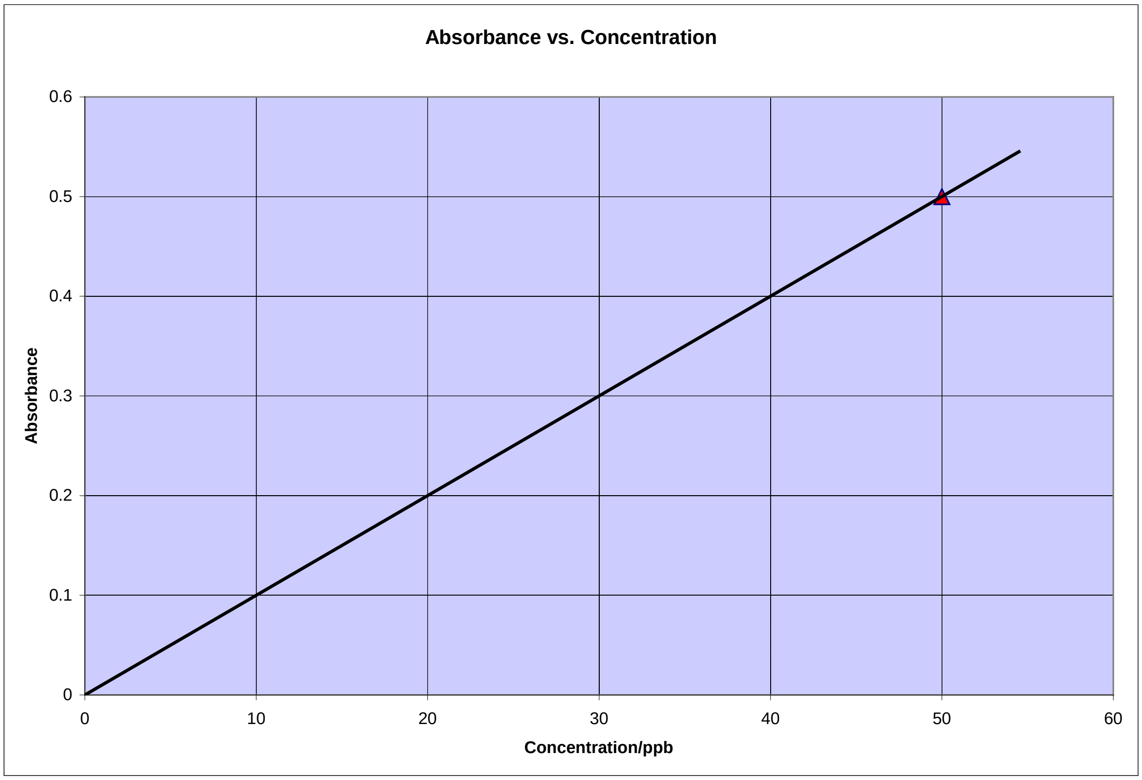


**Figure 2-8. Calibration Plot of Absorbance vs. Concentration**

## QA/QC for OP-FTIR Instrumentation

Several quality checks should be performed on FTIR instrumentation prior to deployment to the field and for the duration of the field campaign.[15] Prior to field deployment, the spectral baseline is checked to determine the amount of signal intensity, instrument noise, and baseline drift. Baseline drift is due to detector signal fluctuations that cause the signal to increase gradually over time. Typically, instruments are powered on and allowed to warm up for at least one hour prior to data collection to minimize baseline drift effects. Baseline noise should be checked prior to initial data collection and on each subsequent day of a field campaign to determine the amount of baseline signal due to the instrument's electronics and detector noise. All checks must be in accordance with the method or test protocol being performed.

On the first day of a field study, a stray light instrument check should be performed. This involves collecting, measuring, and identifying stray light as either background or instrument-related. All QC checks must be conducted prior to actual data collection and the results must indicate that the instrument is operating within the acceptable criteria range as specified in the method or protocol appropriate for the field testing campaign.[15] Typical quality control for this technology includes method quality objectives of 10-25 percent accuracy depending on path length and a precision target of 10 percent. Spectral quality is verified through the procedures and guidelines set by the manufacturers and specific EPA method in use.[16]

In addition to the QC checks performed on the FTIR, the quality of the instrument signal (interferogram) should be checked regularly during the field campaign. This is done by ensuring that the intensity of the signal is at least five times the intensity of the stray light signal and instrument noise. In addition to checking the strength of the signal, checks should be done regularly in the field to ensure that the data are being collected and stored to the data collection computer.[15]

## Data Quality Indicators for Precision and Accuracy for OP-FTIR

Instrument baseline noise and signal intensity are key data quality indicators for OP-FTIR measurements. Some investigators evaluate the precision and accuracy of the PIC measurements collected with an FTIR instrument by analyzing nitrous oxide concentrations in the atmosphere. A typical background atmospheric marker concentration for nitrous oxide is about 315 ppb.[17] However, this value may fluctuate due to seasonal variations in nitrous oxide concentrations or the topographical elevation of the site.[17]

The precision of the OP-FTIR measurements should be evaluated by calculating the relative standard deviation of ubiquitous IR active compounds (e.g., nitrous oxide) in each data subset. A subset is defined as the data collected along one particular path length during one particular survey or sampling episode.[15] The number of data points in a data subset depends on the number of sample events conducted in a particular survey. For a stable air parcel, the standard data quality indicator (DQI) criterion set forth for precision is ±10 percent.[15]

The accuracy of the analyte PIC measurements can be evaluated by comparing the calculated nitrous oxide concentrations from the data subsets to the typical background concentration of 315 ppb.[11] The standard DQI criterion for accuracy is ±25 percent.[15]

### 2.1.4 Example Applications and Vendors

Details on the OP-FTIR application of open path technologies are provided in Section 3 of this Handbook. The OP-FTIR has been used for a wide variety of source emission measurements in the field including applications such as line of sight optical remote, bLS modeling and RPM. Table 2-2 summarizes optical technologies and the typical applications of each of the technologies.

**Table 2-2. Typical Applications for OP-FTIR.**

| Technology | Applications |
|---|---|
| OP-FTIR | bLS, RPM, SOF, Tracer Gas Correlation, TO-16 |

We are aware of multiple vendors that currently manufacture OP-FTIR units; two of these vendors have verified their instrumentation through the EPA's ETV program. The cost of an OP-FTIR field ready system can range from $75,000 to $120,000 in 2010 U.S. dollars, depending on configuration and application. Gas standards used in fixed path length enclosed cells to confirm instrument calibration can range between $300 and $500. Table 2-3 lists several of these vendors and indicates which have verified their OP-FTIRs. The table also lists potential vendors for FTIR gas standards.

**Table 2-3. FTIR Supply Vendors**

| OP-FTIR Instruments | |
|---|---|
| KASSAY FSI –<br>*Ail Systems Inc.[18] | www.kassay.com |
| *Spectrex, Inc.[19] | http://www.spectrex-inc.com |
| IMACC Instruments | http://www.ftirs.com/ |
| MIDAC Corporation | http://www.midac.com/ |

| | |
|---|---|
| ruker Optics | http://www.brukeroptics.com/opag.html |
| ABB/Bomem | http://www.abb.com/analytical |
| **Gas Standard Suppliers**** | |
| Air Gas | http://www.airgas.com/ |
| Linde | http://www.linde.com/ |
| Matheson Gas | http://www.mathesongas.com/index.aspx |
| Spectra Gas | http://www.spectragases.com |
| Praxair | http://www.praxair.com/ |

*ETV Verified Technologies
** Requires gas regulator in addition to gas cylinder

In addition to instrumentation and gas standards, tables of absorbance coefficients are available and standard reference spectra for numerous compounds can be purchased. Suppliers of reference spectra include Pacific Northwest National Laboratory, which continues to develop the NWIR spectral library of quantitative infrared absorption spectra[13] and Harvard University, which compiled the HITRAN database.[14] These spectra have been measured under tightly controlled conditions using state-of-the-art instrumentation.

### 2.1.5 Strengths and Limitations

FTIR can be used as a qualitative tool to provide specific information about volatile IR energy absorbing molecules. It can also be used as a quantitative tool to provide the concentration of many gas-phase molecules. A summary of strengths and limitations is shown in Table 2-4 and Table 2-5. One of its limitations is that gas-phase water and $CO_2$ are a very strong IR absorbing species. Water has strong absorption features in the 3200–4000 wave number range.[5,17,20] Molecules that have coincident vibrational frequencies with water cannot be reliably analyzed using frequencies in this range. FTIR is also limited to measuring gaseous compounds that absorb IR radiation. Homonuclear diatomic gases such as nitrogen, oxygen, and halogen gases cannot be measured by FTIR.

FTIR's major strength is that it can provide real-time, simultaneous analysis of multiple gaseous contaminants.[6] Additionally, the FTIR is a robust field instrument that allows for unattended sampling for as long as a week period. Not only can the FTIR be used for open path concentration measurement of a variety of contaminants, but it can also be used for leak and hotspot detection.

**Table 2-4. Summary Table of the OP-FTIR's Strengths**

| Feature | Strength |
|---|---|
| Economical | Relatively low instrument cost (about \$80,000 - \$125,000)<br>Low-cost long term deployment |
| Compact Instrumentation | FTIR equipment is fairly rugged and easily portable |
| Multiple Wavelength Operation | There are a large number of compounds that are infrared active (absorb IR light) |
| | Large number of compounds can be analyzed simultaneously. Spectra can be saved and post analyzed. |
| Ease of Calibration | No gas calibration standards necessary for field testing (uses standard reference spectral library). Gas standards are only needed for laboratory confirmation of instrument performance and calibration. |
| Multiple Applications | FTIR can be used to locate discrete emissions hotspots at a facility/area source |
| | Multi-compound coverage makes FTIR ideal for leak detection or source location where the facility being monitored has multiple compounds present (e.g., chemical plants) |
| Automated Real-time Measurements | Equipment can be allowed to run with minimal attention for months at a time with remote access to check instrument operation, schedule cryogen replenishment and recover data. |
| | No sample collection, handling, or preparation is necessary |

**Table 2-5. Summary Table of the OP-FTIR's Limitations**

| Feature | Limitation |
|---|---|
| Spectral Interferences | Gas-phase water spectral interference as well as CO and $CO_2$ interference[5,16,17] |
| Diatomoic Molecules | Not applicable to homonuclear diatomic gases such as chlorine, oxygen, and nitrogen[1,2,3] |
| IR Wavelength Range | Weak IR absorption features for many inorganic molecules such as sulfur dioxide and nitrogen oxides[6] |
| | Infrared beam has a limited range and may not be sensitive enough to meet ambient data quality objectives. |

| | |
|---|---|
| Path Length Range | Maximum path length is on the order of 400–500 meters |
| Field Implementation Requirements | Typical infrared detectors require cryogenic cooling to operate. Liquid nitrogen used for detector cooling must be refilled and maintained regularly (weekly). |
| | Field implementation and data collection requires highly experienced personnel |
| Setup Time Consuming and Costly | Typical set-up time usually requires about 5 to 8 hours and a minimum of two people |
| | Multiple vertical or horizontal path measurements necessary to calculate plume flux, can require significant time and cost to set up and implement |
| Measurement Limitations | Single beam open-path method measures concentration along a path. The path must capture most if not all of an analyte plume to provide accurate measure of emissions. |

### 2.1.6 References

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## 2.2 Tunable Diode Laser

Light amplification by stimulated emission of radiation (LASER) is a technique to generate a narrow wavelength of light with a small cross sectional area. Diode lasers generate this beam of light using a semiconductor material that emits light when electrical current is "injected" into the semiconductor junction. When the TDL was first introduced, its measurement applications were limited to laboratory functions because of the instrument functionality and cost. The rise of the fiber-optics communication industry in the 1980s led to the development of open-path TDL (OP-TDL) instrumentation that is compact and affordable.[1] Since that time, the OP-TDL has become recognized as a reliable technology for use in the field for *in situ* measurement of a variety of gaseous pollutants. New laser development demonstrated in 1994 using a repeated stack of thin semiconductor layers (Quantum cascade lasers) offers the possibility to produce LASER beams at additional wavelengths and add to the list of compounds that can be measured.[2]

Laser-based gas detectors are now being used in a wide variety of applications for process and quality monitoring, and safety and environmental compliance. Laser detectors combine semiconductor TDLs and optical fibers developed by the telecommunications industry with detection techniques based on frequency or wavelength modulation (similar to radio). Laser detectors measure gas concentrations by shining a laser beam through a sample of gas and measuring the amount of laser light absorbed. Lasers emit light at a single wavelength. In TDLs, the wavelength can be "tuned" over a small range to match the exact absorption wavelength of a target compound by adjusting temperature and bias current. The wavelength of the laser is tuned over a selected absorption feature of the target species. The measured absorption spectra is recorded and, combined with measured gas temperature and pressure, effective path length, and known line strength, used to determine a quantitative measurement of concentration. These properties give laser detectors a combination of selectivity, sensitivity, dynamic range and rapid response time. The OP-TDL is able to make quantitative measurements of select gases based on the principals of Beer-Lambert law. Gas molecules absorb energy at specific wavelengths based on rotational and vibrational motion within the molecule. By measuring the energy absorbed for a compound-specific wavelength over a laser's path, the OP-TDL can determine the concentration present of a specific gaseous compound. This technology can be used for several open-path and point monitoring applications.

The OP-TDL is a relatively inexpensive technology that emits very narrow wavelengths in the near IR ranges. While mid-IR wavelength lasers are available, they are much more difficult to operate or are currently cost prohibitive for general use. Because the wavelength emitted is very narrow and can be chosen specific to a vibration or rotation of a specific compound, the OP-TDL eliminates most interference. Lack of interference and high intensity of the laser beam allows longer open path lengths, up to 1 to 2 km and therefore, higher sensitivity for the compounds TDL can measure. The near-IR OP-TDL units currently in use are limited by the small number of compound specific wavelengths available from commonly available TDLs and the necessity to use a different TDL for each compound of interest.

### 2.2.1 Basic Operation

TDL Absorption Spectroscopy instruments rely on spectroscopic principles and sensitive detection techniques, coupled with advanced diode lasers and optical fibers developed by the telecommunications industry. Gas molecules absorb energy at specific wavelengths in the electromagnetic spectrum. At wavelengths slightly different than these absorption lines, there is essentially no absorption. Measurement of the relative strengths of off-line to on-line transmission yields a precise and highly sensitive measure of the target gas concentration along the path transited by the laser beam. Measurements are made by (1) transmitting a beam of light through a gas mixture sample containing a quantity of the target gas, (2) tuning the beam’s wavelength to one of the target gas’s absorption lines, and (3) accurately measuring the absorption of that beam. The concentration of target gas molecules can then be integrated over the beam’s path length.

While results generated by traditional optical instrumentation are generally in concentration units such as ppb, the output generated by the OP-TDL, similar to all open-path technologies, represents units of concentration over distance, such as ppb(m). This is also known as a PIC.

Each gaseous compound absorbs energy at different wavelengths, usually more than one, depending on vibrational and rotational excitement within the molecule. Therefore, each compound has its own "signature" of bands from which energy may be absorbed. Each band is highly selective, with virtually no absorption occurring outside of a specific wavelength. Because the OP-TDL emits a laser at a very narrowly tuned wavelength range, it is an ideal instrument for single compound measurement. The OP-TDL's laser is selected for an overtone band specific to the compound of interest. The absorption of energy over the laser's path length is measured by the instrument's detector. The absorption is used to determine the concentration of the target gaseous compound using the principals of Beer-Lambert Law as described in Equation 1.

$$A = \varepsilon c l \qquad \textbf{Eq. 1}$$

Where: $A$ = absorbance intensity
$\varepsilon$ = absorption coefficient
c = sample concentration
l = sample path length

There are a number of instrumental configurations for OP instruments. The simplest OP-systems are bistatic configurations. The arrangement of the components of this design for OP-TDL is shown in Figure 2-9. This configuration derives its name from the fact that both the transmitter and receiver must be fixed in a static position and precisely aimed at each other. The OP-TDL equipment projects the laser beam directly along a path to a detector/receiver. Bistatic configurations, in general, have the requirement of supplying power at both the receiver and transmitter, which can be a disadvantage in some locations. Additionally, there is a requirement for alignment at both receiver and transmitter, which can be time-consuming for mobile systems.[11]

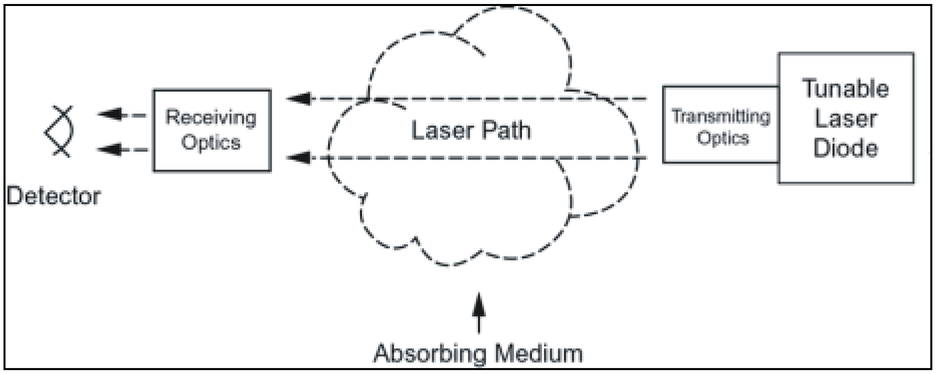


**Figure 2-9. TDL Bistatic Configuration**

Monostatic configurations were developed to address issues raised with bistatic designs. In a monostatic configuration, all of the optical components of the transmitter and receiver are in the same location, and a retro-reflector is used to return the light from the transmitter to the receiver. This configuration derives its name from the fact that only the transceiver portion of the instrument needs to be precisely pointed as the retro-reflector returns light to its source regardless of orientation. A diagram of two monostatic configurations is shown in Figure 2-10.

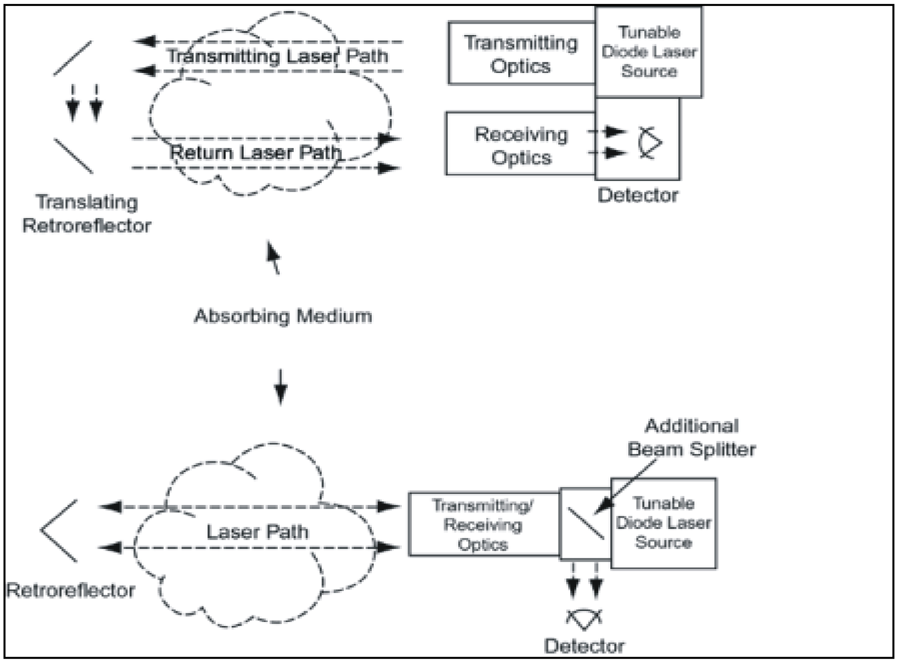
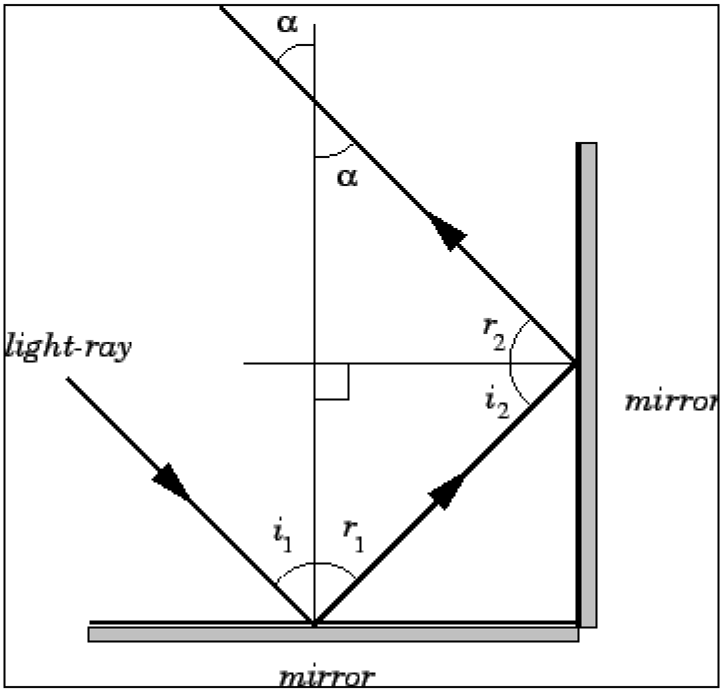


**Figure 2-10. TDL Monostatic Configuration**

Retro-reflecting mirrors, as they are called, are configured with three perpendicular reflective surfaces in the shape of a corner. A combination of three mutually perpendicular mirrors reflects light incident from any direction through 180° as shown in Figure 2-11. Such a combination of mirrors is called a corner-cube reflector. Corner-cube reflectors beam TDL light back to its exact point of origin. This property reduces the divergence of the beam on its return path back to the detector compared to divergence that would result from a flat mirror. Also the retro-reflector array can be very large to capture and return essentially the entire divergent signal from the telescope.



(http://farside.ph.utexas.edu/teaching/316/lectures/node133.html)

**Figure 2-11. The Corner-cube Reflector**

In the mono-static mode, the IR laser beam is split twice, once leaving the OP-TDL and once on its return. This design requires a beam splitter in the optical path that removes 50 percent of the light from the outgoing beam and 50 percent of the light from the return beam for an overall loss of 75 percent of the total light intensity.

The dual-telescope monostatic configuration has lower detection limits because it does not utilize a beam splitter in the optical path. A translating retro-reflector, which is essentially a portion of a very large cube, is used to return the light beam offset to align with the receiving telescope.

This single, large retro-reflector does not have the divergence reversal properties of the corner-cube array. The second telescope adds cost and complexity to the system.[3] However, when compared with mono-static mode, bi-static systems are harder to align and maintain because any shift in the transmitter or detector can result in system misalignment.[4,5] Both operating modes measure only the compounds that are in the beam path. Emissions outside the beam path are not measured. In these situations, measurements have been conducted along multiple beam paths to more accurately characterize the emission plume.

OP-TDL units are designed to operate under computer control, where the interfacing software controls the function of the OP-TDL, controls the tuning of the laser, and collects resulting data from the detector. Commercially available OP-TDL units can be equipped with multiple lasers, allowing the measurement of several compounds at one time. Field units typically include a hardware controller, a laptop, a telescope receiver, and a reflector. Instruments can run unattended via computer control for extended periods of time.[6]

### 2.2.2 Pollutants and Relative Levels That Can Be Measured

Near-IR TDLs have been used to measure approximately 20 compounds that have absorbencies in the 1.4 – 1.8 micrometer (μm) wavelength range. Using an open-path setup, concentrations into the low ppm range can be detected over a path length of approximately 1000 m to 2000 m. Table 2-6 lists airborne compounds that can be measured by OP-TDL systems and their approximate wavelengths. The compounds measured by TDLs are limited by the wavelength range commonly available using electrical current driven semiconductor lasers. Quantum Cascade Laser (QC-Laser) development offers the possibility of expanding the list by extending available laser wavelengths into the mid-infrared range, where many compounds of interest strongly absorb these wavelengths. However, one issue is that the measurements are also limited by the ability of fiber optic cables to transmit the raw LASER energy in those instruments using remote modules. Current TDL light sources cost $2,000 to $3,000. Experimental QC-Lasers are available at a cost up to $100,000.

**Table 2-6. Example List of Gaseous Compounds Measured by Near IR OP-TDL Systems**

| Species | Approximate near-IR λ (nm) | Reported Detection Limit (ppm-m) |
|---|---|---|
| ammonia | 760, 1500 | 0.5-5.0 |
| carbon monoxide | 1570 | 40-1,000 |
| carbon dioxide | 1570 | 40-1,000 |
| **hydrogen chloride** | 1790 | 0.15-1 |
| hydrogen cyanide | 1540 | 1.0 |
| **hydrogen fluoride** | 1310 | 0.1-0.2 |
| hydrogen sulfide | 1570 | 20 |
| methane | 1650 | 0.5-1 |
| nitric oxide | 1800 | 30 |
| nitrogen dioxide | 680 | 0.2 |
| oxygen | 760 | 50 |
| water | 970, 1200, 1450 | 0.2-1.0 |

Compounds in **bold** are EPA Hazardous Air Pollutants (HAPs)

CAA – 112 Title 42, Chapter 85, Subchapter I, Part A U.S. Code 7412 (b)

**Table 2-6. Example List of Gaseous Compounds Measured by Near IR OP-TDL Systems (continued)**

| Species | Approximate near-IR λ (nm) | Reported Detection Limit (ppmm) |
|---|---|---|
| acetylene | 1520 | These compounds are not commonly measured, therefore detection limits are not readily available. |
| ethylene | 1693 | |
| **formaldehyde** | 1930 | |
| hydrogen bromide | 1960 | |
| hydrogen iodide | 1540 | |
| nitrous oxide | 2260 | |
| phosphine | 2150 | |
| propane | 1400, 1500, 1700 | |

Compounds in **bold** are EPA Hazardous Air Pollutants (HAPs)

CAA -112 Title 42, Chapter 85, Subchapter I, Part A U.S. Code 7412 (b)

### 2.2.3 Typical QA/QC

Three major QA requirements are necessary when using a TDL system: (1) selection of the appropriate laser and absorption line for the compound of interest, (2) establishment and use of an appropriate calibration procedure, and (3) establishment of QC procedures that ensure the instrument's performance as measurements are made.[6]

## Selection of the Laser and Absorption Line

A TDL optical system is typically built to generate one wavelength at a time. The range of wavelengths from each type of laser limits measurement to one compound at a time. Therefore, laser and instrument selection must be carefully considered. A few lasers can be configured for one of a limited range of wavelengths, while others provide a wider selection of wavelengths. It is also important to note that many compounds have multiple absorption bands in both the near- and mid-IR regions. However, the availability of mid-IR lasers is limited and may not be available for open-path monitoring or measurement programs. Table 2-7 lists commercially available lasers producing wavelengths in the near-IR range. Table 2-8 lists other laser types that have been developed for mid-IR applications. While this list covers most of the lasers available, TDLs represent a limited set from a larger array of laser types.

**Table 2-7. Near-IR Laser Types Available for OP-TDL Systems**

| Laser Type | Tunable λ Range (nm) | Target Compounds |
|---|---|---|
| **InGaAsP** | 1200-2000 | CO, $CO_2$, NO, $CH_4$, $C_2H_2$, **HF**, **HCl**, HBr, HI, HCN, $NH_3$, **$H_2CO$**, $PH_3$, $H_2O$ |
| **Antimonide*** | 2000-4000 | CO, $CO_2$, NO, $N_2O$, $CH_4$, **HCl**, HBr, $H_2CO$ |

*****Laser emits wavelengths in both the near-IR and mid-IR spectrums.

**Table 2-8. Potentially Usable Mid-IR Lasers**

| Laser Type | Tunable λ Range (nm) | Target Compounds |
|---|---|---|
| **AlGaInP** | 630-690 | $NO_2$ |
| **AlGaAs** | 750-1000 | $O_2$, $NH_3$ |
| **Vertical Cavity** | 650-1680 | $H_2O$, $C_2H_2$, **HF**, $H_2S$, $O_2$, $H_2O$, $NH_3$ |
| **Antimonide*** | 2000-4000 | CO, $CO_2$, NO, $N_2O$, $CH_4$, **HCl**, HBr, **$H_2CO$** |

| | | |
|---|---|---|
| **Quantum Cascade**** | 4000-12000 | $H_2O$, CO, $CO_2$, NO, $NO_2$, $N_2O$, $SO_2$, $C_2H_2$, HCN, $NH_3$, $PH_3$, $0_3$ |
| **Lead-salt**** | 3000-30000 | $H_2O$, CO, $CO_2$, NO, $NO_2$, $N_2O$, $SO_2$, $CH_4$, $C_2H_2$, **HCl**, HBr, HCN, $NH_3$, **$H_2CO$**, $PH_3$, $O_3$ |

*****Laser emits wavelengths in both the near-IR and mid-IR spectrums.
** Laser emits wavelengths in the mid-IR spectrum. http://www.swsciences.com/technology/sensors.html
Compounds in **bold** are EPA Hazardous Air Pollutants (HAPs) CAA **-**112 Title 42, Chapter 85, Subchapter I, Part A U.S. Code 7412 (b)

Because compounds often have multiple absorption bands that can be detected by a TDL system, it is also important to consider which band is best for quantitative purposes.[7] Higher intensity absorption bands provide the best sensitivity. However, interference from other compounds may eliminate the use of the most sensitive wavelengths. It also may be worthwhile to measure the concentrations from a second absorption band to verify the nonexistence of interferences. It is highly unlikely that the same interference would exist for both absorption bands.[6]

## Calibration

In a closed-gas cell TDL instrument, known concentrations of the compound of interest are introduced into the white cell used for sample analysis. Calibration gas is added through the same line used to collect the sample. Varying concentrations of one compound can be introduced by adjusting the inlet flow of the calibration gas relative to the dilution gas. For each concentration step in the calibration curve, the absorption trend should be recorded and the mean and standard variation calculated.[8]

The calibration factors are typically determined in the laboratory with short path length gas cells. One instrument vendor provides an insertion slot that can contain a gas cell of known concentration into the path of the optical beam during measurement. Other OP-FTIR instruments can also be calibrated with gas cells of known concentration by introducing the cell into the laser's path for measurement. Field calibration checks can be accomplished using the absorption signal provided by the calibration gas cell added to the open path field absorption signal. The signal increases above the open path signal, proportionally to the gas concentration and path length of the gas cell. The instrument response is checked using the difference of the measurements with and without the gas cell. An example of a calibration curve for methane is provided as Figure 2-12.

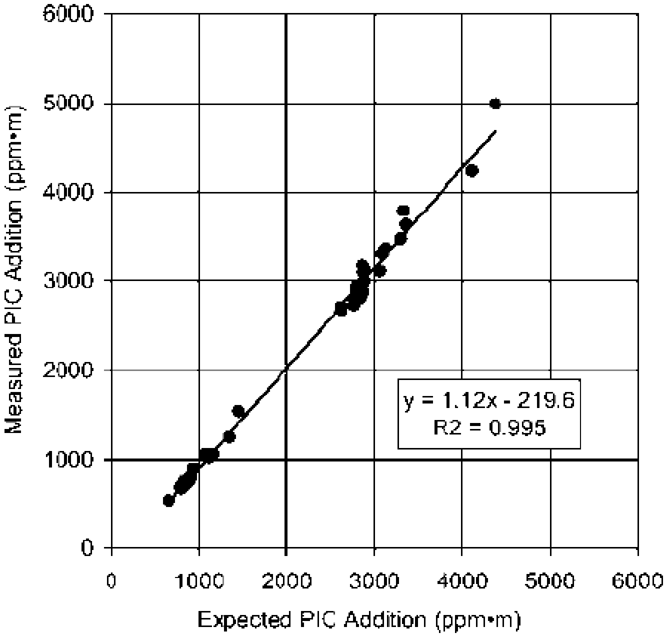


**Figure 2-12. Calibration Data for an OP-TDL System.**[9]

Calibration frequency depends on the duration of the measurement period as well as the concentrations of compounds that are measured. Shorter term measurements projects need calibration verification at the beginning of a measurement episode. Also note that regulatory requirements may also dictate calibration frequencies. Low concentrations in ambient conditions may require background and calibration determinations on a weekly or monthly basis[6] because a small drift in instrument response is more significant at lower measured concentrations.

### Quality Control Procedures

Each OP-TDL manufacturer recommends its own QC procedures; however, it is necessary to verify the accuracy of the calibration throughout a set of field measurements. This can be done by reinserting a calibration standard cell periodically during a measurement episode to ensure correct measurement. Recalibration during field measurements may be necessary due to instrument drift and is typically performed using the instrument's system software.

## 2.2.4 Example Applications and Vendors

### Applications

Details on the near-IR TDL application of open path technologies are provided in Section 3 of this Handbook. The OP-TDL has been used for a wide variety of source emission measurements in the field including applications such as line of sight optical remote, bLS modeling, RPM, and mobile tracer release correlation. Table 2-9 summarizes optical technologies and the typical applications of each of the technologies.

**Table 2-9. Typical Applications for OP-TDL.**

| Technology | Applications |
|---|---|
| OP-TDL | , bLS, RPM, Tracer Gas Correlation, TO-16 |

### Vendors

While there are many sources for TDL instrumentation that is suitable for laboratory applications, there are only a few vendors currently offering field ready OP-TDL instrumentation. Vendors offering instrumentation exclusive to fire detection and monitoring have not been included. The cost of a TDL field ready system can range from $35,000 to $75,000 in 2010 U.S. dollars depending on the configuration and application. Table 2-10 lists example vendors and their internet contact address.

**Table 2-10. Near-IR OP-TDL Vendors**

| Vendors | |
|---|---|
| Boreal Laser | www.boreal-laser.com |
| OPSIS AB | www.opsis.se |
| Leister Process Technologies, Axetris Division | www.ir-microsystems.com |
| Norsk Elektro Optikk (NEO, Norway) | www.neo.no |
| PKL Technologies, Inc. | www.pktechnologies.com |
| PSI Physical Sciences, Inc. | www.tdlas.com<br>www.psicorp.com |
| Senscient | www.senscient.com |
| Simtronics group | www.simtronics.eu |
| Unisearch Associates, Inc. (Concord, Canada) | www.unisearch-associates.com |

### 2.2.5 Strengths and Limitations

The TDL has an array of strengths and limitations that must be considered for each OP-TDL application. A summary of strengths and limitations is shown in Table 2-11 and Table 2-12, respectively. Perhaps the most striking limitation is the fact that each TDL laser can detect only one compound at a time and each laser can scan only a limited range of wavelengths. It is also true that only compounds with overtone absorbencies in the near- and mid-IR ranges can be detected and quantified, of which there are approximately twenty.[9] The instrument’s sensitivity is limited because of noise created by the laser[10], though this can be improved by either of the modulations described above. However, because the laser emits such a narrow bandwidth, interferences from other gaseous compounds are unlikely.

The TDL’s strengths in field application are numerous. Technological developments originating from the fiber optics communication field have allowed the TDL to become compact, robust, and economical compared to other technologies. The TDL can be used for several applications, including open-path, RPM, and cavity ring-down spectroscopy (CRDS) measurements. The high-powered laser source also promotes fast instrument response times (as low as one measurement per second) and longer path lengths up to 1,000 meters. Commercially-available

TDL instrumentation allows for optical beam path flexibility, as well as automated real-time measurements. Calibration is also simplified by the ability to insert a gas cell standard into the instrument.[9]

**Table 2-11. Summary Table of the TDL's Strengths**

| Feature | Strength |
|---|---|
| Automated Real-time Measurements | 24/7 remote monitoring |
| | Can provide near real time data |
| | Unattended measurements collection |
| Compact instrumentation | Field units are lightweight, typically under 75 Kg, and relatively easy to transport and setup |
| Economical | 0.5 to .01 the cost of alternative technologies |
| High intensity light source | Wide linear response over a wide dynamic range resulting in measurements from 0.1 to 1000 ppm |
| | The ability to measure longer path lengths (1 km compared to other ORS technologies) |
| Solid state technology | Robust field use with low maintenance, minimal consumables to operate |
| Low response times | Rapid response – typically 1 second |
| High spectral resolution | Minimizes interference from other gases resulting in high compound specificity |
| Uses fiber optics for signal processing | Lower equipment cost per measurement, ability to multiplex signals |
| Vendor-specific calibration cells | Self calibration, zero and span drift correction |

**Table 2-12. Summary Table of the TDL's Limitations**

| Feature | Limitation |
|---|---|
| Single wavelength operation | Detects only one compound per laser, fewer measureable compounds, and limited sensitivity |
| Mid-IR wavelength range | Quantitation limited to compounds with overtone absorbencies in the near- and mid-IR range |
| Dust and objects block the laser beam | With all open path optical measurements, blocked beams result in no measurements |

### 2.2.6 References

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## 2.3 Ultraviolet Differential Optical Absorption Spectroscopy

The UV-DOAS is an optical remote sensing technology that quantifies concentrations of gaseous compounds by measuring the absorption of UV light by chemical compounds in the air and applying the Beer-Lambert law.[1]

A significant strength of the UV-DOAS is its extremely long path-length capability – typically 500 meters with some research applications up to 10 kilometers.[2] UV-DOAS has been deployed in a wide variety of environmental measurement applications. It is most frequently used to measure or monitor criteria and smog-related air pollutants. It is also able to accurately monitor several pollutants that do not produce ideal IR absorption bands. However, because the absorption bands for UV-DOAS are very wide, there are many compounds that cannot be accurately quantified by UV-DOAS. Nitrogen and oxygen molecules in the air cause broad spectral scattering and interfere with many of the compounds that can be measured. The UV-DOAS is reported[2] to have detection limits in the low (ppb) range and can reach parts per trillion in some research applications when used with optimum measurement path lengths.

### 2.3.1 Basic Operation

In general, UV, visible, and near-IR light is that radiation within the 180-780 nanometer wavelength range that causes changes in energy between the bonding electrons in molecules that absorb the light. While wavelength ranges produced by UV-DOAS instrumentation include the rotational and vibrational transitions caused by near-IR light, the typical application of UV-DOAS restricts the UV light to a wavelength range of 245 to 380 nanometers. Due to the range of excitations measured, molecular absorption bands tend to be far broader than that of IR instrumentation. Compounds that can be accurately detected and measured with the UV-DOAS possess specific chemical structure characteristics that allow for unique absorption bands, which limits the number of compounds that can be monitored.[3]

DOAS is based on the principal that the Beer-Lambert Law (Equation 1) and cannot be used to directly measure the concentration of the compounds of interest because the initial intensity of the signal cannot be measured.

$$A = \varepsilon c l \qquad \textbf{Eq. 1}$$

Where: $A$ = absorbance intensity
$\varepsilon$ = absorption coefficient
c = sample concentration
l = sample path length

Interferences in the atmosphere cause absorption to occur at all points in the measurement spectrum. In the atmosphere, the light of the beam undergoes extinction processes by air molecules and aerosols, turbulence, and absorption by many trace gases. DOAS overcomes the effects of the beam extinction by mathematically separating and removing the nonspecific beam extinction from the target gas absorption.[4] To address this issue, DOAS measures the difference between the absorption peak caused by the compound of interest and absorption peaks at wavelengths on either side of that targeted peak.[3] The concentration is determined by the light intensity in the absence of a structured absorption band, rather than the light intensity in the absence of all absorption.

A typical UV-DOAS system consists of a light source, optics, a spectrometer, and depending on the system configuration, a retro-reflector. Most systems employ a tungsten halogen or xenon arc lamp, though some use deuterium lamps.[2] From the source, the light is focused and directed into the atmosphere by means of a transmitting telescope. A receiving telescope retrieves and focuses the attenuated light beam and the spectrometer measures the change in absorbance caused of the UV light. Data collected by the UV-DOAS can be stored in the analyzer and can be transferred off-site via external storage or Internet connection.[5] The digital signal from the spectrometer is collected by a computer system and compared to laboratory-developed reference spectra to ensure a match between all absorption bands associated with a targeted compound are present to confirm its identification and quantification.[7] Some technologies use specific gas calibrations to fine tune the library reference spectra and improve instrument performance. Figure 2-13 shows an Opsis DOAS source unit.

**Figure 2-13. Opsis DOAS Unit**

UV-DOAS instruments can practically measure path lengths up to 500 meters. Optimum light path length depends on the compound of interest, the desired detection limit, the clear line of sight available, and the expected interferences (e.g., dust and fog). Measurement noise increases and beam intensity decreases as path length increases.[1]

Certain chemical species can also pose interference issues at particular wavelengths. For example, when trying to measure nitrous oxide ($N_2O$) in the presence of other nitrogen oxides (NO, $NO_2$), absorption from NO and $NO_2$ can cause interference.[8] Special considerations must also be made when measuring concentrations of aliphatic hydrocarbons in ambient air since oxygen is a major interferent for these compounds.[5]

Additionally, there are several operational concerns that must be considered when operating a UV-DOAS in the field. These instruments are approved for use in temperatures of 5 - 30°C with humidity ranging from 0 - 80 percent. High humidity can cause fog to build up on the receiver mirrors and windows, which can substantially decrease the detected light intensity and deteriorate the condition of the instrument optics and mirrors. This can be corrected by installing heaters on the mirrors and windows or by changing the site where the UV-DOAS is installed.[5]

## UV-DOAS Field Implementation

There are a number of instrumental configurations for open-path UV-DOAS instruments. UV-DOAS instrumentation can be deployed in both bistatic and monostatic open-path configurations.

The simplest OP-systems are bistatic configurations. The arrangement of the components of this design for UV-DOAS is shown in Figure 2-14. This configuration derives its name from the fact that both the transmitter and receiver must be fixed in a static position and precisely aimed at each other. The UV-DOAS equipment projects the light beam directly along a path to a detector/receiver. Bistatic configurations, in general, have the requirement of supplying power at both the receiver and transmitter, which can be a disadvantage in some locations. The receiver and transmitter must be accurately aligned to optimize signal intensity.[9]

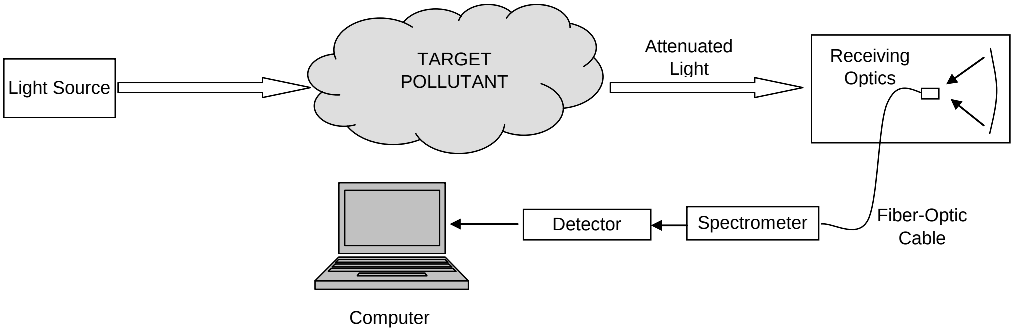
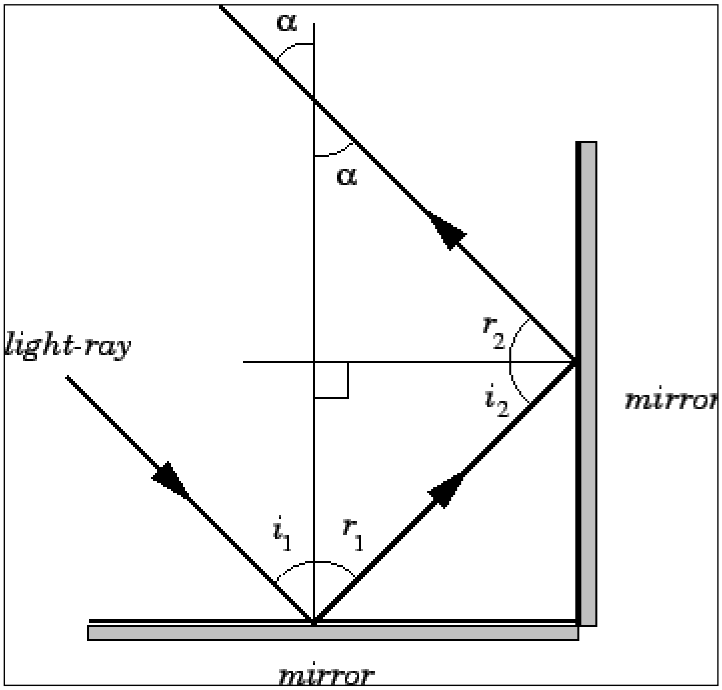


Figure 2-14. Bistatic Configuration of UV-DOAS

Monostatic configurations were developed to address issues raised with bistatic designs. In a monostatic configuration, all of the optical components of the transmitter and receiver are in the same location and a retro-reflector is used to return the light from the transmitter to the receiver. A noted disadvantage of a monostatic system is that the physical path is only half the distance of a bistatic system.

“Retro-reflecting” mirrors are configured with three perpendicular reflective surfaces in the shape of a corner. A combination of three mutually perpendicular mirrors reflects light incident from any direction through 180° as shown in Figure 2-15. Such a combination of mirrors is called a “corner-cube reflector.” Corner-cube reflectors beam light back to its exact point of origin. This property reduces the divergence of the beam on its return path back to the detector compared to divergence that would result from a flat mirror. Also the retro-reflector array can be very large to capture and return essentially the entire divergent signal from the telescope.



(http://farside.ph.utexas.edu/teaching/316/lectures/node133.html)

**Figure 2-15. The Corner-cube Reflector**

The monostatic configuration derives its name from the fact that only the transceiver portion of the instrument needs to be precisely aimed because the retro-reflector returns light to its source.

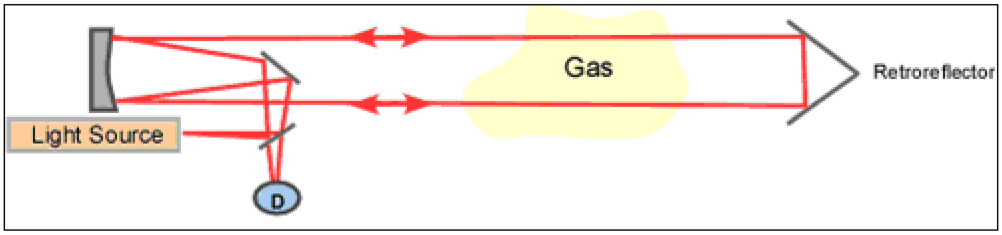


**Figure 2-16. Basic Setup Used to Make Monostatic Open-path UV-DOAS Measurements**

When compared with monostatic mode, bi-static systems are harder to align and maintain because any shift in the transmitter or detector can result in system misalignment.[10,11] Both operating modes measure only the compounds that are in the beam path. Emissions outside the beam path are not measured. Siting and additional QA procedures for ambient measurements found in 40 CFR Part 58 provide basic guidance for criteria pollutants using open-path measurements. In addition, EPA QA Handbook Volume II[12] has siting requirements and other useful information on using UVDOAS in ambient/background monitoring situations.

**Passive UV-DOAS**

A third configuration is known as passive UV-DOAS. Passive UV-DOAS uses ambient lighting, such as sunlight, as its light source and does not require a transmitting telescope. Passive UV-DOAS instruments can be fitted into balloons and used to measure concentrations of pollutant gases at differing heights in the atmosphere.[1,2]

### 2.3.2 Pollutants and Relative Levels That Can Be Measured

Table 2-13 lists compounds that have been measured with UV-DOAS systems. The list is not exhaustive and includes only compounds reported in recent literature.[2,12] UV-DOAS systems have the most widespread environmental use in the detection and measurement of inorganic gases and vapors, monoaromatics (i.e., benzene), and aldehydes.

**Table 2-13. Species Measured with UV-DOAS Systems***

| Species | Species | Species |
|---|---|---|
| **1,3-Butadiene** | **Formaldehyde** | Ozone |
| **Acrolein** | Hydrogen Fluoride | **Sulfur Dioxide** |
| **Ammonia** | Isoprene | **Styrene** |
| **Benzene** | **Mercury** | **Toluene** |
| **Carbon Disulfide** | Nitric Oxide | **m,p-Xylene** |
| **Chlorine** | Nitrogen Dioxide | **o-Xylene** |
| **Ethyl Benzene** | Nitrous Acid | |

*Compounds in **bold** are EPA Hazardous Air Pollutants (HAPs).

Detection limits have been reported in the ppb with at least one research application reporting cases of detection down to parts per trillion ranges.[2] Detection limits vary based on factors such as the deployment configuration, light path length, measurement noise, and meteorological conditions.[1,2] Table 2-14 gives example detection limits found in the literature.

**Table 2-14. Approximate Detection Limits for UV-DOAS**

| Pollutant | Lower Detection Limit (ppb) | Path Length (m) |
|---|---|---|
| Ammonia | 800 | 200 |
| Benzene | single digit ppb | 500 |
| Carbon Disulfide | 500 | 5000 |
| Formaldehyde | single digit ppb | 500 |
| Nitrous Acid | single digit ppb | 500 |
| Nitrogen Dioxide | single digit ppb | 1000 |
| Nitrogen Oxide | 240 | 200 |
| Ozone | single digit ppb | 1000 |
| Sulfur Dioxide | single digit ppb | 1000 |
| Toluene | single digit ppb | 200 |
| m,p-Xylene | 10 | 500 |
| o-Xylene | single digit ppb | 500 |

### 2.3.3 Typical QA/QC

QA/QC ensure the validity of data and calculations performed by UV-DOAS systems. Each instrument manufacturer establishes its own quality assurance procedures based on the specifications of the individual instrumentation, but there are several procedures that should be followed universally.

#### Record Keeping

As with all environmental measurements, it is necessary to keep accurate records during measurement periods to ensure accurate data collection. For UV-DOAS, information such as meteorological conditions, path lengths, UV filter numbers, lamp type, light intensities and measurement times should be recorded.[5] Light intensities must be recorded anytime the UV emitter or receiver is adjusted and compared to the intensities measured when the UV-DOAS was installed. The measured recoveries of standard gas cells with known concentrations should also be documented.

## Instrument Performance

Before measurements are begun and throughout the measurement process, several instrument performance checks are required to make sure the instrument is accurately collecting data. Individual vendors recommend specific instrument performance checks such as correcting for slight variances in the reference spectrum (i.e., the lamp spectrum with no concentration bands) caused by changes in the spectrometer and instrument electronics. This is performed by periodically re-recording the lamp spectrum and comparing it to the initial reference spectrum for agreement. The reference spectrum is critical to the analysis of collected data and performing regular reference checks also minimizes noise collected by the instrument.[5]

Calibration checks are also very important for the collection of accurate data. The analyzer is checked by measuring gas standards of known concentrations for accuracy. Calibration cells are filled with the gas standard, allowed to stabilize, and the absorption is measured. A valid calibration curve should contain six equally-spaced calibration points, including zero, and cover at least 80 percent of the perceived measurement range. Because UV-DOAS measurements are based on absorption and, therefore, the number of target compound molecules in a specific path length, the calibration points can be obtained either by decreasing the measurement path or diluting the gas standard.[5]

A function check is also required to periodically validate the instrument’s performance. During a function test, a cell with a known concentration of gas is placed in front of the receiver. The instrument measures the concentration of the compound in the cell plus the concentration of the compound in ambient air. This check serves two purposes: (1) to ensure that the analyzer is producing accurate measurements and (2) to ensure that no cross-sensitivities occur between the test gas in the cell and other gases. Function tests must be performed in stable ambient pollution conditions because spikes in pollutants may cause the results of the function test to be difficult to interpret.[5]

Accuracy and precision tests are defined by the EPA regulations at 40 CFR part 58 (Ambient Air Quality Surveillance). Often these values are determined by performing calibration checks against known gas standards and verifying the MDL provided by the instrument manufacturer. Instrument manufacturers provide their own instructions on how to perform accuracy and precision tests in accordance with EPA regulations.

### 2.3.4 Example Applications and Vendors

#### Example Applications

UV-DOAS has been deployed in a wide variety of environmental measurement applications which are discussed for specific applications in Chapter 3 of this Handbook. UV-DOAS is most frequently used for monitoring smog-related air pollutants, where its long range is used to verify Eulerian models that are used in air quality management. Multiple pathways have been used to create 2-D and 3 dimensional (3-D) tomographic depictions of pollutants around a large area source or urban area. UV-DOAS is used for fenceline monitoring of air pollutant emissions. Benzene has been measured in residential areas downwind of chemical manufacturing plants and ammonia has been monitored in areas around large-capacity swine feeding operations. UV-DOAS was also used to measure mercury emissions from a chlor-alkali plant.[6] These types of ambient and fugitive or area source measurements have been useful to government agencies to identify places where harmful levels of pollution exist and determine the level of injunctive relief necessary.[2] Table 2-15 summarizes those applications that utilize UV-DOAS technology.

**Table 2-15. Typical Applications for UV-DOAS.**

| TECHNOLOGY | APPLICATIONS |
|---|---|
| UV-DOAS | OTM 10, Tracer Gas, bLS |

One developing application for UV-DOAS is known as Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS). The application provides the ability to derive a vertical profile of pollutants by completing multiple scans simultaneously using either passive or active techniques.[2]

### Vendors

There are currently five vendors of field-ready UV-DOAS instruments, as summarized by Table 2-16. Opsis, Inc., has had two separate instruments verified through the EPA's ETV program.[14] The Opsis System has also been designated as an "Equivalent Method" for the measurement of $SO_2$, $NO_2$ and $O_3$ in ambient air.

**Table 2-16. UV-DOAS Vendors**

| Vendors | Websites |
|---|---|
| Argos Scientific | www.argos-sci.com |
| Environnement S.A. Sanoa UV/Visable DOAS | www.environnement-sa.com |
| ETG Risorse e Tecnologia | www.etgrisorse.com |
| IMACC | www.ftirs.com |
| Opsis, Inc. | www.opsis.se |
| Spectrex | www.spectrex-inc.com |
| Cerex Monitoring Solutions | www.cerexms.com |

### 2.3.5 Strengths and Limitations

Tables 2-17 and 2-18 summarize the strengths and limitations associated with the use of the UV-DOAS. Some UV-DOAS can provide concentration data for up to three compounds simultaneously. In the field, the instrument is portable[15] and can be deployed long-term for continuous remote *in situ* monitoring.[14] UV-DOAS quantifies compounds more successfully that have strong UV light and weak infrared absorption characteristics. Since $NO_2$ measurement by UV-DOAS does not require conversion to NO and measurement by difference, as conventional chemiluminescent monitors operate, this ORS technology provides a direct rather than indirect measure of the criteria pollutants.

**Table 2-17. Summary of UV-DOAS Strengths**

| Feature | Strengths |
|---|---|
| | |
| Automated Real-time Measurements | 24/7 remote monitoring |
| | Can provide near real time data |
| | Unattended measurements collection |
| Economical | Relatively low instrument cost<br>(about $60,000 - $200,000)<br>Low-cost long term deployment |
| Multiple Wavelength Operation | Broad spectrum instruments allow monitoring of three criteria pollutants and trace species simultaneously. Spectra can be saved and post analyzed |
| Range of Measurement | Long measurement path length – up to 500 m. |
| Detectability | Many compounds are detectable in the low ppb range |
| Compact Instrumentation | Portable |

However, the number of species that can be analyzed with UV-DOAS is limited due to the lack of appropriate absorption characteristics in the UV-visible wavelength range of many compounds.

**Table 2-18. Summary of UV-DOAS Limitations**

| Feature | Limitations |
|---|---|
| Difficulty in Deployment | Alignment of remote receiving optics or reflectors can be difficult at long path length. |
| Meteorological Limitations | Fixed observation area. Long term deployment depends on constant wind direction. |
| | Affected by poor visibility conditions |
| Limited Compounds | A number of species do not have appropriate UV-visible absorption structures making them undetectable by UV-DOAS |
| Application Limitations | Some bistatic systems are more difficult to use for radial plume mapping due to difficulty aligning optics from multiple paths |

### 2.3.6 References

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## 2.4 Differential Absorption Light Detection And Ranging Systems

LIDAR is a technology used to measure area source, fugitive or ambient air pollutants without the requirement for line of sight or retro-reflector measurement paths. LIDAR operates on the same principles as radio detection and ranging (RADAR) except light is used rather than radio waves. In early applications of LIDAR, investigators used search lights, a telescope, and a photoelectric light detector to collect information about Earth's atmosphere. The technology was used to determine atmospheric density by studying the backscattered light intensity along the path of the searchlight beam. Since the 1930s, the use of LIDAR has expanded to applications in aerial surveying, three-dimensional imaging, chemical warfare agent detection, and forestry. LIDAR is also used to study atmospheric parameters such as aerosol and cloud properties, temperature, wind velocity, and species concentration.[1,2]

There are three generic LIDAR applications:

- range finders
- Differential absorption LIDAR (DIAL)
- Doppler LIDARs

In 1964, a new LIDAR application called DIAL was proposed to locate and measure trace chemical concentrations in the atmosphere.[1] The goal of LIDAR–based DIAL technique was to precisely measure constituents of ambient air using a simple remote sensing technique that lacked the complexity of traditional optical techniques such as FTIR. Since then, DIAL has developed into a commercially available technology capable of mapping concentrations of multiple atmospheric pollutants.

DIAL uses lasers directed into the atmosphere to measure species concentrations of target aerosols, dust, and gases in the lower few kilometers of the atmosphere. Using the DIAL approach, spatial concentrations are obtained from the reflected or backscattered light from two wavelengths of light: one that is strongly absorbed by the species of interest and the other just outside of the absorption range of the target compound, which is used to measure background light scattering. As these wavelengths of light are emitted from the laser source, the ratio of the backscattered light intensity between the two wavelengths is measured and coupled with the time delay of the return signal. The target compounds absorb or reflect and scatter the light back to a telescope or receiving optics, where intensity of the backscattered light is detected and evaluated. Concentration is determined based on the amount of light absorbed and the location of the observed compounds is based on the time delay of the backscattered light at the detector.[3] By measuring the backscatter at different angles from the source, the data can be processed to show the two-dimensional plume shape of the target compound emission profile.

The main advantage of DIAL over other ORS technologies is the ability to spatially resolve the concentration of a single compound, or class of compounds, based on the radiation absorption characteristics of the pollutants being measured.[3, 4] The ability to spatially resolve concentration data is a unique advantage when compared to alternate remote sensing methods, which yield average concentration data over a predetermined path length. The main limitation in using DIAL is the limited number of wavelengths that can be generated by current laser technology at the precise wavelength for compounds of environmental interest to be monitored. Additionally, the use of DIAL in the United States has been limited due to limited availability and the high cost of the associated equipment.[5]

### 2.4.1 Basic Operation

LIDAR technology operates by transmitting a laser into a medium containing gaseous compounds. The laser light can be transmitted in the UV, visible, or IR wave range.[6] For the DIAL application of LIDAR, an appropriate wavelength is chosen for the species to be measured along with a nearby wavelength that will not be absorbed by the target compound.[7]

During operation, light generated by a laser is directed through a wavelength switching unit. As the laser pulses, the switching unit alternates the laser between the two different wavelengths designated as “on” (the wavelength that is absorbed by the target compound) and “off” (the wavelength just outside of the target compound’s absorption). Some DIAL systems use separate lasers to produce both wavelengths. A continuous laser is used when the measurement range is short or for long measurement time periods. A pulsed laser is used when higher energy is needed for long measurement ranges or short time intervals.[6]

A small portion of the laser output is directed to a calibration cell. The cell is filled with a known concentration calibration gas and the absorption for a given path length is measured. The remaining narrow beam of laser light is expanded or widened to make it “eye safe” and then directed into the atmosphere by a series of mirrors and optics.[7] The expanded laser beam interacts with molecules and particles, and is scattered by them. As the light travels through the atmosphere, the “off” wavelength is scattered elastically by atmospheric particles. The “on” wavelength is absorbed by the target gaseous compound(s) and scattered at a reduced intensity.[3] Light is scattered in various directions and a small portion is reflected back towards its source. This backscattered light is collected, focused, and a detector converts the light information into a digital signal for use in determination of pollutant location and concentration.[7]

DIAL laser systems are chosen based on the absorption characteristics of the compounds under study. Requirements for lasers include low beam divergence, adequately low pulse repetition frequency (PRF), and appropriate wavelength specificity.[1] Capture of the entire beam by the receiving optics is preferable to reduce background noise. A low beam divergence (narrow beam) is necessary to retain the beam in the receiving optics field of view. If a pulsed laser is used, a low PRF ensures measurement cycles are separated by a sufficient length of time to avoid inference from one measurement to the next.

Wavelength specificity defines which compounds can be measured by DIAL systems. Although other applications of LIDAR, such as measuring aerosols, are operated across a range of wavelengths, DIAL wavelengths are specific to the absorption characteristics of the pollutants being measured.[1] Advances in tunable laser technology have allowed simultaneous multi-wavelength, hence multi-component, measurements to be made.[8]

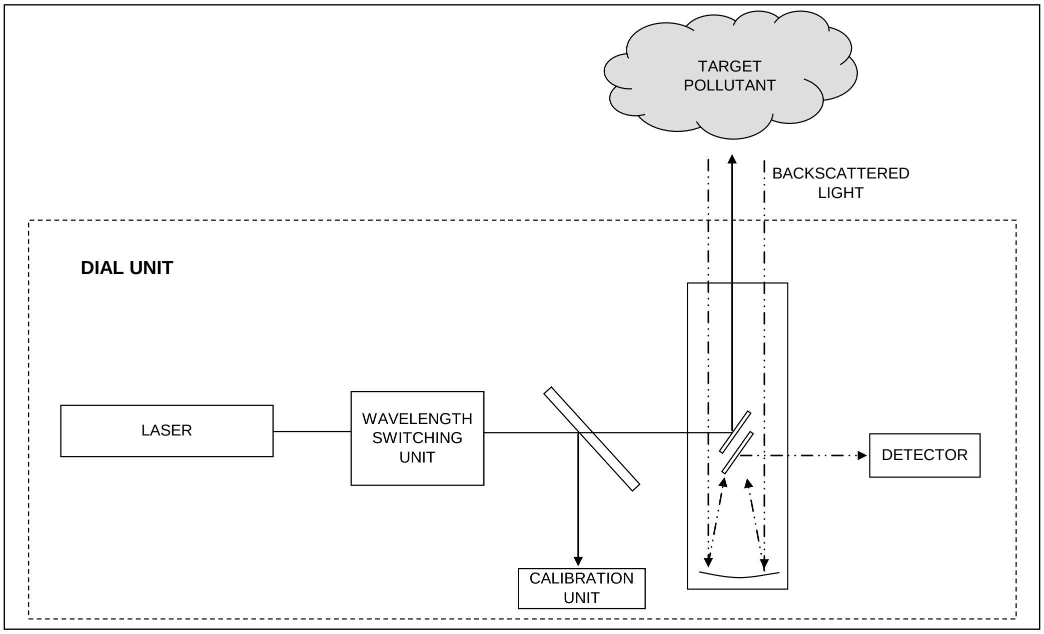


**Figure 2-17. Beam Path and Major Components of DIAL Unit.**

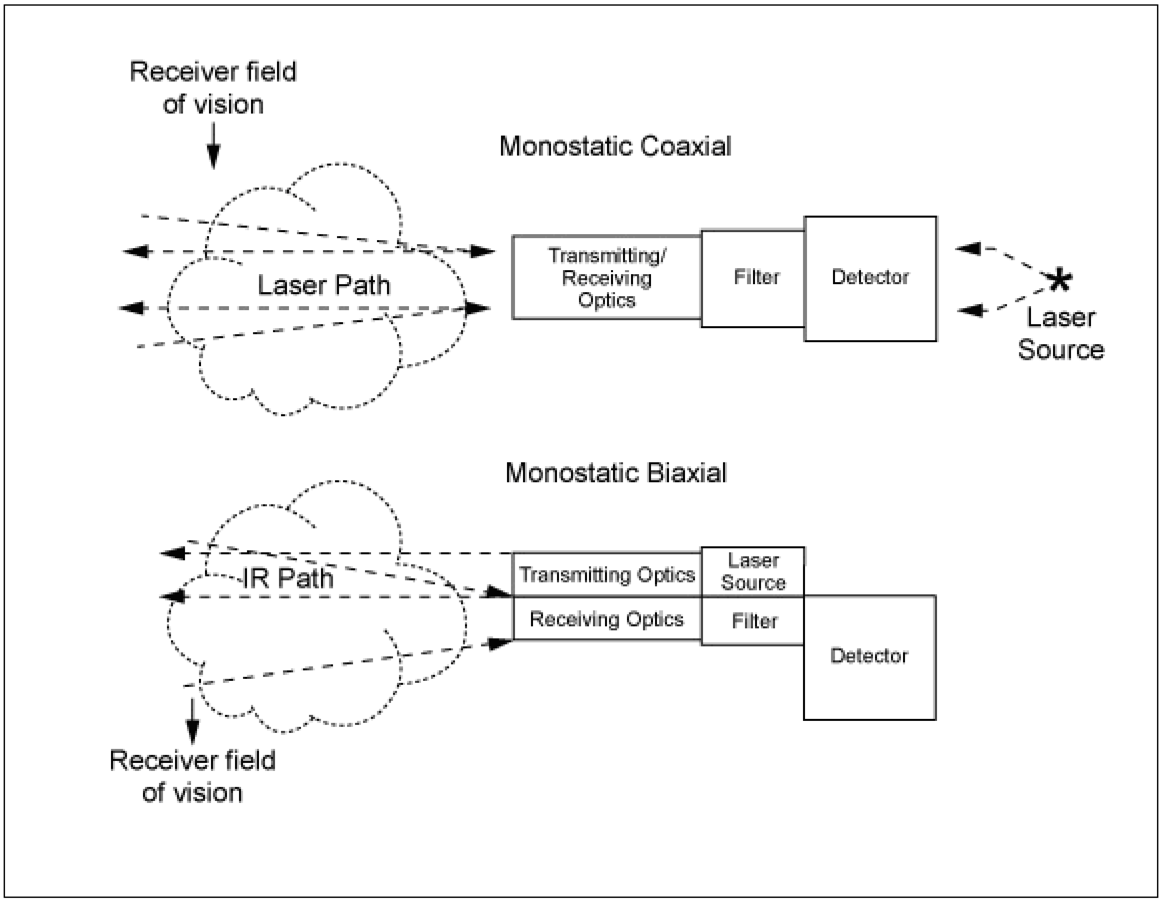
The difference in the backscattered intensity between the “on” and “off” wavelengths allows for a concentration of the compound to be calculated. The “off” wavelength is reflected predictably and decreases in intensity (P) by the inverse square of the distance the light has traveled (R) shown in Equation 2.[9]

$$P = \frac{1}{R^2} \qquad \textbf{Eq. 2}$$

The “on” wavelength is absorbed by the target pollutant and backscattered at a reduced intensity to that of the “off” wavelength. The two intensities are divided by one another and transformed into concentration data using the Beer-Lambert law.[9] When the time delay of backscattering is added into the calculation, the distance from the laser to the compound can be determined.[3,10,11]

DIAL measurements collect pollutant concentration data over a relatively long path length. Beam path lengths range from a few hundred meters to 3,000 meters.[5] Since DIAL systems do not require a remote detector or reflector, a 2-D scan can be completed in approximately 10 minutes.[4, 5, 8] Pollution emission flux is calculated by collecting wind speed data and plume concentration during DIAL testing. Wind speed is multiplied by the pollutant concentration across the emission plane to obtain a flux value.[3]

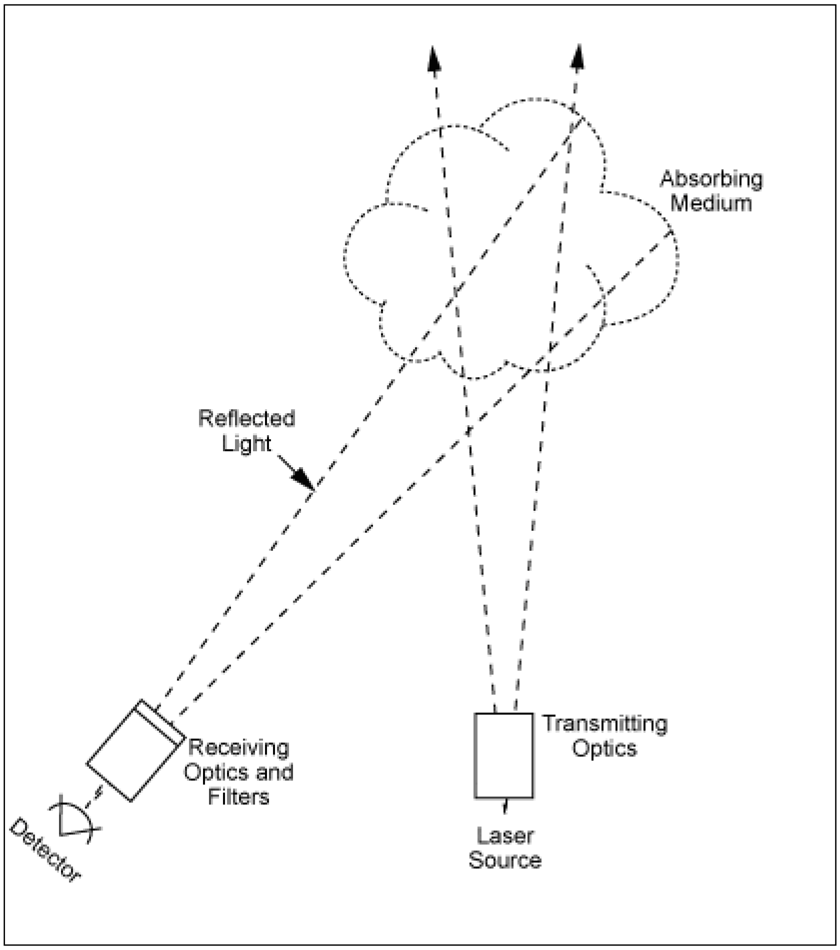
The majority of atmospheric sensing DIAL systems operate in a monostatic mode where light is emitted and received at the same location. A monostatic mode may be deployed in two sub-configurations; monostatic coaxial mode, where light is received by the same optics through which it was emitted, and monostatic biaxial mode, where light is received by optics located adjacent to the originating optics. The monostatic system allows multiple measurements to be completed quickly without the need of retro-reflectors or line of site detection systems. Figure 2-18 illustrates the monostatic coaxial and biaxial modes.



Adapted from "Measurement and Monitoring Technologies for the 21$^{st}$ Century [21M$^2$] Open Path Technologies: Measurement at a Distance LIDAR." Avalable: http://www.clu-in.org/programs/21m2/openpath/lidar/

**Figure 2-18. Monostatic Coaxial and Biaxial Configuration for DIAL**

The use of a bistatic DIAL configuration is less common. In bistatic mode light is produced and detected at separate locations. The bistatic configuration requires frequent repositioning of the detector to obtain an emissions concentration profile.[1, 5] Figure 2-19 illustrates a bistatic DIAL system.

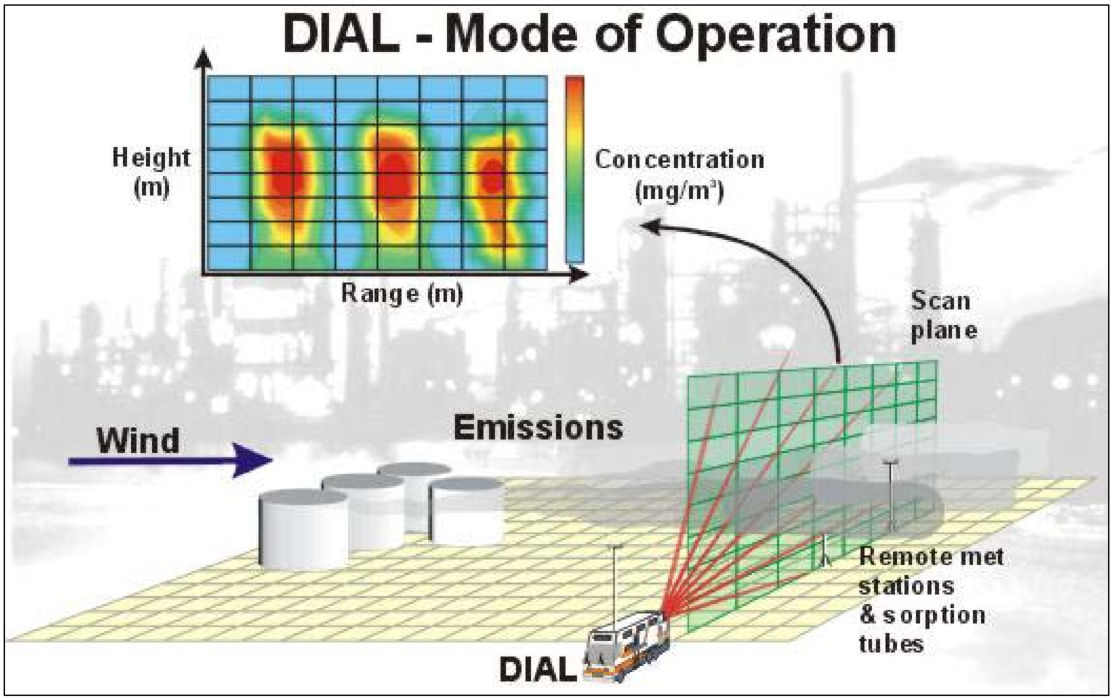


**Adapted from "Measurement and Monitoring Technologies for the 21st Century [21M$^2$] Open Path Technologies: Measurement at a Distance LIDAR." Avalable: http://www.clu-in.org/programs/21m2/openpath/lidar/**

**Figure 2-19. Bistatic Configuration for DIAL**

The signal receiving and detection system consists of primary optics, a spectral filtering unit, a detector, and a photon counter. Receiving optics collect the backscattered light for analysis. Primary optics vary by application and can include Cassegrain or Newtonian telescopes, multiple small mirrors, and liquid mirror telescopes among others.[1, 6] Spectral filtering systems remove background light and reduce signal noise. Spectral filtering can be accomplished by using simple systems such as narrow bandwidth interference filters or more complicated systems such as depolarization techniques.[1] A detector converts the incoming spectral signal into a digital signal for photon counting. Typical detectors include traditional Photomultiplier Tubes (PMTs), Charge Coupled Devices (CCDs), mercury-cadmium-telluride (MCT) detectors, and avalanche photodiodes.[1, 6] The photon counter performs two steps. The first step removes dark counts, which are a type of signal noise created by the detector. The second step counts the number of photons based on the time they were received. By counting photons on a sequential basis, range resolved measurements are realized.[1]

The DIAL system yields a spatially resolved concentration measurement along the specified path length. Multiple closely spaced scans are often performed over a cross section of an emission plume to produce concentration maps as illustrated in Figure 2-20. This type of output is unique compared to that of measurements such as OP-FTIR spectroscopy, for which the output is a PIC without spatial resolution along the path length.



Used with permission from Spectrasyne Ltd (J. Moncrieff, personal communication, April 1, 2010). Obtained from http://www.spectrasyne.ltd.uk/html/technique.html

**Figure 2-20. Illustration of DIAL unit mapping an emission plume**

Wind characteristics play a major role in how the DIAL system should be positioned to take measurements, as well as the validity of data obtained from those measurements. Equipment set up is recommended to be at least 50 meters from the plume cross section and measurements should be taken perpendicular to the wind direction. During the measurement period, wind direction may change, which effectively skews the measurement plane.[12] Therefore, wind direction is typically analyzed throughout the measurement process to accurately adjust the measurement plane for skew.[12,13] Changes in wind direction and speed may cause variation in the emission plume over time and affect the results of a scan along a measurement plane, which takes about 10 to 15 minutes to complete. Averaging multiple scans of the same cross section helps to suppress the error associated with a dynamic emission plume.[12] Wind speed analyzed using dual wind monitors typically do not vary more than 20 percent between the independent wind measurements. Wind data from three elevations ranging from 15 to 25 meters, provide sufficient information to determine plume flux through the plane.[14]

### 2.4.2 Pollutants and Relative Levels That Can Be Measured

A variety of atmospheric parameters can be measured with DIAL techniques including: temperature, pressure, water-vapor concentration, and selected atmospheric gases. Additionally, back scatter and light absorption of cloud particles and aerosols can be investigated.

DIAL has historically been used to measure criteria pollutants in the upper atmosphere. Approximately 15 species in the spectral range of ultraviolet to infrared can be detected by DIAL systems. Table 2-19 lists compounds that can be measured with DIAL systems. The list is not all-inclusive but displays compounds reported in literature.

**Table 2-19: Reported Species Measured with DIAL Systems**

| COMPOUND | COMPOUND | COMPOUND |
|---|---|---|
| Acetylene | **Hydrogen Chloride** | Nitrous Oxide |
| Alkanes | **Mercury** | Ozone |
| **Benzene** | Methane | **Sulfur Dioxide** |
| Ethane | **Methanol** | **Toluene** |
| **Ethyl Benzene** | Nitric Oxide | **Xylenes** |
| Ethylene | Nitrogen Dioxide | |

Compounds in **bold** are EPA Hazardous Air Pollutants (HAPs).

Detection limits in the ppb range have been reported at distances of 500 to 3000 meters.[6,15] Detection limits vary based on a number of factors. Atmospheric effects, such as laser beam wander from atmospheric turbulence, influence the accuracy of DIAL measurements. Laser type and internal instrument noise can also have a negative influence on detection limits.[16,17] The path length also affects the resolution of the system. Reported minimum detection limits range from 0.001 ppb for mercury to 90 ppb for hydrogen chloride gas at a 200 meter absorption path length.[9] Detection limits are given as estimates in Table 2-20 and are based on various absorption path lengths.

**Table 2-20. Approximate Detection Limits for DIAL[6]**

| Compound | Reported Minimum Detection Limit (ppb) | Detection Range (m) |
|---|---|---|
| Acetylene | 26 | 800 |
| Alkanes | 10 | 800 |
| Benzene | 3 | 800 |
| Ethane | 16 | 800 |
| Ethylene | 9 | 800 |
| Hydrogen chloride | 13 | 1,000 |
| Mercury | 0.06 | 3,000 |
| Methane | 76 | 1,000 |
| Methanol | 153 | 500 |
| Nitric Oxide | 4 | 500 |
| Nitrogen Dioxide | 5 | 500 |
| Nitrous Oxide | 56 | 800 |
| Ozone | 3 | 2,000 |
| Sulfur Dioxide | 4 | 3,000 |
| Toluene | 3 | 800 |
| Xylenes | 5 | 500 |

The specific wavelength used for detection depends upon the absorption characteristics of the target compounds. The number of identifiable pollutants is further limited by the number of absorbing wavelengths that are unique to a specific compound without additional interferences, as well as the laser technology that is currently available. This technology is improving with expectation that the range of detectable pollutants will expand.[6]

DIAL systems can also be used in a mode like a fugitive source monitor. In this mode, an entire class of chemicals can be measured using a single laser wavelength that the entire chemical class absorbs. DIAL results from such a study must be interpreted as an average.

### 2.4.3 Typical QA/QC

While the EPA provides information by general reference in Other Test Method 10 (OTM10)[13], the verification of DIAL measurements is challenging due to its unique ability to produce spatially resolved concentration data. Limited QA/QC guidelines exist that verify such data in the literature. Information specific to LIDAR technology has been published by the Association of German Engineers (VDI) in VDI 4210 Part 1 (1999) Remote sensing, Atmospheric measurements with LIDAR, Measuring gaseous air pollution with DAS LIDAR.[18]

#### Record Keeping

As with all environmental measurements, it is necessary to keep accurate records during measurement periods to ensure accurate data collection including records of calibrations, meteorological conditions, path lengths, and measurement times.

#### Instrument Performance

Initial measurements should be conducted over a time period so that emission source fluctuations may be considered during data analysis; one half to an entire day is recommended for an initial measurement.[14] Scanning the same plume over different days and varying conditions is also recommended to assess the impact of varying conditions on measurement results.[12] An initial site assessment should also be conducted to determine any interference that may disrupt data acquisition. Interferences include geographic constraints and off-site upwind emissions sources.[13]

Some DIAL systems are programmed with verification systems to ensure that quality measurements are taken. One reported DIAL system employs an internal “wavelength” verification system, known as a wavemeter, to identify and dispose of any data produced from the emission of an inconsistent wavelength.[8] This prevents erroneous data from being produced if the light source emits radiation outside of the specified wavelength.

### 2.4.4 Example Applications and Vendors

#### Applications

With the ability to develop spatial concentration information of particular air pollutants, DIAL systems have been implemented in a variety of applications including fenceline monitoring, fugitive emissions measurement, and plume fate analysis. DIAL may also be used to measure flare efficiency from industrial processes.[5,11] For each application, the strengths and limitations of a DIAL system must be considered to produce results that meet users' DQOs. For example, the use of $CO_2$ laser assumes sufficient aerosol concentration in the atmosphere to provide sufficient backscatter. High wavelength visible and UV light sources rely on molecular backscatter.

**Table 2-21. Typical Applications for LIDAR.**

| TECHNOLOGY | APPLICATIONS |
|---|---|
| LIDAR | DIAL |

DIAL systems are either in a fixed or mobile arrangement. Fixed DIAL units used in laboratories are typically less complicated than mobile systems used for field operation.[9] A number of mobile systems have been constructed based on an enclosed truck platform. The truck is driven to the testing site and positioned accordingly to obtain emissions data.[3, 7, 19] DIAL systems have also been implemented onboard ocean vessels and in airborne systems, collecting emissions information while flying over a target area.[11, 20] Figure 2-21 illustrates a truck-based mobile DIAL platform.

**Figure 2-21. Mobile DIAL Unit**

Specific field implementation examples include studies completed on gas processing plants and oil refineries. These studies used DIAL systems and plume mapping techniques in Canada and European nations. Measured fugitive emissions were four to 20 times greater than factor estimated fugitive emissions.[5,6,14,21] While these studies have concluded emissions factors may underestimate actual fugitive emissions, objection to using annual emissions figures calculated by DIAL measurements is apparent. Industry objects to using DIAL-based calculated emissions due to the short time-period of measurement relative to the long time-period of annual operation.[6]

In other studies, DIAL systems have been implemented to measure emissions from mobile sources such as air and highway traffic. Additional DIAL systems have been developed to detect chemical warfare agents as well as natural gas pipeline leaks from airplane mounted platforms.[6]

### Vendors

A number of vendors manufacture laboratory-scale DIAL applications; however, field-ready measurement instruments are only offered by a small number of vendors. Table 2-22 lists vendors that manufacture or provide field-ready DIAL instruments.

**Table 2-22: DIAL Vendors**

| Vendors | |
|---|---|
| Spectrasyne | http://www.spectrasyne.ltd.uk/ |
| LASEN | http://www.lasen.com/ |
| National Physical Laboratory | http://www.npl.co.uk/ |
| ITT | http://www.itt.com/ |

### 2.4.5 Strengths and Limitations

A significant limitation of DIAL technology is the cost and limited availability of the measurement service. Multiple measurements in North America have relied on importing the instrumentation from the United Kingdom.[12,15,21] Additionally, the number of chemical species measurable by DIAL is restricted to the unique absorption characteristics of those species and the availability of laser technologies able to produce the absorption wavelengths.

The most notable strength of a DIAL system is the ability to spatially resolve pollutant concentration information in three dimensions in a short period of time. Concentration gradient data obtained in short periods of time enables DIAL to be deployed in a number of applications and a number of configurations. DIAL has been used in scenarios from ground-based emissions plume monitoring to helicopter and fixed-wing aircraft aerial surveys. Table 2-23 and Table 2-24 summarize the strengths and limitations of DIAL systems.

**Table 2-23: Summary of the DIAL Strengths**

| Feature | Strength |
|---|---|
| Concentration data is spatially resolved | In contrast to PIC measurements taken by other instrumentation system, DIAL relay concentration data as a function of distance along the beam path |
| Beam Path | Reported path lengths up to 3000 meters |
| Receiving Optics | Collects backscattered light without the use retro-reflectors |
| Measurement Time | Scan along measurement plane requires 10 to 15 minutes |
| Mobile Platform | Instrumentation is moved around measurement site obtaining multiple plume scans from various locations increasing accuracy of plume characterization |
| | Instrumentation can also be mounted on airborne platform for increased mobility and expanded applications |
| Near Real Time Data | Real time data allows for leak identification and inputs to process change decisions |
| Multi-Wavelength Operation | Allows for simultaneous concentration measurements of multiple species and classes of species |

**Table 2-24: Summary of the DIAL Limitations**

| Feature | Limitation |
|---|---|
| Unique Chemical Absorption Bands | Measureable species are limited to those with unique absorption bands. Chemical species with common absorption characteristics can only be measured as classes of compounds |
| Chemical Species Absorption Dependencies | The absorption wavelengths of species are temperature and pressure dependent. It is necessary to check the applicability of wavelengths selected for measurement based on temperature and pressure variation in target absorption. |
| Backscatter Requirements | Sufficient aerosol or molecular material must be in the atmosphere to create sufficient backscatter |
| Wind speed and direction | Rapidly changing wind speed or direction may cause measurements to change rapidly and may affect mixing ratios of measured surrogates to compounds of interest. |
| Vendors | Small number of vendors providing DIAL systems and services |
| Expense | High system cost has limited to amount of commercial DIAL studies in the United States |
| Site Arrangement | Beam path is limited by the geographical constraints of the measurement location |

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## 2.5 Thermal Infrared Cameras

Thermal IR cameras for environmental measurements come from a class of camera known as thermographic or forward-looking IR which uses IR radiation to form an image in a manner similar to the way photographic cameras use visible light. The original thermal IR camera development was funded largely by the astronomy and defense communities for the purposes of "night-vision" for aircraft and other vehicles and development of heat-seeking missiles.[1] Private companies have adapted military IR technology that does not require sophisticated cooling or optics to produce commercial IR cameras for environmental applications.

IR cameras have been applied to monitor watershed temperature in game habitats, to detect energy loss or insulation defects in buildings, to track and aid in target acquisition by the military, to improve piloting of aircraft in low visibility conditions, to pinpoint ignitions sources during firefighting, and to aid in search and rescue operations of missing persons. Environmental applications include the detection of industrial gas leaks that are invisible to the naked eye. By filtering light to detect IR radiance characteristic of hydrocarbon or VOC, an existing IR video camera allows the user to see images of hydrocarbon gases on the camera screen in real time.[2] These cameras have the ability to identify the source and flow path of escaping gases in a wide variety of applications[3], such as tank vents and gas line leaks.

The major advantages to using the thermal IR camera for leak detection are the technology's portability and its qualitative ability to display a wide field of view that allows major leaks to be detected more efficiently than classical leak detection and repair procedures that require each flange, seal and valve to be tested individually. Additionally, IR camera technology allows leak detection in parts of facilities that may be difficult or hazardous for personnel to access. The thermal IR camera's major drawback is its inability to measure the quantity or concentration of gas present in radiant vapor cloud. A second limitation due to the simple optics employed in portable IR cameras is the technologies inability to identify individual chemicals in a complex gas leak mixture.

### 2.5.1 Basic Operation

The IR camera creates images based on the IR absorption/emission characteristics of chemical species within the camera's field of vision. IR absorption detection typically occurs in the 3 – 5 µm wavelength range[4], but a special lens and filter arrangement is used to narrow the IR spectrum of wavelengths detected, therefore, allowing the camera to identify some specific compounds or compound classes present that are not detectable in the UV or visible range.[5] Lens and filter arrangements have been developed to allow the camera to detect a wide variety of gaseous VOCs. Emissions appear on the camera's screen as a clouded area or smoke in real time, as shown in Figure 2-22.[6-11]

**Figure 2-22. Detection of Gaseous VOC Emissions from a Chemical Storage Tank[14]**

IR camera operation is fairly straightforward. At start up, the IR camera must be allowed to reach operating temperature since the technology primary detection is based on changes in temperature between a target and its surroundings.[5] Operators are trained to scan each piece of relevant equipment or area of potential leaks from one end to another and, if possible, to perform the scan from two different locations or fields of view relative to air flow or wind direction to ensure all leaks are detected.[2] The first field of view is often from a wider angle with a larger viewpoint, while the second field of view is at a closer viewing angle. The same areas can be scanned repeatedly to improving the likelihood leaks are detected.[5]

Several factors affect the IR camera's imaging and, therefore, the sensitivity of the technology. Ambient light plays an important role in the sharpness or resolution of the IR camera's image. Variations in lighting can require that any of a number of settings be adjusted, such as focusing the lens and switching between automatic and manual camera modes to ensure no leak detections were missed.[5] The IR camera's leak detection sensitivity is affected by temperature, not only ambient, but that of the target gas and the equipment surface as well. Reflectivity (reflection of IR light) and emissivity (emission of energy due to the absorbance of IR light) also plays a role in the camera's sensitivity, as well as gas concentration, distance, and wind speed and direction.[12] It is possible under certain conditions that the radiance of the leaking gas and background are equal, and the leak to be invisible to the IR camera and, therefore, the operator. Proper operator training is required to ensure each of these factors is considered to make sure leaks or vapor clouds are detected.

The images collected by modern IR cameras are digital. Even older IR cameras generated a video feed that was recordable and allowed archiving for remote viewing and review. The cameras can operate using battery power for up to eight hours of continuous use, or connected to AC power for 24-hour monitoring purposes.[9] Additionally, IR cameras used for vehicle inspections have been adapted to use a 12-volt power source. Some IR cameras area available with global positioning systems (GPS) to automatically record the location of the camera's use.[10]

IR camera models' basic operation modes can include additional contrast adjustments allowing easier visualization of leaking gaseous compound against the stationary backgrounds. One such mode is a non-uniformity correction (NUC) mode.[13] The NUC mode uses the camera's internal histogram equalization algorithm to create a display that highlights time dependant scene-based variables, thus allowing the operator to see much smaller leaks. Another version is the GasFindIR's High Sensitivity Mode, in which the manufacturer claims a much clearer image that detects smaller leaks and allows for quicker repair.[7-11]

If quantification of a leaking gas is required, it is also possible to couple the IR camera with additional technology, such as a passive FTIR system or more traditional leak detection and repair instrumentation such as a portable instrument meeting EPA Method 21 requirements or mass flow measurement using a bagging technique. Coupling the IR camera with another technology not only provides means for quantification, but can verify a detected leak as well as determine its chemical composition.[6]

### 2.5.2 Pollutants and Relative Levels That Can Be Detected

Thermal IR cameras can detect chemical compounds that have absorptions in the 8 – 12 µm wavelength IR absorption range. Typically the 3 – 5 µm wavelength range is used for organic VOC. Depending on a variety of factors, including lens focal point[13], distance from the source, and meteorological conditions, gaseous compound concentrations in the hundreds of ppm range (> 500 ppm) are detectable by the camera.[6] Table 2- 25 provides an example list of compounds that have been detected using an IR camera. This list is not all-inclusive, but shows that many compounds can detected with the technology.

**Table 2-25. Example List of Gaseous Compounds that can be Detected by Thermal IR Cameras**

| SPECIES | SPECIES | SPECIES |
|---|---|---|
| Acetic Acid | Ethyl Cyanoacrylate | Octane |
| Anhydrous Ammonia | Ethylene | Pentane |
| Benzene | Heptane | 1-Pentene |
| Butane | Hexane | Propane |
| Carbon Monoxide | Isoprene | Propylene |
| Chlorine Dioxide | Methane | Sulfur Hexafluoride |
| Dichlorodifluoromethane | Methanol | Toluene |
| Ethane | MEK | Xylene |
| Ethanol | MIBK | |
| Ethylbenzene | Nitrous Oxide | |

### 2.5.3 Typical QA/QC

Maintenance records should be kept for any equipment adjustments or repairs that could affect measurement performance. Records should include the date and description of maintenance performed. When the instrument is turned on, it must be allowed to warm up to the manufacturer’s recommended operating temperature. Once at the appropriate temperature, the camera can be used to scan a known concentration of a detectable gaseous compound to demonstrate that the IR camera is producing a visible image.[5]

When a leak is detected, a video record should be taken from an angle and distance that promotes optimum leak visibility. The video should be at least 10 seconds in length and stored with a unique video tag.[2] Information about the leak (such as component type, model or style of component, service, size, process unit, process stream, pressure, vent location and ambient or process temperature[15,16]) should also be entered into a log sheet to further document the leak.[5] For leak detection and repair (LDAR) applications, once the leak has been identified, the leaking component should be marked with a leak detection ID tag so that it can be easily identified by maintenance and repaired.[2] For vents, tanks or other major gas emissions detected by the IR camera, the GPS location and a visible light photograph should be used to document the observation.

### 2.5.4 Example Applications and Vendors

#### Applications

Thermal IR cameras have a wide range of applications, though they are most commonly used to detect large leaks from process equipment and storage tanks at refineries and chemical plants.[6] The technology now allowed as a replacement in the current LDAR requirements for federal rules.[5,16] The cameras have also been used to detect leaks in natural gas pipelines through aerial viewing on helicopters.[2,3,6] Thermal IR cameras can also be used to monitor other plant activities that could potentially create fugitive emissions such as truck and barge loading and unloading and incinerator activities. The cameras can also identify flares that would otherwise be unnoticed by the naked eye.[14] An image of such a flare is included as Figure 2-23. Table 2-26 provides a general description of the applications for thermal IR camera.

**Figure 2-23. Flare Detection by Thermal IR Camera.**[14]

**Table 2-26. Typical Applications for Thermal IR Camera.**

| TECHNOLOGY | APPLICATIONS |
|---|---|
| Thermal IR Camera | Leak Detection |

## Vendors

While there are several vendors for standard thermal imaging IR cameras, only a few companies promote their products primarily as optical remote sensing IR cameras for pollutants. A standard thermal imaging IR camera used for pollutant detection costs approximately $75,000, though that cost is expected to decrease as the technology improves.[2] Table 2-27 summarizes these vendors and their Website information.

**Table 2-27. Thermal IR Camera Vendors**

| VENDORS | |
|---|---|
| FLIR, Inc. | www.flir.com |
| Gas Imaging Technology, LLC | http://www.gitint.com/ |
| Leak Surveys, Inc. | www.leaksurveys.com |

### 2.5.5 Strengths and Limitations

The thermal IR camera has a variety of strengths and limitations that should be considered for each application. A summary of strengths and limitations is shown in Table 2-28 and Table 2-29, respectively. Utilizing a thermal IR camera is typically a more economical approach to leak detection than traditional methods. The camera can identify the exact source of a leak from safe distances within a plant. However, training is required for operating personnel, and quantitative results cannot be obtained without introducing additional measurement technology. Additionally, for outdoor use, the IR camera cannot be used on overcast or rainy days.

**Table 2-28. Summary Table of the IR Camera's Strengths**

| FEATURE | STRENGTH |
|---|---|
| Economical | Fast screening speed compared to conventional leak detection methods[15] |
| | Leak assessment can be done without interruption to plant operations[2,3] |
| | Cost-effective compared to traditional leak detection methods.[2,3] |
| Qualitative Results | Accurately assess the size of each leak[15] |
| Leak Identification | Better able to isolate the exact source of a leak despite close proximity to other leaking sources in real time and record in a video format.[2,3,15] |
| Leak Detection from a Distance | Wide field of view: More likely to identify leaking components in unconventional places.[3,15] |
| | Exposure risk minor because leaking components can be viewed at a distance.[2,3,15] |

**Table 2-29. Summary Table of the IR Camera's Limitations**

| FEATURE | LIMITATION |
|---|---|
| Qualitative Results | Cannot quantify the concentration of a leak without additional technology[3] |
| Training Requirements | “Camera use requires individuals with specific training.” Some models are easier to use than others.[3,15] |
| Meteorological Limitations | Cannot be used during rain or fog and is not as effective during overcast skies.[15] |
| | The camera has a specified nominal operating range for ambient temperature.[15] |
| Safety Requirements | Operation is not intrinsically safe and use is limited in hazardous areas.[15] |

## 2.5.6 References

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## 2.6 Cavity Ring-Down Spectroscopy

There are multiple variations on cavity enhanced absorption techniques based on the property of the time required to reduce the signal due to the absorption or scatter of laser light. CRDS and Integrated Cavity Output Spectroscopy (ICOS) are examples of laser absorption spectrometry that measures optical extinction of compounds that scatter and absorb light in a closed sample path. This chapter describes first generation Cavity Ring-Down Laser Absorption Spectroscopy (CRLAS) as an example of this widely used optical technology to measure *in situ* concentrations of gaseous samples that absorb light at specific optical wavelengths down to the part-per-trillion level. Although noteworthy for a broad range of applications, this technology is most often used for measurements of weakly-absorbing or highly-dilute atmospheric samples.

Traditional absorption spectroscopy techniques measure the absolute change in light intensity after passing through a sample relative to the original intensity of the light. CRDS techniques improve on these methods by measuring the rate of decay of light intensity exiting from a high-finesse optical cavity. Using the rate of decay rather than the change in light intensity makes the CRDS technique less sensitive to fluctuations in the source laser intensity or variations in ambient conditions (such as humidity). Moreover, the reflectivity of the closed optical (or ring-down) cavity yields much longer effective sample path lengths for greater detection sensitivity.

In CRDS applications, the measured rate of decay of light intensity over time is a function of the cavity length, the ability of the optical mirrors to achieve perfect reflectance, and the absorptivity ($\varepsilon$) of the sample. Because the cavity length and mirror reflectance are constant between successive analyses, the amount of time required for the light intensity to decay to $1/e$ of is initial intensity (herein referred to as the ‘rate of decay’) within an empty ring-down cavity and one where the target sample is present is entirely the result of the sample absorbance.[1]

### 2.6.1 Basic Operation

Each gaseous compound absorbs energy at different wavelengths, usually more than one, depending on vibrational and rotational excitement within the molecule. Therefore, each compound has its own “signature” of bands from which energy may be absorbed. Each band is highly selective, with virtually no absorption occurring outside of a specific wavelength. Once a compound has been identified, its spectrum can also be used to measure the compound's concentration because the amount of infrared radiation absorbed from the IR beam is proportional to the concentration of the compound in the sample or open path. According to the Beer-Lambert law, there is a linear relationship between absorbance and concentration as shown in Equation 1.

$$A = \varepsilon c l \qquad \textbf{Eq. 1}$$

Where: $A$ = absorbance intensity
$\varepsilon$ = absorption coefficient
c = sample concentration
l = sample path length

Note that the absorption path length may or may not be equal to the cavity length, depending on the experimental design; the total reflection pathway may be used instead, as with prism cavities.[2] The CRDS technique enhances sensitivity to target analytes by significantly increasing the pathlength through the use of an optical resonator (or ring-down cavity). Increased sensitivity of the CRDS technique relative to that of conventional absorption spectroscopy was demonstrated in the inaugural experiments published by O'Keefe and Deacon [1988] in the visible region of the electromagnetic spectrum.

The absorption spectrum (or collection of spectral features for a single species over a range of wavelengths) of a gaseous molecule is the spectroscopic equivalent to a fingerprint as each compound will absorb energy a different wavelengths depending on the quantum properties of that compound. Given the simplicity of CRDS systems, there are no intrinsic limitations to the spectral region of which CRDS can be applied.[4] Indeed, studies have proven that successful measurements from the far-IR (12 μm)[5] to UV (197 nm)[6] are possible with current technologies. Theoretically, any spectral region can be probed with CRDS if the following three conditions are satisfied:

1. Mirrors of sufficiently high reflectivity are available in the spectral region of interest.

2. High-speed detectors are employed that can confidently measure very small differences in duration on the order of microseconds (μs) or less.
3. Tunable pulsed lasers or optical wavelength modulation for continuous-wave CRDS applications are available.

## General Experimental Design

A general schematic diagram of the essential components of a CRDS apparatus is shown in Figure 2-24. The heart of this technique is the sample cell which is bounded by highly reflective, dielectric-coated, concave mirrors. Traditionally, the technique evolved using two of these mirrors as depicted in Figure 2-24, but many mirror configurations that employ three or more mirrors have been attempted (some of which are available through commercial vendors) and are shown to improve the measurement quality from CRDS applications. Regardless of how many mirrors are utilized, the ability of the highly reflective mirrors to achieve maximum reflectivity over the full wavelength range of interest largely depends on the nature of the dielectric coating selected.

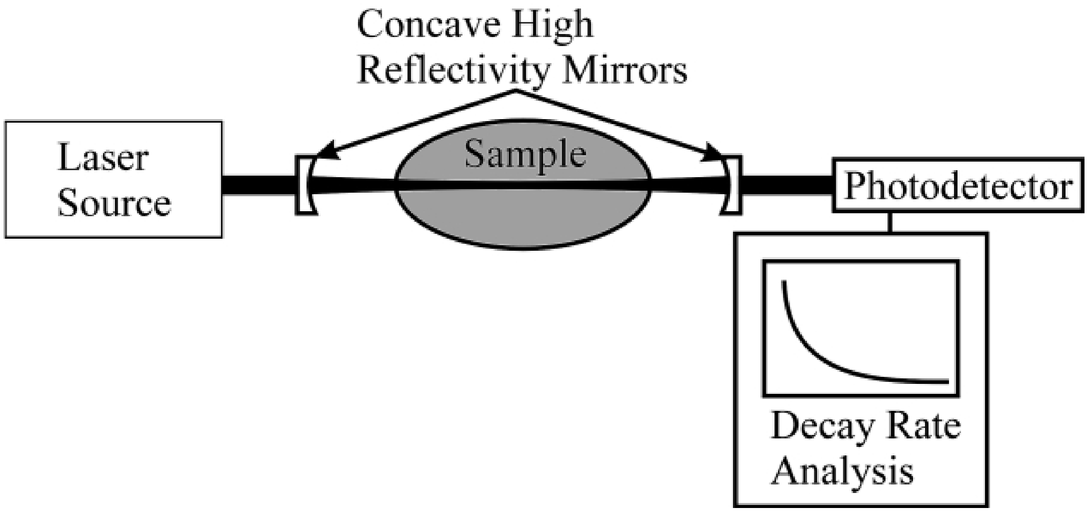

**Figure 2-24. The essential components of any CRDS experimental set-up.**[2]

As shown in Figure 2-24, basic CRDS measurements are acquired by optically coupling laser light through the input mirror of a closed sample chamber bounded by two (input and output) non-cofocal, highly-reflective optical mirrors and measuring the rate of light intensity decay over time. To achieve proper optical coupling and cavity reflectance, the bandwidth of the laser radiation needs to be sufficiently narrow enough to excite only a single optical mode of the cavity while also being sufficiently narrower than that of the spectral features of the sample to obtain well-resolved results (this is illustrated later in Figure 2-26).

When the laser light enters the closed optical cavity, it reflects off the bounding mirrors with a known amount of light exiting the cavity on each reflection (defined by the mirrors' reflectance). If the optical cavity is empty, this rate of light intensity decay is characterized by a steady, exponential decrease to zero (similar to the single-exponential function plotted in Figure 2-25). If a gaseous species that absorbs the laser light is introduced into the cavity, then the intensity decay rate will be faster depending on the concentration of the absorbing species.

The time it takes for the light intensity in an optical cavity to decay to 1/*e* of its original value is called the cavity ring-down time (RDT or $\tau$) and is illustrated in Figure 2-25. This illustration depicts the light lost from the cavity with each pass of the reflecting light as measured by a PMT detector. The smoothed exponential curve above the oscillating data in the figure was derived from an algorithm applied to the data by instrumental software. The difference between the RDT curve of an empty cavity and the RDT curve of a cavity that contains sample is directly proportional to the concentration of the absorbing gas species in the sample. If the empty cavity ring-down time, $\tau$, is known, measurements of the decay rate of light intensity obtained as each laser wavelength is scanned yields a complete absorption spectrum for each analyte.

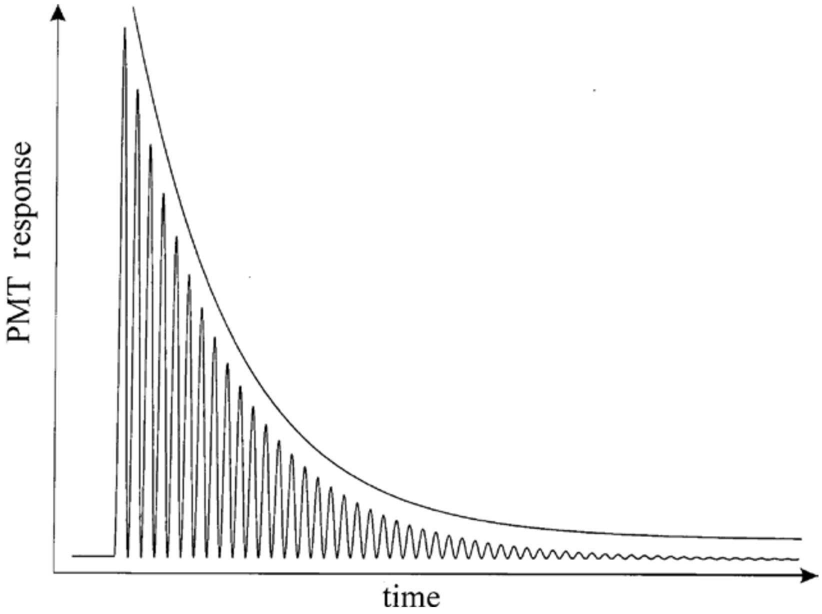

**Figure 2-25. Schematic representation of the expected rate of decay.**[1]

The laser light source can be pulsed or continuous wave (CW), the differences in the experimental design between the two techniques is mostly in the number and arrangement of optical components. Romanini *et al.* [1997] demonstrated the first application of CRDS with a continuous laser source (or CW-CRDS) such as a TDL. In their study, Romanini *et al.* [1997] found that this change in the laser light source lead to gains in spectral resolution, signal intensity, and data acquisition rate. Instead of receiving a signal in the shape illustrated in Figure 2-25, the instantaneous power of a continuous laser is lower, but usually concentrated into a narrower bandwidth.[2] Figure 2-26 illustrates the difference between the incident pulsed laser light and that of the CW laser light.

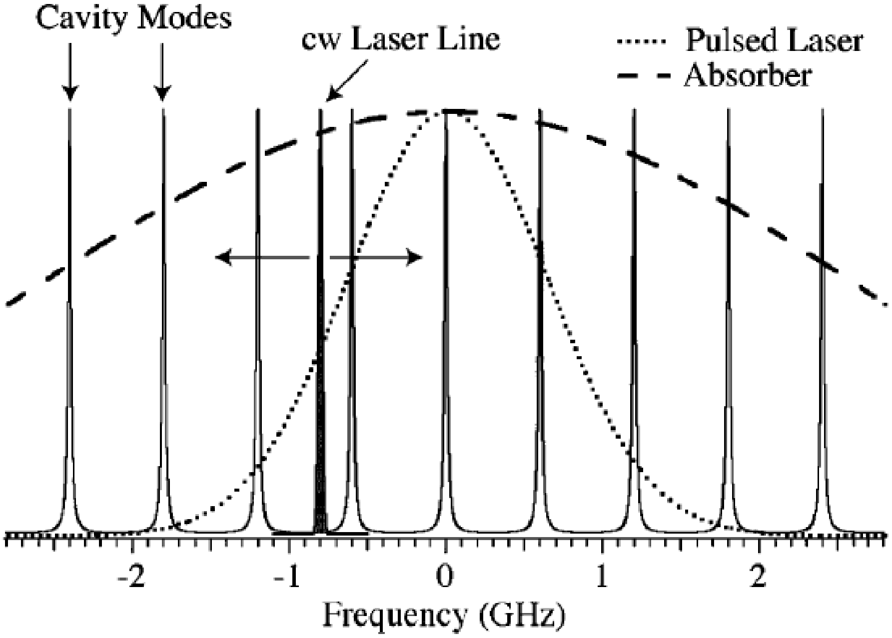

**Figure 2-26. Comparison of Pulsed and Continuous Wave Laser Light.**[8] Illustrating the overlap between the bandwidths of the absorbing species (Absorber), the pulsed laser source, the CW laser source, and the optical cavity resonance frequency modes.

The CW laser bandwidth must be matched to the narrow transmission limits of the optical cavity to allow injection of the light into the cavity; this can be done by adjusting the length of the optical cavity, modulating the laser properties, or a combination of both.[2] Looking at Figure 2-26, it is easy to observe the more passive mode matching of the pulsed laser source with a wider bandwidth capturing a complete cavity mode versus the more difficult mode matching of the thinner CW laser source to superimpose on a narrow cavity mode.[9] While the CW-CRDS method is more optically complicated than the pulsed CRDS method, the low-cost, high-performance, and practical energy requirements of the TDL allows more flexibility for field applications.[2]

Once the light is transmitted into the cavity, the light source must be turned off to observed the decay in light intensity in one of two ways:  the operator can either configure the optics to allow build-up of the light intensity through constructive interference to a predetermined threshold before extinguishing the light source, or he can turn the light source off immediately once a signal is produced from the detector.  There are many ways to turn off the light source, but the most common is through the use of an acousto-optic modulator (AOM) as a laser ‘shutter.’

Optical components are added to the experimental design of a CW-CRDS system to optimize the laser source properties as discussed above.  Figure 2-27 provides a more detailed illustration of the experimental design for CW-CRDS applications.  An optical isolator can be installed immediately after the laser source to reduce on-axis back reflections and increase the signal-to-noise ratio.[10]  A piezoelectric transducer (PZT) is added to modulate the cavity length with a triangular signal to achieve greater cavity resonance, increasing sensitivity, and further improving the signal-to-noise ratio.[11]  Optical filters and lenses can be added immediately before the PZT to augment the laser spectral line selectivity and improve cavity mode-matching if necessary/desired.  Additional optics may be incorporated into the experimental design after the ring-down cavity for similar purposes, depending on the experimental application and the selection of the optical detector type.  It is important to note that the PZT is included for CW applications only.

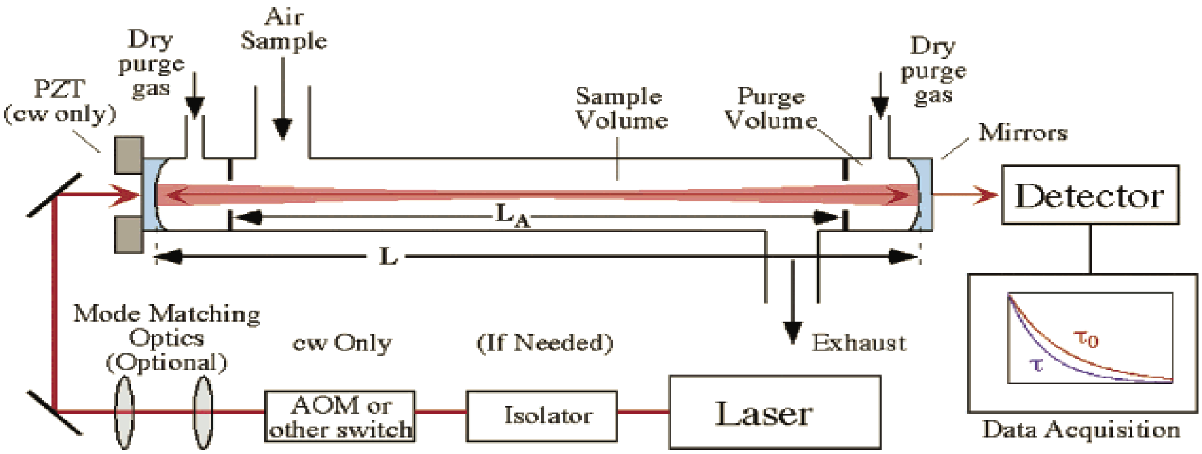

**Figure 2-27.  Optical components schematic of a cavity ring-down spectrometer.[8]**

When the light is coupled out of the laser, a detector generates a signal that is ultimately relayed to a personal computer for processing and storage. The type of detector integrated into the experimental design largely depends on the application and the required signal format. Most commonly, researchers will use a PMT to detect the CRDS signal because it has good quantum efficiency, good spectral range, and a high gain in addition to being lower in cost. Alternatively, a CCD has comparable, if not better, spectroscopic properties while providing a two-dimensional read-out and having multiple channel capabilities. PMT and CCD detectors are the two most frequently cited detectors used in CRDS studies. Figure 2-28 illustrates the difference between the signals received by either detector.

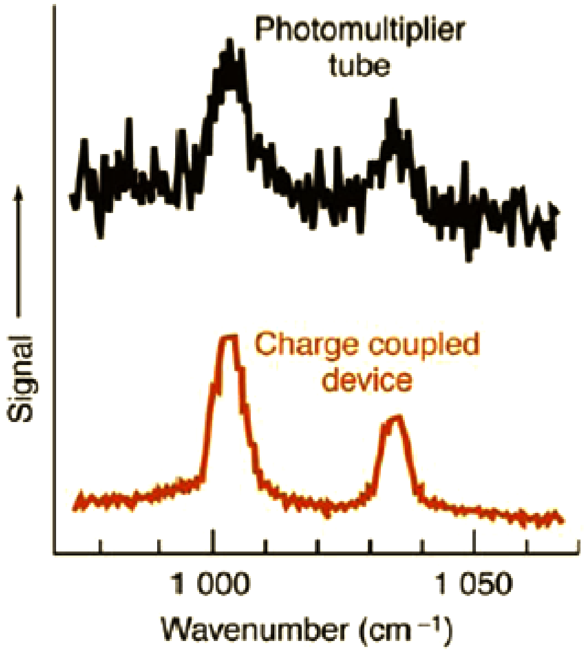

**Figure 2-28. Differences between photomultiplier tube (PMT) and charge-coupled device (CCD) detector outputs.** (Adapted from Pemberton, 1989).[12]

## Current Method Developments

Developments of CRDS technology for vast disciplines and environments have led to many variations to the aforementioned experimental design. Due to the simplicity of the CRD approach, there are only three zones in the experimental design where changes can be made that would significantly alter the technology:

1. (a) the light source (laser technology, spectral design, and the incorporation of input/output optical components);

2. (b) the construction and design of the internal components to the ring-down cavity; and
3. (c) the methods and algorithms utilized for data processing.

The most extensive application of CRDS technology has been atmospheric studies. Pulsed laser CRDS has evolved through many design permutations and is currently manufactured using off-axis cavity-enhanced absorption (OA-CEA) techniques with advancements to the construction of the reflective cavity components. Although appropriate for both pulsed and continuous wave light source applications, CEA or ICOS and off-axis integrated cavity output spectroscopy (OAICOS or OA-CEA) are more frequently used with the CW approach.[8]

Most CRDS experiments are performed on gaseous samples due to the simplicity with which gases can be introduced into the sampling cell. However, attempts to broaden the applicability of the technology have lead to a few studies that sample surfaces, thin films, liquids, and solids, although no sample medium has been as extensively studied with CRDS than air.

### 2.6.2 Pollutants and Relative Levels That Can Be Measured

The applications for pulsed CRDS and its numerous variants (such as CW-CRDS, FT-CRDS, CEA/ICOS, etc.) and the studies performed on these techniques are limitless. Therefore, the list of detectable pollutants provided in Table 2-30 is only a cursory list and does not represent all possibilities.[8]

**Table 2-30. Example list of detectable pollutants by CRDS.** Wavelength (λ), sensitivity, and minimum detectable mixing ratio at 1σ noise level for common gaseous species.

| Species | Method | Approximate λ (µm) | Sensitivity ($cm^{-1}$) | Mixing Ratio (ppbv) |
|---|---|---|---|---|
| $CH_4$ | CW CRDS | 1.65 | $1.5 \times 10^{-8}$ | 52 |
| $C_2H_2$ | CW CRDS [a] | 1.5 | $\sim 4 \times 10^{-9}$ | 4 |
| TNT | Pulsed CRDS [b] | 6 – 8 | $9 \times 10^{-9}$ | 0.075 |
| Chlorobenzenes | Pulsed CRDS | 0.266 | -- | ppmv levels |
| $CO_2$ | CW CRDS | 1.57 | $\sim 4 \times 10^{-9}$ | 2500 |

Samples were analyzed ambient or lab air unless otherwise noted. [a] Sampled in a flame matrix. [b] Synthetically prepared sample. [c] Sampled from a lab source, pure gas or carrier gas mixture matrix. [d] Sampled in human breath. [e] Sampled from prepared standard.

**Table 2-30. Example list of detectable pollutants by CRDS (continued).** Wavelength (λ), sensitivity, and minimum detectable mixing ratio at 1σ noise level for common gaseous species.

| Species | Method | Approximate λ (μm) | Sensitivity ($cm^{-1}$) | Mixing Ratio (ppbv) |
|---|---|---|---|---|
| CO | CW CRDS [c] | 1.57 | ~ $4 \times 10^{-9}$ | 2000 |
| $NH_3$ | CW CRDS [c] | 1.5 | ~ $4 \times 10^{-9}$ | 19 |
| NO | CW CRDS [d] | 5.2 | $5 \times 10^{-8}$ | 0.7 |
| $NO_2$ | CW CRDS [c] | 0.410 | $7 \times 10^{-9}$ | 0.4 |
| $NO_3$ | CW CRDS [c] | 0.662 | $1 \times 10^{-9}$ | 0.002 |
| $N_2O_5$ | CW CRDS | 0.662 | $1 \times 10^{-9}$ | 0.0012 |
| HONO | Pulsed CRDS [c] | 0.354 | $2 \times 10^{-8}$ | 1.7 |
| OH | Pulsed CRDS | 0.309 | -- | ppmv levels |
| Hg | Pulsed CRDS | 0.254 | -- | 0.001 |
| $H_2{}^{18}O$ | Pulsed CRDS [e] | 0.95 | -- | 7 ‰ |
| Aerosol | Pulsed CRDS | 0.532 | $1 \times 10^{-10}$ | -- |

Samples were analyzed ambient or lab air unless otherwise noted. [a] Sampled in a flame matrix. [b] Synthetically prepared sample. [c] Sampled from a lab source, pure gas or carrier gas mixture matrix. [d] Sampled in human breath. [e] Sampled from prepared standard.

The sensitivity of the CRDS method is determined by the fractional loss of light intensity per round-trip in the cavity. The absorption of laser light intensity for a single pass through the optical cavity is given by the Beer-Lambert law in Equation 1, which is used to approximate the minimum detectable absorption in CRDS. Equation 3 below shows that the minimum detectable absorbance per pass is dependent upon the reflectivity (R) of the mirrors and the accuracy in the determination of τ and the precision of Δτ (or the precision of the number of round trips in the cavity (N).[1,4]

$$\delta I_m \approx (1-R)\frac{\Delta\tau_{\min}}{\tau} = (1-R)\frac{\Delta N_{\min}}{N} \qquad \textbf{Eq. 3}$$

Where:
$\delta I_m$ = the minimum detectable change in absorbance
$R$ = mirror reflectivity
$\Delta\tau_{min}$ = minimum detectable change in ring-down time (i.e. precision of Δτ)
$N$ = the number of round trips in the cavity
$\Delta N_{min}$ = the accuracy to which N can be measured

### 2.6.3 Typical QA/QC

There are three main requirements in the experimental design when CRDS is used. First, the laser source must emit the wavelength absorbed by the target analyte or a range of wavelengths that includes the absorption wavelength. Also, the cavity mirrors must be able to reflect the light in the wavelength region of interest. Finally, the detector must be fast enough to detect changes that occur in very short time intervals (µs). The rest of the instrumental configuration involves adjustments (such as cavity length modulation or cavity resonance mode matching) to achieve an absorbance signal. The optical modes of the entire system must then be harmonized to acquire a signal from the detector.

Accuracy, precision, linearity, zero/calibration drift, and response time can be evaluated through the use of known concentrations of gas standards and/or zero air. Simultaneous measurements based on a reference method such as EPA CTM-027 could provide the reference data for assessing CRDS comparability. The data completeness is simply a measure of the amount of valid data points achieved versus the total amount of data points expected for a given period of time. Other factors that become important during operation such as maintenance requirements, consumables used, ease-of-operation, and frequency of repairs are being assessed through EPA verification tests.[15]

### 2.6.4 Example Applications and Vendors

#### Applications

Although the technology is new to regulated environmental applications, it is not foreign to experiments involving the direct monitoring of environmental contaminants. A work by Berden *et al.* [2000] lists a comprehensive overview of published findings with CRDS technology from the official date of inception (with O'Keefe and Deacon in 1988) to the date of publication (2000).[3,4] This list contains well over 200 spectral features detected by CRDS and includes absorption wavelengths, almost continuously, from 205 nm to 10,617 nm. Moreover, Atkinson [2003] and Brown [2003] individually identified chemical divisions for the most potential applications of CRDS in direct environmental contaminant monitoring into the following classes:[2,8]

1. Nitrogen oxides and Nitrous Acid (HONO)
2. Ammonia
3. Elemental mercury and volatile mercury compounds
4. Carbon monoxide and carbon dioxide
5. Methane, hydrocarbons, and formaldehyde
6. Atmospheric aerosol particulates

The limitations to the application of CRDS technology depend on the development of individual optical system components. The overall applicability and usefulness of the method has only begun to be explored and various transfigurations of CRDS will enjoy extensive application in environmental analytical chemistry as the merits of these methods are proven in time. Table 2-31 summarizes the common applications for CRDS technology.

**Table 2-31. Typical Applications for OP-TDL.**

| Technology | Applications |
|---|---|
| CRDS | Tracer Gas Correlations |

### Vendors

There are currently three known proprietors of commercial CRDS systems: (1) Picarro, Inc., (2) Los Gatos Research, Inc., and (3) Tiger Optics, Inc. Each manufacturer has developed a system different from the others. The main technological differences between each manufacturer's designs have primarily to do with the ring-down cavity configuration and construction materials. The cost of a CRDS system ready for field use ranges between $40,000 to $150,000, depending on specific application and configuration. To date, the EPA's ETV is still in the process of testing the method and anticipates reporting their results sometime towards the end of the 2010 calendar year. Table 2-32 lists CRDS vendors and their internet contact information.

**Table 2-32. CRDS Vendors**

| Vendors | |
|---|---|
| Picarro, Inc. (CRDS) | www.picarro.com |
| Tiger Optics | www.tigeroptics.com |
| Los Gatos Research (ICOS) | www.lgrinc.com |

### 2.6.5 Strengths and Limitations

CRDS can be used as a qualitative tool to provide specific information about volatile IR energy-absorbing molecules. It can also be used as a quantitative tool to provide the concentration of many gas-phase molecules. A summary of strengths and limitations is shown in Tables 2-33 and 2-34. One of the main strengths of CRDS is that it measures time and not absorbance, making the technique immune to environmental variations and laser intensity fluctuations while concurrently increasing the linear dynamic range. Moreover, through the use of a high-finesse optical cell, CRDS has greatly increased the technology sensitivity to target compounds without adding complicated sample pre-conditioning steps. The use of the optical cell further enhances the technological design to withstand vibration making field applications of the technology simpler.

The CRDS application is limited mostly by the properties of the high-reflectivity optical mirrors. The mirrors used for CRDS have a high amount of wavelength specificity but lack the flexibility necessary to allow simultaneous multiple species detection and/or a broad species application range. High-reflectivity optical mirrors currently are only able to reflect about 15 percent of the target wavelength on either side.

**Table 2-33. Summary Table of CRDS Strengths**

| Feature | Strength |
|---|---|
| Simple design | Minimal maintenance required and no consumables are needed. Turnkey operation with the potential for remote access and control. "User friendly." |
| Fast detector | Ability to measure very small changes in short time frames. Can rapidly scan spectra continuously for high temporal resolution and real-time results. |
| Multi-pass, high-finesse, stable optical cell | Greatly increases sensitivity with much longer effective pathlengths. Insensitive to vibrations during measurements. |
| Broad-band source capable | Allows for extended wavelength range scanning, increasing sensitivity by probing multiple absorption lines while also eliminating other interferences. |
| Internal temperature and pressure controls | Minimal-to-no drift making frequent calibration unnecessary. Enhanced accuracy and system stability. |
| Measures time, not absorbance | Renders the method immune to ambient changes (such as relative humidity and temperature) and laser intensity fluctuations. |
| Direct sampling | Little-to-no sample pre-conditioning or treatment required before analysis. |

**Table 2-33. Summary Table of CRDS Strengths (continued)**

| Feature | Strength |
|---|---|
| Compact system | Easy field deployment and installation. Quick sample exchange in a smaller volume cavity with moderate flow rates. Advances in components allow for a fairly rugged portable system |
| Can use low power optical sources | Logistically simpler for field use to eliminate the need for a large power source. |

**Table 2-34. Summary Table of CRDS Limitations**

| Feature | Limitation |
|---|---|
| Measures only total extinction | May need to apply sample filtering components to avoid interferences. |
| Laser light source | Limits the method to the laser spectral ranges available. |
| High-reflectivity mirrors | Are only able to reflect over a small wavelength range (about ± 15%) relative to the center wavelength. Multiple species detection difficult. |
| High quality lasers and mirrors | Key components that typically drive up the cost of the instrumentation, depending on application. |

## 2.6.6 References

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# 3.0 Measurements Applicable to Emissions Flux

Optical remote technologies have been applied to answer a variety of fugitive and area source emissions questions. The range of applications spans both short-term characterization and measurement of emission flux to long-term monitoring of trends in control strategy performance. ORS technologies have been used in mobile applications to screen pipelines or industrial sites for leaks or major sources and in stationary applications to measure flux from landfills, waste lagoons, and petrochemical plants.

The technologies described in Chapter 2 can be used alone or in combination to provide three major types of data: plume characterization, short-term flux measurements and long-term monitoring studies.

Short-term flux measurement applications (e.g. DIAL, RPM, SOF, Tracer Release Correlation etc.) are useful to determine the emissions from a complex area sources at one point in time. These measurements provide an estimate of the emissions plume size and concentration of selected target compounds or surrogates.

Concentration profiling involves using ORS such as line of sight open-path optical techniques. Profiling periodic changes of emissions in one dimension is often the precursor of pilot stage of long-term monitoring at an area or fugitive emissions site.

Long-term monitoring is used to determine average trends of area sources emissions and to provide an indication of seasonal or industrial cycle emissions profiles. Continuous concentration profiling is also useful to determine process upsets or to diagnose the potential source of emissions from a complex industrial area through the use of back trajectory calculations. Typically long-term monitoring needs to be associated with a short-term measurement characterization of the size and composition of the emissions plume to relate trends in monitoring data to emissions and emissions factors.[1]

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These three types of data provide essential information on the annual emissions rate of fugitive and area sources as well as a measure of the effect of emissions reductions efforts.

Chapter 3 of this Handbook provides an introduction to the use of ORS technologies by describing applications that measure short-term flux or mass emission rates from open or un-ducted sources.

## Reference

1 Hashmonay, Ram, Long Term Monitoring of Greenhouse Gas Emissions from Fugitive and Area Sources, presented at the AWMA Symposium on Air Quality Measurements Methods and Technology, Los Angeles, CA November 2010

## 3.1 Radial Plume Mapping: Other Test Method 10

RPM is an ORS method used to determine fugitive emissions from non-point emissions sources including fugitive emissions and area source emissions. Its main goals are to identify emission "hot spots" over large scanned areas and measure emission fluxes. Fugitive emissions include air pollutants released into the ambient air from pressurized equipment due to leaks and various other unintended or irregular releases of gases. Examples of fugitive emissions include $O_3$ precursors, benzene, and methane.[1] For some source categories, fugitive and/or area source emissions are a significant portion of the total pollutant emissions; therefore, it is important to be able to locate and quantify these emissions.

The open-path configuration for ORS technologies was originally used to determine the average concentration of a compound of interest over a path of known length. The line-of-sight, or one-path, configuration provides an average of the compound of interest concentration per path length (i.e., ppmm). Open-path monitoring expanded to include the measurement of the average concentration over several distances along the open path length. These interval measurements enabled estimation of the concentration profile of the plume. However, the survey of leaks and hot spots over a large area is not possible with just one optical path. Directing the ORS path over different lengths, as well as different horizontal and vertical paths, allows additional characterization of the horizontal or vertical emissions plume profile. RPM, as discussed in this section, is the outgrowth of multidirectional, multi-pathlength ORS and is used in combination with mathematical algorithms to characterize the concentration profile over a horizontal or vertical optical path plane.

### 3.1.1 General Description of Approach

Measuring the total amount of a fugitive emission over a large area is not simple. Earlier efforts used traditional point sampling instruments like canisters, sorbents methods, flux boxes, PID/FID and others.[2] However, the traditional point methods only provide concentrations from a single point and fail to capture the temporal and spatial distribution of fugitive emissions over a large area. These methods also fail to identify, if any, "hot spots" of fugitive emissions. RPM provides a more complete survey of a large area. Open-path ORS measurement technology mounted on a programmable aiming platform or scanner can be configured in a vertical plane to measure emissions flux. When scanning in the horizontal plane (HRPM), results can be used to locate hot spots at ground level. Emission fluxes are obtained when scanning in the vertical plane (VRPM) downwind of the area source along with meteorological measurements data. One-dimensional RPM, which scans along one line, such as an industrial fence line, is used to profile pollutant concentrations downwind from a source and coupled with wind direction may also be useful in locating emissions sources.[2] Determining which scanning setup to use depends entirely on the objectives of the project and data quality indicators.

## Horizontal RPM Algorithm

The HRPM approach provides horizontal differentiation to path-integrated measurements by optical remote sensing. This technique yields information on the two-dimensional distribution of the concentrations in the form of chemical-concentration contour maps. In this application, the plume mapping identifies chemical "hot spots," the location of high emissions. Horizontal radial scanning is usually performed with the ORS beams located close to the ground. The survey area is divided into a Cartesian grid of rectangular cells. A mirror is located in each of these cells and the OP-FTIR sensor scans to each of these mirrors, dwelling on each for a set measurement time. The measurement equipment scans to the mirrors in the order of either increasing or decreasing azimuth angle. The path-integrated concentrations measured at each mirror are averaged over several scanning cycles to produce time-averaged concentration maps. Meteorological measurements are made concurrent with the scanning measurements. Equation 4 is used in an iterative process to calculate the average concentration for each rectangular areas of the surveyed zone as shown by example in Figure 3-2

$$PIC_k = \sum_k K_{km} c_m \qquad \textbf{Eq. 4}$$

*PIC* = path-integrated concentration
*K* = kernel matrix
*k* = number index for the beam paths
*m* = number index for the pixels
*c* = average concentration in the m$^{th}$ pixel.

The kernel matrix includes the specific beam geometry as shown in Figure 3-2 where the diagonal lines represent the *K*. Each value in the kernel matrix *K* is the length of the $k^{th}$ beam within the $m^{th}$ pixel; therefore, the matrix is specific to the beam geometry. The HRPM procedure solves for the average concentrations (one for each pixel) by solving the non-negative least squares best fit for the data. Then the algorithm multiplies the resulting vertical vector of averaged concentration by the matrix *K* to yield the end vector of predicted PIC data. The second stage of the plume reconstruction involves interpolation among the reconstructed pixel's average concentration, providing a peak concentration not limited to the center of the pixels. A triangle-based cubic interpolation procedure (in Cartesian coordinates) is currently used in the HRPM procedure.[2] The ORS instrument is typically placed at the origin (in the first quadrant of the Cartesian convention) of the rectangular area to be measured. Once the HRPM measurement area and the number of path-determining components (PDCs) have been determined, the area is divided into smaller rectangular areas called pixels. The total number of pixels required is smaller or equal to the total number of beam paths.[6]

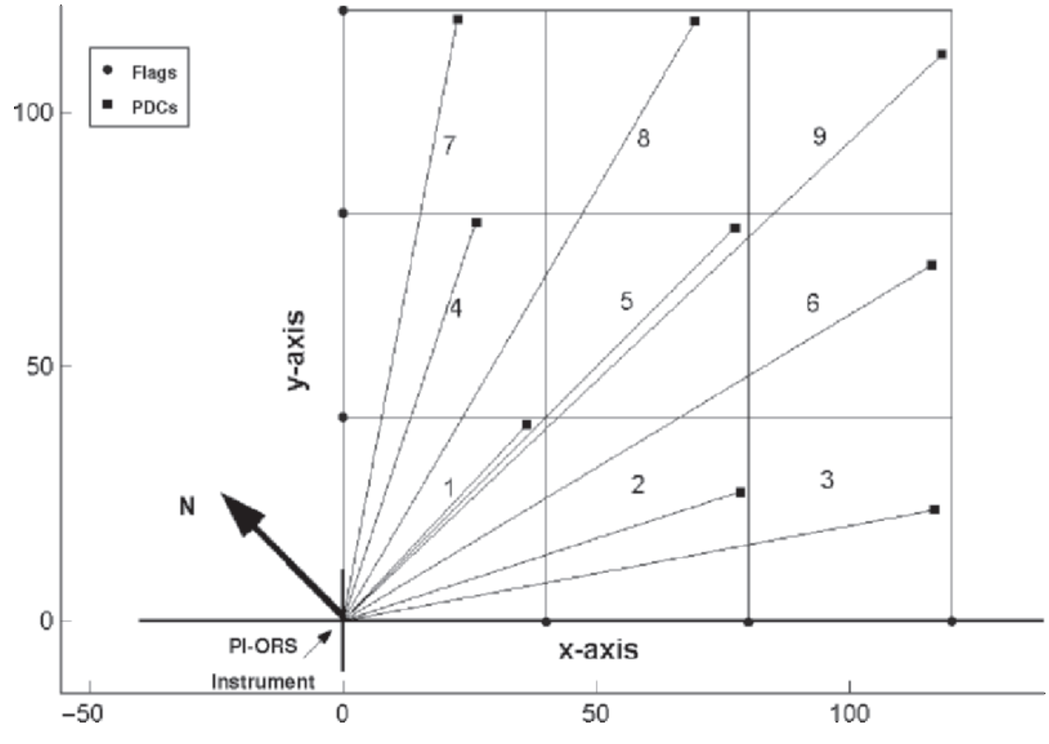

**Figure 3-1. Horizontal RPM setup, taken from Hashmonay et al., 2008.**

### Vertical RPM algorithm

The VRPM algorithm uses multiple beam paths to survey the vertical pollutant concentration profile as a function of distance from the measurement equipment. Two different beam configurations of the VRPM methodology have been used: the five-beam (or more) and the three-beam VRPM configuration. Figure 3-3 shows a VRPM configuration using six beams. In the five-beam (or more) configuration, the ORS instrument sequentially scans the paths of five PDCs. Three PDCs are along the ground-level crosswind direction, and the other two are elevated on a vertical structure. Additional beam configurations provide better spatial definition of the plume in the crosswind direction. In the three-beam configuration, the ORS instrument sequentially scans over three PDCs. Only one beam is focused at ground level, while the other two are elevated on a vertical structure. Pollutant data are collected over time as the measurement equipment cycles between each PDC.[2]

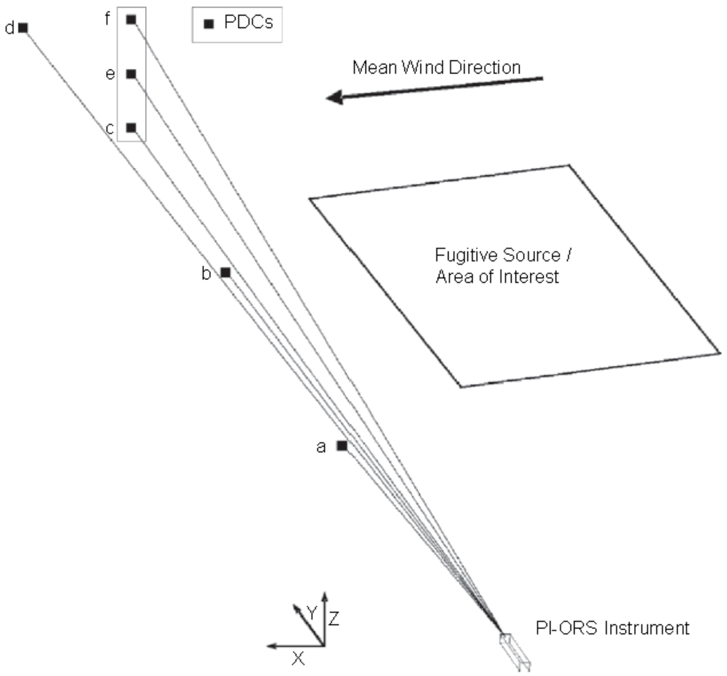

**Figure 3-2. Vertical RPM setup, taken from Hashmonay et al., 2008**

Once the PIC for all beam paths are averaged for the gas species of interest, the VRPM calculations reconstruct a plume map in the vertical downwind plane. A two-phase smooth basis function minimization (SBFM) approach is applied when there are three or more beams focused along the ground level (5-beam or more configurations). In the two-phase SBFM approach, a one-dimensional SBFM (1D-SBFM) reconstruction procedure is applied to reconstruct the smoothed ground level and crosswind concentration profile. The reconstruction is applied to the ground level segmented beam paths of the same beam geometry to find the cross wind concentration profile. A univariate Gaussian function is fitted to measured PIC ground level values.[2] The 1D-SBFM is also the sum of the squared errors (SSE), which is also the error function for the minimization procedure. The equation for calculating SSE is:

$$SSE(B_j, m_{yj}, \sigma_{yj}) = \sum_i \left( PIC_i - \sum_j \frac{B_j}{\sqrt{2\pi}\,\sigma_{yj}} \int_0^{r_i} \exp\left[ -\frac{1}{2}\left( \frac{m_{yj} - r}{\sigma_{yj}} \right)^2 \right] dr \right)^2 \qquad \textbf{Eq. 5}$$

$B$ = area under the on-dimensional Gaussian distribution
$r_i$ = pathlength of the ith beam
$m_y$ = mean (peak location)
$\sigma_y$ = standard deviation of the jth Gaussian function
$PIC_i$ = measured PIC value of the ith path

The SSE function is minimized using the simplex minimization procedure to solve for the unknown parameters (Press et al. 1992). When there are more than three beams at the ground level, two Gaussian functions are fitted to retrieve skewed and sometimes bi-modal concentration profiles. This is the reason for the index *j* in Eq. 5.[6]

Once the 1D-SBFM phase is completed, the 2-D phase is applied. The bivariate Gaussian function used in the second phase is:

$$G(A, \sigma_z) = \frac{A}{2\pi\sigma_{y-1D}\sigma_z} \exp\left\{ -\frac{1}{2}\left[ \frac{(r \cdot \cos\theta - m_{y-1D})^2}{\sigma_{y-1D}^2} + \frac{(r \cdot \sin\theta)^2}{\sigma_z^2} \right] \right\} \qquad \textbf{Eq. 6}$$

Where $\sigma_{y-1D}$ is the standard deviation along the crosswind direction found in the 1D-SBFM; $m_{y-1D}$ is the peak location along the crosswind direction found in the 1D-SBFM procedure and A and $\sigma_z$ are the unknown parameters to be retrieved in the second phase of the fitting procedure. To solve for the unknowns an error function (SSE) is used which is minimized using the simplex method to solve for the two unknowns.

If measurement equipment uses the three-beam setup (one at the ground level and the other two elevated), the one-dimensional phase calculation can be skipped, assuming a wide plume. The standard deviation in the crosswind direction is assumed to be about 10 times that of the ground-level beam path (length of vertical plane). Thus, if $r_1$ is the length of the vertical plane, to determine the vertical gradient in concentration we use:

$$G(A,\sigma_z) = \frac{A}{2\pi(10r_1)\sigma_z}\exp\left\{-\frac{1}{2}\left[\frac{\left(r\cdot\cos\theta - \tfrac{1}{2}r_1\right)^2}{(10r_1)^2} + \frac{(r\cdot\sin\theta)^2}{\sigma_z^2}\right]\right\} \qquad \textbf{Eq. 7}$$

When the parameters of the function are found for a specific run, the VRPM algorithm calculates the concentration values for every square unit in a vertical plane (pixels). Then, the algorithm integrates the values incorporating wind speed data at each height to calculate the flux.

## One-dimensional RPM algorithm

For 1-D plume mapping, the scanning ORS instrument and three or more PDC are placed in a crosswind direction along a line, such as an industrial site fence line, and PIC measurements are made. A minimum of three PDCs are needed, but four to six are recommended, as shown in Figure 3-4, to provide a more detailed concentration profile. PDCs should be placed on the line-of-sight with an equal distance between each subsequent PDC, if possible. The 1D-RPM configuration uses the same equations for the VRPM, 1D-SBFM, which reconstructs a mass-equivalent plume concentration profile along a line-of-sight measurement.

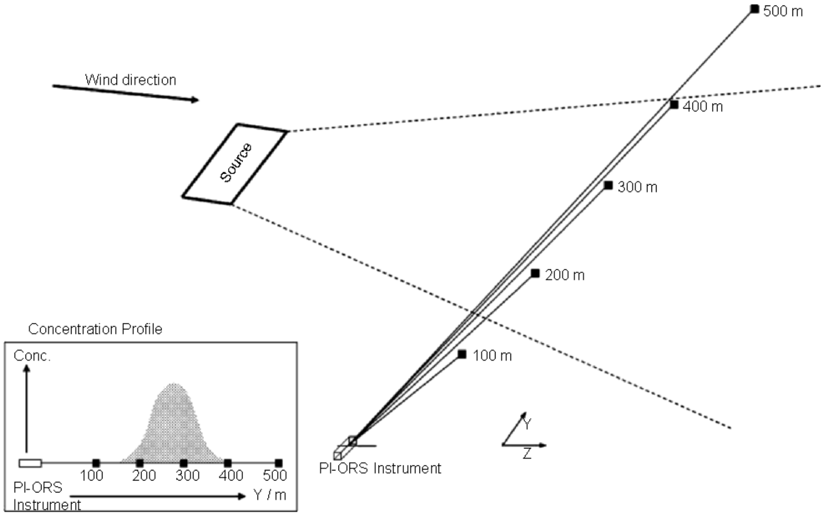

**Figure 3-3. One-dimensional RPM setup, taken from Hashmonay et al., 2008.**

The RPM model and ORS technique are coupled together by a series of steps. First, the ORS pollutant concentration data along with wind vector information are processed with the VRPM algorithm to yield a mass emission flux for the source.[2,5,6,7] In a similar way, HRPM and 1D-RPM algorithms are processed with the concentration data to provide hot spots info or concentration downwind for the source. The output of the concentration data and algorithm process looks like a contour map. Figure 3-5 displays VRPM and HRPM contour map outputs where the concentration patterns are evidence of the distribution of the fugitive emission.

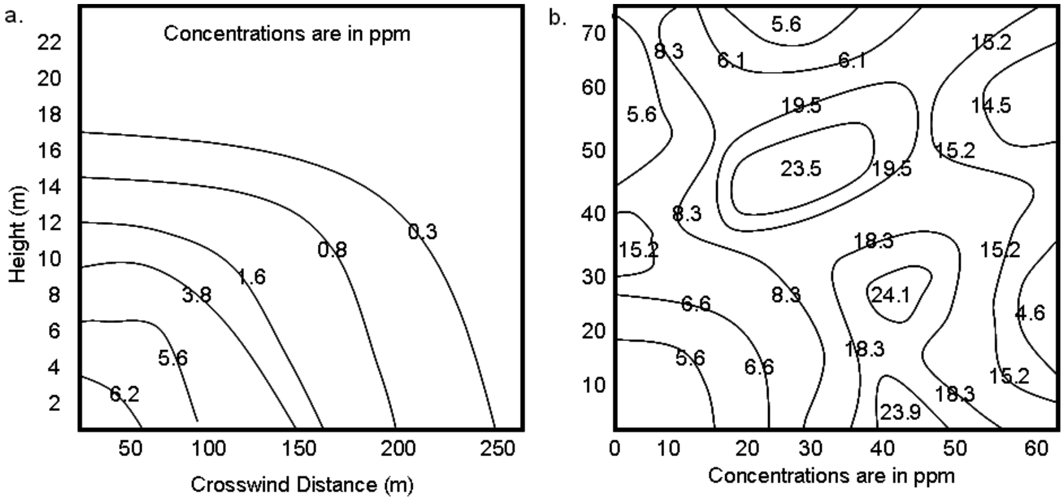

**Figure 3-4. Examples of RPM algorithm outputs.** Panel a. corresponds to the VRPM output and panel b. is HRPM output.

## RPM-ORS Technologies

Technologies appropriate for characterizing ground-level area sources and non-point emission sources such as landfills, lagoons, and industrial complexes[3] using RPM methodologies are: OP-FTIR, open-path Tunable Diode Laser Absorption Spectroscopy (OP-TDLAS), UV-DOAS, and DIAL. Each technology has its own strengths and limitations and, depending on the objective of the project, some are more effective than others. The following is a discussion of the conditions and requirements to deploy each technology.

OP-FTIR has an optical range of 100 – 500 m; it can detect multiple compounds simultaneously at high temporal resolution with detection limits in the ppb range. The instrument setup is time-consuming and it requires liquid nitrogen to cool the instrument, so OP-FTIR is best for campaigns that do not require constant relocation and multiple setups. Another consideration is that $CO_2$ and water are interfering species in FTIR measurements. OP-FTIR data has to be processed to quantify path-integrated concentrations, so if real-time is needed, OP-FTIR is not the best choice. For more details about OP-FTIR technology see section 2.1.

OP-TDL has an optical range of up to 1 km. Depending on the topography and location of physical barriers at the survey area, the distance between the control box and the telescopes may require a large amount of fiber optic cable, which can be difficult to deploy[2]. OP-TDL can detect CO, $CO_2$, $NO_x$, ammonia, methane ($CH_4$) and hydrogen sulfide with detection limits in the ppb range, but can only detect one compound of interest at a time. The instrument can produce multiple beam paths, is lightweight, and is easily deployed. The OP-TDL generates real-time path-averaged concentration data in the field. When only a single gas is of interest, OP-TDL offers a cost-effective choice compared to OP-FTIR. OP-TDLAS has been used to monitor the exhaust from natural and mechanical ventilation systems used in houses, farms and other facilities. The technique has also been used to measure the flux from a traveling gun sprayer applying swine lagoon liquid to the farm field.[4] For more details about OP-TDLAS technology, see section 2.2.

UV-DOAS detects unstable species like radicals, nitrous acid, aromatic species, and BTX at low concentrations in the ppb levels. The UV-DOAS can be setup to scan multiple or single beam paths. For more details about UV-DOAS technology, see section 2.3.

### 3.1.2 Verification/Validation Studies

The RPM algorithm’s capacity to locate/identify sources of fugitive emissions and provide accurate measurement of emissions flux of fugitive emissions and area sources has been assessed in two different ways: (1) measurement of known concentration tracer gas releases and (2) comparison with the measurement results of selected instruments in collocated systems. RPM data is verified by assessing if the collected data satisfies the objectives of the study.[1] The following are several examples of studies performed to test RPM and the selected ORS instruments to survey fugitive emissions.

**OP-FTIR and OP-TDLAS comparison studies: Thoma et al., 2005 and Modrak et al., 2005**

During the Fort Collins measurement campaign[8], methane measurements from two OP-FTIR instruments were compared. Both OP-FTIR instruments contain a Nicolet bench, 12-inch telescope, and collected data at resolutions of 0.125 $cm^{-1}$, 0.25 $cm^{-1}$, 0.5 $cm^{-1}$, 1 $cm^{-1}$, 2 $cm^{-1}$, 4 $cm^{-1}$, and 8 $cm^{-1}$. The data comparison showed that the instruments were extremely stable and reliable for the duration of the campaigns. In separate studies[7,8], investigators used OP-TDLAS and OP-FTIR to compared methane measurements obtained by both instruments and found similar results. During the experiments, the two instruments were deployed side-by-side and aligned to an identical mirror. Methane concentration data were collected with each instrument for a period of 30 minutes.[7] The results of the experiment found that methane concentrations measured with the OP-TDLAS were slightly higher (3 percent) than concentrations measured with the OP-FTIR instrument. These results are significant because they show that methane concentration data collected by the two instruments are comparable, and that both can be used interchangeably in RPM configurations.[3]

### OP-FTIR and UV-DOAS comparison: Colorado Springs field study[3]

The Colorado Springs field campaign occurred in September 2003 at a former landfill site as part of an effort to rehabilitate the site for recreational use. The current owners of the landfill and the State of Colorado requested assistance from the EPA to perform a site assessment to search for the presence of any fugitive gas emissions from the site. The study used OP-FTIR, OP-TDLAS, and UV-DOAS instruments. The UV-DOAS instrument was deployed at the site to collect data concurrently with the OP-FTIR instrument. The UV-DOAS detected the presence of BTX. The concentrations of toluene measured with the UV-DOAS instrument correlated well with gasoline concentrations measured with the OP-FTIR instrument during the same time period.

### VRPM plume capture validation study[3]

During June and July 2006 at Orange County Municipal Landfill, the EPA and ARCADIS performed a VRPM plume capture validation study. The objective was to capture the emissions from hot spots located a large distance upwind of the measurement configuration. The experimental design used OP-FTIR for VRPM measurements and a known concentration of tracer gas released to determine plume capture. The effectiveness of the RPM configuration in capturing plumes (horizontal and vertical planes) was evaluated by comparing the actual release rate of the tracer gas to the calculated flux values as tracer gases were released at different distances upwind of the configuration. Releases were made at different distances; 20, 60, 100, and 140 m from the VRPM measurement plane. The study found that if there is no statistical significant difference between the averaged concentrations along each beam (i.e., no vertical concentration gradient), the VRPM configuration is not vertically capturing the plume. If the difference between the average concentrations along each beam is less than 10 percent (i.e., a slight vertical concentration gradient exists), the VRPM configuration is sufficiently capturing the plume from the upwind release point. If the difference between the average concentrations along each beam is greater than 10 percent (i.e. a substantial vertical concentration exists), the VRPM configuration is vertically capturing the plume from the upwind release point and the releasing location is not close enough to the maximum upwind location for complete plume capture.

### 3.1.3 Typical QA/QC

This section describes the QA/QC activities that pertain to the RPM as described above. QA/QC activities normally depend on pre-determined data quality indicators that address the project unique objectives. The technologies used for RPM have their own specific QA/QC associated with the instruments. If interested in the technology QA/QC for OP-FTIR, refer to section 2.1; for OP-TDLAS, refer to section 2.2; and for UV-DOAS, refer to section 2.3.

The general QA/QC steps are: (i) equipment calibration, (ii) assessment of DQI goals and (iii) DQI check for analyte path-integrated concentration measurement. Each ORS instrument has its own calibration procedure as discussed in Chapter 2 of this Handbook, thus is important to follow the instrument's manufacturer instructions. DQI goals depend on the compound of interest and the expected concentration ranges, thus detection limits, accuracy, and precision need to be determined using appropriate traceable standards. On-site verification using a known concentration tracer gas release provides a sampling episode specific QC confirmation of test results.

Because meteorological data is part of RPM calculations, instruments used to measure ambient conditions need to be calibrated and their accuracy and precision tested regularly. Table 3-1 shows the recommended DQIs for the different aspects associated with the measurement of the path-integrated concentration and RPM.[2]

**Table 3-1. Data quality indicators for the QA/QC process, taken from EPA-OTM10**

| Measurement parameter | Analysis Method | DQI |
|---|---|---|
| PI-ORS Instrument | Instrument specific | Instrument specific |
| Wind speed | Side-by-side comparison of two wind monitors | Within 20% |
| Wind direction | Comparison to magnetic north | Within 10% |
| Optical path-length | Measure and compare to known path | Within 2% |
| Beam angle | Measure and compare known angle | Within 2º |
| HRPM, VRPM and 1D-RPM | CCF* | ≥0.8 |
| VRPM flux measurement | Wind direction | -10º to +25º from perpendicular |
| 1D-RPM | Peak location variability | Reconstructed peak locations |

* Concordance correlation factor (CCF) indicates the goodness of fit between measured and predicted path-integrated concentration, CCF = rA.

### 3.1.4 Siting Concerns

Certain weather conditions such as rain, fog or snow can obscure the optical beam of the utilized instrument and affect its ability to continuously measure gaseous concentrations. Transient, but significant, obscuration can occur during heavy precipitation events, particularly with longer path measurements. This limits the sensitivity of the PIC measurements or the instrument's ability to collect data.[2]

Wind conditions can greatly affect the results of field measurements and should be taken into account when interpreting data. Calm wind conditions do not affect the HRPM methodology algorithm for hot spot source location. However, very low wind speeds are not ideal for the VRPM methodology for emission rate estimation, as the source plume may not be carried through the vertical plane in the absence of measurable wind. Very high wind speed conditions are not ideal for any of the RPM methodologies. High winds may displace or vibrate the optical alignment of the components of the ORS system used in the setup, and affect the quality of the PIC values acquired in multiple beam paths. They may also cause displacement of any hot spot identified by HRPM. Based on controlled studies performed in the past, the following wind speed ranges are recommended for optimal results:

- HRPM methodology: Near 0 to 5 m/s
- VRPM methodology: 1 to 8 m/s

- 1D-RPM methodology: 1 to 8 m/s

In optimal conditions, the prevailing wind direction should be as close as possible to perpendicular to the VRPM measurement plane. The wind direction needs to be determined for each field study measurement configuration. These requirements present a challenge when determining sites and setup locations. HRPM data should be collected for at least one hour in ideal conditions, which can be difficult when considering locations with highly variable conditions.

### 3.1.5 Strengths and Limitations

Strengths of RPM-ORS are the ability to measure high time resolution and spatially distributed emission data, directly calculate emission rates, capture the distribution of all major emissions in an area and isolate emissions from specific measurement areas. Depending on the ORS instrument, it can provide real-time PIC data for multiple compounds simultaneously. RPM is limited because it relies on good wind conditions, it has difficulties characterizing emissions from complex terrain, and has larger uncertainty when capturing emissions for sources located a large distance upwind of the VRPM configuration. Depending on the RPM-ORS instrument used, some ambient compounds cause interferences. No ORS instrument can measure all the possible compounds of interest, which may create the need for two systems depending on the experimental design. A summary of these strengths and limitations is presented in Tables 3-2 and 3-3.

**Table 3-2. Summary Table of the VRPM's Strengths**

| Feature | Strength |
|---|---|
| Measurement Capabilities | Measures high time resolution and spatially distributed emission data. |
| | Directly calculates emission rates. |
| | Characterizes the distribution of all major emissions in a large area and isolates emissions from specific areas. |
| | May provide real-time PIC data depending on the technology used. |

**Table 3-3. Summary Table of the VRPM's Limitations**

| Feature | Limitation |
|---|---|
| Meteorological Challenges | Characterization is reliant on optimal wind conditions. |
| Interferences | Each OP technology used has its own interferences that must be considered. |
| Topographical Concerns | Difficulties associated with characterizing a plume from complex terrain (e.g., a side slope) |
| | Large uncertainty when capturing emissions from sources a large distance upwind of the VRPM Setup. |

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## 3.2 Range Resolved Measurements using Differential Absorption LIDAR

”Range resolved” refers to vertical and horizontal profiles of concentrations for compounds of interest coupled with meteorological parameters. Generally, range resolved measurements are performed to study emission rates and fate and transport of the compounds of interest. LIDAR technology is often paired with the DIAL application to measure range resolved concentrations of trace species in the atmosphere. DIAL has been used to monitor pollution species in the lower atmosphere such as water vapor, NO, $O_3$, $SO_2$ and $CH_4$.[1] DIAL can also be used to measure $O_3$ concentrations in the middle and high troposphere.[1] Atmospheric temperature measurements are possible by the DIAL technique if the absorption line selected is temperature-dependent.[1]

### 3.2.1 General Description of Approach

Range resolved measurements of plume flux typically employs some technology to measure a surrogate gas in the plume to estimate the concentration of compounds of interest. DIAL is a dual-wavelength, elastic (the atom absorbs the photon and instantly emits another photon at the same frequency), backscatter LIDAR that transmits one wavelength at the absorption line of the target compound ($\lambda_{on}$) and one wavelength slightly off-line of the target compound to measure backscatter ($\lambda_{off}$). The on-line wavelength is absorbed by the gas of interest, while the off-line wavelength is not absorbed as shown in Figure 3-6.

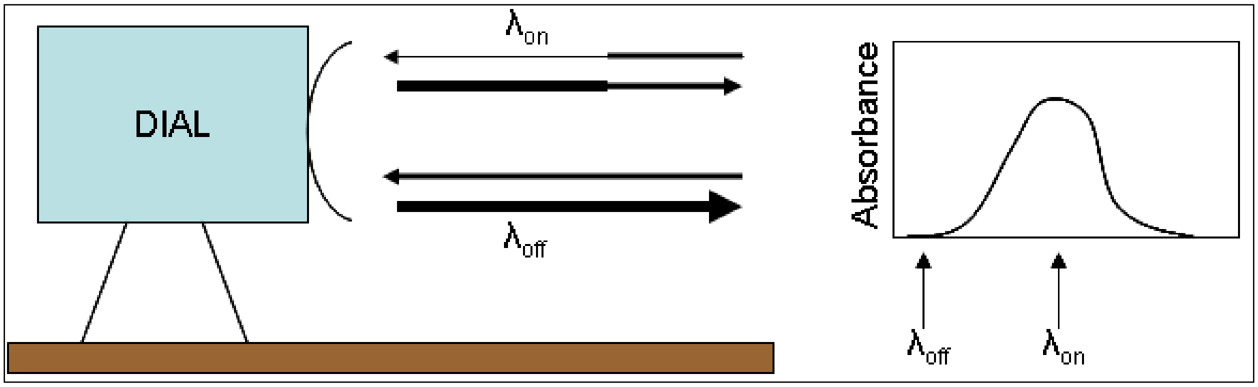

**Figure 3-5. Conceptual picture on the operation of DIAL.** Optical emission is tuned to both the absorbing wavelength and a wavelength that is not absorbed by the target compound. Adapted from Argall, 2003[4].

The differential absorption between the two wavelengths is a measure of the concentration of the gas as a function of range.[2] DIAL is capable of providing a 2-D measure or “contour” of concentrations across a scanning plane. By combining this concentration contour with separately obtained wind speeds, a contaminant flux can be calculated for the measured compound[3], see Figure 3-7.

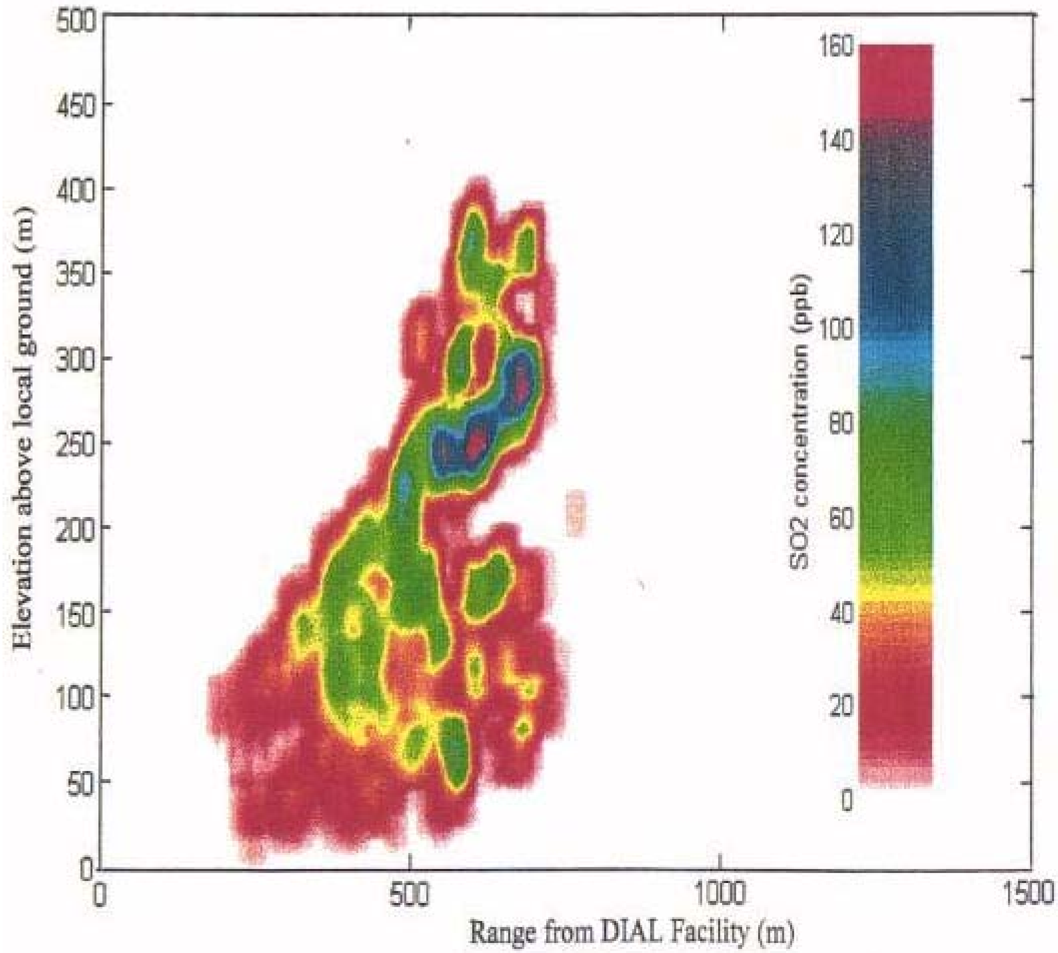

**Figure 3-6. Contour profile of $SO_2$ concentration measured 2.1 km downwind of source, at Cement Works, by Environmental Measurements Group National Physical Laboratory, UK[5].**

### Basic DIAL algorithm to calculate backscatter

The number of photons backscattered correlates to the compound concentration. The basic equation to calculate number of photons backscattered per unit solid angle due to scattering of type *i* (forms of radiation like light, sound) is:

$$P\tau_t(\lambda_l)\int_{R_1}^{R_2}\tau_a(r,\lambda_l)\sigma_\pi^i(\lambda_l)N^i(r)dr \qquad \textbf{Eq. 8}$$

Where $\lambda_l$ = wavelength,
$\tau_t$ = transmission coefficient of the LIDAR transmitter optics,
r = range interval,

$\tau_a(r, \lambda_l)$ = optical transmission of the atmosphere
$\sigma_\pi^i(\lambda_l)$ = backscatter cross section at the laser wavelength,
$N^i(r)$ = number density of scattering centers at range r.[1]

However, to calculate the number of photons incident on the collecting optic of the LIDAR due to scattering of type *i*, one must consider the area of the collecting optic (A):

$$P\tau_t(\lambda_l)A\int_{R_1}^{R_2}\frac{1}{r^2}\tau_a(r,\lambda_l)\tau_a(r,\lambda_s)\zeta(r)\sigma_\pi^i(\lambda_l)N^i(r)dr \qquad \textbf{Eq. 9}$$

Where $\lambda_s$ = wavelength of the scattered light
$\zeta(r)$ = overlap factor

There are two typical types of detectors: photomultiplier and analog. When using photomultiplier detectors, the number of photons detected is:

$$P\tau_t(\lambda_l)A\tau_t(\lambda_s)Q(\lambda_s)\int_{R_1}^{R_2}\frac{1}{r^2}\tau_a(r,\lambda_l)\tau_a(r,\lambda_s)\zeta(r)\sigma_\pi^i(\lambda_l)N^i(r)dr \qquad \textbf{Eq. 10}$$

Where $\tau_r(\lambda_s)$ = transmission coefficient of the reception optics at $\lambda_s$
$Q(\lambda_s)$ = quantum efficiency of the photomultiplier at wavelength $\lambda_s$

Quantum efficiency refers to the percentage of photons incident (hitting) the receiver (photo reactive surface) and it measures the LIDAR electrical sensitivity to light. When using analog detectors, the equations replace the quantum efficiency of the photomultiplier by the gain of the photomultiplier ($G(\lambda_s)$) combined with the gain of any amplifiers used. After some approximations, the analog detector version of equation 10 is:

$$P\tau_t(\lambda_l)A\tau_t(\lambda_s)Q(\lambda_s)\tau_a(R,\lambda_l)\tau_a(R,\lambda_s)\frac{1}{R^2}\zeta(R)\sigma_\pi^i(\lambda_l)N^i(R)\delta R \qquad \textbf{Eq. 11}$$

Where R = range of the center of the scattering volume
$\Delta R = R_2 - R_1$ is the length of the range bin.[1]

### 3.2.2 Verification/Validation Studies

This section presents studies designed to validate the DIAL technique under various conditions. Some studies aim to verify that the application can provide accurate results, thus most of these studies will have other technologies to compare measured concentrations and emission rates.

**Verification of DIAL for Gas Species Measurements**

DIAL has been validated in European studies[10,11] for hydrocarbon emissions with calculated results ranging from ±3 to ±12 percent of the actual value.[3] Two validation studies were performed in Alberta with measured fluxes agreeing within +1 to -10 percent of the known source.[3] Over a four week period during May-June 2003 in Alberta, Canada, DIAL surveys were performed at four gas processing plants, one gas well test site located in the foothills, and two solution gas flare sites. The objective of this project was to field test DIAL technology as a means to:

- monitor ambient $SO_2$ concentrations in the vicinity of sour gas well test flares and track the $SO_2$ plume position,
- measure the combustion efficiency of well test and solution gas flares,
- measure fugitive emissions of methane and other hydrocarbons from gas processing facilities.[6]

The DIAL measurements were performed by Spectrasyne Ltd., UK. When measuring plume concentration profiles, Spectrasyne generally located the DIAL equipment at least 50 meters from the area of interest and relative to the plume source and wind direction so scans could be taken roughly at right angles to the direction of plume travel.[6] Often meteorological changes make this impossible and the measurements were taken at an oblique angle, which results in profiles that appear stretched in the horizontal direction.[6]

The DIAL system included two DIAL lasers, one emitting in the IR range and one in the UV range, and a self-contained weather station for measuring wind speed and temperature. Meteorological parameter data is used in mass rate calculations to reprocess the data to account for the angle relative to the plume direction.[6] With this system, total contaminant flux can be calculated and portions of the plume assigned to specific sources.[6]

The accuracy of the DIAL system was checked by comparing $SO_2$ mass emissions calculated from the DIAL measurements of the $SO_2$ plume with $SO_2$ mass emissions calculated from gas plant CEM instrumentation installed in the incinerator stack.[6] Direct comparison between DIAL and fenceline point source concentration measurements is not possible, since the DIAL measures gas concentration in a relatively large volume in the atmosphere against a point sampling type instrument such as a gas chromatograph.[6] However, the combination of point source measurements for a target compound, combined with meteorological data and dispersion modeling, can provide comparisons useful to verify the DIAL results. Table 3-4 shows some of the results, the scan time, and calculated fluxes for the DIAL and point source. The DIAL and point measurements showed a difference of 11 percent, which is within the range of –18 to + 5 percent from other calibration studies performed by Spectrasyne Ltd.[6] According to this Spectrasyne study and others, DIAL plume measurements generally underestimate the total mass because some areas of the plume contain compound concentration below DIAL's detection limit and are not included in the plume mass. Additional variability among DIAL measurements is believed to originate from variation in wind speed and direction, combined with the 4 - 20 minutes required to do a full DIAL scan across the plume.

**Table 3-4. Results from the comparison of DIAL and plant measurements of $SO_2$ mass emissions** collected on May 26 about 190 m downwind of incinerator stack. Adapted from Chambers, 2003.

| SCAN NUMBER | SCAN TIME | WIND SPEED (M/S) | WIND DIRECTION (DEG) | $SO_2$ FLUX (KG/HR) |
|---|---|---|---|---|
| 1 | 12:37-12:48 | 5.2 | 331 | 372 |
| 2 | 13:00-13:21 | 2.2 | 350 | 223 |
| 3 | 13:31-13:51 | 4.3 | 346 | 394 |
| 4 | 14:00-14:04 | 5.6 | 359 | 196 |
| 5 | 14:07-14:19 | 3.9 | 359 | 145 |
| 6 | 14:42-14:51 | 4.0 | 350 | 333 |
| 7 | 15:10-15:21 | 3.9 | 0 | 394 |
|  |  |  | **Time Weighted Mean of DIAL** | 304 |
|  |  |  | **Plant Data** | 340 |

### 3.2.3 Typical QA/QC

This section describes the QA/QC steps that pertain to the applications described above. QA/QC steps for applications normally depend on pre-determined data quality indicators that address the project unique objectives. The technology used for the applications presented above have their own QA/QC associated to specifics of the instruments. If interested in the technology QA/QC for DIAL, refer to section 2.4.

DIAL measurements are typically verified by running two collocated DIAL systems or one DIAL system along with another ORS instrument, like FTIR or CRDS. Arcadis has verified Dial measurements using OTM10 and developed QA/QC information for conducting Dial measurement projects.[12] However, as noted in OTM10, the unique setup of DIAL requires project specific QA/QC steps with data quality indicators that meet study objectives.

### 3.2.4 Sitting Concerns

The DIAL equipment, optical housing, electronics, computer equipment and other components require a climate control enclosure such as a trailer or an aircraft. Therefore, the operating temperature is controlled to human comfort level ~ 22ºC. Trailers require relatively flat surfaces and road access. Changing weather conditions, physical interferences like buildings, trees, traffic and changing terrain, and interfering chemical species at certain wavelengths will increase variability in the measurement and possibly result in less accurate results.

### 3.2.5 Strengths and Limitations

The most significant limitation to DIAL application is the cost and limited availability of measurement systems. Multiple measurements in North America have relied on importing the instrumentation from the United Kingdom.[6,10,11] Additionally, the number of chemical species measurable by DIAL is restricted to those that are detectable by the Lidar technology. The most notable strength of a DIAL system is the ability to quickly resolve pollutant concentrations in two dimensions. Concentration gradient data obtained in short periods of time enables DIAL to be deployed in a number of applications and a number of configurations. Tables 3-3 and 3-4 summarize these strengths and limitations.

**Table 3-5. DIAL Strengths**

| Feature | DIAL Strengths |
|---|---|
| Measurement Capabilities | DIAL provides spatially resolved pollutant concentration in two dimensions |
| | Measurements are provided in a relatively short period of time. |
| Flexibility | DIAL is deployable in many different applications and configurations. |
| High intensity light source | The ability to measure longer path lengths (1 to 3 km) |

**Table 3-6. DIAL Limitations**

| Feature | Dial Limitations |
|---|---|
| Limited Availability and Expense | Due to limited availability, DIAL systems used in North America are typically imported, which increases the expense of using DIAL for measurements. |
| Range of Measurement | Chemical species that can be characterized and limited to those compounds with the unique chemical properties required to be detected by the LIDAR instrument. Only a few wavelengths are measured; spectral artifacts cannot be fixed or investigated |

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## 3.3 Solar Occultation Flux Measurement

Characterizing and quantitatively measuring fugitive VOC emissions from non-point sources are challenging. The ability to accurately calculate the flux rate of VOC emissions from large area sources such as landfills, refineries, waste retention ponds, process areas, and product holding tanks is highly pursued by government and industry alike. The development and advancement of optical measurement technologies have increased environmental VOC monitoring capabilities and are applied in many new monitoring methods. SOF is a method where optical spectroscopic technologies are used to directly speciate and quantify the chemicals present in a gaseous emission plume using the sun as a light source.

Because the SOF method uses the sun as a broadband light source, the target compound possibilities are limited only by the detection equipment and interferences. Depending on the spectrometer used, the SOF can detect many different gaseous species, even at the same time, including: ammonia, formaldehyde, VOCs, terpenes, vinyl chloride, CO, ethylene, ethylene oxide, hydrofluoric acid, (HF) hydrochloric acid, HCl, $CH_4$, $SO_2$, propane, propylene, and hydrocarbons up to $C_{15}$.[1,2] Due to the ease of mobility with the SOF method, the technique can be used in applications such as total CO columns of megacities, petrochemical industries, agriculture, refineries, ships, and volcanoes.[3]

Volcanic emissions research is a rich source of information on monitoring techniques to determine emission rates of fugitive gases in atmospheric plumes including SOF. Several measurement techniques have been employed to measure volcanic gases such as $SO_2$ (i.e., correlation spectrometer (COSPEC), DOAS, and DIAL). However, the SOF method was developed to improve volcanic activity forecasting capabilities because multiple gas species can be detected using passive FTIR, and direct flux measurements can be made based on movement of the instrument view through the emissions plume.[4]

Environmental applications of the SOF technique have previously focused on measuring fugitive VOCs from oil refineries and industry processes.[5] VOC gases emitted from these source types mostly consist of alkanes, alkenes, and some aromatic compounds.[5] These fugitive VOCs have historically been measured using the DIAL method.[6] The DIAL method, described in Chapter 3.2 of this Handbook, employs short laser pulses directed through the gas plume at different wavelengths to calculate mass flux measurements by multiplying the resulting concentration integrated over the plume cross section at different angles by the wind speed.[7] However, DIAL is rather complex and expensive relative to SOF and is not ideal for periodic regulatory monitoring.[7] In comparison to DIAL, the SOF technique uses solar broadband IR or UV/visible spectral radiation as the light source instead of a laser source, making the SOF method potentially more cost-effective, faster than DIAL, and easier to automate.[7] From the solar spectra, it is possible to retrieve the PIC (molecules/cm$^2$) of VOCs between the sun and the spectrometer.[8] Multiplying this PIC by the local wind speed results in the mass-flux of target VOCs through the area.

Agricultural application studies have established that the SOF method has a detection limit for measured hydrocarbons of 0.3 mg/m[2,3]. Similarly, in applications pertaining to refineries and leak detection, studies conclude that a point source emission of measured hydrocarbons at 0.5 kg/h can be measured 50 meters downwind with a precision of three percent and an accuracy of 30 percent.[1] For simple sources and several traverses ,it has been found that the accuracy can be better than 10 percent. Under more complicated conditions, with emissions occurring from a complex structure with an unknown plume lift, larger systematic errors will occur, primarily due to uncertainties in assessing the plume lift and the associated wind field. Uncertainty in the wind speed in more complex terrain and wind stability can be 15 – 30 percent. Consequently the accuracy in the SOF method depends on the amount of error associated with the ancillary meteorological measurements which can dominate the uncertainty in the emissions results.[1,3]

### 3.3.1 General Description of Approach

There are three main components to the SOF system: an FTIR spectrometer to capture solar radiation spectra, a sun tracker to maintain instrumental orientation to the solar zenith, and a GPS for accurate measurement location relative to the gas plume.[5] Two different sun tracker configurations are shown in Figure 3-8, and a rough schematic of the entire SOF system is provided in Figure 3-9.

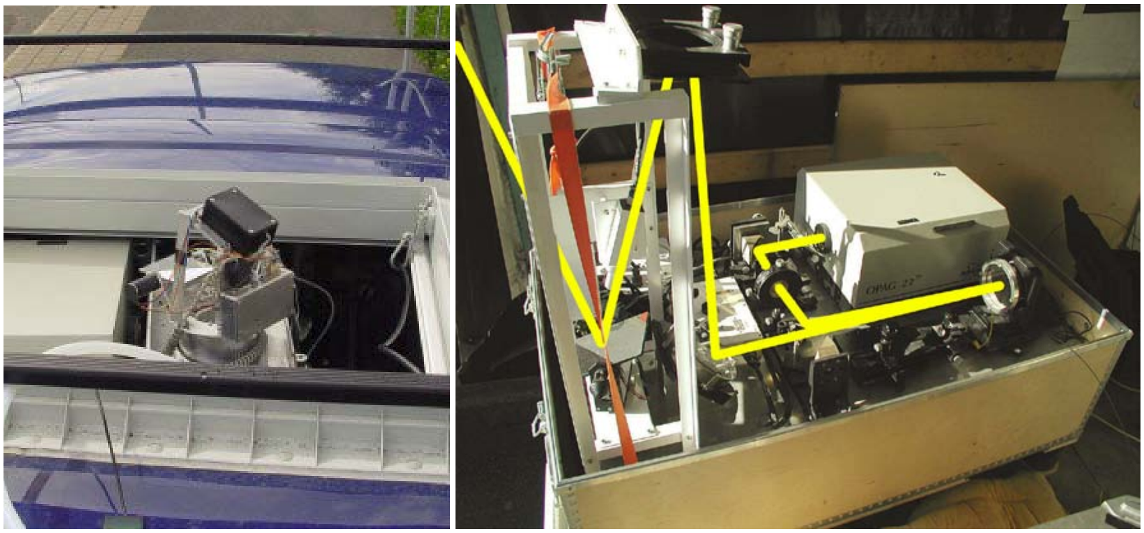


**Figure 3-7. Solar tracker configurations.** The left panel shows the sun tracker and mirrors extending out the top of the vehicle to maintain orientation[9] while the right panel shows the path of the sunlight (in yellow) first striking the mirror of the solar tracker before being directed into the spectrometer.[5]

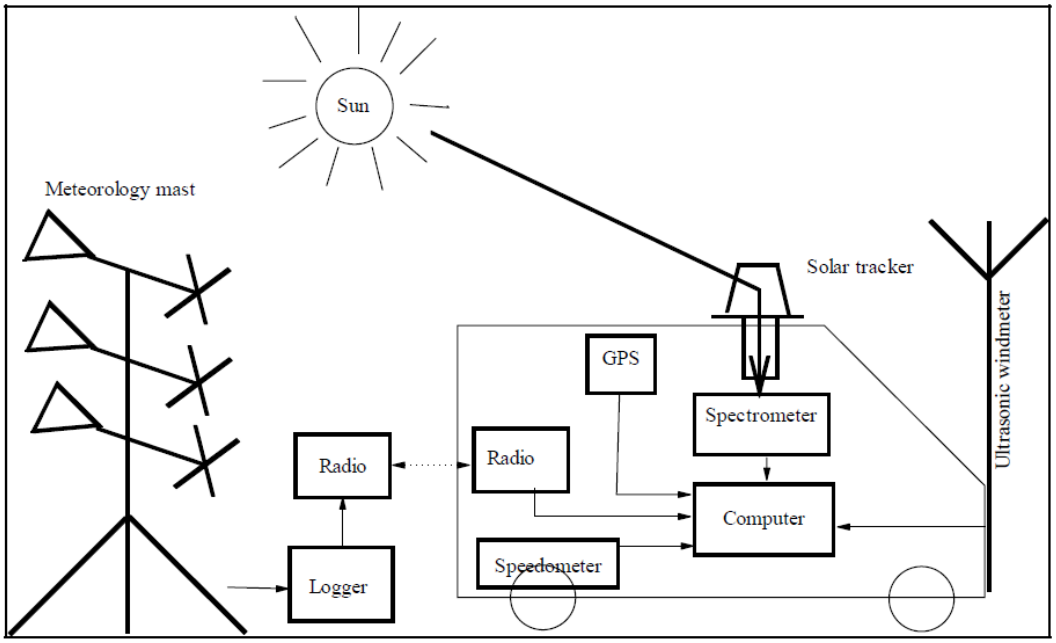


**Figure 3-8. Rough overview of a mobile SOF system.**[1]

Flux measurements are difficult to measure in an atmospheric plume using stationary instrumentation. Figure 3-10 illustrates the capture of a complete plume transect for better constrained source flux calculations using the SOF technique. In the illustration of Figure 3-10, the solar tracker maintains the solar zenith, reflecting the solar light into the spectrometer regardless of the vehicle position as it traverses the width of the plume column.[1,9] As previous methods combined stationary plume measurements with dispersion modeling or tracer gas ratios, the mobile aspect of the SOF technique allows for direct measurements of gaseous flux emissions assuming that the full plume column is captured.[3]

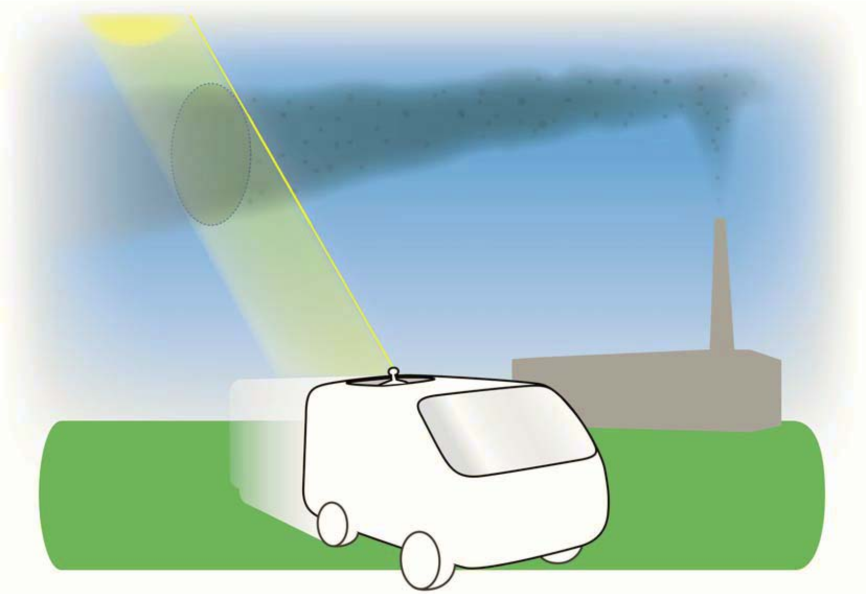


**Figure 3-9. Solar Occultation Flux method** The instrument is placed in a vehicle which travels across the gas plume to capture the plume cross-section (Illustration Karin Sjöberg).[9]

Each gaseous compound absorbs energy at different wavelengths, usually more than one, depending on vibrational and rotational excitement within the molecule. Fundamentally, this measurement is a passive form of IR or UV spectroscopy. Therefore, each compound has its own “signature” of bands from which energy may be absorbed. Each band is highly selective, with virtually no absorption occurring outside of a specific wavelength. When molecules intercept the solar radiation before it reaches the detector, the molecular absorption is seen as an extinction (or occultation) of the solar radiation intensity at the signature wavelengths. Once a compound has been identified, its spectrum can also be used to measure the compound’s concentration because the amount of radiation absorbed from the solar ray is proportional to the concentration of the compound in the sample or open path. According to the Beer-Lambert law, there is a linear relationship between absorbance and concentration as shown in Equation 1.

$$A = \varepsilon c l \qquad \textbf{Eq. 1}$$

Where: $A$ = absorbance intensity

$\varepsilon$ = absorption coefficient
c = sample concentration
l = sample path length

SOF measurements acquired from within the plume column are divided by a reference (background) spectrum recorded outside the plume. This prevents any background sources—such as the atmosphere, inherent structures of the sun, and instrument functionality—from interfering with accurate measurements.[5] Multiple species are simultaneously evaluated for each spectral acquisition using non-linear, least-squares fit routines with published reference spectra from HITRAN 2000, Pacific Northwest National Laboratory, National Institute of Standards and Technology, and Hanst library databases.[7] The resulting spectra are evaluated for gas species absorption intensity to determine concentration using Equation 13 below. Equation 13 is a transmutation of the Beer-Lambert law where spectral line intensity is related to gas concentration.[8]

$$I_m(v) = I_L(v) \cdot \exp\left( -v^4 \cdot \alpha_R \cdot L_R - \alpha_{Mie} \cdot L_{Mie} - \sum_i \sigma_i(v) \cdot conc_i \cdot L_i \right) \quad \textbf{Eq. 13}$$

Where:

$I_m(v)$ = light intensity at each wave number ν after it has passed through the gas.
$I_L(v)$ = light intensity at each wave number ν for the light source.
$\sigma_i(v)$ = absorption cross section ($cm^2$/molecule) of the gas with index i.
$L_i$ = path length where the gas with refractive index i is present.
$conc_i$ = concentration of the gas with refractive index i (molecules/$m^3$).
$\alpha_R$, $L_R$ = Rayleigh scattering which occurs on particles and molecules with a size smaller than the wavelength of the light.
$\alpha_{Mie}$, $L_{Mie}$ = Mie scattering which occurs on particles and molecules with a size about equal to the wavelength of the light.

The PIC is determined by evaluating spectrum measurements individually along a path of continuous analysis to derive the line-integrated concentration represented by each spectrum. GPS measurements taken at the beginning and end of each measured spectrum determine the surface length represented by the spectrum. This value is then multiplied by the line-integrated concentration and summed over the total plume transect to calculate the PIC. An example of this process is shown in Figure 3-11.[8] Multiplying this PIC by the local wind speed results in the mass-flux of target VOCs through the measurement plane (Equation 14).

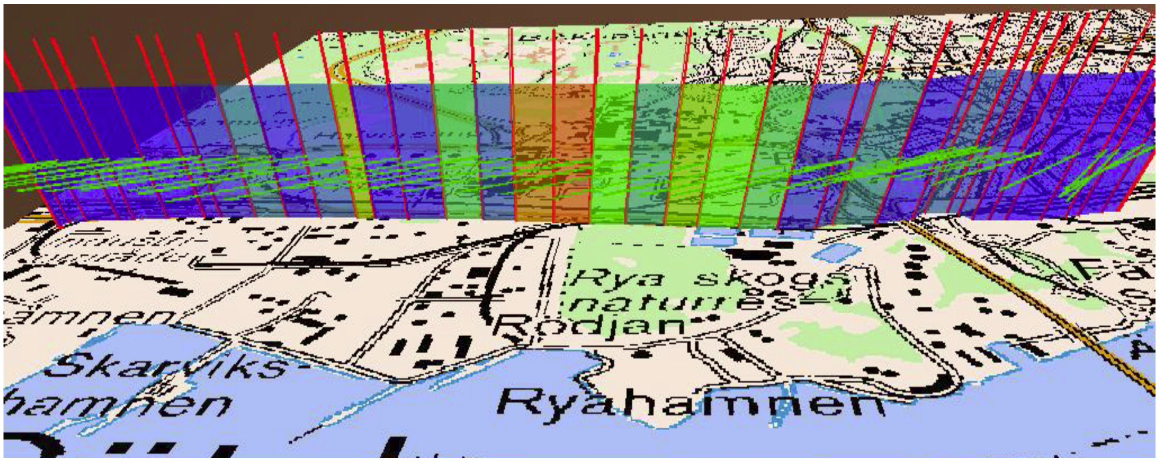


**Figure 3-10. An example of path-integrated calculations determined from SOF measurements.** The red lines indicate individual spectra, the area between the red lines correspond to the surface-integrated concentration, and the green lines illustrate the wind direction vector.[8]

As shown in Figures 3-10 and 3-11, SOF mobile measurements are made crosswind and near downwind (about 0.5 to 3 km) from the target source. The total cross-sectional mass of key species is obtained by summation of all the species measurements over the plume traverse.[10] The process of determining the emissions flux is summarized mathematically by Equation 3 below. This equation shows the prominence of the average wind speed variable in the flux determination, thus explaining that more accurate wind speed measurements yield less overall flux measurement error.[5]

$$Emission = \int_{x_1}^{x_2} column(x) \cdot \overline{u}\ dx \qquad \textbf{Eq. 14}$$

Where:

*column(x)* = the total column at distance x across the plume

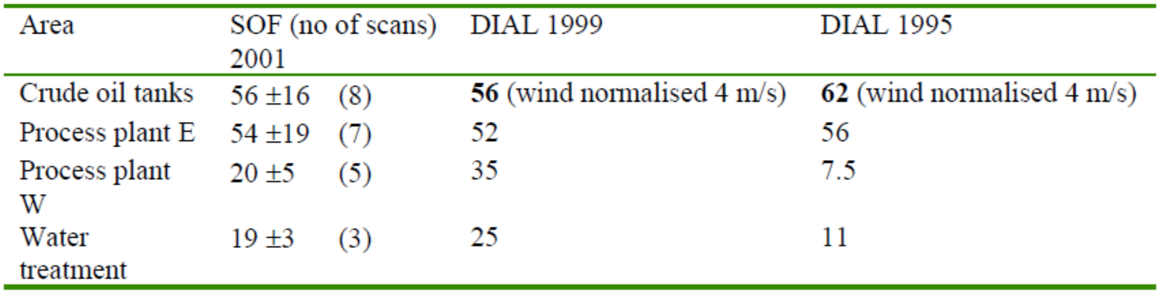
$\bar{u}$ = average wind speed for plume at plume height

The assumption that the wind speed is equivalent to the gas plume velocity is necessary for both the DIAL and SOF techniques as this value is required to calculate the mass flux by multiplying the plume velocity by the cross-sectional integrated gas concentration.[5] Therefore, both methods will be susceptible to the same measurement error associated with the wind speed parameter.

### 3.3.2 Verification/Validation Studies

Because DIAL measurements are a standard method of monitoring VOC emissions at refineries in Europe, Fransson and Mellqvist (2002)[5] performed a comparison between the results of the two different methods during a 2001 SOF field study. SOF measurements by this group were made at the Preem refinery in Göteborg, Sweden for four days starting August 1, 2001. DIAL emissions measurements from 1995 and 1999 were recalculated with the annual average wind speed to compare with the 2001 SOF results; this comparison is shown in Table 3-7.[1]

**Table 3-7. SOF technique VOC emissions compared to DIAL.[1]**



| Area | SOF (no of scans) 2001 | | DIAL 1999 | DIAL 1995 |
|---|---|---|---|---|
| Crude oil tanks | 56 ±16 | (8) | **56** (wind normalised 4 m/s) | **62** (wind normalised 4 m/s) |
| Process plant E | 54 ±19 | (7) | 52 | 56 |
| Process plant W | 20 ±5 | (5) | 35 | 7.5 |
| Water treatment | 19 ±3 | (3) | 25 | 11 |

Although comparing environmental data that is up to six years apart is not recommended, the data in Table 3-7 shows that the emissions measured using SOF are generally consistent with previous DIAL results.[1] Regardless of the amount of measurement error imposed on the SOF result by wind speed approximations, all SOF measurements either match a previous DIAL result exactly or are very near to the average of the 1995 and 1999 DIAL results.

Annual VOC emissions from the Port of Göteborg were reported to be 1100 tons in 1999 and 2300 tons in 1995 by Shell Global Solutions and Spectrasyne, respectively. Fransson and Mellqvist (2002) used an SOF system mounted on a ship to calculate an annual flux of 1770 tons per year based on two measurements—that were not temperature corrected—performed on the same day in August 2001.[5] Again, more than two measurements on a variety of days distributed throughout the year would yield a more accurate snapshot of annual emissions. Nonetheless, a result of 1770 tons per year is almost the exact equivalent to the average of the reported 1999 and 1995 values and is a satisfactory result, validating the application of SOF to measure oil refinery gas emissions flux.

The results from two tracer gas correlation studies plus other validation studies were discussed by Mellqvist et al. (2005) and Kihlman (2005).[3,8] During these studies, sulfur hexafluoride ($SF_6$) was released in an open field (Åby Field) and from the roof of a crude oil tank at the previously mentioned Göteborg refinery in May and June of 2002. Each experiment released $SF_6$ at a rate of about 2.0 kg/h. Tables 3-8 and 3-9 display the results from the open field and tank roof tracer experiments, respectively.[8] As shown in Table 3-8, tracer correlation measurements over four days in an open field validated that the SOF method can accurately retrieve emissions flux measurements within ± 20 percent error; whereas crude oil tank measurements done on a single day shown in Table 3-9 yields emissions flux measurements with up to 50 percent error. It is worth noting that the crude oil tank measurements were conducted in the near field as opposed to a medium or far distance from the emission source in addition to being conducted on only one day. Figure 3-12 illustrates a combination of both scenarios where a tracer experiment in an open field resulted in 72 percent agreement (within 20 percent) of SOF measurements to the actual tracer gas emission, while other measurements can vary up to 50 percent from the actual emission.[1] When averaged together, however, the resulting value is within three percent of the actual emission rate.

**Table 3-8. Summary for measurements on the Åby field, 2002.** [3,8]

| Day | Emitted $SF_6$ | Calculated Average (kg/h) | Number of Accepted Traverses | Ave. Wind Speed (m/s) | Ave. Wind Direction | Error |
|---|---|---|---|---|---|---|
| May 22 | 1.92 | 2.3±1.3 | 4 | 4.9-8.6 | 152˚-169˚ | 20 % |
| May 23 | 1.97 | 2.2±0.6 | 15 | 3.9-5.6 | 120˚-142˚ | 10 % |
| June 03 | 1.97 | 1.6±0.9 | 16 | 2.7-5.3 | 235˚-273˚ | -20 % |
| June 04 | 1.89 | 2.0±1.4 | 9 | 5.9-7.8 | 152˚-191˚ | 5 % |

**Table 3-9. SOF traverse done on day 24-June 2002.** True emitted $SF_6$ was determined to be 2.0 kg/hr.[3,8]

| Time | Emission $SF_6$ | Ave. Wind Speed (m/s) | Ave. Wind Direction |
|---|---|---|---|
| 12:45 | 3.1 | 6.5 | 252˚ |
| 12:54 | 1.8 | 7.2 | 252˚ |
| 13:05 | 1.3 | 6.0 | 259˚ |
| 13:17 | 2.7 | 7.5 | 253˚ |
| 13:29 | 3.1 | 5.4 | 255˚ |
| 13:56 | 5.2 | 7.4 | 264˚ |
| 14:05 | 3.7 | 7.4 | 251˚ |
| 14:24 | 2.6 | 7.3 | 262˚ |

| | | | |
|---|---|---|---|
| 14:31 | 3.4 | 6.5 | 260° |
| Average | 3.0±1.1 | | |

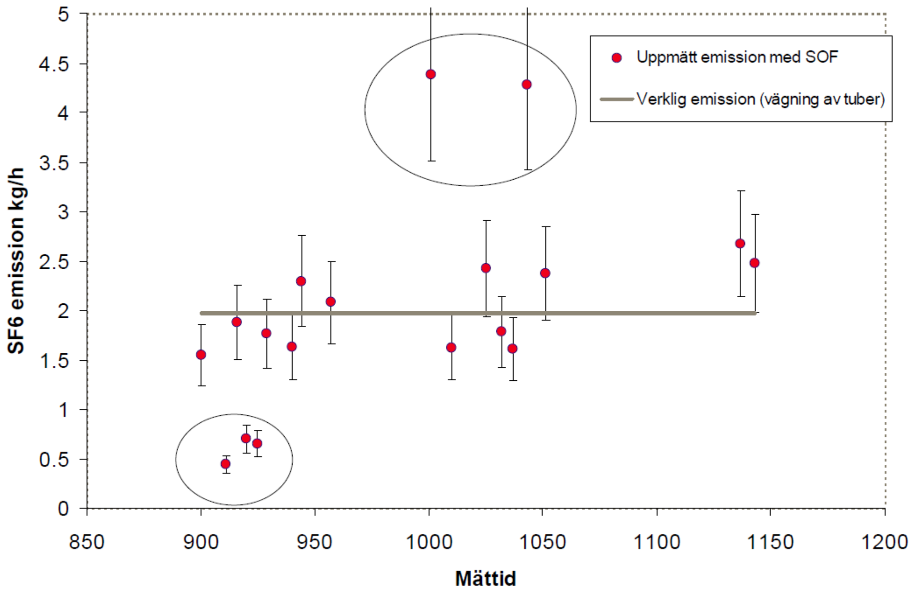


**Figure 3-11. Tracer gas/SOF experiment measuring SF$_6$ emissions in an open field over time of day.** SOF measurements are depicted as red circles while the actual emission release rate is drawn as a grey line.[1]

The results from these studies indicate that multiple measurements in the mid to far field over multiple days are more representative of overall flux rates and reduce the amount of total measurement error. Having enough data points to calculate a statistical average is ideal for eliminating stochastic variances caused my micrometeorological disturbances.

### 3.3.3 Typical QA/QC

In order to make emissions measurements with the SOF method, the operator needs to have meteorological information (distributed in height, surface, and time); a road to travel along that is relatively smooth, downwind of the emissions source and near perpendicular to the wind direction; stable wind conditions; and an unobstructed view of the sun. In addition to meeting these requirements, measurements can be further validated by calculating the expected and observed amounts of measurement error.

The total amount of measurement error associated with SOF results is comprised of statistical and systematic error. Statistical error is described with a normal distribution as this type of error accounts for the natural, stochastic behavior of atmospheric variability. Fransson and Mellqvist qualified this amount using Equation 15 below.[5]

$$Statistical\ error = \sqrt{\sigma_c{}^2 + \sigma_{S/N}{}^2 + \sigma_u{}^2 + \sigma_\theta{}^2 + \sigma_{uH}{}^2} \quad \textbf{Eq. 15}$$

Where:

$\sigma_c$ = Relative error in the absorption cross section (5-10 percent).

$\sigma_{S/N}$ = Relative S/N error and spectral interference effects.

$\sigma_u$ = Relative uncertainty in the wind speed estimation. Typically 15-20 percent for a single plume scan and 5-8 percent for 8 scans.

$\sigma_\theta$ = Relative uncertainty in the total column due to the variability in the wind direction over a plume scan.

$\sigma_{uH}$ = Relative uncertainty in the wind speed due to uncertainties in the estimation of the plume height.

Fransson and Mellqvist (2002) estimated the $\sigma_{S/N}$ (or instrumental precision) from the standard deviation in the baseline of the plume column measurements during their VOC emissions study at oil refineries.[5] This value was about 0.3 to 0.6 mg/m$^2$, which corresponded to an uncertainty of 0.3 percent to 6 percent for a total column measurement of 100 to 10 mg/m$^2$. They also estimated the relative uncertainty in the total column due to wind direction variability ($\sigma_\theta$) to be about 1 percent to 7 percent for eight scans. Fransson and Mellqvist (2002) state that there is an 8 percent effect on column measurements when a plume is traversed at a 90° angle and that this error amount is sensitive to the ability to make measurements perpendicular to the wind direction such that angles of 80° and 70° contribute errors of 16 percent and 25 percent respectively.[5] Relative uncertainty in the wind speed due to plume height estimate uncertainties ($\sigma_{uH}$) are discussed in more detail below.

Using Equation 15, Fransson and Mellqvist (2002) calculated the statistical error assuming various typical scenarios encountered during measurements. The results displayed in Table 3-10 show that even between best and worst case scenarios, the statistical error amount varies from 14 percent to 19 percent.[5] To determine the total error for a measurement, these statistical error values need to be added to the amount of systematic error.

**Table 3-10. Estimation of statistical errors for the SOF measurements**; assuming 8 plume scans.[5]

| Estimation | Comment | $\sigma_c$ | $\sigma_{S/N}$ | $\sigma_u$ | $\sigma_{uH}$ | $\sigma_\omega$ | Statistical 1σ error |
|---|---|---|---|---|---|---|---|
| Best Case | Strong plume 100 mg/m$^2$,<br>90° traversing angle* | 5% | 0.3% | 5% | 12% | 1% | 14% |
| Worst Case | Weak plume 10 mg/m$^2$,<br>80° traversing angle* | 10% | 6% | 7% | 12% | 5% | 19% |
| Typical Case | Intermediate plume,<br>80° traversing angle* | 5% | 3% | 5% | 12% | 7% | 16% |

* Angle between the wind and the direction of movement when traversing the plume.

Output data recovered from SOF measurements do not contain information related to the height of the gas plume in the atmosphere. Plume height estimates are inferred from the corresponding temperature and pressure broadening of the spectral absorption lines if measured from high-resolution (< 0.125 cm$^{-1}$) spectra.[8] This is the largest identified source of error in the SOF method, assuming that the entire plume cross-section is captured and that the total amount of absorption equals the total concentration. As mentioned previously, the integrated concentration of the target species is multiplied by the mass average wind speed of the plume at plume height to determine the emissions flux; therefore, accurate wind speed measurements are crucial to minimizing total flux measurement error. Increasingly complicated site conditions, such as a complex emissions source structure with unknown plume lift, will have larger amounts of systematic error.

Mellqvist (2004) states that measuring emission plumes with heights above 20-30 meters at distances greater than 500 meters downwind are ideal conditions to ensure minimal systematic errors associated with the wind field.[1] This is because of the increased predictability of the wind height profile that corresponds to the plume height while making measurements under these criteria. Figure 3-13 below shows the wind speed profile with height over developed land if a 5 m/s wind velocity was measured at 10 meters. It is clear from this figure that wind speeds above 20 meters from the surface during typical SOF conditions (i.e. sunny, which implies an unstable atmosphere) are past the major inflection point in the profile and have a less prominent height gradient with increasing height. Fransson and Mellqvist (2002) made an estimation from data acquired at 17 meters that ± 5 meters is a realistic amount of error associated with the plume height estimation which translates to about 12 percent error in the wind speed measurement.[5] Further studies into the amount of error in the wind field by height concluded that about 14 percent systematic error in retrieved flux measurements with a 15 percent standard deviation between measurement days is expected.[6]

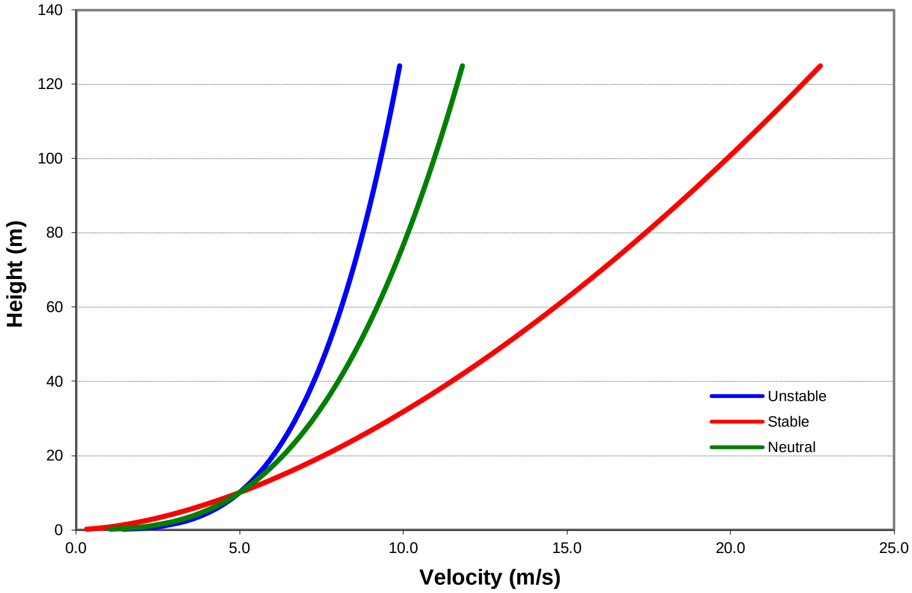


**Figure 3-12. Wind velocity profiles by height.**

### 3.3.4 Siting Concerns

Since the instrumentation for the SOF method is mobile during analysis, issues originating from the site location are few. Most notably, the path of solar light through the plume to the instrumentation needs to be unobstructed, and excessive vibration during the mobile operations can cause noise originating from the interferometer. Therefore, measurement capabilities are constrained to particular weather conditions. In addition to the surrounding area of the mobile path, the line of sight needs to be clear of trees, shrubbery, and buildings that might impede the view of the sun. Moreover, the mobile path needs to be smooth and near perpendicular to the wind direction to minimize the amount of method error.

SOF measurements are more representative in the mid and far field downwind from the emissions source where the plume is well-mixed and the solar transect of the plume will be higher in the wind profile. Plume traverses must be able to capture the entire plume cross-section plus open atmosphere on either side of the plume such that a representative background can be collected. In addition, the measurement site must have a limited amount of well-traveled roads and other transportation operations in close proximity.

### 3.3.5 Strengths and Limitations

One major advantage to the SOF method is also a disadvantage: the solar broadband light source. Using FTIR, the SOF method can precisely and accurately speciate and quantitate multiple gaseous emissions simultaneously using one instrument. The caveat to this advantage is that the method can only do so during specific climatic conditions (high sun and steady winds).[4] Other strengths and limitations associated with the SOF method are presented in Tables 3-11 and 3-12, respectively.

**Table 3-11. Feature strengths of using the SOF method.**

| Feature | Strength |
|---|---|
| Direct Measurement | Increases measurement accuracy by reducing uncertainty. |
| Passive Light Source | Decreases instrumental complexity for field operations and reduces amount of scattering errors in the UV. |
| Broadband Light Source | Multiple species detection over a wide range of wavelengths. |
| Better Mobility | More suitable for frequent field application. |
| Lower technical complexity | Decreased cost and easier field application. |
| FTIR Detection | Higher specificity and better signal-to-noise (relative to DIAL). |
| Measurements during Sunny conditions | Corresponds to unstable meteorological conditions where wind gradients due to convection are smoothed out. |

**Table 3-12. Feature limitations of using the SOF method.**

| Feature | Limitation |
|---|---|
| Interferogram Vibration Sensitivity | System requires vibration reduction platform and a smooth mobile path. |
| Wind Speed Error | Calculations based on wind speed measurements inherently add uncertainty due to the stochastic, uncontrollable, and highly variable nature of wind speed. |
| No Plume Height Measurement | Uncertainty of plume height increases measurement error from wind speed term. |
| Solar Light Source | Inappropriate to make measurements in the presence of clouds. |
| "Open Eye" Detection and Roadway Path Restriction | Difficulty in separating emissions sources that are close together. |

### 3.3.6 References

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## 3.4 Tracer Gas Correlation

Challenges measuring emissions flux from a fugitive or area source such as a landfill, agricultural waste, industrial fugitive, waste water or oil and gas production source include spatial, temporal variability of the emission sources and the uncertainty of the measurement technology. Emissions source variability includes defined and undefined sources like unknown emissions points, delocalized emissions sources, the timing of periodic or episodic emissions, and atmospheric, diurnal, seasonal and process variations in emission flux. Defined fugitive sources cover smaller areas (i.e., less than 1 square kilometer down to a square meter) allowing emissions points to be identified for direct measurement. Undefined area sources typically originate from large areas (i.e., greater than 1 square kilometer). For either defined or undefined emissions sources, the sources of uncertainty cause emissions flux to be difficult to measure and model. Tracer gas correlation provides a ground based technique that can be applied to both well-defined area emissions sources and undefined fugitive sources.

Tracer correlation involves a common practice of measuring pollutant emission rates while releasing a known concentration of a tracer gas. The subsequent simultaneous measurement of this tracer gas and the pollutant of interest downwind from the release provide sufficient information to determine or validate the emissions flux measurements. The release of a known concentration of a tracer gas assists in tracking the plume and sources or sinks of the pollutant of interest into the plume. The majority of tracer gas studies use cell-based technologies, like CRDS and FTIR to measure the tracer gas and the compound of interest. However, some studies are expanding the use of tracer gas release to open-path techniques to evaluate the distribution over a large area.

### 3.4.1 General Description of Approach

The use of a tracer gas is common in projects that aim to study emission fluxes. Normally, emission fluxes are obtained by calculating fluctuations in the vertical and horizontal component of the wind ($w'$), fluctuations in the tracer gas concentration (n’) over either time (T) or space (S) and surface roughness. The following equations provide a method for determining experimentally the surface fluxes of tracer gases by measuring meteorological parameters near the surface as well as the vertical gradient in the concentration of these gases.[1] Equation 16 shows how to calculate vertical fluxes of a tracer gas and basically means that the summation of changes in wind and tracer gas concentrations over the time or distance it takes the gas from release to detection is the emission flux.

$$F = \frac{1}{T(orS)} \int_0^{T(orS)} w'n'\,dt \qquad \textbf{Eq. 16}$$

To calculate horizontal fluctuations, one must consider wind velocity (u(z)) near the surface, friction velocity ($u_*$), which is a measure of the drag exerted by the wind on the surface, and the displacement height (d). The displacement height results from the canopy acting as a displaced lower boundary layer and whose value is typically 70-80 percent of the canopy height.

$$u(z) = \frac{u_*}{k} \ln\left[\frac{z-d}{z_0}\right] \qquad \textbf{Eq.17}$$

Where: k is the von Karman constant and is equal to 0.4 and $z_0$ is the surface roughness.[1]

Using the Tracer Correlation Approach to measure total emissions over a large subject area is an alternative to standard dispersion modeling when attempting surface boundary layer methods as weather conditions are too difficult to measure or estimate accurately. Thus, releasing a tracer gas with known concentration and rate of release assists in calculating emission rates. Assuming that meteorological conditions affect both the tracer gas and the analyte in the same way, the analyte emission rate is calculated from simultaneous measurements of the tracer and analyte gas far downwind from the plume emission source using Equation 18.

$$Q_m = \frac{Q_t \Delta C_m}{\Delta C_t} \qquad \textbf{Eq. 18}$$

Where: $Q_m$ is the analyte emission rate; $Q_t$ is the tracer gas release rate, $\Delta C_m$ is the concentration above the background of the analyte observed in the plume (plume – background concentration); and $\Delta C_t$ is the concentration above background in tracer concentration in the plume, relative to the background.

A tracer gas is released from a canister to transport in the plume along with the analyte. Usually a tracer gas is chemically stable with no significant sources or sinks while in transport and is expected to fully mix in the plume. Typical tracer gas field measurements are performed with cell-based instruments that utilize specific spectroscopic properties to characterize chemical species like CRDS and FTIR. These instruments can be setup as stationary or mobile to obtain one-point or multiple-point samples. Figure 3-14 shows a cartoon of tracer gas release setup. Normally, the tracer gas is released upwind from the source and the cell-based instrument is downwind from the source to measure a well mixed plume with the analyte and tracer gas.

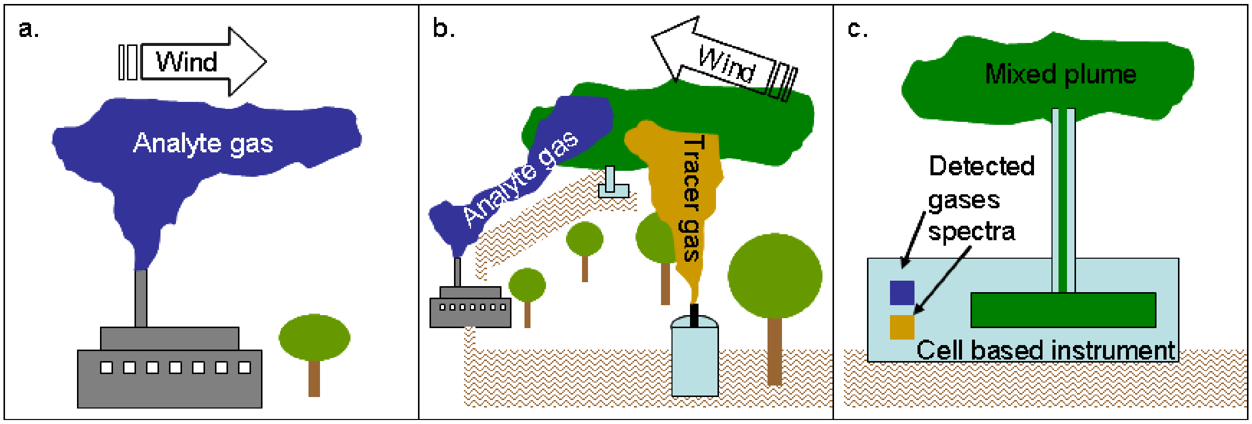

**Figure 3-13 Tracer gas release setup cartoon.** Panel a shows the source with the analyte gas been released to the ambient air. Panel b shows the tracer gas been released and pushed by the wind into the analyte gas area to mix in the plume. Panel c shows the cell-base instrument measuring gases, analyte and tracer.

### 3.4.2 Verification/Validation Studies

Because the tracer gas release concentration is known and there are no significant sources or sinks, the mixing ratio should remain constant while in transport. Thus, verification of correct measurements by the cell-based instrument is done by measuring the known tracer gas concentration with accuracy. Validation is performed depending on the DQOs of the study. Normally, the study will say how accurate the retrieval of the known concentration of tracer gas must be to obtain emission fluxes and the quality of the meteorological parameters to measure. Following are some examples of studies performed to verify and validate the use of tracer gas to calculate emission fluxes, utilizing CRDS and FTIR.

#### Tracer gas characterization using CRDS: Twin Bridges Recycling and Disposal Facility study[2,3]

Mobile plume tracer dilution measurements were taken from May 18 – 21, 2009, driving on Interstate 36 and East Main Street in Danville, IN. Acetylene ($C_2H_2$) tracer gas was released from four sites located on or near to the center of each landfill facility. The stationary measurements for gas tracer correlation measurements, the analyzer was located in the plume sufficiently downwind of the $CH_4$ source and $C_2H_2$ tracer gas release locations for plumes to be well-mixed and appear as a single point emission source. During the measurements, the analyzer is stationary and continuously measures $CH_4$ and $C_2H_2$ concentrations. The CRDS Picarro Model G1203 $CH_4$-$C_2H_2$ analyzer used in this study is a self-contained, stand-alone unit that provides continuous measurements of $C_2H_2$ and $CH_4$ concentrations, ambient temperature, and analyzer location (via high resolution GPS). The $C_2H_2$ tracer gas was released from bottles through a mass flow controller (Alicat Scientific MC Series 16-Bit Mass Gas Flow Controller, model MCP-50SLPM-DIO-SG-30PSIA/5m) which was attached to the gas cylinder line to ensure a constant release rate throughout the study. The range of tracer gas release for the test was 20 L/min to 40 L/min. The release rates were automatically recorded. The following parameters were measured: horizontal wind speed, horizontal wind direction, temperature, vertical and lateral turbulence, and net solar radiation. Results from the study shown in Figure 3-15 demonstrated that the Tracer Correlation Approach is able to measure highly correlated, (correlation coefficient of 0.84) tracer gas to $CH_4$ emissions over a wide range of atmospheric and dispersion conditions.

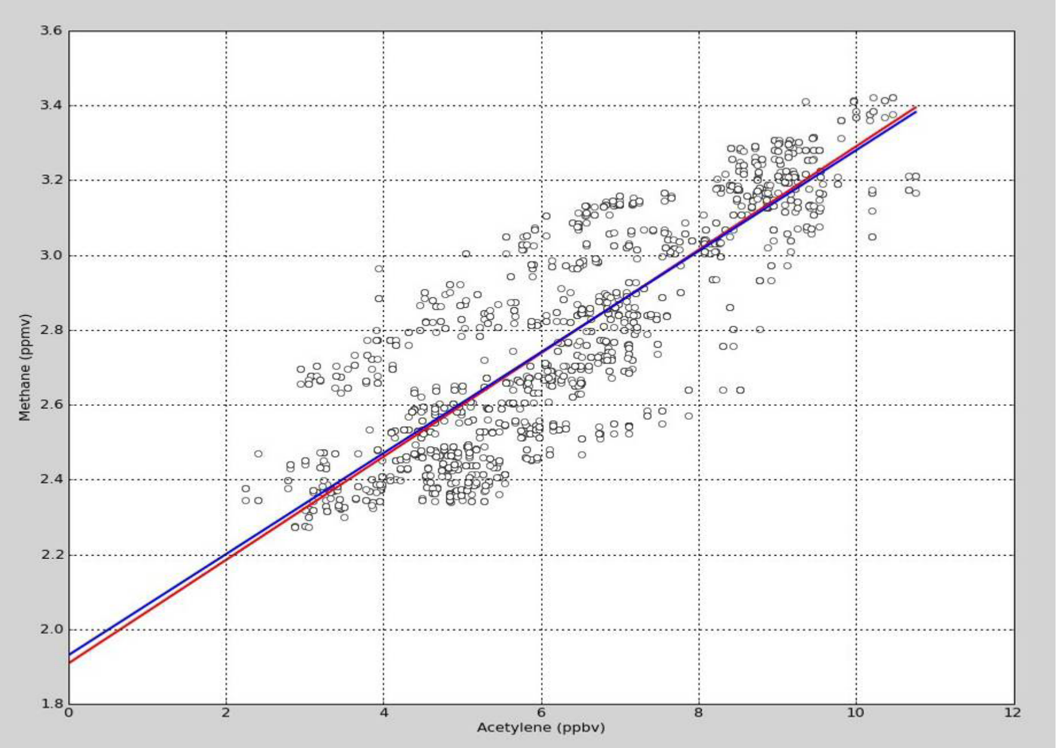

**Figure 3-14 Methane concentration verses acetylene concentration Tracer gas characterization using FTIR: Samuelsson et al., 2001[4]**

FTIR was used to obtain time resolved concentration measurements of methane in the downwind plume of a landfill and $N_2O$ was selected as the tracer gas. FTIR spectroscopy is an optical technique allowing a wide spectral region to be recorded simultaneously, thus the detection of $CH_4$ and $N_2O$ could be done at the same time. Low detection limits and sensitivity of ppb were obtained using a long optical path. In this study, a medium resolution (1 $cm^{-1}$) FTIR spectrometer was connected to an optical multiple-reflection gas cell with an adjustable pathlength, ranging from 9 to 107 meters. Normally a pathlength of 96 m was used, selected to optimize optical throughput and absorption levels. The system was built into a well-tempered and mechanically stabilized optical bench and was located in a normal transport van. The recorded spectra were analyzed by multiple-regression techniques, fitting synthetically derived calibration spectra of all present compounds. $CH_4$ was analyzed in the wave number region at ~2950 $cm^{-1}$, and $N_2O$ around 2200 $cm^{-1}$.[4]

The methodology used to couple the concentration measurements to an actual emission is the Time Correlation Tracer method (Eq. 19). $N_2O$ was released in a controlled way from the methane emitting area by use of several point sources distributed over the landfill. $N_2O$ mixed with the emitted $CH_4$ in the landfill plume, and the emission rate was derived by time resolved analysis of the $CH_4$ and tracer concentrations collected far enough downwind the landfill. The part of the time series where the concentrations correlate, can be assumed to have its origin in the area where the tracer is released, and can be quantified using the known tracer flux according to Eq. 19.

$$Q_{CH_4} = Q_{Tracer} \bullet \frac{C_{CH_4} \bullet M_{CH_4}}{C_{Tracer} \bullet M_{Tracer}} \qquad \textbf{Eq. 19}$$

Where: C corresponds to the concentration in the mixing ratio and M to the molecular weight.

A correlation plot between tracer concentration and analyte helps to identify if sampling is within the plume or outside. If the slopes of the concentration curves coincided as the plume swept in and out of the location, it could be assumed that the tracer release simulated the entire methane release. An estimate of the total landfill emission was obtained using the slope of the regression line of methane. Depending on the meteorological conditions, it is estimated that an accuracy of 15-30 percent in the emission estimate is achievable.[4]

### 3.4.3 Typical QA/QC

This section describes the QA/QC steps that pertain to the applications described above. QA/QC for applications steps normally depend on pre-determined data quality indicators that address the project unique objectives. The technology used for the applications presented above have their own QA/QC associated to specifics of the instruments. If interested in the technology QA/QC for OP-FTIR, refer to section 2.1; for OP-TDLAS, refer to section 2.2; for UV-DOAS, refer to section 2.3; and for CRDS, refer to section 2.6.

When using the tracer gas approach, it is important to consider a gas that is stable and has low reactivity; thus, no significant sources and sinks that will alter the released concentration or, at least, good knowledge of the background concentrations. Spurious releases of tracer gases that reach 20 percent of the known concentration are easily identified CRDS, but anything below is probably not significant. Background levels of the analyte gas must be known to track the boundaries of the plume and to determine whether the measurements are in or out of the plume. The time delay between release and arrival at measurement site needs to be carefully determined before total methane emission results are considered acceptable. Flow rate of tracer gas released from all bottles be carefully monitored and recorded if total methane emissions from a landfill are to be accurately determined. A comparison (correlation plot) of analyte and tracer gas measurements taken close and far away from the source provide a correlation coefficient and the percentage difference or the total emission rate at close and far locations. Large percentage differences indicate insufficient overlap of the analyte plume and the tracer gas plume during stationary tracer-dilution measurements.

### 3.4.4 Sitting Concerns

In general, concerns regarding the use of tracer gases to obtain emission fluxes are associated with possible loss or gain of the tracer gas while in transport, not fully mixing within the plume, and changing weather conditions (wind speed and direction for the most part). Other concerns are associated with calculations of the emission fluxes when estimating surface roughness or assessing vertical and horizontal fluctuations.

### 3.4.5 Strength and Limitations

A key strength of using a tracer gas correlation technique is the ability to determine if varying weather conditions affect the calculation of emission rates, which is possible by knowing release rates and concentration. An additional strength is that emission rates are calculated within 15-30 percent precision. However, stationary and mobile setups have their challenges in terms of logistics, location and whether available roads are near perpendicular to the flow of the plume. Other limitations are cost of tracer gases cylinders and transportation of these, as well as changing weather conditions affecting the calculation of emission rates. Tables 3-13 and 3-14 summarize these strengths and limitations.

**Table 3-13. Tracer Gas Correlation Strengths**

| Feature | Tracer Gas Correlation Strengths |
|---|---|
| Addresses Meteorology | Can determine if varying weather conditions affect the calculation of emission rates. |
| Relatively precise Method | Emission rates are calculated within 15 - 30 percent precision. |
| Portable instrumentation | Field units are lightweight, rugged, and relatively easy to transport and operate. |

**Table 3-14. Tracer Gas Correlation Limitations**

| Feature | Tracer Gas Correlation Strengths |
|---|---|
| Meteorological Concerns | Changing weather conditions affect the calculation of emission rates. |
| Logistical Concerns | Location and the availability of roads perpendicular to the plume create difficulties. |
| Related Expenses | Tracer Gas cylinders can be expensive to purchase and ship. |

### 3.4.6 References

1. Brasseur, G. P., J. J. Orlando and G. S. Tyndall. 1999. Atmospheric Chemistry and Global Change. New York, NY: Oxford University Press.

2. Eastern Research Group, Inc. 2010. Evaluation of Large Area Methane Emission Source Methods: Mobile and Stationary Plume Measurements Using the Tracer Correlation Approach. Final Report for U.S. EPA. May 30.

3. Crosson, E. and S. Tan. 2009. Report on the work undertaken at the Twin Bridges Recycling and Disposal Facility under an agreement with Eastern Research Group, Inc. August 1.

4. Samuelsson, J., G. Börjesson, B. Galle and B. Svensson. 2001. The Swedish landfill methane emission project. http://www.fluxsense.se/reports/Sardinia2001paper.pdf

## 3.5 Backward Lagrangian Stochastic Inverse-Dispersion model

### 3.5.1 General Description of Approach

Identifying and quantifying gaseous emission rates from a fugitive or area source to air (e.g., emissions from an open air waste lagoon, confined animal feeding operations, biofuel production facilities, landfills, etc.) is difficult. Several meteorological techniques are available (e.g., eddy covariance and flux gradient), but they involve complex instrumentation (e.g., concentration measurements at many heights and fast-response concentration sensors). They also require the measurement site to be on a flat location. There is a separate technique that can be used called the Integrated Horizontal flux that can be used for non-flat locations, but can only be used for small source areas because it requires vertical and horizontal concentration measurements for the entire plume. Because many emission sources do not meet these criteria, other techniques must be implemented to estimate emission rates.[1]

The limitations of traditional meteorological techniques can be addressed by using an atmospheric dispersion model to calculate the emission rate indirectly. The “inverse-dispersion” technique provides an accurate and economical alternative for measuring emissions. The technique uses a mathematical model of the dispersion of target gas from an emission source to a downwind location, so that a downwind concentration measurement can establish the emission rate.[1, 2] This approach has the advantage of requiring only a single concentration measurement and basic wind information, with substantial freedom to choose convenient measurement locations. Theoretically, the technique assumes idealized wind conditions; however, with careful selection of measurement locations, inverse-dispersion modeling can provide a simple means of calculating emissions even in non-ideal conditions.[1, 2]

Figure 3-15 illustrates the bLS model for estimating emission rates. An area source of known configuration emits gas at a uniform, but unknown, rate $Q$ in kilograms per meter$^2$ per second (kg/m$^2$/s). A time-average gas concentration $C$ is measured at point $M$ within the plume. The gas concentration $C$ can be determined by ORS measurement methods such as open-path FTIR, TDLAS, UV-DOAS, or point measurements such as CRDS. With a model prediction of the ratio of concentration at *M* to the emission rate $(C/Q)_{\text{sim}}$, the emission rate can be inferred as indicated in Equation 20, where $C_b$ is the background pollutant concentration.[1,2,3,4,5]

$$Q = \frac{C - C_b}{\left(C/Q\right)_{SIM}} \qquad \textbf{Eq. 20}$$

The inverse-dispersion model calculates the ratio of the concentration rise to the emission rate $(C/Q)_{\text{sim}}$ at point *M*. This is the basis of the inverse-dispersion modeling technique. It requires only a single pollutant concentration measurement (assuming $C_b$ is known) with flexibility in the choice of the measurement location *M*. The accuracy of the technique rests on the calculation of $(C/Q)_{\text{sim.}}$[1]

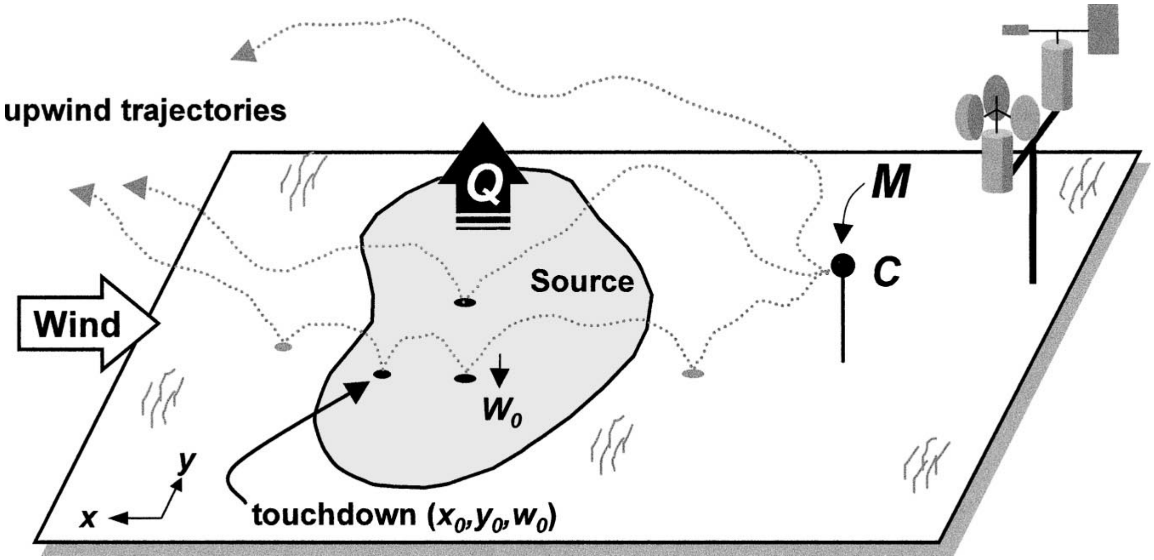

**Figure 3-15. Illustration of an inverse-dispersion model for estimating emission rate *Q*.** Average concentration *C* is measured at point *M* downwind of the source (after Flesch et al., 2004).

One of the most accurate models used to calculate $(C/Q)_{\text{sim}}$ is a bLS model. The model follows the path of a fluid element (e.g., “particle”) from a given location backward in time in order to determine its origin. Particles in the context of the model are considered to be carriers. Depending on the trajectory, the particle may or may not sample the target source (i.e., "touchdown" within the source). The term Lagrangian indicates that the model releases individual particles and follows them along their paths through the air, rather than performing calculations at fixed locations in space. Stochastic indicates that the model mimics the random, turbulent motion of each particle. As these particles travel through the air, they move through different regions of interest. Some particles will touch down in the source region and move to the concentration sensor, contributing to a measured concentration increase.[1,2,6]

For surface area emission sources, all that is needed to invoke the bLS model to calculate $(C/Q)_{\text{sim}}$ are wind statistics, which can be determined from a few key meteorological observations.[1,2] In general, the bLS inverse-dispersion method of modeling emissions is cost-effective, requires only a single field measurement of *C*, and, under the conditions described in this section, generates emission rates with accuracy adequate for many applications.

## Backward LS Dispersion Model for Calculating $(C/Q)_{\text{sim}}$

In a bLS dispersion model, the upwind trajectories of model particles are calculated from location *M* (Figure 3-1). The important information from the backward trajectories is the set of "touchdown" locations ($x_0$, $y_0$) where particles impact the ground, and vertical "touchdown velocities" at impact $w_0$. From the set of trajectories, Equation 21 is used to calculate $(C/Q)_{\text{sim}}$ by summing the reciprocal of $w_0$ for touchdowns occurring within the source boundary.[3]

$$\left(C/Q\right)_{sim} = \frac{1}{n} \sum \left| \frac{2}{w_0} \right| \qquad \textbf{Eq. 21}$$

The variable *n* is the total number of computational particles released from *M* and the summation covers only touchdowns within the source area. In the bLS model, thousands of trajectories are calculated upwind of the prevailing wind conditions.

Commercially-produced software developed and distributed by WindTrax (Thunder Beach Scientific, Nanaimo, Canada) is available to solve bLS equations. WindTrax combines the bLS model with a graphical interface, allowing sources and sensors to be conveniently mapped (see Figure 3-16).[6] To calculate unknown source emission rates and/or concentrations, WindTrax requires the following information:

- upwind and downwind gas concentrations ($C_b$ and C),
- wind statistics (e.g. wind speed and wind direction),
- roughness of the surface ($z_o$), and

- stability of the atmosphere near the ground (Monin-Obukhov stability parameter, L).

The latter wind statistics may be obtained from sonic anemometry or estimated within Windtrax. If concentration is measured in units of ppm or ppb, air temperature and pressure are also needed (pressure is often estimated from elevation). The particle models used in WindTrax are time-independent, so the input data must be values averaged over a period of time, typically 15-30 minutes. This averaging eliminates the unpredictable variability due to turbulence in the atmosphere on short time-scales. Conversely, if the averaging time is too long, the more gradual diurnal variation typical of the surface layer will not be resolved.[6]

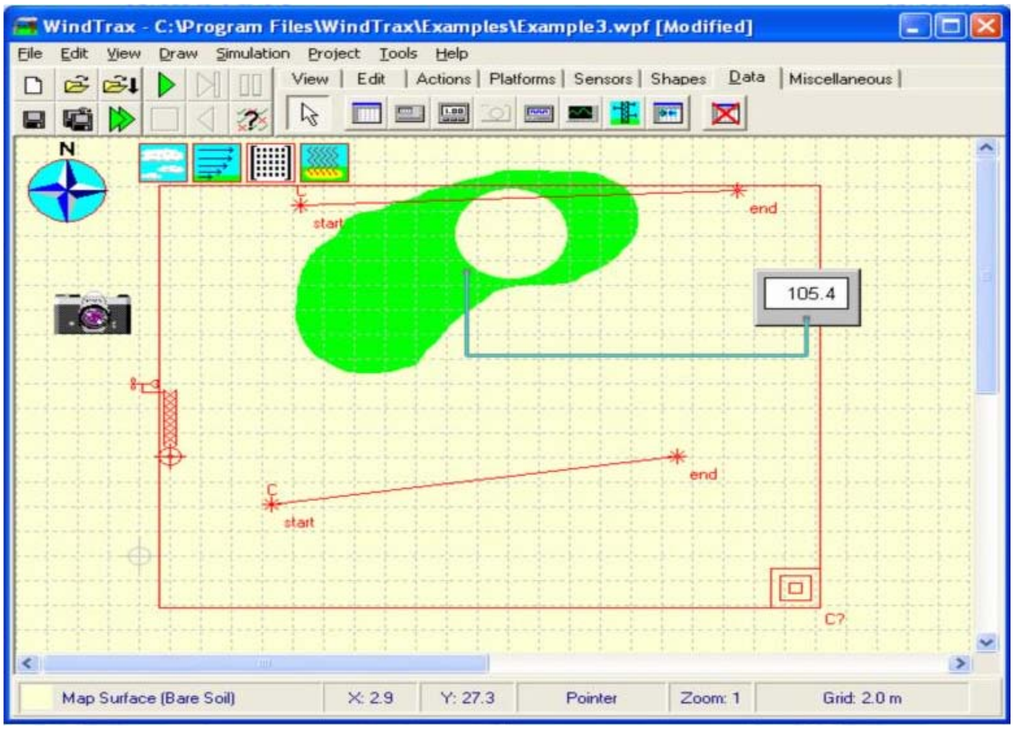

**Figure 3-16. Illustration of the WindTrax bLS Modeling Software Graphical Interface**

## bLS Model Output Units

Open-path ORS (OP-ORS) measurement techniques such as open-path FTIR or TDLAS can be used to make the concentration measurement in a bLS application. Also, point-measurement sensors such as closed-cell sensing techniques including CRDS or cell-based FTIR could be used to measure plume concentration. These techniques provide concentration in units of ppm or ppb over the optical path used in the measurement (ppm*m or ppb*m). Specific temperature and pressure data are needed to convert to absolute concentration (i.e. g/m$^3$), which is used to determine the mass emission rate. The bLS calculation itself produces an emission rate (flux), $Q_{bLS}$, with units of kg/m$^2$/s (for example), but sometimes the emission rate is multiplied by the source area and $Q_{bLS}$ becomes an area integrated emission rate with units of kg/s or kg/h.[1,2,8,9,] (Harper et al, 2010)

### 3.5.2 Verification/Validation Study

One of the foremost leaders in the development and application of bLS modeling as it applies to gaseous emissions for large area sources is Thomas Flesch at the University of Alberta, Canada. He conducted numerous studies using bLS. In this section, a bLS field trial entitled *Deducing Ground-to-Air Emissions from Observed Trace Gas Concentrations: A Field Trial* is summarized as an example of the bLS application.[1] The summary briefly illustrates how bLS can be used and describes the quality of data that can be generated by the model.

In 2004, Flesch *et al.* reported a bLS field trial experiment in which the inverse-dispersion technique was used to determine $Q_{\mathrm{bLS}}$ in an ideal surface-layer setting. A small area source from which methane was released at known rates over a wide range in meteorological conditions was constructed. An open-path laser measured the methane concentration $C$ at positions located up to 100 meters downwind of the source as shown in Figure 3-17. A corresponding $(C/Q)_{\mathrm{sim}}$ was calculated using a bLS dispersion model, and the resulting estimate of the emission rate $Q_{\mathrm{bLS}}$ was compared with the known $Q$. The study objectives were the following: 1) to quantify the accuracy and uncertainty in $Q_{\mathrm{bLS}}$ in an ideal setting; 2) to probe the conditions under which a dispersion model based on the Monin–Obukhov similarity theory (MOST) performs poorly; and 3) to validate an experimental system (i.e., source, sensors, bLS model) for examining the robustness of a bLS estimate in non-ideal conditions.

#### Flesch *et al* Conditions and Setup

The experiment took place over a 6-day period in May and June of 2001, near Ellerslie and Edmonton, Alberta, Canada, in a large clover field. From a meteorological perspective, the site was nearly ideal—wind conditions were uniform, temperatures were not high enough to cause thermal convection of the plume out of the measurement window, and the nearest significant change in land cover was more than 500 m from the source.

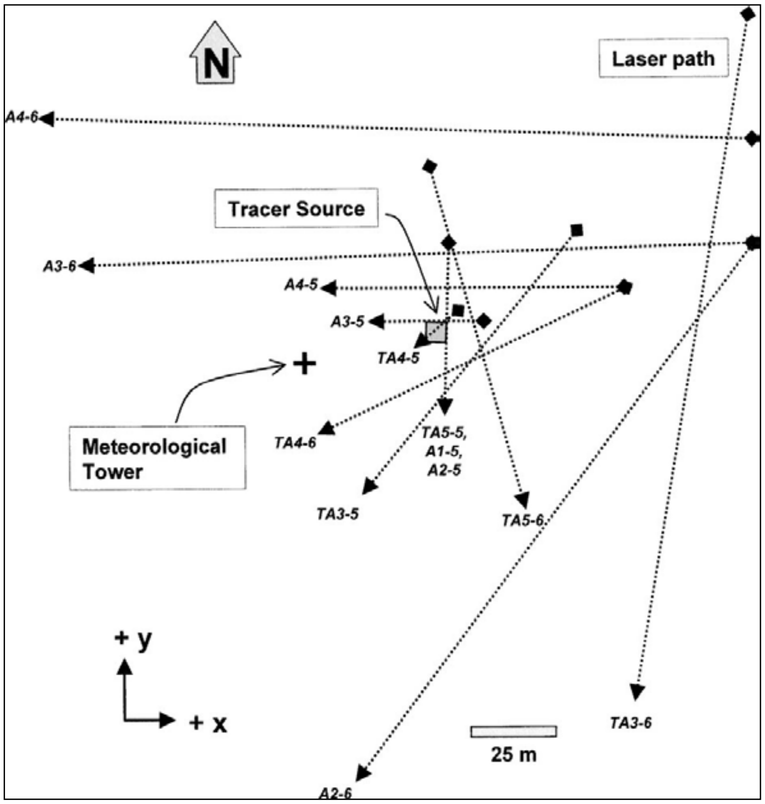

**Figure 3-17. Map of the laser paths used in the 2004 Flesch *et al* experiment.** The shaded square on the map represents the methane tracer source and the large "+" symbol indicates the location of the meteorological tower with the 3-D sonic anemometer.

A synthetic source was created to approximate a 6 m × 6 m square area source. A manifold was constructed out of polyvinyl chloride pipe and 36 0.5 mm outlet holes were drilled into the pipe. A gas cylinder was coupled to the manifold through a regulator and rotometer (flow meter). The methane tracer gas was released from high pressure cylinders (99.1 percent purity) at flow rates between 15 and 50 L/min. Each release lasted from 1 to 3 hours. The cylinder valve was manually adjusted to maintain a nominally constant flow rate, with adjustment occurring every minute or two as necessary. The study estimates a 10 percent uncertainty in $Q$ due to flow-rate fluctuations, observer error in reading the rotometer scale, and gas temperature variability inside the rotometer (which affects calibration).

Methane concentration measurements were made using two open-path lasers. A focused beam from a tunable IR laser was aimed at a distant retro-reflector where it was reflected back to the receiver optics and a detector. The returning signal strength was proportional to the methane concentration $C$ between the laser and the retro-reflector. Background methane $C_b$ was periodically measured at 1.95 ppm. This measured value closely correlated with the average methane background for the Edmonton region during the experiment, as routinely measured by the provincial government of Alberta. The laser units recorded $C$ every minute. These readings were averaged into 15-, 30-, or 120-minute values. To convert concentrations from ppm to absolute concentration in $g/m^3$, Flesch *et al* used the measured air temperature and atmospheric pressure for each observation period. A 3-D sonic anemometer was placed on a tower approximately 2 m above ground and was used to determine values of $u^*$, $L$, $z_0$, and $\beta$ for the bLS simulations. Figure 3-3 shows a map of the various laser paths (dotted lines with arrows) used in the experiment. The code at the tip of each arrow head is associated with the experimental conditions for that trial measurement. The wind direction on the map is from west to east and all laser measurements were made downwind.

### Flesch *et al* Results and Conclusions

When periods of extreme stratification or MOST failure were excluded, the bLS inverse-dispersion technique diagnosed the strength of a small ground-level source with small bias (mean value of $Q_{bLS}/Q$ within 2 percent of unity). Poor results were excluded when using a laser path over the source because this study dealt with a very small area source, meaning the laser path was not always sufficiently inside the plume. In situations involving a large source area, a measurement location above the source is acceptable. The period-to-period variability in $Q_{bLS}$ was acceptably small (standard deviation of $Q_{bLS}/Q$ is approximately 0.2). Using path-integrated values of $C$ enhanced the accuracy with which $Q_{bLS}$ was diagnosed and rendered the experimental procedure very forgiving (the laser could be positioned without being overly concerned about changing wind direction). Based on their field experiments, Flesch *et al* made several recommendations for using a bLS model to infer $Q_{bLS}$ from an area source in an ideal surface layer problem.

- PIC measurement is preferable to a point measurement because PIC gives results that are integrated over the entire beam path length and are, therefore, more representative than a single point source measurement of the actual plume concentration.

- Distance of the detector from the source should be small enough that the concentration rise over background is accurately measured.

- Meteorological averaging times of 10–30 minutes are ideal for calculating concentration and meteorological statistics. Shorter averaging times may not capture an equilibrium state of the atmosphere, a requirement for the application of MOST.

- Periods of extreme atmospheric stability should not be used in assessing $Q_{\mathrm{bLS}}$. An example of an acceptable limit is $|L| \geq 10$m.[4]

- Disregard periods of low $u^*$ (e.g., $u^* \leq 0.15$ m s$^{-1}$).

Because all testing sites are different, the bLS modeling system has been used with varying site locations such as ponds, pastures, and other scenarios. More detailed information pertaining to different types of site locations can be researched in the literature.

### 3.5.3 Typical QA/QC

In order for the bLS dispersion model to accurately calculate the emission rate of a source, it is important to verify that the instrumentation used to collect concentration data for target analytes is appropriate for bLS calculations. QA/QC guidelines identified in this protocol or other EPA literature for the particular technology used should be followed for optimal performance.

Because meteorological measurements are required for the bLS model, it is important to ensure that accurate measurements are used. Meteorological data collected on site should be collected with appropriate instrumentation, and applicable EPA guidelines should be followed. More information on the technology used to collect meteorological data can be found in the *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements, Version 2.0.*[7] If meteorological data are not collected on site, it is necessary to ensure that the data used in the bLS model are taken from a trusted source and the location of the measurements is near the test site. Wind stability determination requires more sophisticated instrumentation (e.g., 3-D sonic anemometer, or temperature measurements at two or more heights).

WindTrax and other modeling software are available for use to perform the bLS calculations. A simplistic data set with known results should be used to test the modeling software before use for field data calculations to verify the software's performance. In special cases, it may be preferable for the user to develop its own software program to perform the necessary calculations, though it is not recommended for accurate modeling. It is necessary to test any and all bLS software on a simplistic data set for which the results are known to verify the software. In all cases, input data should be reviewed for accuracy and possible transcription errors.

### 3.5.4 Siting Concerns

The bLS dispersion model utilizes the average wind and turbulence statistics of the atmosphere to calculate $(C/Q)_{\text{sim}}$. MOST states that the statistical properties of the wind in the surface layer are determined by a few key parameters: the friction velocity $u*$, which is determined by the vertical transport of horizontal momentum near the surface; the Obukhov stability length $L$, which quantifies the stability of the atmospheric surface layer; the surface roughness $z_0$, which is related to the height of the plants, soil, or other elements covering the ground; and the wind direction $\beta$. In the field, these parameters are typically determined with the use of sensors such as a 3-D sonic anemometer. The placement of sensors relative to sources can have a major effect on the quality of the predictions generated by the models. If no concentrations are measured downwind of a source, then emission rates cannot be determined.[6] Upwind ambient gas concentrations must also be measured that may be coming onto the site. The variability of wind direction might cause some simulations to fail while others succeed. When multiple unknown sources are present, the calculations are very sensitive to sensor placement and measurement error. Where flow obstacles such as buildings or fences are present, measurements are often better made further downwind of the source, well away from the obstacles; at least 10 obstacle heights downwind is a useful rule of thumb for measurement location (M) placement.[1,2,5,6]

If the source and the detection point $M$ lie within a horizontally homogeneous surface layer, the application of the bLS dispersion model technique is reasonably straightforward. Many agricultural and environmental source estimation problems potentially fit this category. These problems may include emissions from small soil research plots, feedlots, ponds, industrial grounds, and so on, that often occur in circumstances for which it is reasonable to assume that the local wind flow is uniform (i.e., wind statistics that do not deviate more than 10 to 20 percent from their spatial average over the region from source to detector).[1]

An important advantage of bLS models is the ease with which complex source shapes can be handled. One of the most important factors affecting model error is the size of the regions of interest through which the analytes travel. As more analytes travel through a given region (i.e., the concentration is higher), more samples of the region are taken and the model error is reduced. In practice, this means that the larger the source target, the smaller the error, and conversely, the smaller the source target, the greater the potential for error.[1,2,3] However, the use of bLS within large source areas has been very successful in many studies.

### 3.5.5 Strengths and Limitations

bLS models have several advantages over Gaussian and Eulerian models. For example, bLS models are more physically valid than Gaussian models, which do not incorporate wind shear or other meteorological information, and they do not require artificial diffusivity, as do the Eulerian models for convective transport. A traditional disadvantage of bLS models is their computation time requirements, which can be several orders of magnitude larger than those required to solve algebraically reduced Gaussian models or even Eulerian models. This is because of the need to calculate thousands of unique atmospheric trajectories. However, modern computing power has rendered this problem to be of limited concern for most users. Tables 3-15 and 3-16 summarize the bLS model's strengths and limitations in more detail.

**Table 3-15. bLS Model Strengths**

| Feature | bLS Strengths |
|---|---|
| Simplicity of Measurements | Requires only a single concentration measurement – as opposed to many concentration measurements made in the vertical or horizontal plane of the plume [1,2] |
| | Flexible input requirements: various wind statistics can be entered into software and |

| | |
|---|---|
| | needed conversions are done internally; different types of concentration observations are possible (point or line average).[6] |
| Siting Concerns | Substantial freedom to choose convenient measurement locations [1,2] |
| | Handles complex source shapes and sizes with relative ease [1,2,6] |
| | Can be used in locations with wind disturbances if sensor locations are chosen with care [2] |
| Economical | An economical alternative for determining emissions [8,9] |
| | Free downloadable software available online [6] |

**Table 3-16. bLS Model Limitations**

| Feature | bLS Limitations |
|---|---|
| Meteorological Concerns | Assumes idealized atmospheric conditions [1,2,3,4,5,6] unless particular care is taken with sensor placement.[9] |
| | Rapid atmospheric changes or extreme stability invalidate MOST and cause $Q_{\mathrm{bLS}}$ estimates to be inaccurate [1,2] |
| Training Requirements | Some judgment required to identify poor measurement locations (for both winds and concentration). Poor measurements locations (e.g., close to building) can significantly impact the quality of emission calculation.[1,2,6] |
| | Some basic experience or training in micrometeorology or atmospheric gas transport is required to generate high-quality data from the bLS model |
| Siting Concerns | When multiple unknown sources are present, the calculations are very sensitive to sensor placement [1,2,3] |
| | Where flow obstacles such as buildings or fences are present, measurements are often better made further downwind of the source, well away from the obstacles [1,2] |
| Time Limitations | Can require lengthy computational time [6] |

## 3.5.6 References

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# 4.0 Ancillary Data Collection

Ancillary data used with ORS measurements may include information from a variety of sources. Examples of ancillary data are meteorological measurements, process or site-specific emissions information, off-site sources or sinks of emissions. Emission flux requires both measurement data and meteorological data to complete dispersion calculations and flux calculation validation. Emissions factors can be determined using ORS measurements with the addition of source-specific process information or activity factors. Mobile ORS measurements require GPS data to complete emission flux calculations. Source attribution based on ORS measurements requires site-specific process and interference information on each of the upwind stationary sources to validate the identification of the source generating the emissions of interest. Information on the type and use of ancillary data is described in this Chapter.

## 4.1 Meteorological Measurements

Meteorological conditions at the site of optical remote measurements are an important component of many of the ORS applications. Please note that in-depth description of meteorological measurements information can be found in Volume IV of EPA's QA Handbook series.[1] Quality of the meteorological parameters measurements is as important as the quality of the optical remote sensing results used in emissions flux calculations. The quality of meteorological parameters measurements includes topics such as:

- Meteorological tower siting and setup,
- Wind speed (horizontal and vertical) and direction,
- Relative humidity and dew point,
- Temperature,
- Solar radiation and
- Atmospheric pressure.

Historical meteorological parameters measurements are important to the applications of ORS measurements because emission rates from open sources are affected by ambient conditions (e.g., high wind speed over the source can increase the emission rate). If the ORS data is intended to evaluate exposure or determine emissions factors, the ultimate use of the ORS measurements should include evaluation of how well the meteorological conditions encountered during the ORS test compare to the annual average meteorological conditions for the sampling site. Ideally, the ORS test report summary includes data or commentary that addresses the representativeness of the meteorological conditions. The meteorological conditions recorded during the ORS test can be compared to the historical trends for a site. If site-specific meteorological measurements are not available, current local conditions can be compared to the average statistics available from the nearest National Weather Service (NWS) monitoring station. If there is more than one NWS station in close proximity to the measurement site, then the comparison should be made against the average measurement of the NWS stations.

Wind stability is often important to ORS measurements and refers to atmospheric turbulence. Atmospheric stability or turbulence is the vertical and horizontal transportation of an air mass. Atmospheric turbulence is the collective differences between small-scale air motions driven by winds that vary in speed and directions for a given parcel of air. Measurements that lead to wind stability account for convection, diffusion, buoyancy, rapid variation of pressure and wind velocity. Turbulence is responsible for mixing the atmosphere and is what distributes water vapor, particulate matter and gases.

However, one does not measure or calculate turbulence directly to assess atmospheric turbulence; instead we examine the atmospheric stability and the potential for vertical and horizontal transport, as well as mixing while in transport. Vertical and horizontal transport is normally associated with atmospheric stability (although it is important to note that wind speed will play a major role in the horizontal plane).[2,3,4]

A practical use for “wind stability” or turbulence for ORS measurements is to examine atmospheric stability and assess the atmosphere’s potential to mix and transport (vertically and horizontally). Another concept that is associated with “wind stability” is surface roughness as it relates to topographical and landscape variability. Determining if one is under stable or unstable atmospheric conditions is an important step in evaluating when conditions are appropriate for sampling, depending on the objectives of the measurement application. For example, the combination of vertical and horizontal wind speed and direction with solar radiation can be used to determine the atmospheric stability class of the air parcel by stability categories shown in Table 4-1 (Pasquill-Gifford stability categories).[5] These stability categories can be used as a quality indicator for representative ORS measurements.

### 4.1.1 Meteorological Station Siting

Typically, the terrain associated with an optical remote monitoring measurement program is complex only to the extent that the local elevation provides an elevated or depressed land area with sloped sides. A properly located meteorological monitoring station should provide meteorological measurements for an entire facility.  For facilities or sites that exceed one square mile in area, an additional meteorological monitoring station may be required for each additional square mile of area to obtain accurate local meteorological conditions.

The meteorological monitoring station must be positioned at the center of the highest point near the measurement location.  Winds blowing across the top of elevated areas and winds down the slopes contribute to transport and dispersion characteristics.  By positioning the station at the center and highest land mass near the measurement site (i.e., as determined by Google earth® map elevations), all upwind wind patterns sweeping the source emissions are represented in the wind speed and direction measurements.

Obstructions must also be considered during siting of a meteorological monitoring station.  There is no specified distance that the station must be positioned away from the measurement location.  By positioning the station at the center of the highest elevation, effect/contribution of the winds blowing over elevated areas are normalized with respect to the direction of the wind to the greatest extent possible.

Meteorological measurement sensors are typically setup or positioned at 2 meters above ground level.  The wind/speed direction sensors must be positioned so that they are located no closer than 2 meters from the temperature sensor.  Wind direction sensors are oriented to true north using a digital compass.

The timers/clocks on the meteorological station and the optical measurement equipment should be synchronized to allow the concentration data and meteorological data to be directly compared to the measurement data during post-processing.  If synchronization is not possible, the offsets between the clocks will be recorded at the start and end of data collection of each day in order to estimate any differences in the clock times or rates.

### 4.1.2 Horizontal Wind Speed and Direction

Compact weather stations[6] can provide all-in-one measurement of temperature, horizontal wind speed, and horizontal wind direction at optical remote measurement sites. The compact weather station typically uses 2-D ultrasonic measurement technology for wind speed. For wind direction measurements, the system automatically and continuously self-aligns to magnetic North. Typical units are capable of providing the following performance measurements:

- Wind speed range from 0-50 m/s with an accuracy of ± 0.5 m/s
- Wind direction range 0º - 360º with an accuracy of ± 5º

### Vertical Wind Speed and Lateral Turbulence

If wind stability is required as an ancillary measurement for the optical remote measurement application, then a 3-D Ultrasonic Anemometer may be necessary. Typical accuracy of this instrument is ± 2 degrees compass (1 to 30 m/s) or ± 5 degrees compass (30 to 40 m/s).

### 4.1.3 Relative Humidity

Relative humidity (RH) is important to ORS measurements because it provides information on water interference and predicting cloud or fog formation which interfere with many ORS techniques. Of the many atmospheric variables describing water vapor content in the atmosphere, RH is the most common for routine monitoring programs. RH is the ratio (percent) of actual vapor pressure of moist air to the saturation vapor pressure at the same temperature. A corollary measure, Dew-point temperature (or dew point) is the temperature to which a moist air parcel must be cooled to achieve saturation over water at constant pressure and water vapor content. RH and dew point are measured with electrical hygrometer, chilled mirror, or psychometer instruments. Typical accuracy of this equipment is ± 0.5% RH.

### 4.1.4 Temperature

Temperature is important because it determines or controls vertical transport of air which changes portion of the plume measured by the ORS technology. Standard meteorological equipment includes a thermocouple or thermistor temperature sensor with a temperature range -50ºC to +50ºC and an accuracy of ± 0.2ºC.

### 4.1.5 Net Solar Radiation

Net Solar Radiometer is required for wind stability determination. The typical accuracy of these units is > 90 percent of the Daily Total Solar Radiation.

### 4.1.6 Atmospheric Pressure

For air quality and meteorological purposes, atmospheric pressure is generally measured with mercury, aneroid, or electronic barometers. Most, if not all, of the atmospheric pressure sensors available provide analog or serial output that is directly interfaced with a data acquisition system.

A mercury barometer measures the height of a column of mercury that is supported by the atmospheric pressure. It is a standard instrument for many climatological observation stations, but it does not afford automated data recording.

An aneroid barometer consists of two circular disks bounding an evacuated volume. As the pressure changes, the disks flex, changing their relative spacing which is sensed by a mechanical or electrical element and transmitted to a transducer.

Most electronic barometers of recent design use transducers which transform the sensor response into a pressure-related electrical quantity in the form of either analog or digital signals. Current digital barometer technology employs various levels of redundancy to achieve long-term stability and accuracy of the measurements. One technique is to use three independently operating sensors under centralized microprocessor control. Even higher stability and reliability can be achieved by using three completely independent barometers, incorporating three sets of pressure transducers and microprocessors. Each configuration has automatic temperature compensation from internal-mounted temperature sensors. Triple redundancy ensures excellent long-term stability and measurement accuracy, even in the most demanding applications.[7]

## 4.2 Differential Global Positioning for Tracking Monitoring Locations

Global position information using a high resolution Differential Global Positioning System (DGPS) is required for mobile tracer correlation optical measurements and temporary stationary measurement locations.[8] Global position high resolution accuracy of <0.6 meters will meet most application requirements. The DGPS data collection includes a time stamped data stream acquired in real time. The DGPS clock should be synchronized with the measurement system clock to simplify measurement location and concentration information.

In the field coordinates measured by the DGPS, unit results should be compared to known Google Earth® coordinates for known geodetic marks as a quality check of the location system.

## 4.3 Collection of Process Information

Process information is site-specific data on factors or activities that affect the production or release of pollutants to be measured. Process parameters are measured indicators of process performance such as duct flow, operation temperature, or fuel use. The measurement of emissions rate, also called emission flux, may be extended beyond mass per unit air volume to determining emissions factors when the flux can be related to activity factors of the source. Emission flux is often converted into an emission factor to estimate air pollutant emissions from a process or activity (e.g., fuel combustion, chemical production). The simplest form of an emission factor is an expression of the mass of pollutant emitted per unit of activity generating the pollutant (e.g., pounds of particulate matter emitted per ton of coal burned). Typically, emission factors for stationary point sources are developed by dividing the source’s emission rate by an appropriate parameter (e.g., number of widgets made per hour) that represents the activity responsible for generating the emissions. Therefore, gathering process information related to production, chemical use, energy use, heat or power generation is important to assess the relative rates of pollution produced by a stationary source. Once process information is available, ORS flux measurements of open source activity can yield meaningful emission factors.

In developing emission factors for point sources, identification of the underlying activity that generates the emissions is typically straightforward. For example, particulate matter emissions from fuel combustion are a direct function of the type and amount of fuel burned. However, for open sources (e.g., landfills) the pollutant generation and emission release mechanisms tend to be more complex. This complexity can make the selection of appropriate underlying activity, emission precursor, or process parameter(s) for use as an emissions surrogate more difficult than for point sources. Consequently, emission factor developers should have a thorough understanding of the pollutant generation and emission release mechanisms for a given open source to accurately interpret the results from the ORS test and to properly apply the ORS data for emission factor development.

One strength of ORS techniques is measurement of fugitive emissions from open sources such as landfills, wastewater treatment systems, agriculture operations, and equipment leaks at petrochemical and industrial facilities. At landfills, wastewater treatment systems, and animal agriculture operations, fugitive emissions are generated by biological decay of organic matter present in the waste. The rate of biological activity is affected by ambient conditions (e.g., bioactivity increases with increasing temperature) and process parameters such as chemical conditions (pH, reduction/oxidation potential) in the waste. Pollutant emissions are also affected by site-specific parameters such as the process information on the configuration of the source and the process steps involved in handling and disposing of the waste. At petrochemical and industrial facilities, fugitive emissions from equipment leaks are a function of process information such as the type of equipment; the number of equipment components; the concentration and vapor pressure of pollutants in the in-service gas; and process parameters such as temperature and pressure. The complex transport and diffusion mechanisms, and the chemical/biological reactions inherent in certain types of open sources, mean that the emissions from the open source may not be easily related to an industrial process or activity. For example, an industrial process generates a liquid waste stream that is discharged to an open wastewater treatment system. Although the pollutant loading to the treatment system may be relatively constant over time, the emissions from the system may not consistently track the loading rate due to changes in the rate of pollutant formation caused by increases/decreases in process parameters of the treatment system such as temperature.

The output ultimately obtained from an ORS test is an emission rate in terms of mass of pollutant emitted per unit of time. For point sources, the activity typically selected for emission factor development has a time component such that the use of the activity in the denominator of the factor cancels out the time units of the measured emission rate. For example, the use of a boiler’s fuel feed rate (Mg coal/hr) as the activity converts the measured emission rate (g pollutant emitted/hr) into an emission factor in terms of g pollutant emitted/Mg of coal fired. The activity data selected for use in development of an emission factor based upon ORS measurements may or may not have a time component.

Simple emission factors for a specific site can be developed using the emission rate measured by one of several of the ORS technologies described in Chapter 2 and a characteristic activity factor related to the emissions factor of interest. However, the source characteristic is not necessarily a simple time-dependent activity independent of the site. The addition of site-specific or process-specific information improves emissions factors estimates. For example, a simple emission factor (kg of pollutant/$ft^2$ of landfill surface area) could be developed using ORS test data and the surface area of the landfill. However, because landfill fugitive emissions are also dependent on the type of cover and gas collection system (if applicable), the type of material contained in the landfill, the retention time of the material, and the size and number of landfill cells, the applicability of the simple emission factor to other landfills based solely upon surface area would be limited. A more refined landfill emission factor (e.g., in terms of mass of pollutant emitted/mass of pollutant generated) could be developed using the measured emission rate and an estimated pollutant generation rate, such as one calculated from the site specific biological decay model discussed in Section 2.4.4.1 (Municipal Solid Waste Landfills) of EPA’s AP-42, as the activity. This refinement (i.e., emission factor) would an intermediate estimate and more site-specific than the simple factor, yet less specific than uniquely measuring the emissions flux for every landfill of interest. The additional value of the process parameters necessary to utilize the decay model (e.g., pollutant generation potential of the waste, time since initial waste placement in the landfill) is less costly than multiple field sampling episodes at different landfills.

## 4.4 Attribution of Emissions to Source of Intent

Results from an ORS sampling episode can be used in a dispersion modeling analysis conducted in reverse. In dispersion modeling for point sources, the emission rate from the source is known and the concentrations at receptor points downwind of the source are estimated based on the release characteristics of the source (e.g., stack height, exit velocity, gas temperature) and the meteorological data (e.g., wind speed and atmospheric stability parameters) used in the modeling analysis. In ORS sampling, the sampling path or plane effectively serves as a downwind receptor and the emission rate from the open source is back-calculated based upon measured downwind concentrations and the wind speed and atmospheric stability data measured during the test. Consequently, the open source emission rate is directly dependent upon the ambient conditions encountered during the test.

The emission rates determined using ORS techniques can also be affected by background pollutant concentrations in the atmosphere surrounding the open source, and by how well the placement of the ORS instrumentation (e.g., transmitters, receivers, retro-reflectors) captures the area source emissions. Consequently, ORS data users should determine whether background concentrations were accounted for in the ORS measurements. Typically, background emissions are determined by measuring pollutant concentrations in sampling paths or planes located upwind of the emission source and subtracting those concentrations from the concentration values measured at the downwind locations. For assessing the effectiveness of the ORS instruments to capture the source emissions, the developer should review the placement of the ORS instrumentation, and any assumptions made regarding the prevalent wind direction, relative to the emission source to be measured. The ORS technique could be applied properly, but the configuration of the sampling equipment relative to the emission source and the prevailing wind direction may not adequately capture the source emission plume under varying meteorological conditions.

## 4.5 References

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# 5.0 Data Validation and Verification

This section provides information on validation and verification of remote optical measurements starting from field observation through test report review. The emphasis in this section is how an optical technology report recipient can evaluate and verify the quality of the reported data. Information is provided on how data quality indicators can be used to assess and verify optical monitoring data in the most general way.

Data review, verification, and validation are techniques used to accept, reject, or qualify data in an objective and consistent manner. Verification can be defined as the process of evaluating the completeness, correctness and conformance of a specific data set against the data quality requirements.[1] Verification can be done by examination and objective evidence that the final data meets specified QC recommendations or requirements and fulfills the data users' requirements.

Validation can be defined as a confirmation by examination and objective evidence that the particular recommendations for a specific intended use are fulfilled. The criteria for deciding the degree to which each data item has met its quality specifications should be described in an organization's site specific QAPP. The QAPP should clearly indicate the plan to meet the end user's DQO. The DQO process was described in Chapter 1 Section 1.4.

This data validation and verification section describes the techniques used to make assessments of the application of remote optical air methods to field measurements. In general, the initial assessment activities are performed both by persons implementing the environmental data operations and by personnel "independent" of the operation, such as post test data reviewers and the organization's QA personnel. The procedures, designated personnel, and frequency of assessment should be included in an organization's QAPP. These activities should occur prior to submitting the final data report and before they are used in models or emissions factors development. Field testers should verify results from a field test program before data users validate measurement results and use them to make decisions.

## 5.1 General Approach

Specific QC specifications for each optical technique are provided in the individual technology or applications sections in Chapters 2 and 3. The general information in this section can be used for most optical remote measurement projects. How closely a measurement represents the actual environment at a given time and location is a complex issue that must be considered during development of the sampling design. Testers check (verify) each measurement for conformity to the specifications, including type and location (spatial and temporal). Modelers and other secondary data users should compare project quality specifications to their data needs and determine (validate) if the optical remote measurement data is useful for their purpose. By noting the deviations in sufficient detail, modelers and secondary data users will be able to determine the data's usability for scenarios different from those included in project planning.

Remote sensing methodology and meteorological data are often linked. Pollution enters the atmosphere directly, or is formed by chemical reactions in the atmosphere, or it is the result of a process. Photochemical pollutants, such as $O_3$ and sulfates, are generally produced over a period of time. Ozone forms by the interaction of VOCs and NOx under the right meteorological conditions when low wind speeds, variable wind directions, and relatively high temperatures are present. Other pollutants are generated by point, mobile, and area sources. Winds, a meteorological variable, can transport pollutants from their sources to affect populated areas. Therefore, if possible, meteorological data should be verified and validated at the same time as remote sensing data, not separately.

Figure 5.1 is a simplified illustration of a typical verification and validation process. The left column shows the "levels of data review." These levels of data are described in Section 5.1.1. The right column illustrates the type of verification or validation that usually occurs during the process. The numbers in parentheses reference the section numbers in this document that provide additional details on the data review process at each step in the hierarchy.

### 5.1.1 Levels of Data Quality Review

Generally, there are four "levels" of air quality measurements data review. These levels are similar to those defined by Mueller and Watson[2] and Watson et. al.[3] When a data set has undergone each level of review, it passes on to the next level. The entire process is used to determine the validity of the data.

- Level 0 verification includes raw calibration data and initial setup observation prior to collecting field data. Testing staff should report results of manufacturer calibration and verification that they perform prior to a field campaign. These data can include background and noise measurements made to establish a baseline for sensitivity of the measurements. Level 0 verification also includes field observation of the equipment setup and function. At this level, the data may be reduced and possibly reformatted, but are unedited and un-reviewed. These data have not been adjusted for known biases due to interfering components in the air at the test site or other problems that may have been identified during field maintenance checks or audits. These observations and data may be used to monitor instrument operations during the measurement episode but should not be used for regulatory purposes. Section 5.2.1 provides more details on this level of validation.

- Level 1 data verification involves quantitative and qualitative reviews for accuracy, completeness, and internal consistency. Quantitative checks are performed by instrument software screening programs, and qualitative checks are performed by field staff who manually review the data for outliers and problems. Quality control flags are assigned, as necessary, to indicate the data quality. Data are only considered verified at Level 1 after final QC checks have been completed and any adjustments, changes, or modifications to the data have been made. Section 5.2.2 provides more details on this level of data validation.

- Level 2 data validation involves comparisons with independent data sets. This function includes, for example, making comparisons to other simultaneous emissions measurements or historical data on the source emissions.

- Level 3 data validation involves a more detailed analysis and final screening of the data. The purpose of the final step is to ensure that there are no inconsistencies among the primary optical data and related data (such as meteorological measurements). The reviewer examines the overall consistency of the data and the consistency of related data (i.e., checking emissions patterns against time of day or wind speed and wind direction).

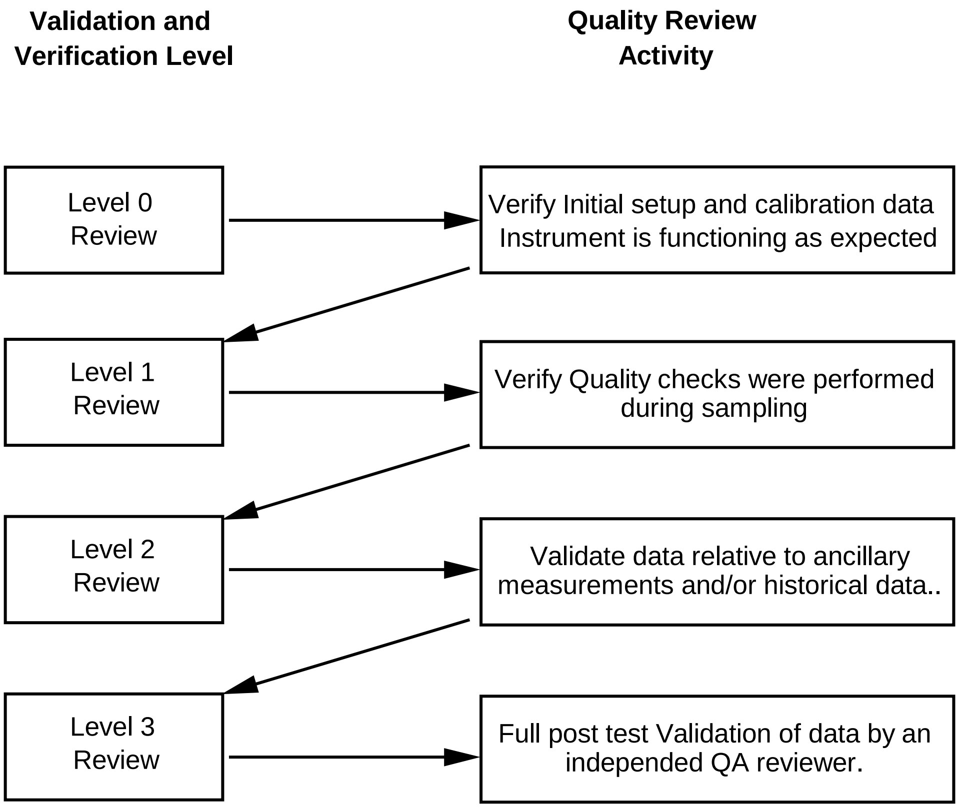

**Figure 5-1 Generalized Data Verification and Validation Process Flow**

## 5.2 Data Verification Methods

Data verification is defined as the confirmation by examination and objective evidence that specified quality requirements have been fulfilled according to the standard procedure for the method. This verification contributes to the confidence that the data will be valid for the original decision or purpose of the data collection. These recommendations should be included in the organization’s QAPP as part of the method quality indicators. The data verification process involves two basic steps: visual inspection and analysis and verification performed by data review. Both techniques are needed to verify optical measurements data. Each is described in the following sections.

### 5.2.1 Visual Data Verification

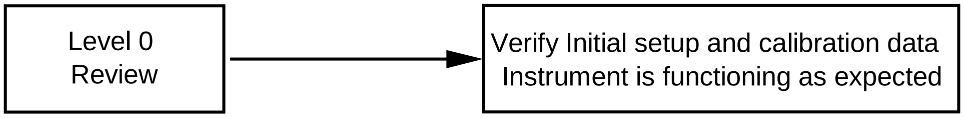

**Figure 5-2 Level 0 Verification Checks the Most Fundamental Quality Requirements**

The monitors and equipment used for remote sensing rely upon a radiation source (UV, visible, or IR) and a detector used together to identify and quantify the levels of certain chemicals in the atmosphere. These monitors are typically used in a continuous monitoring mode and monitor one or several compounds simultaneously. Although the overall design requirements for the different spectral ranges are significantly different, the basic components of these technologies are similar. In general, these monitors contain at least the following components:

- Radiation source
- Optics
- Detector
- Data processing algorithms

The radiation sources for these technologies belong to one of three distinct groups. The monitors operating in the UV region of the spectrum use a continuous or non-continuous lamp that provides broad-band radiation in the UV and visible regions. The monitors, using TDL technology, use a laser to provide radiation over a very narrow spectral range in the near-IR. That spectral range can be tuned over a small range with a single TDL and is selectable over a wider range using multiple TDLs. The FTIR monitors use a broadband IR source. Passive technologies such as IR cameras and Passive FTIR measure natural IR radiance from the compounds being measured. The optical components of these monitors typically are used to guide the radiation from the source, through the atmospheric path to be monitored, to the detector. The detectors and configurations for these monitors vary according to specific applications. They are typically chosen to maximize signal-to-noise ratio for the spectral region and operating temperature.[4]

Level 0 verification includes review of calibration of instruments and equipment. Periodic calibration and/or calibration checks must meet MQOs identified in project QAPPs. Typical MQOs are listed Chapter 2 for each measurement technology. Calibration data should be reviewed by field test staff and data validation staff. The following questions should be answered:

- Were the calibrations performed within an acceptable time prior to generation of data?
- Were they performed in the proper sequence?
- Were they performed using standards at the conditions expected during field measurements?
- Were acceptable linearity checks and other checks made to ensure that the measurement system was stable when the calibration was performed?

Level 0 verification can also include field inspections to visually verify optical measurement technologies performance during field acquisition of data. Field verification can be technical systems audits (internal or external) or simple inspections by field operators. For example, optical equipment often generates visible light as a direct or indirect result of the measurement process. Field inspection can verify measurement equipment is aimed correctly and operating if reflected visible light is apparent from the optical path. Optical equipment and associated reflectors can gather dust or moisture, and observation of these two interferents can be made visually during field inspection. Several questions might be asked during a visual verification process:

- Is the equipment operational? Verification is performed by observing that the optical equipment is collecting and storing data.

- Was the equipment aimed correctly to make measurements? Verification is performed by observing that the data collected is different from zero or full saturation.

- Part of the verification process is a review of the optical remote data over a period of time. A quick visual inspection may reveal some anomalies that do not match other parameters.

Continuous long term optical measurement verification programs should include documentation of periodic field observations that ensure equipment is operating. Figure 5.3 is an example of a visual observation records. Many environmental samples can be flagged (qualified) during the periodic visual inspections.

**Weekly Visual Quality Control Check Sheet**

Optical Remote Instruments
Site ______________________ Month/Year _______________________________
Site Number _______________ Technician ________________________________
Date:_____________________

☐ System is powered and operating
☐ Source is generating adequate radiation for measurements
☐ Optical alignment is correct allowing beam detection
☐ Detector is maintained at the proper temperature and generating spectral signal
☐ Calibration, span, zero checks are performed as appropriate
  ○ Standard Gas mixtures are available if required
  ○ System operation includes periodic QC

All comments must be noted in the system log.

Reviewed by _______________ Date _________________________________

**Figure 5-3 Example of Optical Remote Measurement Visual Check List**

### 5.2.2 Data Review and Verification

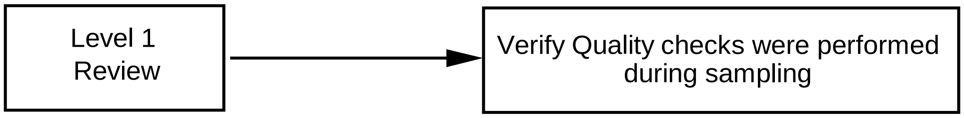

**Figure 5-4 Level 1 Verification Ensures Quality Requirements are Met in the Field**

In the late 1990s, optical remote systems were developed with personal computer compatible data collection routines. Many optical remote instruments offer remote access and download of data from systems that are in continuous use. Steps preparatory to data validation should include the daily transfer of raw data (e.g. signal averaged processed data) to a central data processing facility and the transfer of raw data files to create an edited database. The raw data files should be stored separately to insure data integrity. Backup copies of the data should be prepared and maintained on-site and off-site.

For continuous optical remote monitoring systems, data can be processed and QC operations parameters can be evaluated to determine if equipment maintenance is required. These types of verification techniques can be extremely useful because the program can “sense” a change in operating conditions or instrument response and a prediction of the possibility of equipment failure.

Data reviewers should answer some typical questions during their remote download data review such as:

- Did the signal intensity drift or diminish significantly since the last equipment maintenance?
- Did the regular QC check for noise and or calibration exceed acceptable limits?
- Did the optical system trip any electronic limits or indicate data collection failure?
- Does the data fall within the measurement range of the instrument or was the data saturated or zero?
- Does the system have a minimum detectable limit?

## 5.3 Data Validation Methods

### 5.3.1 Validation of Primary and Ancillary Measurements

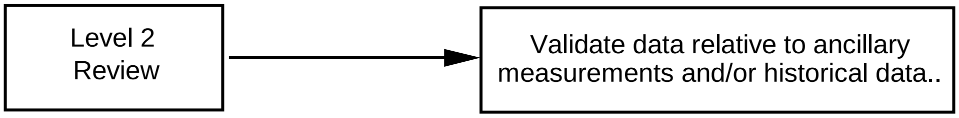

**Figure 5-5 Level 2 Quality Checks Start the Data Validation Process**

Both manual and computer-oriented systems require individual reviews of all data tabulations. As with all environmental measurements, it is necessary to keep accurate records during measurement periods to ensure a complete data collection. A site logbook and calibration sheets should be maintained at the data collection site. The site logbook will include information such as meteorological conditions, path lengths, UV filter numbers, lamp type, light intensities and measurement times. Light intensities must be recorded any time an optical source or receiver is adjusted and compared to the intensities measured when the equipment was installed. Calibration sheets include the record and results of system calibration checks or audits performed with known concentrations of a target or surrogate analyte.

Initial data verification steps should be performed by the station operator and later by data validation staff. All necessary supporting material, such as audit reports and site logs, should be available for Level 2 validation. Access to daily ancillary measurements such as wind speed, direction, should be provided for use in relating suspect data to local and regional conditions. If measurements are taken down wind of a facility, process information and production schedules are useful to interpret trends or excursions in optical remote data. Questionable data, such as data flagged in an audit, manual review should be corrected or invalidated during Level 2 data validation.

For long-term continuous measurements programs, the data should be reviewed on a regular schedule and at least monthly. For short-term measurements programs, the data should be reviewed by the site operators at the end of each day. Optical measurement instruments typically include onboard personal computers that allow operators to view and evaluate data visually. Graphs or plots of data or a summary table of data can be evaluated for outliers or obvious data collection failures. Graphing data can be a quick method of visualizing the data relative to other parameters. Graphs can show longer term trends and relationships that are difficult to see when data validation staff are looking at large amounts of tabular data.

The purpose of manual data inspection is to spot unusually high (or low) values (outliers) that might indicate a gross error in the data collection and to verify signal intensity. Manual review of data tabulations also allows detection of uncorrected drift in the zero baseline of an optical sensor. Zero drift may be indicated when the daily minimum values tend to deviate (increase or decrease) from the expected minimum value over a period of several days.

In an automated data processing system, procedures for data validation can be incorporated into the basic software. As noted in Section 5.2.2, the computer can be programmed to scan data for extreme values, outliers, or ranges. These checks can be further refined to account for time of day, time of week, and other cyclic conditions. Questionable data values flagged on the data tabulation may or may not indicate possible errors. The system operator should check all the data flagged by the acquisition system program and investigate whether the data flagged should remain flagged. In some cases, extreme conditions can occur rapidly and the data may actually reflect real values. For example, if a spill or leak occurs and moves through a measurement area the optical monitor may record high values or extreme interference in the data. The system operator should note such excursions and alert the data validation and reporting staff that these data may actually reflect real conditions. Data validation in Level 2 evaluates the data completeness and representativeness against the project DQO requirements to ensure sufficient data is collected for data users to draw conclusions or make decisions.

A useful data validation method is to compare the difference between successive data values. Logic dictates that rapid changes in values in a 1 to 15 minute acquisition period would normally not be expected. When the difference between two successive values exceeds a predetermined value, the data in question can be flagged for further evaluation. Screening is an iterative process in which range checks and other screening criteria are revised as necessary based on experience. For example, an initial QA pass of a data set using default criteria may result in flagged values which, upon further investigation, are determined to be valid for a particular site. In such cases, one or more follow-up QA passes using revised criteria may be necessary to clearly segregate valid and invalid data.

### 5.3.2 Final Validation and Evaluation of Measurements for Data Users

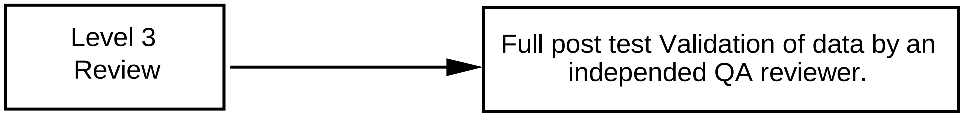

**Figure 5-6 Level 3 Quality Checks Ensure the Data is Usable for the Purpose Intended**

Data validation is a routine process designed to ensure that reported values meet the quality goals and objectives of environmental data operations. A progressive, systematic approach to data validation must be used to ensure and assess the quality of data. The purpose of this step in the process is to detect, compare, and perform a final screening on all data values. Any final data that may not represent actual conditions at the sampling site will be detected at this stage. Effective data validation procedures usually are handled independent of the procedures of initial data verification, that is, by different staff. It is important that data validation staff be independent of field operators.

If data assessment results clearly indicate a serious response problem with the optical technology, the agency should review all related information to determine whether the optical remote assessment data, should be invalidated. Some problems that may escape detection during an audit are often easily identified during data validation. Data validation should be performed by a person with appropriate training in the optical technology who has a basic understanding of instrument operation and typical results from similar measurement projects.

Data flagged by the QC screening should be evaluated by personnel with optical measurement expertise. Reasons for changes in the data resulting from the validation process should be documented. If system problems are identified, corrective actions should also be documented. Edited data should continue to be flagged so that their reliability can be considered in the interpretation of the results of modeling analyses for which the data are used.

Flags can be used in the field and by the data reviewers to signify data that may be suspect due to calibration or audit failure, special events, or failed QC limits. When calibration problems are identified, data produced between the suspect calibration event and subsequent recalibration should be flagged. Because flag combinations can be overwhelming and cannot always be anticipated, an organization needs to review these flag combinations to determine whether single values or values from a site over a particular time period should be invalidated. Procedures for screening data for possible errors or anomalies should also be implemented. When calibration problems are identified, data produced between the suspect calibration event and any subsequent recalibration should be flagged to alert data users.

## 5.4 References

1. Guidance on Environmental Data Verification and Data Validation, EPA QA/G-8, EPA/240/R-02/004, November 2002.

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