Literature Assessment of Remote Sensing Technologies for Detecting and Estimating Emissions for Flares and Fugitives
2008-90

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List of Abbreviations

ANGEL:	Airborne Natural Gas Emissions LIDAR
BTEX:	Benzene, toluene, ethylbenzene and xylenes
DIAL:	Differential Absorption LIDAR
DOAS:	Differential Optical Absorption Spectroscopy
ENVIRON :	ENVIRON International Corporation
EPA:	Environmental Protection Agency
FTIR:	Fourier Transform Infrared Spectroscopy
GPS:	Global Positioning System
HRPM:	Horizontal Radial Plume Mapping
HRVOC:	Highly Reactive Volatile Organic Compound
IR:	Infrared region of the spectrum
LIDAR:	Light Detection and Ranging
Mass Flux:	Mass per unit time (gram/sec or lb/hr)
OP:	Open Path
ORS:	Optical Remote Sensing
OTM:	Other Test Method, used by the EPA for emission characterization using path-integrated concentrations from non-point sources
PFTIR:	Passive FTIR
RPM:	Radial Plume Mapping
SOF:	Solar Occultation Flux
TexAQS:	Texas Air Quality Study
TCEQ :	Texas Commission on Environmental Quality
TDLS:	Tunable Diode Laser Spectroscopy
UV:	Ultraviolet region of the spectrum
VOC:	Volatile Organic Compound
VRPM:	Vertical Radial Plume Mapping

Executive Summary

The TCEQ wishes to remain familiar with the current state of optical remote sensing (ORS) technology available for commercial use. To this end, ENVIRON was directed to conduct a literature search and develop and assess a list of commercially available ORS technologies capable of detecting and estimating emissions of volatile organic compounds (VOC) and specific VOC contaminant species from flares and fugitive areas.

This evaluation is conducted in four tasks:

1. Identify ORS technologies capable of quantifying VOC emissions from flares and, to a lesser extent, process fugitives.

2. Evaluate TCEQ-selected ORS technologies with respect to: technical ability to detect and quantify emissions, known uncertainty in emission estimation levels, reliability, commercial availability and field use.

3. Rank ORS technologies.

4. Provide operational cost estimates for TCEQ-selected ORS technologies.

Thirteen ORS technologies are identified for inclusion in the evaluation. Of these, six are selected for further evaluation:

- Differential Absorption LIDAR (DIAL)
- Solar Occultation Flux (SOF)
- Vertical Radial Plume Mapping (VRPM)
- Hyperspectral Imaging (TELOPS FIRST)
- Imaging Spectrometry (GIT Sherlock FE)
- Passive Fourier Transform Infrared Spectroscopy (PFTIR)

These technologies are evaluated, ranked and, with the exception of VRPM, operating cost estimates prepared. VRPM is not considered further because of limitations, at this time, on use of the technology for measuring emissions from elevated flares.

It should be noted that suppliers were given the opportunity to provide information regarding the technical performance and cost of their technologies. This included the opportunity to review and comment on draft sections of the report that pertained to their technology.

Rankings and costs for a field survey in Texas lasting 20 days are presented in Table 1. Rankings are a compilation of scores in five areas: technical ability to detect and quantify

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emissions (0-25 points), known uncertainty in emission estimation levels (0-25 points), reliability (0-10 points), commercial availability (0-10 points) and field use (1-10 points).

Table 1: Summary of ORS Technologies.

Technology	Numerical Evaluation Score	Estimated Operating Costs for 20-Day Survey (US$)
DIAL	70	295,000 – 445,000+
SOF	65	128,000 – 175,000
VRPM	50	--[1]
TELOPS FIRST	40	100,000
GIT Sherlock FE	45	80,000
PFTIR	50	45,000

[1]Not evaluated for cost.

1 Introduction

1.1 Project Purpose

The Texas Commission on Environmental Quality (TCEQ) wishes to remain familiar with the current state of remote sensing technology available for commercial use. For this project, ENVIRON International Corporation (ENVIRON) identified and evaluated commercially available remote sensing technologies capable of detecting and estimating mass emissions of volatile organic compounds (VOC) and specific VOC contaminant species from flares and fugitive areas.[1]

1.2 Project Background

VOC and highly reactive volatile organic compound (HRVOC) emissions from flares and fugitive sources, such as brine ponds associated with underground salt domes, may be under-quantified in current inventory practices.[2] Remote sensing technologies, using passive and active spectrometry, have been successfully used to detect and estimate certain VOC emissions from some sources. The TCEQ is considering a potential field evaluation of flares and fugitive sources using current technology to detect and estimate these emissions.

1.3 Scope of Work

The scope of work includes the following tasks:

Task 1. Develop work plan.

Task 2. Generate list of remote sensing technologies capable of quantifying VOC emissions. From this list, the TCEQ selected technologies for further evaluation.

Task 3. Evaluate remote sensing technologies selected by the TCEQ.

Task 4. Rank the technologies using five criteria and weighting factors identified by the TCEQ. From this list, the TCEQ selected technologies for further evaluation.

Task 5. Estimate operational costs for remote sensing technologies selected by the TCEQ.

Task 6. Prepare final report.

[1] VOC is defined in 40 CFR 51.100(s).
[2] HRVOC is defined in 30 TAC 115.10.

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2 Identification of Remote Sensing Technology Candidates

2.1 Process Used to Identify Candidate Technologies

A set of pre-requisite conditions is used to shortlist the candidate technologies. These are as follows:

- The technology has been used or has the potential to be used to identify and quantify individual and total VOCs from process fugitives and flares. Process fugitives are defined as emissions sources which have non-smokestack emissions points, e.g., cooling towers or storage tanks. The term 'quantify' used here and in this report hereon, refers to the ability of the remote sensing technology to compute individual and total VOC mass emission rates rather than just calculating the path-average concentration or relative concentration based on spectral radiance or absorbance.

- The technology has been used or has the potential to be used to detect and quantify a wide range of individual VOCs as well as total VOCs. The individual VOCs include but are not limited to ethene (C_2H_4), propene (C_2H_6) butene (C_4H_8 - all isomers), 1, 3-butadiene (C_4H_6) and other VOC species containing three to fifteen carbon atoms. In addition to identifying and quantifying VOCs, the technology should have also demonstrated the capability of detecting and quantifying nitrogen oxides (NO_x), carbon monoxide (CO) and sulfur dioxide (SO_2) emissions, though this is not a necessary condition.

- Preferably, the technology is passive and does not involve the use of an active energy source or laser for inducing absorbance spectra. However, based on discussions with TCEQ personnel, including the project representative, a decision was made to not exclude technologies that use an active source.

- The technology is primarily land based with the possibility of having an airborne variant.

- The technology is capable of operating at a safe distance from the source with good accuracy.

- The technology is commercially available for use in the United States.

2.2 Remote Sensing Technology Summaries

2.2.1 Overview

Candidate technologies are sub-divided into three groups based on their potential to measure mass emission rates from flares and/or fugitives and also their commercial applicability. Technologies are grouped based on literature and publicly-available information, and conversations with individuals involved with developing and/or using the technology. The groups are:

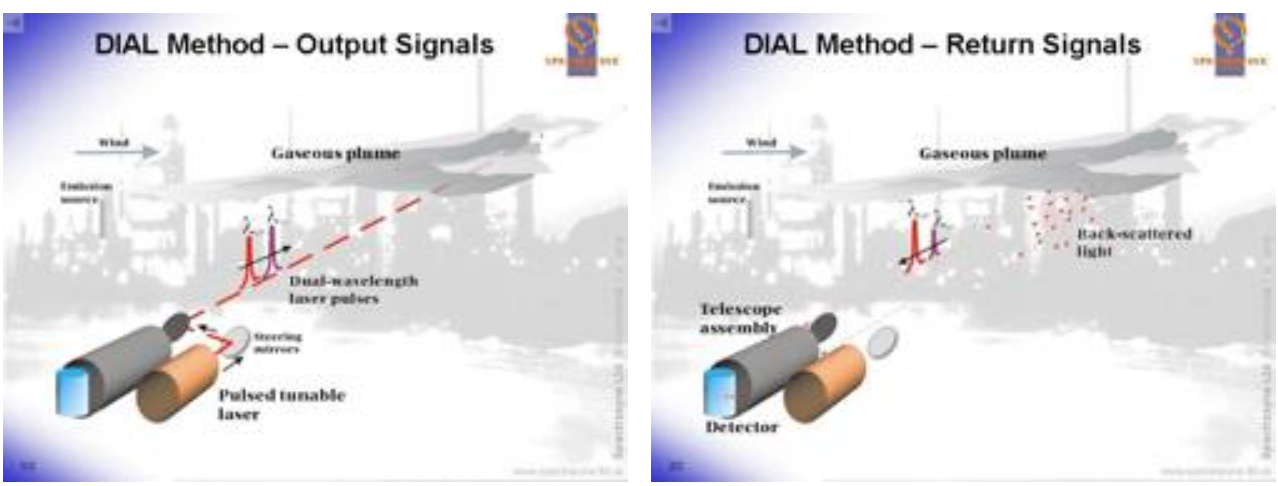
- Technologies that have been used commercially to measure mass emissions from flares and/or process fugitives
- Technologies that may have the potential to measure mass emissions from flares and/or process fugitives but have not been used to do so in commercial applications
- Technologies that do not seem to have the potential, at this time, to measure mass emissions from flares and/or process fugitives

Thirteen optical remote sensing technologies are considered by ENVIRON. These are discussed individually in the following sections.

2.2.2 Differential Absorption LIDAR (DIAL)

DIAL is an active laser-based technique used to measure mass emission rates and concentrations of various chemical species. This technique gives two dimensional concentration profiles and mass fluxes of various molecules. The measurement is based on the unique absorption spectrum of each molecule. A laser is used as the Light Detection and Ranging (LIDAR) light source. The tunable laser source gives the LIDAR the ability to be tuned on and off in pulses, sending out two beams of different wavelengths. Dust particles and aerosols act as reflectors and back scatter small portions of light to a sensitive detector. The DIAL system measures the round trip time for the differential pulses from leaving the system, being scattered and then returned to the detector. The intensity ratio of the return signals at different distances along the laser beam path indicates the concentration along the measurement line. These concentrations can be converted into mass emission rates by making a series of scans along different lines within the plume and them combining these with meteorological data. DIAL measurements are made from a mobile truck. The DIAL truck is equipped with portable meteorological masts to measure meteorological and wind speed data. A representation of the DIAL technique is shown in Figure 1.

Figure 1: DIAL Technique



(Source: Spectrasyne Ltd.)

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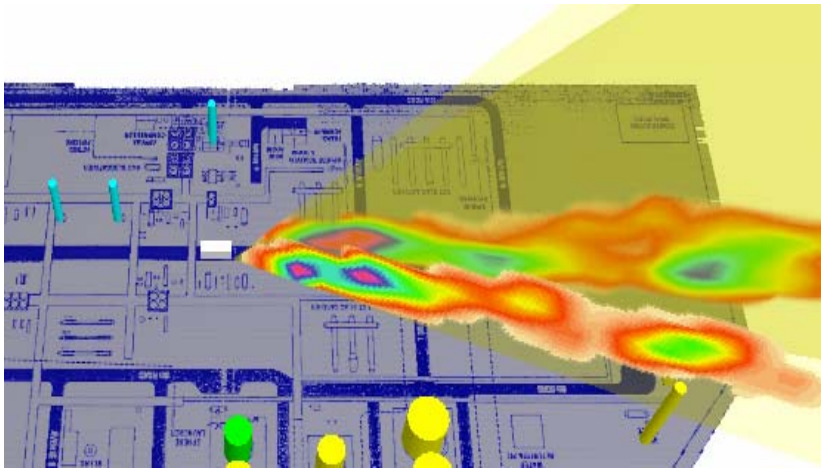
DIAL lasers can be tuned to appropriate wavelengths in the infrared (IR), visible and ultraviolet (UV) regions of the spectrum to measure any compound for which the absorption spectrum is known. Since 1990, DIAL has been used in more than 150 measurement surveys across the world to quantify emissions from a wide variety of sources. These sources include petroleum refineries, chemical plants, storage terminals, natural gas plants, flares, barges and ships and airport operations. DIAL technique has been used for measurements from both process fugitives and flares to quantify individual VOC species. The individual compounds and compound groups that have been measured using DIAL include alkanes, alkynes, benzene, toluene, xylene and other higher aromatics, ozone, NO_2, SO_2, NO and diesel vapors. A three-dimensional representation of a DIAL scan is shown in Figure 2. The violets and blues correspond to higher concentrations of the pollutant being surveyed.

Figure 2: DIAL Survey Graphic



(Source: NPL)

The primary limitation with DIAL is the time it takes to retune the lasers to scan for multiple compounds that absorb in different wavelengths. As a result, DIAL is typically used to measure emissions of a single compound of interest or to measure absorption in a wavelength where multiple compounds of interest are absorbed. However, if the later approach is taken, another method must be used to resolve the measurement for specific compounds of interest. This can be done by analyzing physical samples or by using Fourier Transform Infrared ("FTIR") spectroscopy to scan the plume at the same time the DIAL survey is conducted.

Additional information on DIAL can be found on the internet at:

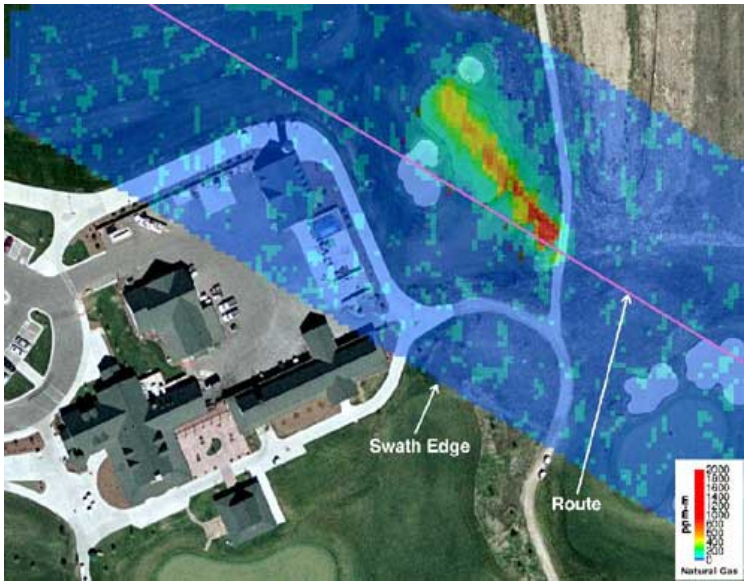
http://www.spectrasyne.ltd.uk/html/about_dial.html

http://www.npl.co.uk/server.php?show=ConWebDoc.1441

2.2.3 Airborne DIAL

Both ITT's Airborne Natural Gas Emissions LIDAR (ANGEL) and ALMA's Airborne Laser Methane Assessment (ALMA) are based on DIAL discussed in Section 2.2.2 and both are DIAL on an airborne platform. They have been used almost exclusively to monitor methane leaks from natural gas pipelines. The DIAL laser is pulsated approximately 1000 times per minute, collecting information on methane concentration as the plane flies a route parallel to a pipeline right of way. The concentrations are integrated with digital mapping imagery. An example is shown as Figure 3. The darker reds correspond to higher concentrations of methane.

Figure 3: Airborne DIAL Imagery



(Source: ITT ANGEL Service)

The technology can be used to detect any pollutant that absorbs energy in the infrared region of the spectrum. However, both ITT and Pergam-Suisse, the parent companies of ANGEL and ALMA, respectively, have decided to limit the commercial application to the detection of methane at this time. Recently, ALMA has also developed a motor vehicle version of ALMA for detection of gas leaks from buried and above ground pipelines.

In its current form the technology does not allow for three dimensional measurements or estimation of mass emission rates from process fugitives or flares. However, ITT recently communicated that it is working to integrate information from meteorological arrays into their ANGEL system to allow for estimation of mass emission rates. That work is in the early stages and no timeframe for delivery of these capabilities has been publicly communicated.

Additional information on airborne DIAL can be found on the internet at:

http://www.pergam-usa.com/main.asp

http://www.ssd.itt.com/angel/overview.shtml

2.2.4 Solar Occultation Flux (SOF)

SOF is a passive infrared method based on the measurement of IR intensity spectra of the sun from a mobile vehicle in combination with point measurements with a parallel IR system coupled to a White-cell. In order to obtain the flux from a particular source, the vehicle is driven in such

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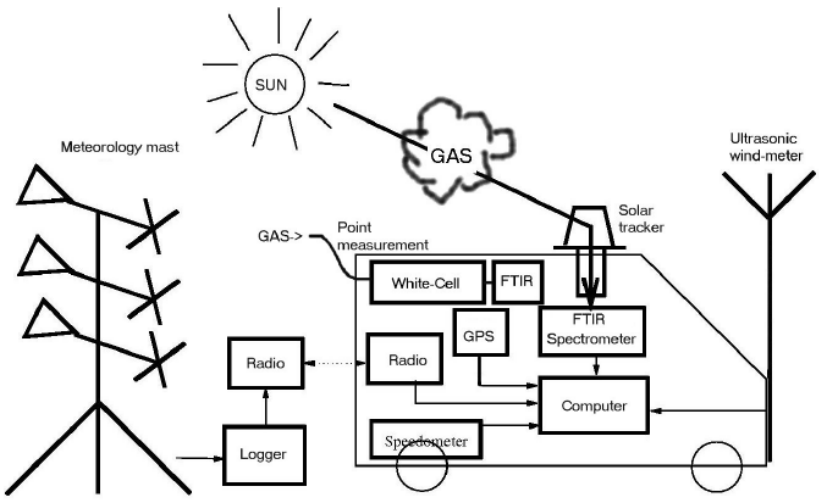
as way that the detected solar light traverses across the actual emission plume. The flux is then obtained as the integrated sum of the retrieved path averaged concentrations, multiplied by the wind speed. Wind speed and wind direction are measured using high masts and GPS balloon sondes. A representation of the SOF technique is shown in Figure 4.

Figure 4: SOF Technique



(Source: FluxSense AB website: www.fluxsense.se)

The SOF technique has been used for over five years in Sweden to quantify emissions from refineries. It was also used to measure reactive VOCs in the Houston Ship Channel area during the second Texas Air Quality Study (TexAQS II). SOF measurements are conducted in the mid-IR (MIR, 2.5-8 µm) range and thus this technique can be effectively used to detect and quantify many VOCs (including alkanes and olefins, but except aromatics), formaldehyde, NO_2 and SO_2.

The SOF technique works well for both process fugitives and flares. However, it only works in daytime under sunny conditions as the plume needs to be between the SOF receiver and the sun. Measurements conducted near the source are associated with larger uncertainties as the plume is closer to the ground and the wind field is more disturbed. Thus in the SOF technique, measurements are usually made at some downwind distance, usually between 0.5 to 2 km, to avoid uncertainty due to turbulence and mixing. Wind speed and direction are the largest known sources of error for the SOF technique. To reduce this fluctuation, the time spent in the plume is minimized by driving the SOF vehicle at speeds ranging from 30 to 35 mph.

Additional information on SOF can be found on the internet at:

http://www.chalmers.se/rss/EN/research/research-groups/optical-remote-sensing/

http://www.fluxsense.se/

2.2.5 Active Open-Path Fourier Transform Infrared (OP-FTIR)

OP-FTIR is an active technique in which a telescope is used to send an IR beam through air. Each molecule has a unique IR signature and the amount of light absorbed or emitted is proportional to the concentration. As a result, specific compounds can be identified and their concentrations can be measured using the strength of absorption or emission spectra. This telescope-based technique can operate in two modes, monostatic and bistatic. In the monostatic mode, a single telescope is used as an active IR source and a passive reflecting mirror is used at the other end to reflect the IR beam. The bistatic mode uses transmitting and receiving telescopes on both ends of the path.

OP-FTIR can be used to measure path average concentrations of any chemical pollutant that absorbs energy in the IR region of the spectrum. Besides urban air and accidental release monitoring, this technology has been used for fenceline monitoring of industrial facilities. Operated in monostatic or bistatic modes, OP-FTIR provides path-average concentrations but does not allow for quantification of emissions. However, OP-FTIR can be used to quantify emissions when used as part of the radial plume mapping (RPM) configuration, as described in EPA's Other Test Method (OTM)-10 document and later in this section.

Additional information on OP-FTIR can be found on the internet at:

http://www.ftir.bz/

http://www.unisearch-associates.com/ftir.htm

2.2.6 Differential Optical Absorption Spectroscopy (DOAS)

DOAS is an active technique that uses specific narrow band absorptions of chemical species in the UV, visible and near-IR (NIR) spectrum to determine their concentrations. This technique depends on the measurement of the absorption spectra instead of the intensity of light at a particular wavelength, which makes it possible to separate the absorption spectra of several chemical species based on the wavelength of absorption. In order to measure the concentration of chemical species, DOAS separates the absorption cross section into low and high frequency (broad and narrow parts of absorption) parts by specific numerical filtering. A typical DOAS instrument consists of a light source and an optical setup to send and receive light through the atmosphere.

DOAS can be used to measure path average concentrations of any pollutant that absorbs energy in the UV, visible or NIR regions of the spectrum. DOAS has been used in the past to measure the concentrations of several trace gases involved in photochemical smog formation. UV-DOAS has found its most widespread use in detecting inorganic gases and vapors such as SO_x, NO_x, NH_3, H_2S, and HF, aromatics such as benzene, toluene, ethyl benzene, xylene and aldehydes such as formaldehyde. The instrument's ability to detect BTEX compounds at low concentrations is one of the major advantages of this technique. DOAS has been primarily used for industrial fenceline monitoring.

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In a typical configuration, DOAS provides path-average concentrations and does not quantify emissions. However, DOAS can be used to quantify emissions when used as part of the RPM configuration as described in EPA's OTM-10 document and later in this section.

Additional information on DOAS can be found on the internet at:

http://www.opsis.se/

http://www.spectrex-inc.com/safeye/Xenon700.htm

2.2.7 Open Path Tunable Diode Laser Spectroscopy (OP-TDLS)

OP-TDLS is an active technique that uses tunable diode lasers having line-widths of only a few megahertz and therefore is well suited for high resolution spectroscopy. The tunable diode lasers are designed to focus on single absorption wavelengths specific to a pollutant of concern. The laser beam is sent through the optical path to a reflector and back again. This generates a signal which varies with the concentration of the target gas in the path. Typically, the OP-TDLS lasers have a long lifetime and are reliable over long service intervals.

The OPTDLS has been used to detect HF, NH_3, O_3, HCl, H_2O, CO and CO_2. Major advantages of using an OP-TDLS instrument are that they are lightweight and easy to setup and operate at ambient temperatures.

In a typical configuration, OP-TDLS provides path-average concentrations and does not quantify emissions. However, OP-TDLS can be used to quantify emissions when used as part of the radial plume mapping (RPM) configuration, as described in EPA's OTM-10 document and later in this section.

Additional information on OP-TDLS can be found on the internet at:

http://www.psicorp.com/products/tdlsensors.shtml

http://www.opsis.se/

http://www.unisearch-associates.com/ftir.htm

http://www.boreal-laser.com/products/mcoview.htm

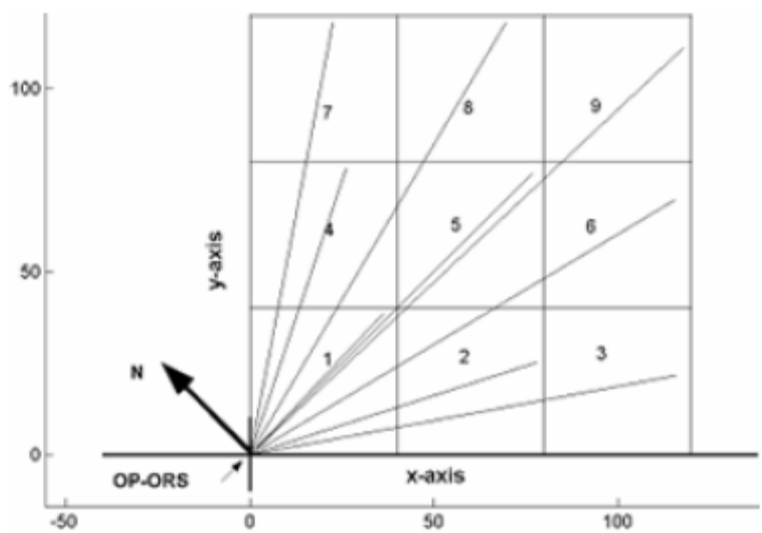
2.2.8 Radial Plume Mapping (RPM)

RPM is an active optical remote sensing technique that uses an OP optical instrument to measure the path-integrated concentration data along multiple beam paths. Each configuration uses multiple retro-reflecting (mirrors that reflect the beam parallel to the incidence beam, but in opposite direction) mirrors along different beam paths in the survey area. Usually, either OP-FTIR or OP-TDLS or UV-DOAS are used as optical remote sensing instruments for RPM. Path-

integrated concentration profiles are obtained by scanning along various beam paths. RPM and its variations have been listed in category C of the OTM by the USEPA for emission characterization and obtaining path-integrated concentrations from non-point sources.

If the optical remote sensing instrument is used along a horizontal plane to produce surface concentration profiles, the configuration is called horizontal RPM (HRPM). HRPM configuration typically uses between 4 and 12 mirrors in a radial pattern along the survey area, as shown in Figure 5. The optical remote sensing instrument scans each path length in the configuration, thereby generating a path-integrated concentration data. The path-integrated concentration data is processed using various HRPM algorithms to produce concentration contour maps for the survey area. This technique can be used for survey areas with dimensions as large as 250 meters. However, the technology is a qualitative tool and not capable of generating a mass emission rate.

Figure 5: HRPM Configuration



(Source: USEPA, National Risk Management Laboratory)

The RPM technique is referred to as vertical RPM (VRPM) when the optical remote sensing instrument is used to scan a vertical plane downwind of the area of interest. VRPM is an active OP, path-integrated optical remote sensing system. This technique maps the concentrations in the vertical plane of measurement. In VRPM, the instrument is set to send light to various retro-reflectors deployed perpendicular to and at horizontal distances across the plume path downwind of the source. Multiple retro-reflectors are placed in various locations along a vertical plane in-line with an OP-FTIR or other light source. A typical VRPM configuration uses between 5 and 8 mirrors in the vertical and horizontal plane of the survey area. Plume concentration profiles and path integrated concentrations are obtained by scanning in a vertical plane downwind of the area source. Meteorological data is collected concurrently along with the concentration measurements. With the help of various algorithms, the meteorological and

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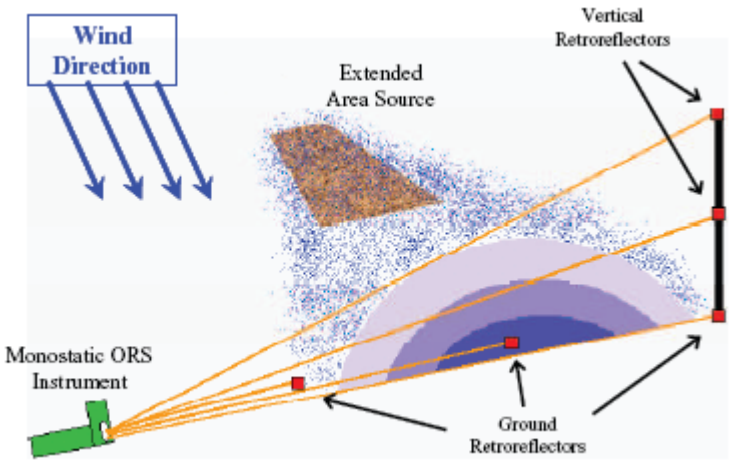
concentration data are processed to calculate the downwind emission flux. A typical VPRM configuration is depicted in Figure 6.

Figure 6: VRPM Configuration



(Source: USEPA, National Risk Management Laboratory)

The VRPM technique has been used in EPA landfill, EPA Superfund and Brownfield sites and gas station and refinery emission studies. VRPM has been mostly used to detect and quantify compounds that absorb in the NIR region of the spectrum. These include alkanes and alkenes. Coupled with UV-DOAS, VRPM has been used to measure emissions of aromatics and inorganics, including hydrogen sulfide (H_2S) and mercury. VRPM has also been used with OP-TDLS to measure gases such as HF, ammonia and methane.

The VRPM technique requires the placement of multiple retro-reflectors places in various locations along the vertical plane of measurement. Therefore, there are practical limitations to the vertical reach of the technology. VRPM is a good application for obtaining emissions information over longer periods of time. However, the array of retro-reflectors is fixed and unable to be repositioned quickly as wind direction changes.

Additional information on VRPM can be found on the internet at:

http://www.arcadis-us.com/Service+Types/Environment/Operating+facilities+services+management/Air+quality/

http://www.epa.gov/ttn/emc/prelim/otm10.pdf

2.2.9 Passive Infrared Gas Imaging Camera

Over the last several years, use of Passive IR Gas Imaging Camera technology has grown rapidly for detection of leaks in the chemical, petroleum refining, and hydrocarbon extraction, processing, storage and transportation industries. This is a passive technology that records the

difference in absorption of specific IR wavelengths in the field of vision and produces the appearance of a cloud where the chemical is present. The technology uses different combination of lenses, detectors and filters for detecting different VOCs.

The camera has been used to detect natural gas, propane, butane, methane, pentane, propylene and ethylene leaks. The technology allows the camera to detect any compound which absorbs IR energy in the wavelength seen by the camera. The camera has been used in combination with other technologies to provide a visual record of the source of the release as well as its chemical composition. The HAWK leak system from Leak Surveys Inc. (LSI) uses the FLIR GasFindIR camera to detect leaks. Electrophysics Corporation offers a series of cameras for detection in short, medium and long-wave IR region of the spectrum.

Current technology cannot quantify or speciate individual chemical species. New software and interfaces are being developed that may enable the camera to quantify individual species. These enhancements include development of software that may interpret gross emission rate based on video imagery. LSI is currently working to develop an integrated system that would deliver these capabilities.

Passive IR gas imaging cameras have found widespread use throughout the industry for leak detection. The TCEQ has extensive experience using this technology as part of the “Find-It-and Fix-It” program. Besides industrial applications, the camera has also been used in TCEQ campaigns in the Houston Ship Channel region and the EPA and Louisiana Department of Environmental Quality (LDEQ) post Hurricane Katrina campaign. The camera has been used to detect the presence of unburned hydrocarbons in flare plumes outside of the flame. An IR camera is used to shoot the plume in passive FTIR technology for determination of combustion efficiency.

Additional information on passive infrared gas imaging cameras can be found on the internet at:

http://www.leaksurveysinc.com/hawkdetails.html

http://www.electrophysics.com/Browse/Brw_ProductLineCategory.asp?CategoryId=187&Area=IS

2.2.10 Hyperspectral Imaging – TELOPS FIRST

Infrared Hyperspectral Imaging is a passive, FTIR-based technique that combines two individual well-established techniques of spectrometry and imagery and provides high spectral resolution and radiometric accuracy in the thermal IR region. The method – as with any passive FTIR-based system – relies on the imbalance of emission and absorption spectrum of chemical species in the field of view of the instrument. Natural radiance from the background (sky) will have a definite absorption spectrum. In the presence of a hot gas this spectrum will be modified. This difference or imbalance in the absorption spectra is used to measure the concentration based on the radiance of the hot gas being measured. An estimate of the difference in temperature of the background (sky, if measuring a flare) and the flare gas has an effect on the

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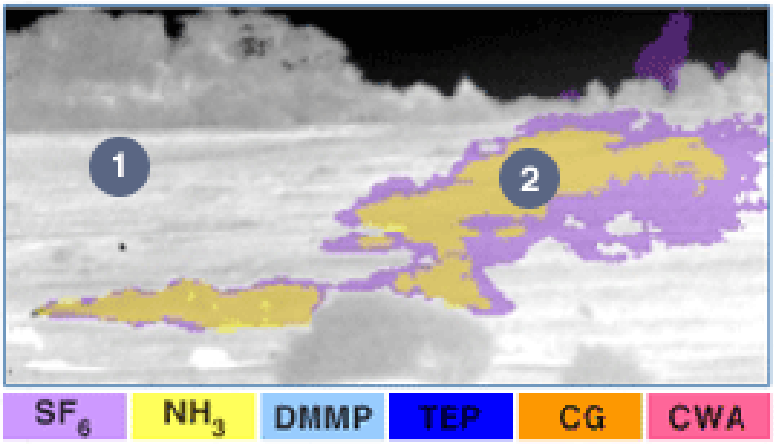
strength of TELOPS FIRST measurement, in the same way as does the concentration of the gas. Spectral bands of the gaseous molecules appear in the absorption data if the gas is colder than the background but these bands are seen in the emission data if the gas is warmer than the background. The advantage of using thermal IR is that objects at room temperature emit radiation in the 3 to 12 µm range, thus making the technique passive.

TELOPS has developed an IR based passive FTIR technique named "FIRST" that operates in long wave (8-11 µm) and medium wave (3-5 µm) region of the spectrum. FIRST has been used in two testing programs to measure concentrations of different gases. Most recently FIRST has been used to measure the SO_2 concentrations from a refinery in 2006.

Data is acquired as relative concentration. The algorithms needed to post-process the relative concentration data into mass emissions have not been developed yet. Optimal range of measurement is 0.003 km to 3 km. However, on a dry day when there is reduced moisture in the air, measurements can be made from a greater distance.

Figure 7 shows a TELOPS FIRST image. The brightness corresponds to temperature. The colors indicate gas detection. In this case, the gas released was a mixture of SF_6 and NH_3.

Figure 7: TELOPS FIRST Image



(Source: TELOPS website: www.telops.com)

Though FIRST is capable of detecting and identifying most chemical species of interest, it's ability to measure mass emission rates for flares and process fugitives has not been demonstrated. Certain enhancements -- such as improved gas detection and quantification algorithms and inclusion of meteorological data into such algorithms -- to the current technology seem necessary before it could be used to measure mass emission rates. Also, since this method relies on temperature differences causing imbalances of emission and absorption spectra, it may be difficult to use this technique successfully, for process fugitives.

As noted previously, TELOPS is currently working to develop software that would allow for quantifying emissions using the pixel content of the image.

Additional information on the TELOPS FIRST system can be found on the internet at:

http://www.telops.com/html/english/aerospace/products_detail.php?pro_id=7

2.2.11 Imaging Spectroscopy – Sherlock

Imaging spectroscopy is a passive, dispersive-type hyperspectral imaging spectrometry using the image multi-spectral system (IMSS) developed by Gas Imaging Technology, LLC (GIT). The IMSS technique uses both optics and image signal processing. It images a scene and then measures the spectral and radiative content of each pixel within the scene. It can also be used to monitor gas emission ratios to measure flare efficiencies.

GIT has two different versions of the imaging spectrometric instruments, namely Sherlock VOC and Sherlock FE. Sherlock VOC is a remote imaging spectrometer which has been used to measure fugitive gas concentrations of most chemical species of interest, including methane and benzene. Sherlock VOC is reported to measure the mass emission rate of a fugitive equipment leak – often referred to as “smart” leak detection and repair, or smart-LDAR. Sherlock FE is another remote imaging system developed by GIT which has been used to determine the combustion efficiency of flares. Both models contain various individual components including a compact FTIR spectrometer, IR camera, data logger and computer, all in a single piece of instrument.

Sherlock FE uses a combination of Beer’s Law and the Ideal Gas Law for calculating concentrations and then the mass of pollutants. If the hydrocarbon loading to a flare is known, measured combustion efficiency could be used to estimate the destruction efficiency and, thus, the mass emission rate of total and/or individual hydrocarbons. Algorithms required to compute mass emission rates from either the concentration per unit volume or mass have not been tested. The Sherlock system has been field tested at the British Petroleum (BP) refinery in Naperville, Illinois. The results of these tests have yet to be reported.

Additional information on the GIT Sherlock VOC and FE can be found on the internet at:

http://www.gitint.com/products/index.htm

2.2.12 Passive Fourier Transform Infrared Spectroscopy (PFTIR)

The PFTIR spectroscopy technique analyzes the amount of thermal radiation emitted by a hot gas, as opposed to traditional spectroscopic methods that use the amount of light absorbed to quantify the species of interest. As the name suggests, the technique is passive as no active IR light source is used. The hot gas in the plume acts as an IR source and the PFTIR measures the energy radiated from the plume. IR radiation emitted by a hot gas has the same wavelength as that of the absorption spectra. Thus, by measuring the emission spectra it is possible to

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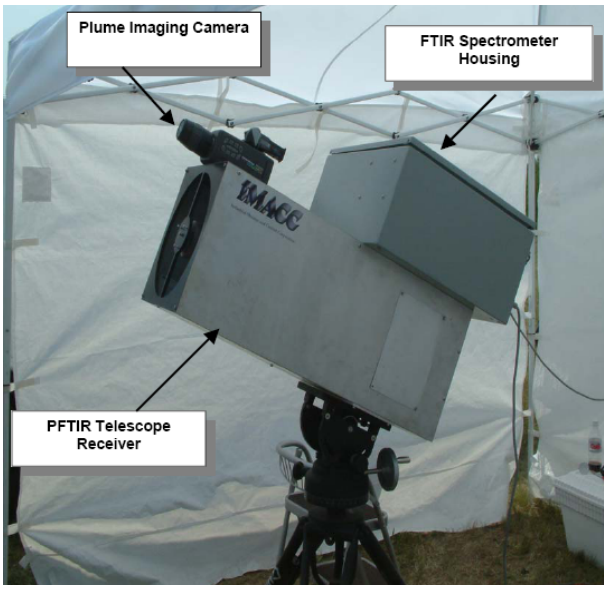
identify and quantify the path-average concentration of the species in the flare plume. As explained earlier, the strength of the emission spectrum is proportional to the concentration and the temperature of the hot gas. Use of PFTIR requires a radiant gas with a temperature of at least 120°C. A photograph of the PFTIR system is shown as Figure 8.

Figure 8: PFTIR



(Source: PFTIR Phase I Testing, Final Report, TCEQ, June 2004)

PFTIR technology has been successfully demonstrated on a trial basis for measuring the combustion efficiency of flares. Combustion efficiency is the ratio of CO_2 to the sum of CO, CO_2, total hydrocarbons (THC) and Soot. The technology has also been used to measure CO, CO_2, butane, ethylene and propylene concentrations and could be potentially used to measure other C_1 to C_5 hydrocarbon species. A passive IR gas imaging camera is used to visually detect the presence of hydrocarbons in the flare plume (beyond the flame) and to aim the PFTIR system.

In 2003, the TCEQ commissioned a testing of PFTIR capabilities. The study was conducted under controlled conditions on a simulated flare. From the test results it was concluded that the PFTIR technique was a potentially viable technology for determining the combustion efficiencies of flare systems and concentrations of select species. If the hydrocarbon loading to a flare is known, measured combustion efficiency could be used to estimate the destruction efficiency, and thus the mass emission rate of total hydrocarbons. The technology, however, does not currently allow for determination of the destruction efficiency of individual hydrocarbons.

As a passive technique which relies on the heat of gases emitted, use of PFTIR to monitor fugitive emissions is limited to applications where the gas temperature is in excess of 120°C.

Even when feasible, PFTIR measurements of fugitive sources will only provide path-average concentrations of the pollutants, not the emission rates.

Additional information on PFTIR can be found on the internet at:

http://www.ftir.bz/

2.2.13 Imaging Differential Optical Absorption Spectroscopy (I-DOAS)

DOAS is a passive technology in which the gas is monitored at two different wavelengths: one where gas absorbs and another where the gas does not absorb. The wavelength at which the gas does not absorb serves as a reference. The ratio of gas absorption spectra is compared to the background absorption spectra to calculate the concentrations of gaseous species. I-DOAS measures a hyperspectral image in two dimensions. Scattered sunlight is used as a light source for the first dimension, with an imaging spectrometer that simultaneously acquires spectral information on the incident light in one spectral dimension. A moving mirror is used in the vertical viewing direction for the second dimension. Thus, the technology may be able to detect and measure the concentrations of VOCs and other chemical species of interest.

The DOAS technique in theory can be used to measure path average concentrations of any chemical species that absorb energy in UV, visible and NIR region of the spectra. Most VOCs and other chemical species of interest lie in the NIR (3 µm to 5 µm) region of the spectrum. UCLA has proposed to develop a technology based on multi-axis DOAS (MAX-DOAS) that may be used to construct vertical profiles of species of interest. This will be done by either training one telescope in different directions or at different angles using a mechanical motor drive or by using multiple telescopes for simultaneous measurements along different directions. It is ENVIRON's understanding that the Houston Advanced Research Center (HARC) Science Advisory Committee (SAC) has agreed to fund this work. As proposed, the work will be completed in 2009.

I-DOAS remains in development and is not commercially available. The technology has the potential to detect and measure the concentrations of various chemical species but its ability to calculate mass emission rates has not been demonstrated.

2.2.14 Raman Spectroscopy

Raman Spectroscopy is an active open path technique that can identify chemical species and measure their path average concentrations. This technique relies on inelastic scattering of monochromatic light. The incident light excites the electrons in a molecule causing them to vibrate from ground in what is known as Raman Scattering. The concentration of gaseous molecules is proportional to the signal strength. The detectors measure the portion of light that is scattered inelastically from the gas molecule.

Basic open path Raman Spectroscopy is capable of detecting a wide range of chemicals, both organic and inorganic, in vapor, liquid and solid phase. The detection limit depends on the

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length of the path, the excitation wavelength used and the Raman cross-section of an individual chemical. Typical detection limits range from low ppm to percent levels. This technique has been suggested for use in identifying air pollutants but based on the available information, no commercial application to such use has been identified by ENVIRON.

Based upon ENVIRON's research, the only identified use of Raman Spectroscopy for monitoring of air pollutants is a 2001 EPA funded study by Radiation Monitoring Devices Inc. for monitoring automobile emissions.

2.3 Technologies Identified for Further Evaluation

The following criteria are used as a guideline to shortlist technologies from those listed in Section 2.2:

- The technology should be able to identify VOCs of interest and quantify their mass emission rates.
- The technology should be able to detect VOCs of interest over a wide range of the spectrum. Most VOCs of interest lie in the near- to mid-IR (3 µm to 8 µm) region of the spectrum.
- The technology should be passive and not require an active source such as a laser to detect VOCs.
- The technology should be able to identify and quantify VOCs from industrial flares and/or process fugitives.
- The technology should be land based.
- The technology in its current form should qualify for use in an industrial setting.
- The technology should be commercially available.

Table 2 summarizes the characteristics of the 13 technologies evaluated.

Based on the listed criteria, six technologies are chosen for further evaluation. These technologies are:

- DIAL
- SOF
- VRPM
- Hyperspectral Imaging

- Imaging Spectrometry
- PFTIR

DIAL and VRPM are both active techniques. These technologies are included for further evaluation based on the number of relevant surveys conducted and the potential for quantification of emissions from flares and/or process fugitives. Since 1990s, DIAL has been used to conduct more than 150 surveys covering refineries, chemical plants, rail loading, shipping terminals, natural gas plants etc, which merits its inclusion in this discussion on remote sensing technologies. VRPM has also been used in a number of studies USEPA landfill, refinery and gas station emission studies.

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Table 2: Summary of candidate remote sensing technologies.

Technology	Has the Technology Been Used or Has the Potential to be Used to:						Passive or Active?	Land-Based?	Commercially Available?
	Quantify Total VOC Emission Rates from:		Quantify Individual VOC Emission Rates?	Quantify Emission Rates of:					
	Process Fugitives?	Flares?		NO_X?	CO?	SO_2?			
DIAL	✓	✓	✓	✓	✓	✓	Active	✓	✓
Airborne DIAL	X	X	X	X	X	X	Active	X	✓
SOF	✓	✓	✓	✓	✓	✓	Passive	✓	✓
OP-FTIR	X	X	X	X	X	X	Active	✓	✓
DOAS	X	X	X	X	X	X	Active	✓	✓
OP-TDLS	X	X	X	X	X	X	Active	✓	✓
VRPM	✓	X	✓	✓	✓	✓	Active	✓	✓
Passive IR Camera	X	X	X	X	X	X	Passive	✓	✓
TELOPS FIRST	P	P	P	P	P	P	Passive	✓	✓
Sherlock Systems	P	P	P	P	P	P	Passive	✓	✓
PFTIR	X	✓	P	P	P	P	Passive	✓	✓
I-DOAS	P	P	P	P	P	P	Passive	✓	
Raman Spectroscopy	X	X	X	X	X	X	Passive	✓	✓

P – Indicates potential for use in this application, assuming developments and advancements in the technology as discussed within this report.
✓- Indicates that the technology in its current form is capable of quantifying various compounds of interest from flares or process fugitives.
X – Indicated that the technology in its current form is not capable of quantifying various compounds of interest from flares or process fugitives.
.

3 Evaluation of Remote Sensing Technologies

3.1 Process Used to Evaluate Remote Sensing Technologies

The technologies are evaluated based on the following criteria:

- The technology should have the ability to passively detect and quantify emissions of chemical species of interest from flares and process fugitive emissions, under ambient conditions.
- The technology should have known detection limits for the species of interest and this should have been validated using various validation and comparison studies.
- The technology should be able to operate reliably in a continuous operation, with minimum downtime for maintenance.
- The technology should be commercially available for use in the US.
- The technology should have been commercially used in industrial survey campaigns for chemical species of interest. The technology should be portable.

These criteria are discussed in detail for each technology.

3.2 DIAL

3.2.1 Technical Ability to Detect and Quantify Emissions

As discussed in Section 2.2.2, DIAL is an active laser-based technology that measures the ratio of intensity of the return signals at different distances along the laser beam path. This ratio of signal strengths indicates the concentration of the target compound(s) along the line of measurement and time gating the return signal gives the concentration range resolution. Mass emission rates are computed by measuring along a series of scan lines through the plume to determine the plume profile, then integrating the concentration in the measurement plane and combining these with the meteorological data. DIAL has been routinely used to detect and quantify methane, C2+ hydrocarbons, benzene, toluene, ethyl benzene, xylene, NO_x, SO_2 and various other species. A high resolution mass flux measurement can take under 10 minutes. The technique has been used to measure emissions from both flares and process fugitives.

3.2.2 Known Uncertainties in Estimating Emissions

Sensitivity: Sensitivities and detection limits depend on the atmospheric conditions. For an IR DIAL system, the sensitivity ranges from 10 ppb to 50 ppb at a distance of about 1 km for methane, alkanes and alkenes. For an UV/visible DIAL system, the sensitivity ranges from 5 ppb to 10 ppb for NO_x, SO_x and O_3 at a distance of 0.5 km to 2 km. The sensitivity ranges from 10 ppb to 20 ppb for benzene, toluene and xylene at a distance of 0.5 km to 0.8 km. Detection

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limits for compounds of interest are listed in Table 2. DIAL has a fast response rate of only a few minutes for most chemical species. Like other OP techniques, DIAL measures a path-integrated concentration, usually expressed in units of ppm-m, but can also detect the distance of the plume from the detector and allow the generation of a two-dimensional plot of concentration and distance. The detection limit will vary with the path length. The DIAL detection limit varies with range from the DIAL, getting progressively worse the further from the DIAL. The DIAL detection limit, particularly in the IR region, is sensitive to atmospheric conditions.

Interferences: Meteorological measurements are important for calculating mass emission rates from concentrations measured using DIAL. Thus, any atmospheric turbulence that affects the measurements of wind speed and direction will also affect the calculation of mass fluxes from the concentration data. It may sometimes be difficult to isolate a source, particularly in downwind measurements, due to changes in wind speed or wind direction. However, DIAL can be used to scan specifically to isolate sources, although simultaneous flux measurements may not be possible.

Spectral Overlap: Many chemical species usually absorb at multiple wavelengths in the IR spectral region. IR absorbance spectra of ethylene, benzene and carbon dioxide are shown in Figure 9. All three of these compounds absorb strongly at more than one location in the IR spectrum. This may result in spectral overlap when using DIAL, or another optical remote sensing technology that uses absorbance, to detect a compound of interest from a complex mixture of gases having overlapping IR absorbance patterns. In addition, atmospheric absorption, in particular water vapor, CO_2 and methane, may interfere with absorbance in either the on or off wavelengths. For this reason, DIAL, particularly IR DIAL, employs laser lines with narrow spectral width, allowing the DIAL to probe in between interfering spectral lines.

For example, benzene and carbon dioxide both show an absorption peak in MIR (wavenumber of around 650 cm^{-1} or a wavelength of approximately 15.4 µm) range. Therefore, if carbon dioxide is present, it will be difficult to survey for benzene with the laser tuned to this wavelength. Benzene also shows an absorption peak in the NIR (wavenumber of 3050-3100 cm^{-1} or a wavelength of approximately 3.5 µm) range; however, ethene also absorbs at this wavelength. Therefore, the presence of ethene could interfere with a benzene survey conducted with the laser tuned to this wavelength. Because of these spectral overlaps, benzene surveys are often conducted in the ultraviolet portion of the spectrum.

It is crucially important to know beforehand the compounds present in a mixture to select the appropriate DIAL detection wavelengths for the target compounds and eliminate or minimize interference from other compounds. However, when examining a complex mixture, it may not be possible to completely exclude this interference. Other tools, such as OP-FTIR, can be used to scan for the presence of compounds with spectral overlap and, as necessary, retune the laser to a different wavelength or adjust the results to reflect the absorption of other compounds.

Validation studies have been conducted by both commercial suppliers of the DIAL technology, the National Physical Laboratory (NPL) and Spectrasyne Ltd. Following is summary of those validation tests.

Validation Studies:

- DIAL in-field validation measurements carried out by NPL include measurements of a known source of methane which were within 10% of the actual emitted value. For aliphatic hydrocarbons, the measurements were within 12% of the actual emissions. For toluene, the measurements were within 15% of the actual value and for VOC emissions, the measurements were within 8% of the actual value calculated by standard point method.

- The NPL DIAL has also been validated using the OP calibration facility developed at NPL. This is a 10 m long windowless calibration cell which can generate controllable test gas regions for testing the sensitivity, accuracy and spatial resolution of DIAL and other OP techniques.

- The NPL DIAL was also used in parallel with the USEPA DOAS system for side by side comparisons of benzene measurements during recent studies for the TCEQ.

- Spectrasyne carried out its first mass emission validation study in 1991 at Spadeadam, Cumbria in the UK, a defense site. In this study, DIAL measurements were carried on a controlled release of methane, 200 m-400 m downwind. Agreement between release measurements and DIAL was within 10%. The NPL DIAL was also involved in this study.

- Another mass emission study was carried out in by Spectrasyne in collaboration with the European Oil Industries Association for Environment, Health and Safety (CONCAWE), using a river barge tanker vent as a single emission source. In these studies, the maximum deviation in DIAL measurements was 15%. [http://www.spectrasyne.ltd.uk/html/dial_accuracy.html; http://www.spectrasyne.ltd.uk/html/reports.html]

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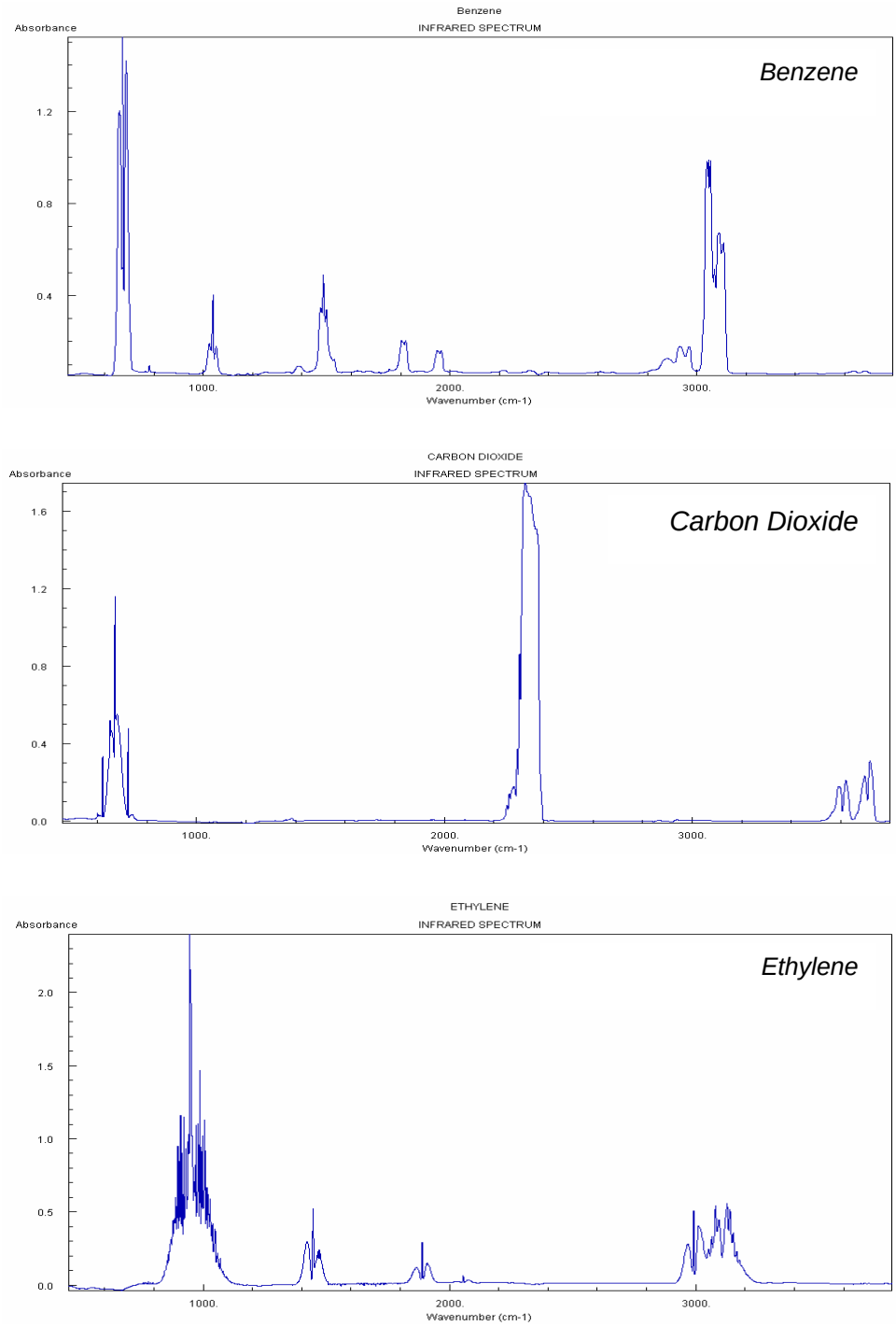
Figure 9: Gas-Phase IR Spectra of Benzene, Carbon Dioxide and Ethylene



(Source: NIST chemistry database)

Summary:

Table 3: Summary of DIAL ability to detect and quantify emissions

Contaminant	Optimal Operating Distance (km)	Detection Limit (kg/h / ppb)[1]	Flare		Fugitive	
			Detect?	Quantify?	Detect?	Quantify?
Total VOC	0.05-2	0.01/<10-50	Yes	Yes	Yes	Yes
Ethene	0.8	0.01/10	Yes	Yes	Yes	Yes
Propene	0.05-2	0.01/<10-50	Yes	Yes	Yes	Yes
1,3-butadiene	0.05-2	0.01/<10-50	Yes	Yes	Yes	Yes
Butenes (all isomers)	0.05-2	0.01/<10-50	Yes	Yes	Yes	Yes
Formaldehyde	0.05-2	0.01/<10-50	Yes	Yes	Yes	Yes
Acetaldehyde	0.05-2	0.01/<10-50	Yes	Yes	Yes	Yes
Toluene	0.8	0.01/10	Yes	Yes	Yes	Yes
Xylene	0.50	0.01/20	Yes	Yes	Yes	Yes
Isobutane	0.05-2	0.01/<10-50	Yes	Yes	Yes	Yes
Trimethylbenzenes	0.05-2	0.01/<10-50	Yes	Yes	Yes	Yes
Isopentane	0.05-2	0.01/<10-50	Yes	Yes	Yes	Yes
Carbon Monoxide	0.05-2	0.01/<10-50	Yes	Yes	Yes	Yes
Nitrogen oxide	0.5-0.8	0.01/5-100	Yes	Yes	Yes	Yes
Sulfur dioxide	0.05-3	0.01/10	Yes	Yes	Yes	Yes

[1]Detection limit is a function of the temperature of the plume and concentration of other compounds present.
(Source: The application of DIAL for monitoring industrial emissions. NPL; Reflections on 20 years of DIAL VOC measurements in the oil and gas industries. Spectrasyne Ltd.)

3.2.3 Reliability

DIAL surveys are conducted using a highly sophisticated, complex mobile laboratory that, in addition to the lasers, contains all of the technology required to:

- Continuously calibrate the lasers;
- Receive and record the DIAL signals;
- Analyze and process the signals into two-dimensional concentration contours; and
- Collect and integrate data from one or more meteorological masts.

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In addition to the DIAL system, there are the mechanical systems required to maintain and move the mobile laboratory and support the crew.

In general, the more complex the system, the more key components, the more opportunity there is for failures that affect, or potentially preclude, the system from obtaining the sought-after information. This certainly applies to DIAL. However, a trained and knowledgeable DIAL system crew, sufficiently equipped with key spare components, can minimize downtime associated with potential component failures.

Based on discussions with NPL and Spectrasyne personnel, it is ENVIRON's understanding that system failures that affect data acquisition have been rare. In 18 years of DIAL surveys, Spectrasyne has had less than 3 weeks of equipment failure time on site, which corresponds to about 1.2% of time on site[3]. Assignments typically last from one week to one month. Following each assignment, the systems are put through a thorough evaluation and the necessary preventive maintenance is performed. Should a key component fail during a DIAL survey and the necessary spare part is not on-hand, both DIAL providers maintain an extensive network of parts suppliers and can typically obtain the required part within a day or two.

3.2.4 Commercial Availability

Currently there are no commercial suppliers of the DIAL technology in the United States. The two commercial suppliers of the technology, Spectrasyne and NPL, are both based in the United Kingdom and their mobile laboratories and crews are located in the UK as well. Consequently, there are some significant logistical barriers involved in executing DIAL engagements in the U.S. These include:

- *Importation of the mobile laboratory*. This includes arranging for marine shipment as well as receipt and release through U.S. Customs. [Given the heightened security concerns in the United States since 2001, one should not disregard the possibility of a mobile laboratory containing highly sophisticated technical equipment, including one or more lasers, being detained by U.S. Customs for longer than expected periods.]

- *Obtaining worker visas*. To perform work in the United States, foreign nationals must obtain proper authorization from the U.S. State Department. Authorizations that may be used include obtaining an H1-B (specialty occupation) or O-1 (extraordinary ability) temporary worker visa. The number of H1-B visas issued is currently limited to 65,000 per year. They are released on April 1st of each year and are typically exhausted within one day. Therefore, obtaining an H1-B visa for conducting a DIAL survey does not appear to be a viable option.[4] According to Jan Moncrieff of Spectrasyne, no work permit is required

[3] Based on information provided by Jan Moncrieff, Spectrasyne Ltd.

[4] ENVIRON provides this information for discussion purposes only. ENVIRON does not have expertise in immigration law and/or State Department regulations and policies. The TCEQ or anyone else relying

under the US immigration 'traveling tailor' program, if only the measurements are taken in the US and the post-processing and reporting are done in the UK. However, ENVIRON has not been able to verify this.

- *Scheduling*. Even if workers can obtain proper authorization and importation of the mobile laboratory goes smoothly, there are still only two DIAL mobile laboratories that can perform this work. Under the best of circumstances it will take several months to schedule the field investigations. If both DIAL systems are highly committed to conducting surveys for other clients – it is ENVIRON's understanding that both Spectrasyne and NPL are currently receiving more requests for DIAL surveys than historical averages – it may take many months (or longer) from the time the order is placed until the equipment is in-the-field and ready to take measurements.

- *Cost*. The logistical difficulties of importing DIAL to the United States will add significantly to the cost of the survey.

However, despite these issues, both DIAL systems have been deployed successfully on US measurement campaigns in previous years.

Contact information is as follows.

Spectrasyne Ltd.
3 The Ringway Centre
Edison Road
Basingstoke, Hampshire
RG21 6YH, U.K.
Contact: Tony Wootton or Jan Moncrieff
Telephone: +44 (0) 1256 331555
Email: info@spectrasyne.ltd.uk
Website: www.spectrasyne.ltd.uk

(Source: Spectrasyne Ltd.)

National Physical Laboratory
Hampton Road
Teddington, Middlesex
TW11 0LW U.K.
Contact: Rod Robinson
Telephone: +44 20 8943 7146
Email: rod.robinson@npl.co.uk
Website: www.npl.co.uk

(Source: NPL)

3.2.5 Field Use

Field Applications During the Last Three Years: Since 1990, the two DIAL providers – Spectrasyne and NPL – have collectively conducted nearly 200 DIAL surveys. Since 2005,

upon the content of this report is advised to seek legal counsel on this matter.

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Spectrasyne has conducted 13 surveys and NPL has conducted two surveys.[5] These surveys are listed in Table 4.

Table 4: Summary of DIAL surveys conducted in the last three years.

Company	Location	Pollutants Surveyed	Date
Spectrasyne	UK Storage Terminal	Total HC, benzene	2005
Spectrasyne	Norwegian Methanol Plant	Unknown	2005
Spectrasyne	Norwegian Refinery	Unknown	2005
Spectrasyne	Norwegian Gas Plant	Unknown	2005
Spectrasyne	Canadian Oil Sands Productions Plant	Total HC, CH_4, benzene and NO_x	2005
Spectrasyne	Canadian Refinery	Total HC, Benzene	2005
Spectrasyne	Norwegian Gas Plant	CH_4, ethane, C3+ HCs and benzene	2006
Spectrasyne	Danish Refinery and Flare	Total HC, CH_4, Benzene and NO_x	2006
Spectrasyne	Danish Refinery	Total HC, CH_4 and Benzene	2006
Spectrasyne	Norwegian Gas Plant and Flare	CH_4, ethane, C3+ HCs, NO_x and benzene	2006
NPL	Landfill (unknown location)	CH_4	2007
Spectrasyne	Norwegian Marine Oil Terminal	Total HC, CH_4 and Benzene	2007
NPL	U.S. Refinery, Storage Terminal	Total HC, Benzene	2007
Spectrasyne	U.S. Refinery	Total HC, Benzene	2007
Spectrasyne	European Refinery & Gas Plants	Unknown	2008

Mobility & Portability: Both Spectrasyne and NPL DIAL systems are housed in mobile laboratories that can gain access to most areas that allow for vehicular traffic. Since both DIAL systems are housed in large vehicles, sufficient horizontal and vertical clearance is required. For example, the Spectrasyne DIAL truck is 2.4 meters wide and 4.1 meters tall (without meteorological mast attached). It weighs approximately 24 metric tons.

Power Supply: The DIAL mobile laboratories generate their own power via diesel generators. These can be run continuously or an overnight power supply can be used to keep systems warm and minimize daily startup times. Spectrasyne requests 3 phase 380/415/440 volts with a

[5] During much of this time period NPL was refurbishing their mobile laboratory and, therefore, were not available to conduct surveys.

starting current of approximately 50 amps and a running current of approximately 20 amps. Alternatively, they can use single phase 240v able to supply 1.5 kW.

3.3 SOF

3.3.1 Technical Ability to Detect and Quantify Emissions

SOF is a passive infrared based technology that has been used to measure most chemical species of interest. It has been used to quantify VOC emissions from refineries but only works in daytime in fair weather conditions. The uncertainty in detection varies with the compound of interest and ranges from 20-50%. With the ability to measure solar absorbance in the mid-infrared (2.5-8 µm) and the UV/visible region (0.3-0.7 µm), as the vehicle passes under a plume, SOF can detect most compounds of interest including alkanes, alkenes, HCHO, NH_3, HCl, HF, NO_2 and SO_2. Spectral overlap in the infrared spectrum limits the ability to use SOF to measure aromatics compounds such as benzene, toluene and xylene. For aromatic compounds, canister measurements are usually taken from the plume of interest and the ratio of aromatics to alkanes is used to estimate the emissions.

3.3.2 Known Uncertainties in Estimating Emissions

Limitations: SOF measurements conducted near the source are associated with larger uncertainties as the plume is closer to the ground and the wind field is more disturbed. Wind speed and direction are the largest known sources of error for the SOF technique. Wind uncertainties as high as 30% have been reported. For ethene, propene, NO_2, SO_2 and alkanes, the summed uncertainty for flux measurements has been reported to range from 33% to 38%. The SOF vehicle is typically driven at speeds ranging from 30 to 35 mph for far-field measurements. This may be a limitation when attempting to make measurements on-site where sources are much closer and vehicle speeds usually range from 10 to 20 mph.

Other considerations for SOF:

- To minimize uncertainty due to turbulence and mixing, where feasible, SOF measurements should be taken at some downwind distance (0.5-2 km) from the source. However, at those distances it may be difficult to isolate the source of emissions due to changes in wind speed or wind direction. The measurements conducted in near-field, close to sources, are rescaled to far-field measurements (0.5-2 km) to account for the disturbed wind field.

- As noted previously, SOF surveys are limited to daytime under sunny conditions. However, recently time correlation tracer (TCT) method has been used along with SOF to measure emissions from loading areas and tanks. A tracer is released near the VOC leakage area, upwind of the tank. A dilution factor is obtained from the measurements

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made by driving through the plume, downwind of the tank. This dilution factor of the tracer gas is used to estimate the VOC emissions.[6]

- SOF works better in a relatively flat terrain as wind variation is less than 20% between 20 and 100 meters, thus reducing the uncertainty in measurements.

Spectral Overlap: As discussed in Section 3.2.2 for DIAL, spectral overlap may limit the ability to use SOF for detection and measurement of certain compounds. For example, the spectral overlap between benzene and carbon dioxide in the MIR region may limit use of SOF for measuring benzene emissions.

Validation Studies: Several validation studies have been conducted by FluxSense AB, the commercial suppliers of SOF. These include the following.

- Several validation studies were conducted at a refinery in Sweden. These tests used SF_6 as the tracer gas and on an average the difference between actual emissions and emissions measured by SOF was 11% for a simple measurement, such as a gas release. However, various individual single emission measurements differed by almost 50% from the known emissions, depending on the proximity of the source to SOF.

- During TexAQS II (summer of 2006), SOF measurements of ethylene differed by a factor of 2 when compared to simultaneous emission measurements conducted by a NOAA aircraft during the same campaign. Average emissions over several days were within 15% of the NOAA measurements.[7]

- SOF measurements of alkanes conducted at a crude oil refinery in Sweden were within 4% of similar measurements conducted by DIAL at the same refinery, but at different times.

- In another campaign, emissions from a crude oil tank were measured at a Bitumen refinery. Emissions were measured using three independent techniques and SOF differences were between 20-30%, when measuring from a few tank heights away.[8]

Summary:

Table 5: Summary of SOF ability to detect and quantify emissions

Contaminant	Optimal	Detection Limit	Flare	Fugitive

[6] Information provided by Johan Mellqvist, Chalmers University of Technology, Sweden.
[7] An Overview of Solar Occultation Flux method, Johan Mellqvist, Chalmers University of Technology, Sweden, 2007.
[8] Information provided by Johan Mellqvist, Chalmers University of Technology, Sweden.

			Detect?	Quantify?	Detect?	Quantify?
Total VOC	0.05-1	0.5	Yes	Yes	Yes	Yes
Ethene	0.05-1	0.5	Yes	Yes	Yes	Yes
Propene	0.05-1	0.5	Yes	Yes	Yes	Yes
1,3-butadiene	0.05-1	0.5	Yes	Yes	Yes	Yes
Butenes (all isomers)	0.05-1	0.5	Yes	Yes	Yes	Yes
Formaldehyde	0.05-1	0.5	Yes	Yes	Yes	Yes
Acetaldehyde	0.05-1	0.5	Yes	Yes	Yes	Yes
Toluene	-	-	No	No	No	No
Xylene	-	-	No	No	No	No
Isobutane	0.05-1	0.5	Yes	Yes	Yes	Yes
Trimethylbenzenes	-	-	No	No	No	No
Isopentane	0.05-1	0.5	Yes	Yes	Yes	Yes
Carbon Monoxide	0.05-1	0.5	Yes	Yes	Yes	Yes
Nitrogen oxide	0.05-1	0.5	Yes	Yes	Yes	Yes
Sulfur dioxide	0.05-1	0.5	Yes	Yes	Yes	Yes

[1]Detection limit is a function of the temperature of the plume and concentration of other compounds present.
(Information presented in the table has been provided by the manufacturer.)

3.3.3 Reliability

SOF is run from a mobile van which contains highly sophisticated and complex instruments which are used for the following:

- Track the solar path through the plume;
- Receive and record the absorption spectra;
- Collect and integrate data from the ultrasonic windmeter and meteorological mast.

Based on discussions with FluxSense personnel, it is ENVIRON's understanding that system failures that affect data acquisition have been rare. Assignments typically last from two weeks to one month, depending on the size of the survey area. Typical SOF components such as, solar tracker, FTIR spectrometer, speedometer, GPS etc are commonly available and should not appreciably delay the survey if such a situation arises.

3.3.4 Commercial Availability

At this time there are no commercial suppliers of the SOF technology in the United States. The only commercial supplier of the technology, FluxSense AB, is based in Sweden and there are some significant logistical barriers involved in executing SOF engagements in the U.S.

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However, the company has plans to provide monitoring service in the US by collaborating with a local partner. These barriers are discussed in more detail in Section 3.2.4, but include:

- Importation of the SOF equipment;
- Obtaining worker visas;
- Scheduling; and
- Cost.

Contact information is as follows.

FluxSense AB
Sörensens gata 13
SE-416 79 Göteborg
Sweden
Contact: John Mellqvist
Telephone: +46 70 30 88 777
Email: johan.mellqvist@fluxsense.se
Website: www.fluxsense.se

3.3.5 Field Use

Over the past three years, FluxSense has conducted approximately 16 SOF surveys. These include:

- Since 2001, as part of the KORUS measurement program FluxSense has conducted annual SOF surveys of emissions from three Swedish refineries as part of the KORUS program. Measurements have been made for total alkanes.
- Since 2001, FluxSense has conducted annual SOF surveys of two Swedish chemical plants. Measurements have been made for total alkanes.
- Participation in TexAQS II during the summer of 2006. Measurements were made for alkanes, olefins, NO_2 and SO_2.

Mobility & Portability: SOF is housed in a light-duty truck or van that can gain access to most areas that allow for vehicular traffic.

Power Supply: SOF operates from power generated by the truck or van that it is housed in. There are no additional power supply requirements.

3.4 VRPM

3.4.1 Technical Ability to Detect and Quantify Emissions

VRPM can be applied to any open path survey technique. Using OPFTIR, VRPM can be applied to detect and quantify most alkanes, alkenes and most organics and inorganics from process fugitives that absorb in the IR region of the spectrum. UVDOAS based VRPM has been used to identify and quantify emissions of aromatics as well as inorganics such as NO_x, and mercury. VRPM has also been used with OP-TDLS to measure gases such as, HF, ammonia and methane.

3.4.2 Known Uncertainties in Estimating Emissions

Sensitivities: VRPM is used with OP-FTIR, UV-DOAS or OP-TDLS, all of which have low to moderate detection limits for species of interest. Typical sensitivity ranges for species of interest range from 0.5-50 ppb, 0.1-1 ppb and 1-50 ppb for OP-FTIR, UV-DOAS and OP-TDLS respectively. Typical response times range between 5-7 minutes with data updated every 2-2.5 minutes to give a moving average.

Limitations: The following should be integrated into the decisions on when and where to use VRPM.

- Measurements are best conducted on flat terrain.
- Optimally, the wind should be perpendicular to the plane of VRPM configuration. Of course, the wind direction may shift during the course of a VRPM survey. Since the VRPM array cannot be easily redeployed (a disadvantage when compared to DIAL or SOF), multiple VRPM arrays may be necessary dependent upon data needs.
- The use of retro-reflectors – deployed perpendicular to and at horizontal distances across the plume path downwind of the source – limit the practical vertical reach of VRPM. Therefore, VPRM may be unsuitable for measuring certain elevated sources, such as process flares.
- Currently, post field-measurement QA/QC of VRPM field data is required. However, software such as *IMACCQuant* and *ARCADIS Real-time RPM* are being evaluated and may give real-time concentrations in the field.
- Considerable effort is required to deploy the VRPM system. This includes placement of the light sources, retroreflectors, receivers as well as supporting data collection and processing systems and housings. Alignment for the UV-DOAS instrument may be difficult and time-consuming.
- For detection using VRPM, the target compound concentration should be three times the detection limit of the optical remote sensing instrument used in the configuration [EPA OTM-10].

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- Using OP-TDLS instrumentation with VRPM may require the use of fiber optic cable for telescopes, which may be difficult to deploy at certain survey locations. However, fiber optic cables have been used only in multiple-path fixed installations for long-term monitoring.

Spectral Overlap: As discussed previously, spectral overlap can limit the ability to use any emission detection and measurement technique that uses light absorption. However, since VRPM can be conducted using OP-FTIR, DOAS or OP-TDLS light sources, a very wide range of spectral analysis (IR, visible and UV) is available for use with this survey technique.

Validation Studies: In July 2006, ARCADIS, the commercial supplier of VRPM, and the USEPA conducted several validation studies. Recovery percentages for known tracer gas emissions were used to validate VRPM capture, with acetylene and SF_6 used as the tracer gases. VRPM was demonstrated to capture 86%-97% of the acetylene emissions and 75%-95% of the sulfur hexafluoride emissions across various VRPM configurations.

Summary:

Table 6: Summary of VRPM ability to detect and quantify emissions

Contaminant	Optimal Operating Distance (m)	Optimal Detection Concentration (ppm)[1,3]	Flare[2]		Fugitive	
			Detect?	Quantify?	Detect?	Quantify?
Total VOC	100-500	0.02	Unknown	Unknown	Unknown	Unknown
Ethene	100-500	0.05	Unknown	Unknown	Yes	Yes
Propene	100-500	0.05	Unknown	Unknown	Yes	Yes
1,3-butadiene	100-500	0.01	Unknown	Unknown	Yes	Unknown
Butenes (all isomers)	100-500	0.05	Unknown	Unknown	Unknown	Unknown
Formaldehyde	100-500	0.02	Unknown	Unknown	Yes	Yes
Acetaldehyde	100-500	0.05	Unknown	Unknown	Yes	Unknown
Toluene	100-500	0.02	Unknown	Unknown	Yes	Yes
Xylene	100-500	0.02	Unknown	Unknown	Yes	Yes
Isobutane	100-500	0.05	Unknown	Unknown	Unknown	Unknown
Trimethylbenzenes	100-500	0.05	Unknown	Unknown	Unknown	Unknown
Isopentane	100-500	0.05	Unknown	Unknown	Unknown	Unknown
Carbon Monoxide	100-500	0.05	Unknown	Unknown	Yes	Yes
Nitrogen oxide	100-500	0.05	Unknown	Unknown	Yes	Yes
Sulfur dioxide	100-500	0.05	Unknown	Unknown	Yes	Yes

[1] Most of the above chemical species can be detected by OP-FTIR, OP-TDLS or UV-DOAS. However, detection and quantification in the above table is solely based on the surveys conducted. [2]The VRPM is not designed for flares. However, the VRPM may be able to detect and quantify chemical species downwind of the flare if a tower high enough can be erected.
([3] Information provided by Ram Hashmonay, ARCADIS.)

3.4.3 Reliability

VRPM uses optical remote sensing equipment such as OP-TDLS, OP-FTIR or UV-DOAS that have a long history of field service and are considered to be robust, requiring limited maintenance and having a long service life. If a malfunction occurs during the course of a survey, parts and replacements are readily available in the US so, as necessary, units can be repaired or replaced quickly. OP-FTIR requires the least maintenance over long periods of time [EPA/600/R-07/032; EPA/600/R-05/042]. Of the three optical technologies that may be used in the VRPM, the OP-TDLS is the smallest and easier to use.[9]

3.4.4 Commercial Availability

ARCADIS is the commercial supplier of VRPM. It is ENVIRON's understanding that it typically takes at least a couple of months from the time the order is placed to design and install the VRPM system.

Contact information is as follows:

ARCADIS
P.O. Box 13109
Research Triangle Park, NC 27709 USA
Contact: Ram Hashmonay
Telephone: 919 544 4535
Email: ram.hashmonay@arcadis-us.com
Website: www.arcadis-us.com

3.4.5 Field Use

Following is a list of VRPM surveys conducted by ARCADIS in the last three years:

- Conduct of a landfill methane emissions survey during 2005-2006.
- Conduct of a survey for mercury emissions at a manufacturing facility during 2006.
- Conduct of a comprehensive refinery survey for various alkanes, alkenes, ketones, formaldehyde and aromatics.

Mobility & Portability: Once established the VRPM system is not portable or mobile.

Power Supply: The OP-FTIR system typically requires 120 volts of AC power, the OP-TDLS works on two 12 volt batteries and the UV-DOAS requires 230 volts of AC power.

[9] Information provided by Ram Hashmonay, ARCADIS

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3.5 Hyperspectral Imaging – TELOPS FIRST

3.5.1 Technical Ability to Detect and Quantify Emissions

TELOPS FIRST passive FTIR imaging system is capable of detecting most chemical species of interest from flares. The technology in its current state can identify all chemical species that absorb in the long wave IR region of the spectrum. The medium wave version, which would be able to identify aromatics and some additional VOCs, is not currently available for use.

TELOPS FIRST software is not currently designed to measuring mass or mass emission rates. However, the sensor has the capability to provide such measurements and research groups have used the FIRST sensor to perform such measurements in the past. TELOPS is currently working to perform flare measurement tests with the FIRST system to visually detect emissions of hydrocarbons and perform a spectral analysis to identify the individual hydrocarbons present. The project team members are also working to develop software that would allow for quantifying emissions using the pixel content of the visual image.[10]

3.5.2 Known Uncertainties in Estimating Emissions

The following should be taken into consideration for TELOPS FIRST.[11]

- Radiance requirements preclude the use of the TELOPS FIRST for evaluating process fugitives that are at the same temperature as the background. However, even a temperature contrast as small as 1°C between the background and emissions would generate a successful detection. When sky is the background, as in case of flare measurements, the contrast is generally good.

- For TELOPS FIRST, higher humidity has shown to decrease the instrument range. For fugitive emissions, as noted in the above section, good contrast between the background and emissions will result in higher instrument sensitivity and vice versa.

- The optimal range of measurement is between 0.3 Km and 3 Km. However, on a dry day when there is reduced moisture in the air, measurements can be made from a greater distance.

- Since TELOPS FIRST uses light absorption for compound detection and measurement, spectral overlap may limit its ability to detect unique compounds in the presence of spectrally overlapping compounds. However, TELOPS FIRST gas detection algorithms are based on clutter matched filter (CMF) and correlation calculations to separate a chemical of interest from a similar, interfering spectral signature.

- At this time, TELOPS FIRST software cannot be used to measure mass emission rates.

[10] Information provided by Vincent Farley, TELOPS.
[11] Ibid.

- Several gas detection and identification validation tests have been conducted with many chemical species. Flare measurement validation tests are planned for summer of 2008.

Table 7: Summary of TELOPS FIRST ability to detect and quantify emissions

Contaminant	Optimal Operating Distance (km)	Detection Limit (kg/h / ppb)[1]	Flare		Fugitive	
			Detect?	Quantify?	Detect?	Quantify?
Total VOC	Unknown		Unknown	No	Unknown	No
Ethene	0.003-3		Yes	No	Yes	No
Propene	0.003-3		Yes	No	Yes	No
1,3-butadiene	0.003-3		Yes	No	Yes	No
Butenes (all isomers)	0.003-3		Yes	No	Yes	No
Formaldehyde	0.003-3		Yes	No	Yes	No
Acetaldehyde	0.003-3		Yes	No	Yes	No
Toluene	0.003-3		Yes	No	Yes	No
Xylene	0.003-3		Yes	No	Yes	No
Isobutane	Unknown		Unknown	No	Unknown	No
Trimethylbenzenes	Unknown		Unknown	No	Unknown	No
Isopentane	Unknown		Unknown	No	Unknown	No
Carbon Monoxide	0.003-3		Yes	No	Yes	No
Nitrogen oxide	0.003-3		Yes	No	Yes	No
Sulfur dioxide	0.003-3		Yes	No	Yes	No

[1]Detection limit is a function of the temperature of the plume and concentration of other compounds present.
(Information provided by Vincent Farley, TELOPS Inc)

3.5.3 Reliability

The optimal operating temperature range for the camera is 0°C to 35°C (32 F to 95 F). Higher temperatures require the addition of a cooling module to the instrument.

3.5.4 Commercial Availability

TELOPS is the commercial supplier of the FIRST passive FTIR imaging system. Currently, TELOPS has one long wave camera available for rental purposes. The time between placing an order and conducting a survey varies but is usually between 2-3 weeks.

Contact information is as follows:

TELOPS
100-2600 Avenue St. Jean-Baptiste
Quebec, Qc Canada G2E 6J5
Contact: Vincent Farley
Phone: (418) 864-7808 x 481
Fax: (418) 864-7843

(Source: www.telops.com)

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Email: vincent.farley@telops.com
Website: www.telops.com

3.5.5 Field Use

The TELOPS camera is relatively heavy (weight ~ 60 lbs) and tripod mounted. It currently uses a separate computer for data acquisition. The camera works on either 120 volts of AC power or 28 volts of DC power.

Following is a list of TELOPS FIRST surveys conducted in the last three years[12]:

- Refinery survey for SO_2 conducted during 2006.
- Several field tests for monitoring of many chemical releases, mostly of chemical warfare agents (SF_6, NH_3, acetic acid, phosgene, etc) between 2008-2008.
- Flare tests planned in the summer of 2008.

3.6 Imaging Spectroscopy - Sherlock

3.6.1 Technical Ability to Detect and Quantify Emissions

Imaging spectroscopy (Sherlock VOC and FE) is based on dispersive hyperspectral imaging. Most chemical species of interest, including, 1,3-butadiene, methane, ethane, propane and butane, can be detected by Imaging Spectroscopy with varying detection limits based on the temperature of the gas and ambient conditions such as wind, rain, etc.

Each image pixel of the image corresponds to a certain volume which results in a concentration per unit volume. The Ideal Gas Law can be applied to calculate the actual mass from concentrations. However, algorithms and technology required to compute mass emission rates from either the concentration per unit volume or mass have not yet been tested.

Sherlock FE has been used to measure the combustion efficiency of flares. If the hydrocarbon loading to a flare is known, measured combustion efficiency could be used to estimate the destruction efficiency and, thus, the mass emission rate of total and/or individual hydrocarbons. The technology has been field tested for detecting emissions from flares at a distance of 5 km.[13]

3.6.2 Known Uncertainties in Estimating Emissions

Wind speed can have a dramatic effect on the detection limits of Sherlock VOC which is used primarily to image fugitive leaks (typically low concentration leaks that diffuse in the atmosphere rapidly). The Sherlock FE imaging spectrometer is not affected by wind since it analyzes

[12] Information provided by Vincent Farley, TELOPS.
[13] Information provided by Michele Hinnrichs, Gas Imaging Technology.

plumes from stacks and flares based on their temperatures. According to published test results of API sponsored testing in 2006, detection thresholds for various compounds including benzene, ethylbenzene and pentane, are dependent on wind speed. Most of these compounds have lower thresholds at no wind condition. However, the detection threshold increases with higher wind speeds [AWMA manuscript 06-A-159-AWMA].

Table 8: Summary of Sherlock camera ability to detect and quantify emissions

Contaminant	Optimal Operating Distance (km)	Detection Limit (ppm)[1]	Flare		Fugitive	
			Detect?	Quantify?[2]	Detect?	Quantify?[2]
Total VOC	0.001-5	100-1000	Unknown	Yes	Unknown	No
Ethene	0.001-5	100-1000	Yes	No	Yes	No
Propene	0.001-5	100-1000	Yes	No	Yes	No
1,3-butadiene	0.001-5	100-1000	Yes	No	Yes	No
Butenes (all isomers)	0.001-5	100-1000	Yes	No	Yes	No
Formaldehyde	0.001-5	100-1000	Yes	No	Yes	No
Acetaldehyde	0.001-5	100-1000	Yes	No	Yes	No
Toluene	0.001-5	100-1000	Yes	No	Yes	No
Xylene	0.001-5	100-1000	Yes	No	Yes	No
Isobutane	0.001-5	100-1000	Unknown	No	Yes	No
Trimethylbenzenes	0.001-5	100-1000	Unknown	No	Yes	No
Isopentane	0.001-5	100-1000	Unknown	No	Yes	No
Carbon Monoxide	0.001-5	100-1000	Yes	Yes	Yes	No
Nitrogen oxide	0.001-5	100-1000	Yes	Yes	Yes	No
Sulfur dioxide	0.1-1	100-1000	Yes	No	Yes	No

[1]Detection limit for Sherlock VOC (fugitive emissions) only. [2]ENVIRON does not have any knowledge of quantification into mass emission rates that may have been carried out by the Sherlock spectrometer. However, according to the manufacturer, quantification into mass emission rates has been carried out but not verified or certified.
(Source: Sherlock FE product presentation, Gas Imaging Technology, LLC; Michele Hinnrichs, Gas Imaging Technology, LLC)

3.6.3 Reliability

Information on reliability of the Sherlock spectrometer is not available. However, the manufacturer has brought to ENVIRON's attention that in one case the Sherlock VOC camera was used successfully to measure fugitive emission concentrations for seven consecutive years, with little or no maintenance.[14]

[14] Ibid.

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3.6.4 Commercial Availability

Gas Imaging Technology, LLC is the manufacturer and commercial supplier of both Sherlock VOC and Sherlock FE cameras in the US. Sherlock FE and VOC cameras are built to order and typically take between 3-4 months for delivery.

Contact information is as follows:

Gas Imaging Technology LLC
85 Industrial Way
Buellton, CA 93427
Telephone: +1 805.688.2088
Email: info@gitint.com
Website: www.gitint.com

3.6.5 Field Use

The Sherlock imaging spectrometers are portable, lightweight (weight < 12 lbs) and can be setup and operated by a single individual. The camera is operated using a standard 12 volt battery.

Sherlock's suppler, GIT, has provided the following information regarding commercial applications where either the VOC or FE models are currently being used. However, till date, ENVIRON has not been supplied with any documentation to this effect.[15]

- Sherlock VOC is being currently used by service companies in Japan, Italy, Argentina, Canada and other parts of the world to monitor fugitive hydrocarbon leaks.
- The Sherlock FE is being used in Russia for flare stack analysis.

We do know that the technology has been field tested at the BP refinery in Naperville, Illinois; however, the results of those tests have not been made available.

3.7 PFTIR

3.7.1 Technical Ability to Detect and Quantify Emissions

In 2003, the TCEQ evaluated use of PFTIR for measuring emissions from a flare under simulated and controlled conditions.[16] As noted in the Executive Summary of the June 2004 Final Report:

[15] Information provided by Michele Hinnrichs, Gas Imaging Technology.
[16] Texas Commission on Environmental Quality and the University of Houston, "Passive FTIR Phase I Testing of Simulated and Controlled Flare Systems," Prepared by URS Corporation, June 2004.

> *"The PFTIR testing on the actual flare was performed on August 27, 2003. A series of measurements were made in which the field of view of the PFTIR was moved to a number of different locations in the flare plume. Overall, the results suggest that PFTIR should be capable of measuring the emissions from industrial flares under the rigors of actual field conditions . . . The results of the Phase I testing suggest that PFTIR can be a viable approach for continuous near-real-time measurement of flare emissions and calculation of flare efficiencies."*

The report goes on to recommend additional field studies. However, the report also states:

> *"Based on the results of the Phase I Study it appears that further effort is needed to refine the analytical methodology used to process the PFTIR data."*

To the best of our knowledge, additional field studies have not been conducted and status on refinement of the analytical methodology used to process the PFTIR data is not known. However, plans are being developed by private industry to conduct further tests at Texas refineries, possibly in the summer of 2008.

During the controlled field studies of 2003, PFTIR was used to measure path-average concentrations CO, CO_2, butane, ethylene and propylene. This information is used to estimate combustion efficiency, defined as the concentration of CO_2 divided by the sum of the concentrations of the CO_2, CO, total hydrocarbons and soot. In its current state of development, PFTIR does not provide estimates of mass emission rates or destruction efficiencies. However, coupled with information on mass loading to the flare, combustion efficiency could be used to estimate emissions of total hydrocarbons.

Flares in the Houston-Galveston-Brazoria non-attainment area that are subject to the monitoring provisions of the HRVOC program are required to continuously monitor the mass of ethylene and propylene going to the flare. Affected facilities in Harris County must also monitor for 1,3-butadiene and isomers of butene. In order to calculate the heating value of the material going to the flare, some facilities are monitoring for more hydrocarbons than just HRVOCs. Therefore, it is possible, for some flares there may be sufficient information on total hydrocarbon loading to the flare to be able to use PFTIR-estimated combustion efficiency to perform a mass balance on the flare and calculate total hydrocarbon emissions. However, to the best of ENVIRON's knowledge, this has not been done either in a field study or in a commercial setting.

3.7.2 Known Uncertainties in Estimating Emissions

The Mercury Telluride Cadmium (MCT) detector used in the PFTIR is not sensitive for short (<3 µm) wavelengths and is not able to detect >C5+ hydrocarbons if the plume temperature is below 200°C. However, to overcome this limitation, a sandwich MCT-Indium Antimonnide (InSb) detector has been proposed. This would combine the high response of the MCT at long wavelengths with the high response of InSb at shorter wavelengths. These detectors are readily available commercially.

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The PFTIR technology cannot be used to detect and quantify emissions from most process fugitives since it involves analyzing the amount of thermal radiation emitted by a hot gas. To be detected, the gas should be at a temperature of at least 120°C.

Validation tests comparing the relative accuracies of PFTIR to extractive FTIR have been conducted. The test results are:[17]

- The relative accuracies are reported to be about +/-50% for CO_2, CO and ethylene. Due to lack of system response in the 3000 cm^{-1} region, >50% relative accuracies have been reported for butane and propylene.
- Sky background for reducing data and the absolute radiance calibration of the instrument may introduce a large bias in PFTIR measurements.
- This will have little effect on CO and CO_2 spectral signatures which are found between 2000 cm^{-1} and 2500 cm^{-1} and total hydrocarbon signature found between 2900 cm^{-1} and 3000 cm^{-1}, as the sky radiance is dominant between 700 cm^{-1} and 1700 cm^{-1}. However, the concentrations of ethylene, propylene and propane, which are measured in the 700 cm^{-1} to 1700 cm-1 range will be most influenced.
- The overall uncertainty for combustion efficiency ranges from 0.11% to 0.82%. In terms of run-to-run precision, coefficient of variation has been reported to be 5.4% and 29% for ethylene and butane, respectively.

The technology has not been used in a commercial application and greater effort is needed in understanding and analyzing the results of the only field test that was conducted almost 4 years ago.

Table 9: Summary of PFTIR ability to detect and quantify emissions

Contaminant	Optimal Operating Distance (km)	Detection Limit (ppm)[1]	Flare		Fugitive	
			Detect?	Quantify?	Detect?	Quantify?
Total VOC	Unknown	Unknown	Yes	Unknown	No	No
Ethene	50-200	0.11-0.18	Yes	No	No	No
Propene	50-200	0.42-0.71	Yes	No	No	No
1,3-butadiene*	Unknown	Unknown	Yes	Unknown	No	No
Butenes (all isomers)*	Unknown	Unknown	Yes	Unknown	No	No
Formaldehyde*	Unknown	Unknown	Yes	Unknown	No	No
Acetaldehyde*	Unknown	Unknown	Yes	Unknown	No	No
Toluene	Unknown	Unknown	Unknown	Unknown	No	No

[17] Ibid.

Table 9: Summary of PFTIR ability to detect and quantify emissions

Contaminant	Optimal Operating Distance (km)	Detection Limit (ppm)[1]	Flare		Fugitive	
			Detect?	Quantify?	Detect?	Quantify?
Xylene	Unknown	Unknown	Unknown	Unknown	No	No
Isobutane*	Unknown	Unknown	Yes	Unknown	No	No
Trimethylbenzenes	Unknown	Unknown	Unknown	Unknown	No	No
Isopentane*	Unknown	Unknown	Yes	Unknown	No	No
Carbon Monoxide	50-200	0.89-1.36	Yes	No	No	No
Nitrogen oxide*	Unknown	Unknown	Yes	Unknown	No	No
Sulfur dioxide*	Unknown	Unknown	Yes	Unknown	No	No

[1]Detection limit is a function of the temperature of the plume and concentration of other compounds present.
(Source: Passive FTIR Phase I Testing Final Report, June 2004)

3.7.3 Reliability

There is not enough information available to independently assess the reliability of the PFTIR instrument. However, in discussions with the PFTIR supplier, IMACC, they have conveyed their opinion that PFTIR is reliable for long term commercial use. The optical remote sensing equipment used in the technique is identical to that used in the active FTIR system which, over the years, has proven to be reliable and stable in industrial environments, under most weather conditions and only requires moderate maintenance.

3.7.4 Commercial Availability

Industrial Monitoring and Control Corporation (IMACC) is the commercial provider of the technology in the US. Currently, IMACC has one PFTIR unit in operation and available for short term surveys. Availability varies with the number of field tests or surveys being conducted.

Contact information for IMACC is as follows:

Industrial Monitoring & Control Corporation
800 Paloma Drive, Suite 100
Round Rock, TX 78664 USA
Contact: Robert Spellicy
Telephone: +1 512.341.8189
Email: rls_tx@earthlink.net
Website: www.ftir.bz

3.7.5 Field Use

PFTIR has been used in field tests for determining the combustion efficiency of a John Zink flare. The field tests were conducted using commercial grade propane as fuel at 10,000 lb/hr. The regions monitored by the PFTIR were as close 2 m and as far as 4 m from the plume tip. The average plume temperature during the field tests ranged from 225°C at 4 m to 416°C at 2m.

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Detailed information on the testing can be found in the 2004 report prepared by URS for the TCEQ.[18]

Mobility & Portability: The PFTIR system uses a wheeled cart to move very short distances within the survey area. However, it requires a pick-up truck in order to be transported to longer distances.

Power Supply: The PFTIR system requires 120 volts of AC power.

[18] Ibid

4 Ranking of Remote Sensing Technology Candidates

4.1 Ranking Process

As per the objectives of this project, the ranking system is heavily weighed towards the ability of a technology to detect and quantify emissions from flares. The following point allocation system is used to rank the short-listed technologies.

Technical Ability

- 25 points: Technology can detect and quantify emissions of all compounds of interest from both flares and fugitive-type sources and has been demonstrated in an industrial setting.
- 20 points: Technology can detect and quantify emissions of all compounds of interest from flares or both flares and fugitive-type sources and has been demonstrated in an industrial setting.
- 15 points: Technology can detect and quantify emissions of some compounds of interest from flares or both flares and fugitive-type sources and has been demonstrated in an industrial setting.
- 10 points: Technology can detect and quantify emissions of some to all compounds of interest from fugitive-type sources, but not from flares.
- 10 points: Technology has the potential to detect and quantify emissions of some to all compounds of interest from flares or both flares and fugitive-type emissions and has been field tested but has not been demonstrated in an industrial setting.
- 5 points: Technology may have the potential to detect and quantify emissions of some to all compounds of interest from flares or both flares and fugitive-type sources, but has not been field tested or demonstrated in an industrial setting.
- 0 points: Technology does not have the potential at this time to detect and quantify emissions of compounds of interest from either flares or fugitive-type sources.

Uncertainty

- 25 points: The technology has low detection limits for the compounds of interest, rapid response rates, operates effectively over short and long distances, and has been validated.
- 20 points: The technology has low detection limits for the compounds of interest, rapid response rates, has been validated, but operates effectively only over short distances.

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- 15 points: The technology has low detection limits for the compounds of interest, rapid response rates, operates effectively over short and long distances, but has not been validated.
- 10 points: The technology has low detection limits for only some compounds of interest.
- 5 points: Measurement and detection limits are unknown for most chemicals on interest.

Reliability

- 10 points: Technology appears to be simple, robust and reliable during field investigations.
- 5 points: Technology is complex, but has generally been reliable during field investigations.
- 0 points: Technology has not been reliable during field investigations or has not been field tested.

Commercial Availability

- 10 points: Technology is commercially available in the US.
- 5 points: Technology is commercially available outside the US but can be imported into the US for use.
- 0 points: Technology is not commercially available.

Field Use

- 10 points: Technology has been used commercially to measure and quantify air emissions at least 5 times in the past three years.
- 5 points: Technology has been used commercially to measure and quantify air emissions at least once in the past three years.
- 0 points: Technology has not been used commercially to measure and quantify air emissions in the past three years.

4.2 Technology Rankings

Table 10: Technology Evaluation Scoring

Technology	Technical Ability	Uncertainty	Reliability	Commercial Availability	Field Use	Total Score
DIAL	25	25	5	5	10	70
SOF	20	25	5	5	10	65
VRPM	10	15	10	10	5	50
TELOPS FIRST	5	15	10	10	0	40
GIT Sherlock FE[1]	10	15	10	10	0	45
PFTIR	10	20	10	10	0	50

[1] Sherlock FE, not Sherlock VOC, is ranked since the primary focus of this investigation is the measurement of emissions from flares.

4.3 Technologies Identified for Operating Cost Evaluation

Based on the rankings and discussions with TCEQ, five technologies are selected for cost evaluation. These technologies are as follows:

- DIAL
- SOF
- PFTIR
- Sherlock FE
- TELOPS FIRST

The detection and quantification of various chemical species from flare emissions is the main objective of this evaluation. VRPM has been extensively used for measurements from fugitive emissions; however, since the technology uses retro-reflectors mounted in a vertical plane, there are some practical limitations to the use of technology for measurements from elevated

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flares which may range from 150 to 600 ft in height. With this in mind, VRPM is not included in the final list of technologies identified for operating cost evaluation.

5 Operating Cost Evaluation

5.1 Cost Estimation Approach

The operating cost evaluation is a rough estimate of the cost of operation of the technology for a field survey in Texas. The estimate built using the following criteria.

- *Remote sensing technology rental rate*: The cost of leasing the technology for field use for surveys lasting one week and 20 days.
- *Staff cost*: The cost of qualified personnel to setup and operate the equipment. The cost is developed based on the number of staff required per day, hours of staff time required for each day of the survey and the hourly rate for the staff.
- *Travel and shipping expenses*: The cost for shipping the equipment and travel expenses for qualified personnel during setup and operation of the equipment during the survey.
- *Post-processing costs*: The cost for processing of the data collected during the field survey, including reporting of methodology and findings.
- *Other capital expenses*: Unspecified or incidental expenses related to the use of technology for the survey.

5.2 Cost Summary

Table 11 presents a summary of cost information for the five technologies evaluated.

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Table 11: Operating Cost Evaluation

Technology	Rental Rate (USD)		Staffing			Travel (USD)	Shipping (USD)	Processing (USD)	Other (USD)	Notes
	5 Days	20 Days	Number	Hrs/Day/ Person	Rate (USD/hr)					
DIAL	100,000 – 140,000	250,000 – 400,000	4	10	--[1]	14,000 – 25,000	15,000 – 20,000	--[1]	See Notes	• Additional costs may include: sorption tube analysis (speciation), additional insurance, etc. • Travel expenses are estimated at $200 per day per person for the duration of the survey plus three days for mobilization and demobilization. Cost also includes $1,500 per person for airfare. • Estimates may vary based on the currency exchange rate, number of species measured and location in the US.
PFTIR	2,000	8,000	1	8	125	2,000 – 5,000	1,000	5,000	See Notes	• Two people are required during the set-up and first day of the survey. • Travel expenses are estimated at $200 per day per person for the duration of the survey plus three days for mobilization and demobilization. • Post-processing includes combustion efficiency calculations. If destruction efficiency is the desired result of the survey, then the post-processing costs are typically 2-3 times the estimate.
SOF	32,000 - 43,000	125,000 - 175,000	2	8	--[1]	--[1]	--[1]	--[1]		• Estimates may vary based on the currency exchange rate. Exchange rate used for this estimate is US$1 = 1 SEK (Swedish Krona).

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Table 11: Operating Cost Evaluation

Technology	Rental Rate (US$)		Staffing			Travel (US$)	Shipping (US$)	Processing (US$)	Other (US$)	Notes
	5 Days	20 Days	Number	Hrs/Day/ Person	Rate (US$/hr)					
TELOPS FIRST	30,000	96.000	1	7.5	--[1]	--[1]	--[1]	175[2]		• After the first week, the equipment rental rate drops to $22,000 per week for subsequent weeks.
GIT Sherlock FE	2,000	16,000	2	8	175	6,000 – 10,000	2,000	--	See Notes	• Travel expenses are estimated at $200 per day per person for the duration of the survey plus two days for mobilization and demobilization. Airfare is estimated at $750 per person • Staff costs may vary and depend on the labor grade of staff associated with the survey. • Post-processing cost may vary significantly and depends on the amount of data collected and the desired output. At this time, GIT does not have an estimate.

[1]Costs are included in the rental rate.

[2]This is the hourly cost for post-processing.

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6 Conclusions and Recommendations

6.1 Conclusions

Based on the investigations conducted for this study, ENVIRON concludes that there are only two optical remote sensing technologies that have been used commercially to measure mass emission rates from flares: DIAL and SOF. Of these, DIAL has a more extensive history of commercial use with approximately 180 field surveys conducted since the early 1990s (not all of these involved measuring emissions from flares). Conduct of a field survey using DIAL, however, is not inexpensive. A 20-day field survey may cost as much as US$500,000. Also, since there are no commercial providers of land-based DIAL surveys operating in the US, there are significant logistical barriers that add time and cost to the conduct of a survey. While less expensive than DIAL, with only a single commercial provider of the technology – and that provider operates out of Sweden – the conduct of a SOF survey has many of the same logistical barriers as DIAL.

Two other technologies, the GIT Sherlock FE and IMACC's PFTIR, have been used to measure flare combustion efficiencies. Sherlock FE has been used in commercial applications whereas PFTIR has been demonstrated in a controlled study only. To be useful in measuring mass emission rates from flares, however, both technologies require that you know what is going to the flare. This means that the flare header must be monitored during the survey for mass loading of the compound or compounds of interest.

There are other, promising ORS technologies in development; however, at this time only the four aforementioned applications are commercially available for measuring mass emission rates from flares.

6.2 Recommendations

ENVIRON recommends that newer technologies that haven't proven their ability to detect and quantify various compounds of interest in a commercial setting and in the presence of overlapping compounds or mixtures should be challenged to do so.

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