

Optical methods for remote measurement of diffuse VOCs: their role in the quantification of annual refinery emissions

Prepared by the CONCAWE Air Quality Management Group's Special Task Force
on remote measurement of VOCs (AQ/STF-72)

M-F Bénassy
K. Bilinska
G. De Caluwé
L. Ekstrom
F. Leotoing
I. Mares
P. Roberts
B. Smithers
L. White

L. Post (Technical Coordinator)

Reproduction permitted with due acknowledgement

© CONCAWE
Brussels
June 2008

ABSTRACT

This report provides a review of the techniques which are currently commercially available for remotely monitoring VOCs from both point and area diffuse emission sources.

The use of recently developed optical gas imaging (OGI) equipment is a relatively simple and cost-effective method to identify fugitive point emission sources. An OGI camera can scan all potential sources on a process plant, which is not possible using conventional hydrocarbon leak detection instruments. Emission factors have been developed to permit quantification of annual emissions using OGI techniques.

For refinery area diffuse emission sources, the use of emission factor methodologies is concluded to be very effective in combination with a procedure to detect any 'significant emitters'.

Complex remote sensing techniques can only provide short-term emission measurements. Extrapolation of these can lead to very large errors in the projected annual inventory values due to the temporal variability of refinery emissions.

The OGI technique permits the cost-effective identification of any tank equipment components causing significant emissions. The complex techniques at best allow the identification of tanks with significant emissions but do not have the capability of pinpointing the equipment components in need of maintenance.

KEYWORDS

Diffuse emissions, LDAR, remote monitoring, optical gas imaging, VOCs

INTERNET

This report is available as an Adobe pdf file on the CONCAWE website (www.concawe.org).

NOTE

Considerable efforts have been made to assure the accuracy and reliability of the information contained in this publication. However, neither CONCAWE nor any company participating in CONCAWE can accept liability for any loss, damage or injury whatsoever resulting from the use of this information.

This report does not necessarily represent the views of any company participating in CONCAWE.

CONTENTS		Page
SUMMARY		V
1.	NOMENCLATURE	1
	1.1. TYPES OF EMISSIONS	1
	1.2. VOLATILE ORGANIC COMPOUNDS (VOCS)	2
2.	INTRODUCTION	3
3.	OVERVIEW	5
4.	TECHNIQUES FOR DETECTION OF POINT SOURCE FUGITIVE EMISSIONS	9
	4.1. CONVENTIONAL VOC 'SNIFFERS'	9
	4.1.1. Background	9
	4.1.2. Monitoring Instruments	9
	4.1.3. User requirements for FID/PID instruments	10
	4.1.4. Component identification	10
	4.1.5. Data handling	10
	4.1.6. Advantages	11
	4.1.7. Disadvantages	11
	4.2. OPTICAL GAS IMAGING TECHNIQUES	12
	4.2.1. Background	12
	4.2.2. Description of technology	12
	4.2.3. Sensitivity, selectivity and detection limits	13
	4.2.4. Developments	13
	4.2.5. Advantages	13
	4.2.6. Disadvantages	14
5.	TECHNIQUES FOR MEASUREMENT OF AREA SOURCE DIFFUSE EMISSIONS	15
	5.1. DIFFERENTIAL ABSORPTION LIDAR (DIAL)	15
	5.1.1. Facilities	15
	5.1.2. Description of the Technique	15
	5.1.3. Calibration	16
	5.1.4. Validation	17
	5.1.5. Range and Sensitivity	17
	5.1.6. Advantages	18
	5.1.7. Disadvantages	19
	5.2. SOLAR OCCULTATION FLUX (SOF) METHOD	20
	5.2.1. Facilities	20
	5.2.2. Description of the Technique	20
	5.2.3. Measurement strategy	21
	5.2.4. Measurement errors	22
	5.2.5. Validation	23
	5.2.6. Advantages	23
	5.2.7. Disadvantages	24
6.	QUANTIFICATION METHODOLOGIES FOR ANNUAL VOC EMISSIONS	26
	6.1. POINT SOURCE FUGITIVE EMISSION QUANTIFICATION	26
	6.1.1. Conventional LDAR using sniffing techniques	26
	6.1.1.1. Methodology	26
	6.1.1.2. Uncertainties	27
	6.1.2. Optical gas imaging technologies	27

6.1.2.1.	Development of the methodology	27
6.1.2.2.	Methodology	29
6.1.2.3.	Validation	30
6.1.2.4.	Uncertainties	31
6.1.3.	Advantages and Disadvantages	31
6.2.	EMISSION ESTIMATION METHODS FOR AREA SOURCES	31
6.2.1.	Storage Tanks	31
6.2.2.	Other Diffuse Emission Sources	32
6.2.2.1.	Loading	32
6.2.2.2.	Water drainage, collection and treatment systems	33
6.2.3.	Advantages	33
6.2.4.	Disadvantages	33
7.	SYNTHESIS	35
7.1.	POINT SOURCES	35
7.2.	AREA SOURCES	36
8.	CONCLUSIONS	38
8.1.	POINT SOURCES	38
8.2.	AREA SOURCES	39
8.3.	OVERALL CONCLUSIONS	39
9.	ACRONYMS	41
10.	REFERENCES	42
APPENDIX 1	COMPARISON OF MEASUREMENTS USING DIAL, SOF, TRACER AND CONVENTIONAL TECHNIQUES FOR A BITUMEN VAPOUR VENT	45
APPENDIX 2	COMPARISON OF DIAL MEASUREMENTS WITH THE API STORAGE TANK ESTIMATION METHODOLOGY	51
APPENDIX 3	COMPARISON OF TRACER GAS MEASUREMENTS WITH THE API STORAGE TANK ESTIMATION METHODOLOGIES	53

SUMMARY

This report provides a critical review of the techniques which are currently commercially available for remotely monitoring VOCs from both point and area diffuse emission sources.

To provide a suitable perspective, and for the sake of completeness, this report includes a description of qualitative and quantitative techniques for detecting emissions from point sources (i.e. from equipment components) as well as of those systems which are designed to visualise or to quantify emission fluxes from area sources such as process plants and tank farms.

In the report it is demonstrated that the use of robust emission factor methodologies is very effective in combination with a procedure to detect those few diffuse sources which emit significantly more (the 'significant emitters') than the majority of similar sources in a refinery.

Recently developed optical gas imaging (OGI) techniques permit remote point source leak detection with relatively simple to use hand-held cameras. All components can be scanned and monitoring surveys can be completed at a much faster rate than with conventional hydrocarbon leak detection ('sniffing') equipment.

An OGI leak detection survey can identify the point source 'significant emitters' permitting focused equipment maintenance and subsequent emission reductions.

Emission factors have been developed so that average annual emissions for all point source fugitive emissions can be determined from OGI leak detection surveys. This eliminates the need to use complex optical techniques to determine remotely the total emissions from point emitters.

The emissions from area sources cannot be measured using conventional instrumentation and so historically they have been quantified using algorithms.

The use of complex optical techniques to determine remotely the emissions from diffuse area sources (e.g. tanks, process plants) provides only short term flux data, which can permit the identification of the 'significant emitters', but cannot provide accurate annual emission estimates. In addition, due to resolution limitations, these techniques cannot identify the individual components within the area source which are the cause of the emissions.

For floating roof tanks the API has invested significant effort into the derivation of methodologies suitable for estimation of annual emissions as required by regulators both in the US and Europe. These methodologies have been proven to be robust where the user has applied the appropriate algorithms and where the tanks are properly maintained.

Tank floating roof surveys using OGI cameras can identify those tanks which are 'significant emitters' due to faulty emission control equipment such as seals. This capability permits repairs to be undertaken and thus return the tanks to within the bounds of operation for which the robust emission estimation algorithms are valid.

1. NOMENCLATURE

This report focuses on the quantification of diffuse volatile organic compound (VOC) emissions. This section clarifies the meaning of those terms, in particular outlining the difference between 'channelled' and 'diffuse' emissions and between 'point' and 'area' diffuse emission sources

1.1. TYPES OF EMISSIONS

Optical methods can be used to measure emissions to air from a variety of sources. The emissions are called 'channelled' when they are monitored within the source (e.g. in a vent pipe, flue or stack) and 'diffuse' when they are monitored externally to the source (e.g. uncovered oil-water separators). So called 'fugitive' emissions (e.g. from pressurised pipe components) are a subset of 'diffuse' emissions.

The definitions of these emissions, as provided in the Monitoring BREF [1], are given below:

Channelled emissions

Emission of pollutants into the environment through any kind of pipe, regardless of the shape of its cross-section. The practicality of measuring flow rates and concentrations is important to decide whether an emission is channelled.

Diffuse emissions

Emissions arising from the direct contact of volatile or light dusty substances with the environment under normal operating circumstances. These can result from:

- inherent design of the equipment (e.g. filters, dryers ...)
- operating conditions (e.g. during transfer of material between containers)
- type of operation (e.g. maintenance activities)
- or from a gradual release to other media (e.g. to cooling water or waste water).

Diffuse emission sources can be point, linear, surface or volume sources. Multiple emissions inside a building are normally considered as diffuse emissions, whereas the general ventilation-system exhaust is a channelled emission. Examples of diffuse emissions include venting from storage facilities during loading and unloading, storage of solid matter in the open air, separation pools in oil refineries, vents, doors in coke plants, mercury emission from electrolysis cells, processes involving solvents, etc.

A subset of diffuse emissions is:

Fugitive emissions

Emissions into the environment resulting from a gradual loss of tightness of a piece of equipment designed to contain an enclosed fluid (gaseous or liquid); typically this could be caused by a pressure difference and a resulting leak. Examples of fugitive emissions include leakages from a flange, a pump or a piece of equipment and losses from the storage facilities of gaseous or liquid products'.

In this report the distinction is made between diffuse emission point and area sources. Emissions from point sources comprise leaks from components which are not fully sealed e.g. pipe flanges, valve stems, pump glands, etc. As noted above, point diffuse emission sources are more commonly referred to as fugitive emission sources.

An example of a diffuse emissions area source is an uncovered oil-water separator, where the emissions originate from evaporation of the entrained hydrocarbons from the surface of the water. Other area sources are open-top floating-roof tanks and process plants. Both of these are classified as area sources because the emissions may be due to multiple point sources e.g. the roof fittings on tanks, equipment components on plants, etc.

Measurements of emissions from point sources can be made in very close proximity to the source whereas measurements of area source emissions have to be made at a distance from the source.

1.2. VOLATILE ORGANIC COMPOUNDS (VOCs)

In Europe, the term VOC is used in a broad generic sense to indicate any hydrocarbon compound which is either a gas or a liquid which can vaporise at ambient temperatures and enter the atmosphere. The driver for reporting VOC emissions is photochemical production of ozone. Methane has a negligible photochemical reactivity, so this compound is excluded from the 'basket' of reactive VOCs which are collectively referred to as non-methane volatile organic compounds (NMVOCs). It should be noted that the term VOC is defined differently by the US EPA; it also considers ethane to have a significantly low reactivity so ethane is excluded from the EPA list of reactive VOCs.

There are, however, a number of specific European regulatory definitions of VOCs; the differences being the lower limit placed on the volatility of the compounds defined as VOCs. For the specific case of fugitive emissions, CEN [2] has defined VOCs as 'all products of which at least 20% m/m has a vapour pressure higher than 0.3 kPa at 20°C. For the petroleum industry this includes all light products and excludes kerosene and all higher (*i.e. heavier*) products'.

2. INTRODUCTION

Volatile organic compounds (VOCs) are relevant to air quality because the photochemically reactive compounds form ozone in the presence of nitrogen oxides. Over recent years there have been wide ranging EU regulations resulting in significant reductions in VOC emissions from both industry and transport sources. Although concerns about tropospheric ozone currently have a low priority with European regulators, there is still strong pressure from local and national authorities to reduce VOC emissions from the oil refining and marketing sectors. Furthermore, EU regulators have set emission ceiling levels for VOC emissions and reduction targets as a percentage of baseline emission levels. As a consequence of this regulatory approach, consistent quantification of VOC emissions has become more important.

National inventories of emissions have to be prepared for submission under the UNECE convention for the long range transport of air pollution (CLRTAP). More recently values of annual emissions have been required of industry by regulators e.g. as input to the European Pollutant Emissions Register (EPER) and for its successor the Pollutant Release and Transfer Register (PRTR). Long-term measurements of emissions can only be made for sources which have a common vent or stack to which a continuous emissions monitor can be connected. This is possible for emissions from, for example, combustion sources but the latter provide a very small proportion of the mass of VOC emitted from a refinery [3]. The majority of VOC emissions are from diffuse emission sources, such as from pressurised piping components (e.g. valves, pumps, etc.), storage tanks, etc.

Over a 12 month period there may be significant variations in the VOC emissions from diffuse sources. For example, the emissions from external floating roof tanks are highly dependent on wind speed. Gross errors would be obtained, therefore, from the extrapolation of data from short-term measurement campaigns to provide annual averages for these sources.

The most common practice used by the refining industry to quantify annual VOC emissions is to apply internationally accepted industry estimation algorithms, such as those published by the US EPA [4] and API [5] [6]. It should be noted, however, that these assume that good operating procedures are in place and the equipment is well maintained.

Depending on the type of emission source these methods have a variety of uncertainties. For example, the uncertainty associated with the quantification of emissions from leaks from piping components is considered higher than those from loading mobile containers such as road tankers.

For this reason some interested parties have expressed the need for monitoring techniques to improve the quality of VOC emission estimates.

A number of optical methods to remotely monitor diffuse emissions are either commercially available or are being developed. These range from hand-held devices which can provide a visual image of the emitted VOCs from point sources to complex systems which aim to quantify area source emissions over short-term measurement periods.

The two complex systems which have been most commonly used in refineries are known as DIAL (differential absorption LIDAR) and SOF (solar occultation flux)

techniques. Like the hand-held devices, these employ absorption methods; DIAL using infrared (IR) or ultraviolet (UV) lasers as the light source and SOF using solar radiation.

For area sources, DIAL has been used to undertake VOC emission measurements since the late 1980s, whereas SOF is a more recent development. In this report the issue will be addressed that the results from measurements using both techniques at refineries have sometimes suggested that the methods commonly used to calculate annual emission estimates from refinery process plant, storage and other area sources of diffuse emissions are providing significant under-estimates.

For point sources, leak detection programmes in which components are monitored for leaks with a hand-held VOC detector can be used to quantify fugitive emissions. Although the detectors only measure VOC concentration, emissions can be quantified using correlations [2] [7]. This procedure can be extended to form a combined leak detection and repair (LDAR) programme which permits focused maintenance, ensuring that those components which are identified to be leaking in excess of a set leak rate are repaired.

The traditional hand-held detectors used in LDAR programmes utilise conventional VOC measurement technologies e.g. flame ionisation. Recent developments in optical gas imaging techniques have provided the opportunity for hand-held cameras to be used to visualise leaks from components, and this report reviews their use for detecting fugitive emissions. This report includes details of traditional non-optical LDAR monitoring techniques to permit comparison with those using optical gas imaging.

Some authorities are promoting remote measurement methods such as DIAL to identify those area sources classified as 'significant emitters' i.e. sources on a site which are emitting significantly more than other comparable sources. The detection of these sources using more localised leak monitoring methods, and their subsequent repair, has been claimed as a successful use of DIAL for reducing VOC emissions [8]. Consequently such systems are referenced in the European Commission Best Available Techniques Reference documents (BREFs) for both Refineries and Storage [9] [10]. These documents are due to be revised in the near future, prompting a need to establish if these systems are BAT.

In the context of these issues, this report provides a critical review of the techniques which are currently commercially available for remotely monitoring VOCs from both point and area diffuse emission sources. To provide a suitable perspective, and for the sake of completeness, this report includes qualitative and quantitative techniques for detecting emissions from point sources (i.e. from equipment components) as well as those systems which are designed to visualise or to quantify emission fluxes from area sources such as process plant and tank farms. The report also discusses the applicability of these techniques for the support of quantification of annual VOC emissions as required by the regulators.

3. OVERVIEW

Regulators require refinery operators to provide annual emissions data for a number of pollutants for national and European inventory purposes e.g. for the forthcoming European pollutant release and transfer register (E-PRTR).

Measurements of channelled emissions, such as with flue or stack gas monitors, are made by multiplying the VOC concentration by the vapour flow. For such sources, therefore, it is possible to determine annual emissions using measurement data. Thus for some VOC sources, such as road tanker gasoline loading, where the vapours are collected and piped to a vapour recovery unit (VRU), the annual emissions could be determined from a knowledge of the volume of gasoline loaded and data from VRU vent emission monitors.

Diffuse emissions, however, require measurements to be made of the VOCs external to the source. For example, the emissions from area sources can only be determined by measuring the plume concentration field data and multiplying by the corresponding wind field data.

Concentration measurements can usually only be made over short periods due to the impracticality of measuring on a continuous basis. However, there are significant temporal variations in refinery diffuse emissions. For example:

- The emissions from external floating roof tanks are highly dependent on wind speed.
- The emissions from fixed roof tanks are dependent on solar radiation; emissions occur as the vapour space above the liquid expands due to solar heating of the tank shell, but contraction at night as the vapour space cools results in air being drawn into the tank.
- The emissions from uncovered oil-water separators are dependent on the waste water temperature and the amount and composition of oil entrained in the water.

Without a full appreciation of these variations and a good understanding of product movements during sampling, extrapolation of data from short-term measurement campaigns (particularly those made only during daylight hours) to provide annual averages for these sources can easily lead to very large errors in the projected inventory values.

For area sources, the practice within the refining industry, therefore, is to quantify annual diffuse VOC emissions by calculation using well established estimation factors and/or algorithms; those recommended by CONCAWE are provided in [3]. It should be noted, however, that these assume that good operating procedures are in place and the equipment is well maintained. Further details of the methodologies for storage tanks and other area diffuse VOC sources are provided in **Section 6.2** of this report.

For point sources, simple emission factors can be used to determine fugitive emissions from pressurised equipment components such as pumps, valves, flanges, etc. The methods include:

- Use of a single factor for emissions from all equipment components based on refinery throughput.
- Where the number of equipment components is known, the use of average emission factors for individual types of components and their process service (i.e. gas or volatile liquid).

To improve accuracy, an alternative approach is to measure the concentration of any potential leak at the surface of equipment components e.g. at valve packings, joints, etc. The methods involve:

- Applying average emission factors based on a leak/no leak criteria, where the measured concentration determines if a leak 'threshold' has been exceeded; or
- Applying empirical emission correlations based on actual VOC concentration values determined at each leaking component.

These methods determine the concentration at a specific time and apply factors and correlations to determine long-term emissions, as outlined in the European CEN Standard [2]. Further details of the VOC monitoring devices used for point sources are given in **Section 4.1** of this report.

Such monitoring is being applied not only to quantify emissions but to reduce them through leak detection and repair programmes (LDAR). Leak detection studies are very time consuming as every accessible equipment component should be monitored, and in a typical refinery there may be in the order of 100,000 equipment components.

For calibration purposes, the emission mass flux has been determined by 'bagging' an equipment component with an impermeable shroud, passing air at a known rate over the component and measuring the resultant VOC concentration. Although this method provides quantified point source mass emission fluxes, it is very cumbersome and time consuming. It is, therefore, not viable as a method to determine total plant fugitive emissions.

A number of companies have developed optical sensing technologies which enable the visualisation of gas leaks, resulting in small, lightweight, hand-held imaging cameras which can detect leaks from process plant equipment components. These are being used for the application of optical gas imaging (OGI) LDAR where components are scanned to identify those that are leaking. This type of LDAR is often called 'Smart' LDAR in the United States.

Optical gas imaging technologies fall into two general classes, active and passive:

- Active systems illuminate the equipment being surveyed with infrared radiation and a scanner picks up the backscattered light. The wavelength of the light is chosen to be strongly absorbed by the gas being detected.
- The passive type uses ambient illumination to detect the difference in heat radiance or absorption of the hydrocarbon cloud.

Details concerning the optical gas imaging techniques being used for 'Smart' LDAR are given in **Section 4.2**.

Details on point source fugitive leak quantification are given in **Section 6.1**.

These hand-held optical gas imaging technologies have been developed primarily to detect leaks from point sources. Other optical techniques have been developed that permit more remote sensing including, in the most advanced methods, the measurement of concentration profiles down-wind of area sources, such as process plants and storage tank farms.

These remote optical systems, like the hand-held devices, employ absorption techniques. The two complex systems that have been most commonly used in European refineries are:

- DIAL, which is a laser-based technique using differential absorption LIDAR (light detection and ranging); this is the optical analogue of RADAR (radio detection and ranging). The technique relies on the scattering of light by the atmospheric aerosol. A small part of each laser light pulse sent out is scattered back to a detector. The amount of light absorbed provides an indication of the gas concentration in the scan line. The time taken for the signal to return provides range resolution.
- SOF (solar occultation flux), which is a technique that utilises the sun as the source of radiation. The system uses a solar tracker to ensure that solar radiation is beamed into a spectrometer. The system is housed in a mobile container which is driven past potential emission sources. As the solar radiation beam passes through a gas plume it is adsorbed, the reduction in signal providing an indication of the gas concentration in the line between the system and the sun.

DIAL has been used to undertake VOC emission measurements since research studies proved the principle in the late 1980s, whereas SOF is a relatively recent development which has been used operationally since 2002.

The SOF system has to be driven past a facility resulting in emission concentrations being measured along the transit line. The height of the plume (or plumes) crossing the scan line, however, cannot be determined. The DIAL system, by comparison, scans from a fixed location permitting two-dimensional range-resolved concentration profiles to be visualized.

In principle both types of system enable quantification of the VOC concentration in a vapour plume for the period that the system scans the plume. In practice this means that great care has to be taken to ensure robust averages are obtained from the large quantity of measurement data and that, when emission fluxes for both systems are quantified by multiplying the concentration data by the wind velocity, the shape of the plume cross-section and the wind profile across it are adequately described.

Further details on the DIAL and SOF techniques are provided in **Sections 5.1 and 5.2**.

Other available remote optical sensing techniques include Fourier Transform infrared (FTIR) spectroscopy, differential optical absorption spectroscopy (DOAS) and tunable diode laser absorption spectroscopy (TDLAS). These extend the measurement capabilities by working with multiple wavelengths so as to potentially identify several species simultaneously. There is an added layer of analysis involved in fitting the measured absorption spectrum to the species. The species that can be detected depend on the operating wavelength range. FTIR and DOAS use broad-band light sources; in the IR range for FTIR and in the IR/UV/visible range for DOAS. This allows simultaneous detection of multiple species. TDLAS uses laser

light which can be targeted to detect more precisely a single species, but different species can be selected by the choice of laser line.

These three systems provide an average concentration over the path between a light source and a receiver and do not provide range resolved information. They are generally used with a retro-reflector which must be re-positioned after each measurement. This makes the application of these techniques less useful for quantification of plant emissions and hence they are not discussed further in this report.

An alternative, non-optical method to quantify diffuse emissions from a point source is to use a tracer gas. This method is briefly described here as it has been used to provide comparison measurements with optical techniques; see **Appendices A1 and A3**. An inert gas, such as SF₆, is released at a known rate close to the suspected leak source. Gas samples are taken at a number of locations down-wind of the equipment and analysed. The ratio of the concentrations of the tracer gas to the process vapour is then determined permitting the leak rate to be calculated. If this method is used it is implicit that the potential emission source has already been identified.

4. TECHNIQUES FOR DETECTION OF POINT SOURCE FUGITIVE EMISSIONS

This chapter provides details of the techniques used to detect VOC emissions from point sources.

Section 4.1 describes traditional sniffing methodologies using conventional instrumentation. These are included to permit comparison with recent developments in the optical gas imaging techniques described in **Section 4.2**, which provide an alternative to the traditional methods.

4.1. CONVENTIONAL VOC 'SNIFFERS'

4.1.1. Background

VOC 'sniffing' is a method to monitor fugitive emissions. It consists of determining the airborne VOC concentration adjacent to a potential leak point (e.g. the packing gland of valves or the seal of a pump) by using sensitive gas detection instruments. VOC sniffing is mostly used in Leak Detection and Repair (LDAR) programmes to identify equipment components needing repair.

The most widely used LDAR programme is included in the US EPA *Protocol for Equipment Leak Emission Estimates* [7] and is based on the use of the American monitoring Reference Method 21 [11]. This protocol was the basis for the European CEN standard on LDAR [2].

This section focuses on the detection of point source fugitive emissions; their quantification is covered in **Section 6.1** of this report.

4.1.2. Monitoring Instruments

There are many different types of analyzers which can be used to detect fugitive emissions. These analyzers operate on a variety of principles, but the three most common types are flame or photo-ionization, infrared absorption and combustion. The choice of the instrument type is generally based on the type of chemical species to be monitored.

Ionization Detectors

These detectors operate by ionizing the gas sample and then measuring the charge (number of ions) produced. Flame ionization (FID) and photo-ionization (PID) are the two methods currently used in LDAR programmes. Photo-ionization detectors use ultraviolet light instead of the flame used in a FID to ionize the organic vapours. Certain organic compounds containing nitrogen or oxygen are difficult to measure with a flame ionization device (e.g. formaldehyde). In oil refinery leak detection programmes the FID is most commonly used.

For both the US and CEN methods, FID analyzers have to be calibrated to operate in a range of 10 ppmv to 100,000 ppmv VOC in air.

Both PID and FID analyzers are available in portable bag pack type sets allowing the operator to carry out measurements over an extended period of time.

Infrared Instruments

These instruments measure light absorption characteristics of gases. These instruments are generally used for streams of specific chemical species at high concentration. The device is set for the infrared absorption wavelength of the species of interest.

Combustion Analyzers

These analyzers are designed to measure either the thermal conductivity of a gas or the heat produced by combusting the gas.

4.1.3. User requirements for FID/PID instruments

As the analyzer is calibrated with a certain reference gas, a correction factor may need to be taken into account for the stream composition that is monitored. This correction factor is called the 'response factor'. A high response factor means that the instrument does not detect the compound very well. Both the US and CEN methods require the response factor to be less than 10.

The response time is defined as the time interval for a step change in VOC concentration at the sampling probe to register 90% of its final value. Method 21 requires the response time to be equal or less than 30 seconds. The CEN method requires it to be equal or less than 5 seconds.

The probe must be placed perpendicular, not tangential, to the surface of the leak interface and within 1 cm of the leak interface for moving components (e.g. pumps, compressors). The probe is moved along the entire leak interface to find the maximum reading. The probe is moved more slowly along those areas where leakage is indicated. The probe inlet is left at the location of the maximum reading for approximately twice the instrument response time. The maximum recorded reading is usually called the 'screening value'. If the screening value exceeds the instrument range, a 'pegged' value is used (e.g. 100,000 ppmv). If the response factor of a stream is greater than 3, the screening value needs to be adjusted.

Other requirements are defined for calibration procedures, precision tests and sample flow rate. For example, the scale of the analyzer should be readable to +/- 2.5% of the 'leak' definition.

4.1.4. Component identification

Potential fugitive emission sources are identified on process flow diagrams (e.g. by a software overlay on an electronic flow diagram). Some applications use field equipment tags for component identification. This can be achieved by using labels or bar codes. Labels have the disadvantage of being prone to getting lost, e.g. during repair works.

4.1.5. Data handling

Monitoring can result in a very large quantity of data being collected. For example a complex refinery typically may contain in the order of 100,000 potential fugitive emission sources of all sizes.

To store and track fugitive emission data effectively a computer database is required, compiling all relevant information such as component type, number,

service, location, screening value, emission estimate, etc. Commercial software applications are available allowing emissions reporting, data analysis for planning monitoring campaigns and for identification of leaking equipment components.

The use of a data logger facilitates collection of field data. These consist of hand-held or wearable computers that are carried in the field along with the sniffing instrument. Data are subsequently downloaded into the database. Some applications have the data loggers integrated into the detection device allowing automatic data recording. Other applications have wireless transmission of data to the database.

4.1.6. Advantages

1. Accepted technique

This technique is widely used and accepted.

2. Instrument costs

Detectors used for sniffing can be relatively simple. Typical costs are in the range of 5000 – 25,000 EUR depending on complexity. However, for practical purposes, several may be needed: for example, if a complete survey of the site needs to be undertaken over a short period then a number of monitoring teams have to be operating at the same time.

3. Applicability

Can be used in hazardous and/or congested areas.

4. Low limit of detection

The detection limit for monitors is of the order of 10 ppm.

4.1.7. Disadvantages

1. Not useable for some equipment components

Sniffing measurements are limited to sources located at grade or on platforms accessible by staircases or ladders. Experience show that typically 15-25% of refinery equipment components are not accessible and hence cannot be monitored. The technique is also limited to use on non-insulated sources.

2. Cannot be used for diffuse area sources

The technique requires contact with the emissions source. It can, therefore, only be used for fugitive emission point sources and not diffuse area sources e.g. uncovered oil-water separators.

3. Costs of pan-refinery surveys

The sniffing method is time consuming and therefore costly. Full monitoring of a complex refinery can take 6 months or more to complete and in one example (2006) reported costs were 0.6 million EUR.

4. Only measures concentration

Detectors only measure the VOC concentration at the leak point. Correlations must be used to derive mass emissions (see **Section 6.1**).

4.2. OPTICAL GAS IMAGING TECHNIQUES

4.2.1. Background

A number of companies, both in Europe and the US, have developed optical sensing technologies which enable the visualisation of gas leaks in real time, so that they appear like 'smoke' on a video recorder. As the plant equipment is also visible on the recorder the operator can easily locate the leak. A number of these devices were originally developed for military applications and have subsequently been used in industrial applications.

Development over recent years has resulted in small, lightweight, hand-held imaging cameras being produced which have provided the oil and gas industry with the means to detect leaks from process plant equipment components, storage tank fittings, pipeline flanges and vents.

The application of this technology in fugitive emission control programs is covered in **Section 6.1** of this report. The emission estimation methodology based on this leak detection technique is also discussed in **Section 6.1**.

4.2.2. Description of technology

Most currently commercially available optical gas imaging (OGI) technologies fall into two general classes; active and passive.

Active systems

The active system produces an optical image by reflected (back-scattered) laser light, where the laser wavelength is such that it is strongly absorbed by the gas of interest [12] [13]. The system illuminates the scene with infrared light and a video camera type scanner picks up the back-scattered IR radiation. The camera converts this back-scattered infrared light to an electronic signal, which is displayed in real-time as an image. Since the scanner is sensitive to illumination from the infrared light source, the camera is capable of displaying an image in either day or night conditions.

Passive systems

The passive type system is based on the image created by reflection of sunlight in the infrared region off the equipment. A gas cloud absorbing the reflected infrared light will appear darker [14] [15]. In addition the contrasting image of the gas is enhanced by the difference in heat radiance of the gas cloud and the background behind the cloud. The passive instrument has a tuned optical lens. It selects and displays a video image of light of a particular frequency range and filters out the light outside of that frequency range. In one design, by superimposing the filtered light (at a frequency that displays VOC gas) on a normal video screen, the instrument (or camera) displays the VOC cloud in real time in relationship to the surrounding process equipment. The operator can thus visualise a plume of VOC gas emanating from a specific component. Even when gases have a low contrast with their surroundings, the movement of the gas in a static environment makes finding leaks feasible.

The image responds to both changes in concentration and in plume size. As plume size and concentration for a fixed release rate depend on ambient weather conditions the plume image is not unique to each release. To evaluate the sensitivity

of the camera a series of measurements are carried out for a range of conditions and leading to a semi-empirical calibration.

Like a conventional camera an OGI device can be used for general or close-up views. In the close-up mode the operator scans areas of equipment components from a distance of a few meters. This enables quick detection of leaking equipment components such as valves, flanges and drains, even in congested areas.

By changing the focal length, the operator can detect relatively large leaks at a distance of several hundred meters. This feature enables monitoring of equipment components which are not accessible during conventional sniffing surveys. For example, safety valves leaking to atmosphere at the top of tall distillation towers have been detected from ground level. Another application of this remote visualisation capability is scanning tank components (e.g. floating roof rim seals, vacuum breakers and roof support legs) from tank-top platforms to detect leakage.

4.2.3. Sensitivity, selectivity and detection limits

A wide range of chemical species can be detected by the OGI technology. These include light aliphatic hydrocarbons, olefins and aromatics which constitute the vast majority of VOC emissions from refineries. The instrument is not designed to be selective for one compound but to have the possibility to detect, to some extent, all of the chemical components that may be present in leaks at oil refineries or petrochemical sites.

Laboratory wind tunnel tests [14] [15] [16] have demonstrated that the sensitivity of the OGI technology largely depends upon the type of molecule and the wind speed. These tests showed that for the most commonly used types of passive IR camera the detection limits for light aromatics are generally higher than for light aliphatic hydrocarbons and olefins. Detection limits increase at higher wind speeds.

For the cameras tested the detection limits for those molecules which are the main constituents of most refinery VOC fugitive emissions were well below 60 g/h. This has also been confirmed by field tests in refineries and chemical plants [17]. In some tests the camera could detect leaks below 1 g/h.

4.2.4. Developments

Although this technology allows efficient visualization of leaks it does not quantify the mass emission rate. The ability to quantify leaks appears to be the next technological hurdle to be overcome as well as decreasing the detection limits for certain molecules, e.g. benzene.

4.2.5. Advantages

1. Manpower requirement

Experience shows that typically a two person team using an OGI camera can screen in the order of 15,000 to 20,000 equipment components per day (i.e. approximately 2000 per hour). This performance is mainly determined by the time needed to tag for repair the identified leaking equipment components as the camera operator has to communicate the location to the assistant. Conventional sniffing techniques are of the order of thirty times slower (i.e. about 500 equipment components can be screened per day).

2. Large monitoring scope

Screening of all equipment components is possible. This enables detection of large leaks in non accessible locations, which would remain undetected in a conventional sniffing survey.

3. Mobility

Size and weight made first generation cameras difficult to manoeuvre in elevated areas and operating in congested areas was not practical. However, current generation OGI cameras are the size of domestic camcorders. This permits these instruments to be taken into process areas and onto tank tops, which is not possible with the more complex systems (see **Section 5.1**).

4 Operator training

Two to three days training is required to enable start of use. Obviously it requires some time before an operator gains sufficient experience to achieve the component screening rate referred to in **Section 4.2.5.1**. Unlike sniffing the camera does not require instrument calibration, thereby reducing the required level of expertise.

4.2.6. Disadvantages

1. Detection limit

The current generation of OGI cameras have a range of detection limits from 1 to 10 g/h for aliphatic hydrocarbons. However, the detection limit for benzene is substantially higher, making this technology less useful for leak detection surveys on benzene rich streams. Even so, the technique can still identify the 'substantial emitters' in this service.

2. Weather Conditions

OGI techniques are not as effective in rain or fog as conventional sniffing methods. They are less effective where there is limited temperature difference with ambient surroundings.

3. Instrument Costs

The cost of commercially available cameras devices is of the order of 70,000 to 100,000 EUR. By comparison the VOC detectors used in conventional sniffing surveys cost between 5000 to 25,000 EUR depending on complexity, but several are needed if a complete survey of the site needs to be undertaken over a short time period.

4. Equipment intrinsic safety

OGI cameras are generally not fully classified for hazardous areas and work permits impose the use of explosion meter to check the areas of survey. Some units, however, have limited hazardous area classification (e.g. one system is classified to NEC Class 1 Div 2). By contrast, the detectors used in conventional sniffing surveys are classified for use in hazardous areas.

5. TECHNIQUES FOR MEASUREMENT OF AREA SOURCE DIFFUSE EMISSIONS

This chapter provides details of the techniques used to measure the concentration of VOC emissions from area sources and quantify their mass emission fluxes.

The emissions from area sources can only be determined by measuring the plume concentration field data and multiplying by the corresponding wind field data. The determination of accurate emission fluxes depends upon certain conditions being met. For example the wind field must be 'stationary' (i.e. sufficiently unchanging in time for an average wind profile to apply) and, similarly, the plume concentration cross-section in a direction normal to the wind must be well-defined and consistent on a timescale that matches the measurement program. Such conditions are rarely met in the field, although they may be simulated in wind tunnel measurements.

Concentration measurements can usually only be made over short periods due to the impracticality of measuring on a continuous basis. The concentrations determined within plumes may be strongly influenced by any plume movement associated with wind direction fluctuations.

5.1. DIFFERENTIAL ABSORPTION LIDAR (DIAL)

5.1.1. Facilities

Two DIAL services are available commercially in Europe for the quantification of diffuse emissions from large industrial complexes like refineries; one facility is operated by the UK National Physical Laboratory (NPL) and the other by Spectrasyne. Both of these operate in the IR and UV spectral regions. Another DIAL with limited measurement capability (i.e. only in the UV) is operated by INERIS. There are other systems available but these require a particulate tracer to be added to the suspect source.

5.1.2. Description of the Technique

DIAL is a laser based technique using differential absorption LIDAR (light detection and ranging), which is the optical analogue of RADAR. The technique relies on the scattering of light by the atmospheric aerosol. A small part of each laser light pulse sent out is scattered backwards in the direction of the instrument (back-scatter). Collection and analysis of the spectral properties of this light, as described below, constitute the measurement. The main advantage over other open-path systems is that both the Spectrasyne and NPL DIAL facilities are 'single-ended' systems; i.e. there is no need for a mirror or retro-reflector to terminate the light path, so these systems can measure upwards.

By sampling the returned light pulse rapidly in time it is possible to distinguish how far each part of the light pulse has travelled and hence range resolve the signal.

The principle of differential absorption is to use two closely spaced wavelengths, one of which is absorbed more strongly by the component being detected than the other. The difference in the size of the two returned signals can be used to determine the concentration of the pollutant along the line of the laser beam. When the laser is pulsed and the back-scattered light is sampled then the basic path-

integrated attenuation measure is obtained. This is path integrated because the light gathered from, say, the second path segment has also to pass through the first path segment (in fact it passes through it twice – once out, once back) and so forth. The length of each segment depends on the sampling capability of the instrument due to the speed of light. A precision of a few metres is achievable in optimal conditions. The gathered signal has to be converted to concentration and then differentiated to give the variation in concentration along the beam. The analysis must also compensate for the attenuation of the light pulse intensity with distance which is calculated from attenuation of the non-absorbed wavelength. Performance will vary with ambient atmospheric conditions.

The two DIAL instruments incorporate scanning systems. The optical system can be rotated in a plane of choice while measurements are being made. By scanning the laser beam a two dimensional concentration map can be generated. This is deemed to be a key feature of the system, allowing plume heights to be determined and emission sources to be back-traced.

The wavelengths used for measurement must be unique to the target material to avoid interference with other materials commonly found in the atmosphere. For example, the wavelengths absorbed by water especially have to be avoided. The measurement capability then depends on the lasers installed in the DIAL system. For example, Spectrasyne use two Nd:YAG pumped dual wavelength dye lasers to provide the multi-wavelength tuneable sources required.

One of the systems is used to generate tuneable UV and visible radiation. In the UV spectral region gases such as SO₂, NO, NO₂, benzene, toluene and ozone are strongly absorbed. NO_x can be measured in the visible region, but due to eye safety issues this is not undertaken in industrial environments.

The other system generates a beam of narrow band, tunable IR radiation, which can be used for the majority of hydrocarbon components. A typical refinery 'general' hydrocarbon measurement can be made which uses an infrared absorption that is common to all hydrocarbons with three or more carbon atoms, linked to the stretch frequency of the carbon-hydrogen bond. The pair of IR wavelengths used can be selected so that the absorption per unit mass does not vary significantly for the typical hydrocarbons found in refinery diffuse emissions.

To obtain mass emission flux values, the concentration data across the entire plume cross section have to be multiplied by the wind velocity perpendicular to the DIAL measurement plane. The determination of accurate emission fluxes depends upon the wind field data at each concentration measurement segment being used. However, because it is not possible to obtain such sets of wind data, generally only one meteorological mast is deployed during a measurement campaign at a fixed location, providing a long-term consistent wind field data set. The use of wind field data obtained at a distance from the measurement plane introduces the greatest error into the flux estimation: see **Section 5.1.7.4**.

5.1.3. Calibration

The attenuation of the laser light by a gas of a known concentration over a known path length needs to be determined to calibrate the instrument. This is achieved using in-line gas calibration cells. These are filled with known concentrations of traceable standard gas mixtures. A fraction of the transmitted beam is split off and directed through the gas cell to a detector. This provides a direct measurement of

the differential absorption at the operating wavelength. The calibration cells are also periodically placed in the output beam to establish that the concentration response of the whole system is as expected.

It is possible to test the assessed fall off in light intensity with distance by targeting a gas expected to be fairly uniformly distributed in the atmosphere, for example methane.

In addition, the NPL has developed a facility for the calibration of open path monitors. This uses a 10 m long windowless cell able to maintain a uniform concentration of gas along its length.

5.1.4. Validation

A number of comparative tests have been undertaken to validate flux measurements derived by DIAL with known or directly measured emission sources. For example, NPL have undertaken measurements downwind of a known flux of methane from a vent in open-field, smooth terrain conditions, and obtained agreement to within +/- 10% [18]. NPL accept that the tests mainly highlight uncertainties in the technique used to calculate flux rates which relies on accurate wind profiling. The accuracy will be significantly worse in the terrain found within refineries, where wind profiles will be very different to those in smooth open-field conditions.

5.1.5. Range and Sensitivity

The ultimate ability of the system to resolve range depends on the sampling rate for the returned light pulse. However, to get a good signal to noise ratio, there must be both sufficient attenuation of the target wavelength and sufficient return reference light. Range resolution, and also the maximum distance over which the measurement may be made, therefore depends both on atmospheric conditions and the concentration of the pollutant. The NPL DIAL has a theoretical range resolution of 7 m along the beam but, in practice, this may be up to a few hundred metres.

The sensitivity of a DIAL system depends on:

- how strongly the laser beam radiation is absorbed by the pollutant being measured;
- the range at which it is being measured; as the back-scattered signal varies approximately as an inverse square function with range, the sensitivity reduces with distance from the DIAL facility;
- the path length over which the pollutant is present.

Typical values for the NPL DIAL, based on performance obtained during field measurements, are given in **Table 1** [18].

Table 1 Capability of NPL DIAL Facility

Pollutant	Spectral Region	Sensitivity ¹ ppb	Maximum Range M
SO ₂	UV	10	3000
Ozone	UV	5	2000
Benzene	UV	10	800
Toluene	UV	10	800
Xylene	UV	20	500
Methane	IR	50	1000
Ethane	IR	20	800
Ethene	IR	10	800
'General' Hydrocarbons (higher alkanes)	IR	40	800
HCl	IR	20	1000
Methanol	IR	200	500
Nitrous Oxide	IR	100	800

Note 1: the concentration sensitivities apply for measurements of a 50 m wide plume at a range of 200 m under typical meteorological conditions.

The resolution permits a DIAL facility to identify the area source 'significant emitters', but it is not adequate to allow individual point sources (e.g. equipment components on a process plant) to be pin-pointed.

5.1.6. Advantages

1. Well established technique

DIAL is well established, having been developed during the 1980s and used commercially for over 15 years.

2. Provides range resolved concentration data

With a scanning system the technique provides two dimensional concentration mapping, permitting plume shape and height to be estimated. If the scanning location is well chosen then plumes from specific area sources (but not point sources) can be visualised although this can compromise the quantitative interpretation depending on the complexity of the atmospheric flow.

3. Can provide quantification of mass emissions

Quantification of mass emission flux over the period of the measurement scan can be made if an estimate of the wind velocity field perpendicular to the scan plane can be determined. The major errors in the quantification are in the wind field measurement.

4. Can identify area source 'significant emitters'

It can be very effective as a screening tool to identify the area source 'significant emitters' if the DIAL can be sited to give a horizontal scan over, for example, an

entire tank farm. However, the resolution is not adequate to permit the identification of individual point source 'significant emitters'.

5. Permits improvement in emission factors for specific sources

It permits improvement of emission quantification of specific sources. For example, the combustion efficiency of flares can be determined from knowledge of the flow and composition of the gases combusted and the measured values of the VOCs in the flare emissions.

5.1.7. Disadvantages

1. Limited availability.

There are only two commercially available DIAL facilities in Europe.

2. Expensive and labour intensive to operate.

The system requires a team of at least 2 highly trained professionals. A typical measurement campaign at a refinery can last about 10 working days with overall costs of about 11,000 EUR per day.

3. Dependent on atmospheric conditions

The accuracy of the concentration measurement is dependent on weather conditions e.g. the degree of atmospheric aerosol. Measurements are not possible if the visibility is severely limited by fog or rain, or in very low wind speed conditions.

4. Potential serious errors in mass flux computation.

To obtain mass emission fluxes ideally requires each concentration data measured at a given point in space to be multiplied by the component of the wind velocity perpendicular to the measurement plane at the same location. This can never be achieved in practice, however, because the wind field cannot be measured at the concentration measurement point. Moreover, either because of physical constraints on the scan line or to improve detection sensitivity, measurement scans may be undertaken close to an emission source. As the emission plume close to the source may be in the wind shadow of a structure, such as a storage tank or process plant, the wind field profile in the scan line will vary with range and be significantly different to that measured in an open area. This may result in a significant over-estimation of the emission flux.

5. Up-wind sources cannot be simultaneously subtracted.

Upwind emission data must be subtracted from those measured downwind of the emission source. However, with only one DIAL system it is not possible to measure both up and downwind simultaneously. The ratio of upwind to downwind measurements depends on whether a significant up-wind source is detected. DIAL facilities are housed in large mobile containers (the Spectrasyne van is 12m long) and moving and setting up these up again to measure upwind of a source is time consuming. During short term monitoring exercises, therefore, there may only be one upwind scan and it is not possible to establish if intermittent upwind emission sources have influenced the measured source emission values.

6. For sources of varying emissions, measurements need to be made continuously during the entire emission cycle (or reporting period) to obtain representative source emission data.

Measurements of any one source tend to be made over short periods – typically 5 to 10 scans downwind of a source will be made providing 1 to 2 hours of measurement. Emissions from many refinery sources have temporal variations (see

Section 3). Short-term DIAL measurements can only provide a ‘snap-shot’ of emissions from these types of sources. The data can assist in the identification of the ‘significant emitters’ but extrapolation to provide estimates for the entire emission cycle or long-term regulatory reporting periods will result in serious error. **Appendix 2** provides details of measurements using DIAL over the medium-term (73 half hour scans) which shows that the range of measured values was between zero and 46 kg/hr and that the maximum value was 3.6 times the average value of all of the scan data.

7. For hydrocarbon measurements, detailed knowledge of the pollutant may be needed.

There are significant overlaps in the absorption spectra of the different hydrocarbons that may be detected by a DIAL system, as well as interference effects from water vapour. To simplify operations, DIAL facilities tend to use the absorption frequency that provides strong signals for the mix of typical hydrocarbons found at a refinery. This will give errors where the pollutant has significantly different absorption characteristics to that for the ‘general’ hydrocarbon mix. Olefins, for example, are more weakly absorbed in the ‘standard’ spectral measurement region used. This may require atmospheric samples to be taken and analysed and the absorption data adjusted to reflect the absorption coefficient for the mix of hydrocarbon components present. The degree of potential error is shown in **Appendix 1** which provides details of comparative measurements on a channelled bitumen vapour vent. In this case the DIAL measurements were >40 times higher than those measured using other techniques. However, it is possible that aerosols formed as the bitumen vapour cooled on contact with air may have contributed to this over-measurement by DIAL.

5.2. SOLAR OCCULTATION FLUX (SOF) METHOD

5.2.1. Facilities

Solar occultation flux (SOF) is a relatively recent development, having been patented in 1997. It has been used operationally to remotely measure emissions from industry since 2002. FluxSense AB is the only commercial supplier of this technique.

5.2.2. Description of the Technique

The SOF technique is an optical method that utilizes the sun as the light source. It is based on the absorption by certain VOCs of the infrared portion of the solar spectrum. The SOF measurements are conducted using a Fourier Transform infrared spectrometer that is connected to a solar tracker. The latter is a mirror device that tracks the sun and reflects the light into the spectrometer independent of its position. From the solar spectra it is possible to retrieve the path-integrated concentration (column) in mg/m² of various species between the sun and the spectrometer. The measurement system is built into a vehicle. To obtain the VOC emissions from a source, the vehicle is driven in such way that the detected solar light cuts through the emission plume.

In the infrared region of the solar spectrum utilized by the SOF method, a large number of species, such as aldehydes, alkanes, ammonia, CO, ethene, ethene-oxide, HF, HCl, NO₂, SO₂, propene, terpenes, and vinyl-chloride, can be measured. Olefins can be measured with good specificity, whereas alkanes have less

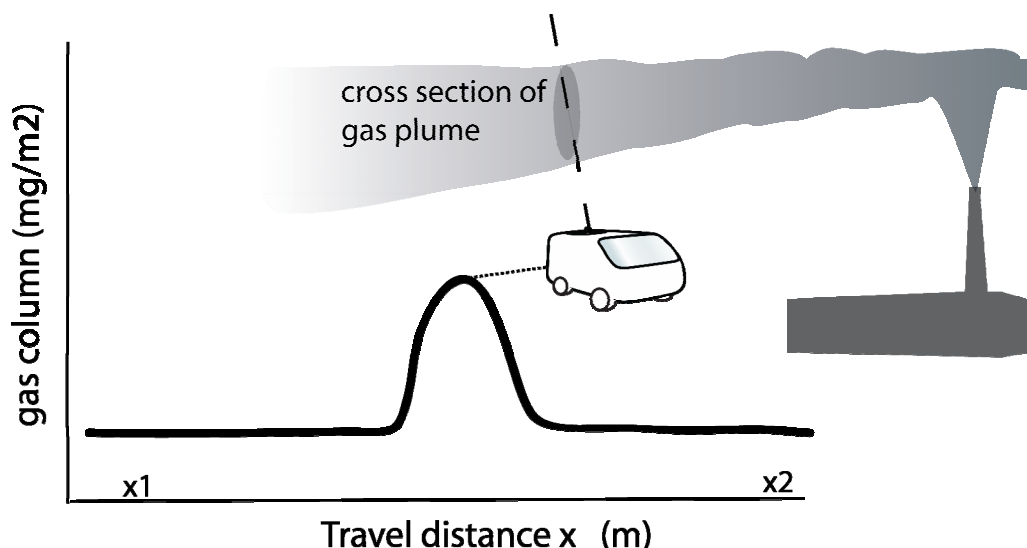
specificity due to spectral overlap. Aromatic species, however, cannot be measured directly. The spectral retrieval is based on using multivariate analysis in which calibration spectra recorded in the laboratory are fitted to the measured spectra. In addition to the target species, various interfering species such as H₂O and CO₂ are also fitted in the retrieval procedure.

The calibration spectra are obtained from published reference libraries, the uncertainty in the absorption strength of the calibration spectra being about 3% for all species. The fugitive VOC emissions from refineries generally correspond to alkanes (by mass). These compounds are retrieved in the infrared region between 3.3 μm and 3.7 μm using the vibration transition in the carbon-hydrogen bond (CH-stretch). The absorption features of the different alkanes are similar and interfere with each other, but since the number of absorbing C-H bonds is directly related to the molecular mass, the total alkane mass can be retrieved, despite the interference, within 5-10% from a typical refinery plume [19].

The emission flux in the SOF method is obtained first by adding the column measurements conducted across the gas plume as illustrated in **Figure 1**. The integrated mass of the key species across the plume is hence obtained. To obtain the flux this value is then multiplied by the average wind speed of the plume. The wind direction and speed are usually measured from high masts, towers and/or GPS balloon sondes.

The measurement and determination of the suitable wind speed for emissions estimation is not straightforward, as winds are usually complex close to the ground and speed increases with the height above surface. The uncertainty in the wind therefore is the largest source of error in the SOF method.

Figure 1 Schematic of SOF concentration measurement technique



5.2.3. Measurement strategy

Multiple measurements of the emission sources are normally conducted to reduce uncertainty and capture possible source variation. To eliminate possible background sources, industrial sites are enclosed in a 'measurement box' by measuring both upwind and downwind, typically from a distance of 0.5 km to 3 km. Because SOF

measurements have to be conducted in sunny conditions which cause unstable meteorological conditions, the wind gradients are smoothed out by convection. Over relatively flat terrain the mean wind varies less than 20% between 20 and 100 m height using standard calculations of logarithmic wind. In addition, for such meteorological conditions with considerable convection, the emission plume from an industrial plant mixes relatively quickly in a vertical direction. This means that at some distance downwind (>500 m) the plume is distributed from the ground up to several hundred meters height and the wind should vary little over the bulk of the plume. However, for sites with rougher surrounding terrain, including for example other industrial complexes or harbour installations, there will be an increase in the variation in mean wind speed resulting in an increased error in flux determination.

The SOF method has also been used to measure close to sources e.g. flares, process areas, crude oil tank farms, water treatment facilities, ship loading, etc. Measurements conducted near to the sources are associated with larger uncertainties than the measurements made at some distance from the site. This is because the plume is closer to the ground and the wind field is more disturbed, which introduces larger errors. In general, the emissions will be over-estimated when measurements are made in close proximity to sources, e.g. storage tanks, because the near-source wind speed will generally be lower than that measured in open terrain. For example, the over-estimation when measuring storage tank emissions at a few tank heights distance is reported by FluxSense to be of the order of 30-50% (see **Section 5.2.5**).

To compensate where measurements with large uncertainties are made close to sources, FluxSense combines these with measurements, with lower uncertainties, made some distance away. The flux estimates for the near-field sources are rescaled so that they add up to the total VOC flux measured at distance. This technique, however, is only valid if the remote measurement location is not affected by emissions from other neighbouring sites.

5.2.4. Measurement errors

The measurement error for the SOF measurements is mainly due to uncertainties in the wind data used in the flux calculation, as discussed above. Since the total emissions from industrial plants are typically measured at distances between 0.5 km and 3 km from the sources the bulk of the plume has risen to several hundred meters by the time it crosses the scan line. In this case, the uncertainty of the wind is estimated by FluxSense to be around 30% [19]. Measurements conducted inside industrial areas, near to emission sources, are associated with larger uncertainties (estimated by FluxSense to be up to 50% but could be greater depending on topography) due to more complexity in the wind field.

FluxSense state that other sources of error are the absorption line parameters of the retrieved compounds with uncertainties of 3% for the spectroscopic part. To this a retrieval uncertainty is added; this is the combined effect of instrumentation and retrieval stability on the retrieved total columns during the course of a plume transect. The composite uncertainty in the flux retrieval at the plume measurement traverse is believed by FluxSense to be within 33% to 38% for all retrieved compounds, as shown in **Table 2**.

Table 2 Uncertainty estimation of the flux measurements for plume measurements made outside of industrial sites.

	Wind Speed ⁽¹⁾	Wind direct	Spectroscopy (cross sections)	Retrieval	Square-root summed uncertainty
Ethene	30%	10%	3%	10%	33%
Propene	30%	10%	3%	20%	38%
NO₂	30%	10%	3%	10%	33%
SO₂	30%	10%	3%	20%	38%
Alkanes	30%	10%	3%	10%	34% ⁽²⁾

Notes:

1 – Error will increase with ground surface ‘roughness’ and also with proximity of scan line to the source.

2 – Includes an error of 6.6% in the alkane composite uncertainty, due to interference in different plume compositions.

5.2.5. Validation

Several validation experiments of the SOF technique have been conducted in which SF6 tracer gas was released at a known rate and then measured using the SOF method. In one experiment SF6 was emitted from the top of a 17 m tall mast in the middle of an open field. Traverses were then done downwind with the SOF measurement system at varying distances from the emission source. The retrieved average emission value differed by 11% but discrepancies of up to 50% were obtained for single measurements. Releases of SF6 from oil tanks have also been conducted at a number of refineries showing discrepancies of 50% for close-by measurements and smaller (about 30%) when measured a distance of several tank heights away.

5.2.6. Advantages

1. An established technique

Although a recent development, the technique has been used internationally on a number of projects and can be considered now to be well established.

2. Can provide quantification of mass emissions

Quantification of mass emission flux over the measurement period can be made if a reasonable estimate of the wind velocity field can be determined. As with DIAL the major error in flux determination is introduced by the wind field data.

3. Less complex method than DIAL

The method is straightforward compared to the other area source method discussed in this report (DIAL). An overview of emissions from a site can be mapped comparatively quickly. The measurements are spectroscopic and make possible the determination of many species such as alkanes and alkenes. Aromatics cannot, however, be measured directly.

4. Cost relative to DIAL

It is expensive but more cost-effective than employing a DIAL system. A typical refinery survey costs of the order of 5500 EUR per day with a duration of 8 to 10 days of measurement. However, the full survey may take up to one month if the weather is not suitable for the utilisation of SOF – see **Section 5.2.7.2**.

5. Can identify area source 'significant emitters'

If used for close-field measurements, it can be effective as a screening tool to identify the area source 'significant emitters', although it is recognised that the flux measurement uncertainties are greater than when used to scan entire facilities. SOF can be used in conjunction with tracer gas techniques to provide improved quantification of these 'significant emitters'. However, the resolution is not adequate to permit the identification of individual point source 'significant emitters'.

6. Permits improvement in emission factors for specific sources

As with DIAL, it permits improvement of emission quantification of specific sources e.g. flares.

5.2.7. Disadvantages

1. Limited availability.

There is only one company providing SOF measurements commercially in Europe.

2. Can only be used in sunny conditions

The SOF technique uses the sun as its source of IR radiation. It can, therefore, only be used in the day-time and then only when there is sufficient sunlight to provide adequate measurement conditions. Emissions from refinery operations tend to be higher during the day-time working hours, and solar radiation increases some VOC emissions e.g. breathing losses from storage tanks.

3. Does not provide range-resolved concentration data

The SOF technique provides a measure of the average concentration of a VOC in the entire column between the sun and the spectrometer. It cannot, therefore, provide the height of a plume, or details of concentration variations along the column length to permit the identification of individual sources contributing to a plume.

4. Does not measure aromatics

The aromatic species cannot be measured directly by this technique. They can be determined by using other methods to establish average concentration ratios with pollutants which are directly measured.

5. Potential serious errors in mass flux computation.

To obtain mass emission fluxes requires the concentration data to be multiplied by the component of the wind velocity at the plume height. This cannot be achieved because the plume height is unknown. This error may be limited when measurements are made at a distance of a few hundred metres to several kilometres due to wind-fields being more stable away from the rough terrain within a refinery environment. However, where a refinery is surrounded by other industrial plant, this far-field measurement strategy may not be possible. Fenceline measurements can be made as long as there are no sources close by. Measurement scans undertaken close to an emission source may result in an over-estimation of the emission flux. As the emission plume close to the source may be in the wind shadow of a structure, such as a storage tank or process plant, the wind

field profile in the scan line will vary with range and be significantly different to that measured in an area of flat terrain. For example, the over-estimation when measuring storage tank emissions a few tank heights away is reported to be 30-50%.

6. Up-wind sources cannot be simultaneously subtracted.

Upwind emission data must be subtracted from those measured downwind of the emission source. The SOF strategy is to drive the system around a plant whilst making continuous measurements. Hence both up and down-wind measurements are made in the same circuit of a facility. However, it is not possible to measure both up and downwind simultaneously, so it is not known if intermittent upwind emission sources have influenced the calculated source emission flux values. To reduce this uncertainty it is necessary to make several measurement circuits.

7. For sources of varying emissions, measurements need to be made continuously during the entire emission cycle (or reporting period) to obtain representative source emission data.

Measurements of any one source are made over relatively short periods, and only during day-light hours. These measurements can only provide a 'snap-shot' of emissions from area sources with temporal variations (see **Section 3**). The data can assist in the identification of the 'significant emitters' but extrapolation to provide estimates for the entire emission cycle, or long-term regulatory reporting periods, will result in serious error.

6. QUANTIFICATION METHODOLOGIES FOR ANNUAL VOC EMISSIONS

This chapter describes the methods available to quantify annual VOC emissions from diffuse sources.

6.1. POINT SOURCE FUGITIVE EMISSION QUANTIFICATION

The major point sources of fugitive emissions are pressurised equipment components installed on process plant.

Emission estimates based on using average component factors give conservatively high values as all similar components are considered to be leaking and all at the same rate. In practice, the majority of emissions are due to a few 'significant emitters': data from the US indicate 90% of fugitives originate from just over 0.1% of point sources.

Those point sources which are leaking can be identified, monitored and the emissions quantified by two methods:

1. Conventional LDAR using sniffing techniques
2. Optical gas imaging technologies

6.1.1. Conventional LDAR using sniffing techniques

6.1.1.1. Methodology

The conventional leak detection procedure [11] involves placing a gas sampling instrument probe at the surface of each piping component seal and measuring the volatile organic compound (VOC) concentration as the probe is moved along the surface of the seal. The instrument readings, referred to as screening values, are compared to a set level which is considered to indicate a leak.

Rather than measuring the actual mass leak rate, this procedure only measures the VOC concentration in the vicinity of the component leak.

The US EPA 1995 Protocol [7] describes two methods to estimate mass emissions from these concentration measurements. Either 'leak' / 'no-leak' factors or correlations can be used. These are provided in the Protocol and differ depending on the type of industry: there are 'Refinery' factors or correlations for refineries and 'SOCMI' factors or correlations for chemical facilities. If correlations are used, separate factors are available for pegged screening values and default factors for equipment components which are below the detection limit.

It should be noted that estimates for the same products and equipment components obtained by using Refinery and SOCMI factors/correlations can differ significantly.

The methodology to determine mass emissions using correlations, described in [7], has been used as the basis for standardisation by CEN [2].

To obtain a value for the total fugitive emissions from a site, the methodology for quantification must cover all the potential point sources at that site. Once all the screening values have been determined, they can be converted into mass emissions using the appropriate correlations and factors for pegged values. In addition, there needs to be an accurate count of non-accessible equipment components. These are assigned an average leak rate, based on the observed leak rates obtained on the leaking components of the site.

The total mass flux from all point sources is the addition of the mass flow rate of all the measured leaking equipment components and an estimate of the mass flow rate of non-measured components according to the average leak rate factors.

'Targeted' monitoring can also be undertaken in which only certain component types are monitored. Component types which are not monitored are assigned an average emission factor, thereby increasing the uncertainty of the emission estimate.

Speciation of emissions (e.g. estimating benzene emissions) can be achieved by using an equipment component database which includes stream compositions. Monitoring results from sniffing are fed into this database yielding both total VOC and speciated emission estimates.

6.1.1.2. Uncertainties

The use of correlations is well established, but it is recognised that there is a relatively poor correlation between screening concentrations and actual mass emissions rates as determined by bagging (see **Section 3**).

One of the reasons for this is that a given mass emission rate from a small point leak can result in a much higher screening value than larger leaks over a broader area. When used in LDAR programs this can result in leaks being missed because of a low screening value or in unnecessary repair efforts for high screening values.

Apart from these uncertainties, during the European standardization process [2], a round robin test was designed to determine precision parameters for concentration measurement and corresponding mass emission estimates. For the screening concentration measurements (in ppm) the repeatability and reproducibility standard deviations were 34.5% and 46.5% respectively. For the estimated total mass emission flux (in kg/year) the repeatability and reproducibility standard deviations were 24.5% and 40.5%.

As described above, the uncertainty of the emission estimate increases as the number of non-measured equipment components increase e.g. in 'targeted LDAR' monitoring campaigns.

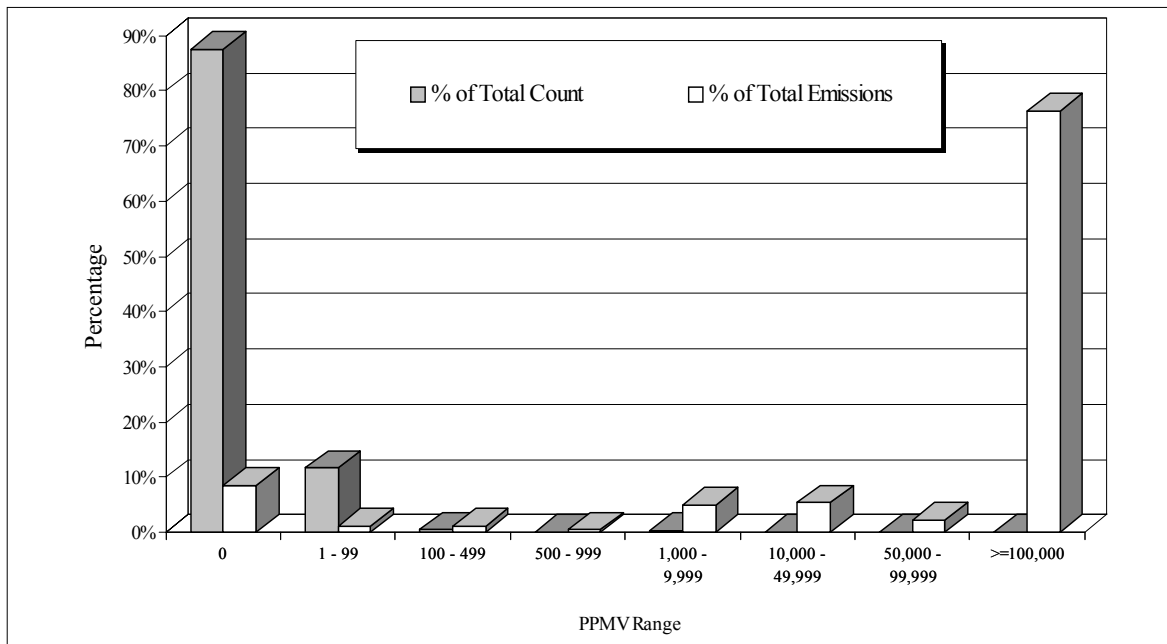
6.1.2. Optical gas imaging technologies

6.1.2.1. Development of the methodology

Analyses by the API have shown that over 90% of controllable fugitive emissions come from only about 0.13% of the piping components [20] [21]. These results are illustrated in **Figure 2** where the vast majority of components are in the lowest Method 21 screening ranges (zero defaults and below 100 ppmv) whilst almost all of the estimated emissions are from the very few components that are measured to be above 100,000 ppmv. This leak distribution was derived from a large US database,

and individual cases may show a different leak distribution. This is the case, for example, for the results from some preliminary, initial monitoring campaigns at European refineries. However, these show greater numbers (in the order of 90%) of components which are below the leak threshold concentration.

Figure 2 Distribution of Component Count and Estimated Emissions by Screening Range [22]



These observations clearly show that a method which economically locates the very high leaking components (the ‘significant emitters’) without having to monitor every individual point source in the plant using the conventional sniffing methods would result in major reductions in costs and emissions.

Optical gas imaging had been identified as such an alternative to sniffing for locating large leaks more efficiently. This technology has been tested in both refinery and chemical plant environment following controlled laboratory calibration of the detection limits of the OGI cameras. It has the potential to meet three key principles, which are:

- scanning components in a plant more quickly;
- identifying the ‘significant emitters’; leading to
- increased emission reductions, and lower survey costs.

As discussed in **Section 4.2**, the emerging OGI technology offers an operator the ability to visualise leaking gas as a real-time video image. The remote sensing and instantaneous detection capabilities of OGI technologies allow an operator to scan areas of potentially leaking components much more quickly, eliminating the need to measure all components individually. Whilst many other technologies can detect the presence of hydrocarbons, OGI provides a real-time image of the gas plume and the equipment from which it is emanating, which permits identification of the exact source.

The US EPA Steering Committee for Alternative Leak Detection Work Practices (AWP) has developed a 'demonstration protocol' to provide petitioners with a reasonable idea of what it will take for a new technology or work practice to achieve equivalent control effectiveness and be approved by the US EPA. This demonstration protocol provides an optional 'approval process' that includes a combination of laboratory testing, field testing and mathematical analysis to quantify the performance of an alternative technology and determine if it can achieve equivalent fugitive emissions control to that achieved using Method 21 as applied in the USA.

To facilitate the demonstration of emissions control equivalence for an alternative LDAR technology, the US EPA has developed Monte Carlo simulation software to help evaluate technologies or work practices [22]. The software performs Monte Carlo simulations (i.e. random statistical simulations) of simultaneous screenings of equipment by the current work practice (conventional LDAR using Method 21) and by a proposed alternative e.g. using OGI techniques. The emission reductions which could be achieved by repairing the equipment components which are identified as leaking can then be derived. These provide quantified environmental benefits from using either the conventional or alternative technologies in a LDAR programme. An environmental benefit equivalent to the current work practice (CWP) is demonstrated when the Monte Carlo simulations show that the emission reductions achievable with LDAR using an alternative technique are the same as, or greater than, those achieved using Method 21.

Using an AWP in which all components are monitored and large leaks are repaired on a common schedule can attain the same or better environmental control as the CWP using Method 21. Required leak detection thresholds for these AWP have been determined by API [23] using the Monte Carlo simulation technique developed by the US EPA. The corresponding frequencies of monitoring are listed in Table 3 of publication [23].

Laboratory testing was used to determine the instrument capabilities for a wider range of chemical species [16] and detection limits for different compounds were determined. As shown in **Section 4.2**, field bagging tests confirmed that OGI camera detection limits for most refinery VOC mixtures are even lower than the required leak detection threshold for the AWP. This observation also supports the effectiveness of the use of OGI where the leak size distribution has less leaks above the AWP threshold compared with the typical leak size distribution found in the US (as shown in **Figure 2**).

6.1.2.2. Methodology

A new set of emissions factors as shown in **Table 3** has been derived for the quantification of emissions when optical gas imaging is used for leak detection [24].

The emissions factors in **Table 3** were derived for valves, pumps and connectors/flanges and for a selected range of OGI camera leak detection thresholds ranging from 3 to 60 g/h. These new emissions factors are designed to be used in lieu of US EPA 1995 protocol 'Leak/No Leak' factors.

The study demonstrates that the use of these new emission factors generates mass emission estimates that are the closest to actual mass emissions rates obtained through the current work practice.

The factors used depend on the detection limit of the OGI camera. With a lower detection limit the camera detects more leaks, hence the factors are lower because they were developed so that the total mass emission flux is the same as that determined by conventional sniffing. Thus if a camera has a detection limit of 6 g/h, the factor used for a non-leaking valve is 0.043 g/h and for a leaking valve is 73 g/h.

Table 3 Set of Emissions Factors to be applied when optical gas imaging is used for leak detection [24]

Component Type	Emission Factor Type	1995 U.S. EPA Protocol Factors ^(*)	Emission Factor (g/hr/component) for Specified AWP Leak Definition (g/hr)			
			3	6	30	60
Valves	No-Leak	0.88	0.019	0.043	0.17	0.27
	Leak	160	55	73	140	200
Pumps	No-Leak	13	0.096	0.13	0.59	0.75
	Leak	420	140	160	310	350
Flanges	No-Leak	0.06	0.0026	0.0041	0.0100	0.014
	Leak	38	29	45	88	120
All Components	No-Leak	0.33	0.0070	0.014	0.051	0.081
	Leak	69	56	75	150	210

(*) The 1995 U.S. EPA Protocol Factors listed were weighted by service according to the proportion of components in each type of service in the model refinery.

The new methodology to estimate mass emissions will require a survey of all the equipment components using optical gas imaging. For each detected leaking point source, application of the new 'Leak' factors will provide mass emission estimates. Likewise, the new 'No Leak' factors will be used for all non-leaking components. The addition of all the leaking and non-leaking component emissions will give an estimate of the mass emission of the unit or site. As with conventional sniffing surveys, there is still a need for reliable equipment component counts.

It should be noted that when sites switch from a conventional sniffing based monitoring programme to an optical gas imaging based monitoring programme they will also change the emission estimation method. This could result in a change in reported emissions merely due the uncertainties of the estimation method.

Speciation of emissions using optical gas imaging can be undertaken in the same way as for are conventional LDAR (see **Section 6.1.1.1**).

6.1.2.3. Validation

Data have been collected on a refinery process unit where optical gas imaging replaced Method 21 for leak detection [25]. Emissions were monitored over a six month period and mass emission rates determined by the two methodologies were in accordance.

Over this period the optical gas imaging procedures resulted in significantly lower emissions to the atmosphere than could have been achieved using Method 21, as a result of more rapid identification and repair of the leaking components. In addition, leaks were found on equipment that were not part of the plant's LDAR programme.

This demonstrated that an OGI leak detection survey can meet all the criteria required to permit its use as an alternative work practice to the conventional sniffing procedure.

6.1.2.4. Uncertainties

The 'leak'/no-leak' factors have been derived from LDAR databases characterized by a leak size distribution as shown in **Figure 2**. This introduces two sources of uncertainty:

- deviations from this type of leak size distribution increase the uncertainty of the estimate;
- as the emission factors have been derived from emission estimates based on sniffing they also reflect the uncertainty associated with quantification based on that method.

6.1.3. Advantages and Disadvantages

The advantages and disadvantages of conventional sniffing and OGI techniques are outlined in **Sections 4.1.6, 4.1.7, 4.2.5 and 4.2.6**.

6.2. EMISSION ESTIMATION METHODS FOR AREA SOURCES

The most common practice used by the refining industry to quantify VOC emissions from diffuse area sources is to apply internationally accepted sector-specific estimation algorithms. This section reviews those methodologies for storage tanks and for other sources such as loading and waste water treatment facilities. The section also discusses the outcome of comparison tests of these calculated emissions with results obtained from methods like tracer gas or DIAL.

6.2.1. Storage Tanks

The most commonly used algorithms for storage tanks have been developed by the API [5] [6] from extensive testing over a number of years. Algorithms are available for external floating roof tanks, with and without a dome roof, internal floating roof tanks and fixed roof vertical tanks. These algorithms are updated or refined at intervals as further work by the API is completed (e.g. reference [26]). They have been accepted and incorporated into emission estimation guidance provided by the US EPA [27]. The latter also includes algorithms for horizontal cylindrical tanks.

The intent of the API in their development was to provide a means of estimating annual losses. It is stated that the estimation techniques 'become more approximate when used to estimate losses for time periods shorter than one year'.

The algorithms use different factors for the variety of stored product, tank features, seal types and roof fittings commonly found in refinery tanks. Average meteorological data for the site are required, e.g. wind speed, solar irradiation and ambient temperatures, as the emissions can be significantly dependent upon these.

There are some options provided in the algorithms to cover the possible state of equipment; e.g. degrees of rust on tank internal shells and tightness of floating roof seals. The user of the algorithms, therefore, must ensure that the factors utilised to derive emissions for a particular tank are appropriate. In particular, the API states

that the algorithms are only 'applicable to properly maintained equipment under normal working conditions'.

Following some reports in the early 1990s, which stated that the API methods under-estimated tank emissions, CONCAWE undertook an exercise in 1994 [28] to compare these with DIAL measurements. Recognising that the API methods were developed for long-term emission estimates, the project was planned to measure continuously the emissions from external floating roof gasoline tanks using DIAL over a period of several days; in practice the maximum period over which DIAL scans were made was four days. The conditions of the tanks were checked and they were considered to be well maintained. The equipment fitted to each roof was identified to permit correct use of the algorithms. During the test the contents of one tank were almost fully turned over, ensuring that any variations in emissions between high and low levels of the floating roof would be covered.

Over the four day period the average of the DIAL remote measurements were within 10% of the value of the tank emissions calculated using the API algorithms.

However, as shown in the case study in **Appendix 2**, the DIAL measurements on a scan by scan basis were up to 3.6 times the average value of the emissions over that four day period, demonstrating the potential errors in extrapolating short-term data.

This exercise by CONCAWE established that the API estimation algorithms and DIAL can provide comparable values if both are used over the same period and the limitations of both are recognised and applied.

Appendix 3 provides details of a comparison of tracer gas measurements with emission estimates made using the API algorithms. Optical gas imaging of leaks was also used to determine whether the tank roof fittings were in good condition. This test demonstrates that the API estimation methodologies are robust where the tank fittings are in good condition i.e. there are minimal leaks seen using the OGI camera.

6.2.2. Other Diffuse Emission Sources

Other sources of diffuse emissions include product loading and unsealed process drain systems and related water collection and treatment facilities such as uncovered separators.

Factors and algorithms are used for estimating emissions from product loading. For waste water drainage, collection and treatment there are emission factors, algorithms and estimation models available.

Those factors and algorithms considered the most appropriate for the refining sector are collated in CONCAWE report 3/07 [3]. The factors, derived from test measurements, are applicable to equipment that is well maintained and good operating procedures are in place.

6.2.2.1. Loading

Loading emissions are well characterised being dependent on a small number of parameters e.g. product true vapour pressure, design of loading system (e.g. top or bottom loading), etc. Hence emissions from this source can be relatively accurately

estimated using algorithms. The emission factors for gasoline road loading provided in CONCAWE Report 3/07 [3] are empirical having been derived from extensive measurements at European refineries and terminals.

Those for marine loading (ship and barge) are from API publication [29]. During the CONCAWE exercise to compare the results of API algorithms versus DIAL measurements described in the section above, direct measurements of the VOC concentration in a barge cargo tank vent were made during gasoline loading [28]. The results were within 3% of the value estimated using the empirical emission factor developed by the API [29].

6.2.2.2. Water drainage, collection and treatment systems

The emissions from oily-water systems vary significantly with time, depending, for example, on the amount and volatility of the entrained oil, waste water temperature, etc. Emissions from this source can be estimated using either simple emission factors [3], algorithms requiring data for a limited number of parameters [30] or complex models available as software packages [31]. Considerable sampling and analysis have to be undertaken to achieve accurate estimates of emissions.

Within CONCAWE report 3/07 [3], a simple, pragmatic methodology is recommended for uncovered oil-water separators which, it is known, provides conservatively high estimates of emissions. Measurements on uncovered waste water treatment plants at two Canadian refineries varied by two orders of magnitude [32]. The factor in reference [3] was confirmed by the greater of these measurements.

6.2.3. Advantages

The advantages of the NMVOC annual emission estimation methodologies recommended in CONCAWE report 3/07 [3] are:

1. Well established

The methodologies are well established and widely used internationally. Algorithms and emission factors have been published in the public domain e.g. in the US Environmental Protection Agency publication AP 42 *Compilation of Air Pollutant Emission Factors* [4] [27].

2. Low cost, easy to use

The methods are, in general, easy to use with the necessary data available from refinery operational records. The algorithms for storage tanks are less easy because they require a detailed equipment database to be established for all volatile product storage tanks. However, once this has been initially established, only limited operational and meteorological data are required on an annual basis.

6.2.4. Disadvantages

There are specific disadvantages due to the differences in the methodologies:

1. Storage

a) The algorithms developed by the API are applicable to properly maintained tanks under normal working conditions. They cannot be used, therefore, where the tank conditions or operations are outside of the limits defined within each algorithm.

b) The algorithms were developed to provide estimates of annual VOC emissions. The estimates are less accurate if used for time periods shorter than one year.

2. Uncovered oil-water separators

The simple emission factor provided in CONCAWE report 3/07 [3] gives conservatively high emission estimates. To achieve more accurate estimates of emissions requires the use of an algorithm, for example as provided in reference [30], for which considerable sampling and analysis have to be undertaken.

7. SYNTHESIS

Diffuse NMVOC emissions are defined as those which are not emitted from a vent pipe or stack, and hence for which the flux (concentration × vapour flow) cannot be measured by conventional methods.

These emissions can be classified as emanating from either 'point' or 'area' sources. Emissions from point sources comprise leaks from components which are not fully sealed e.g. pipe flanges, valve stems, pump glands, etc. As they are point sources, the emission concentration at the leak point can be determined by measurement with a hydrocarbon detector.

An example of an area source is an uncovered oil-water gravity separator, where the emissions originate from evaporation of the entrained hydrocarbons from the surface of the water. The largest number of area sources at a refinery comprise the open-top floating-roof tanks. Although classified as an area source because the emissions vent from the open top of the tank shell, the emissions are actually due to a number of point sources e.g. the roof fittings, peripheral seal, etc. During normal operation, access to the roof is not permitted and so it is not possible to measure the concentration of the NMVOC emissions from these using conventional instruments.

The quantification of the emissions from these two types of sources has historically been undertaken in different ways, and hence point and area sources are considered separately below.

7.1. POINT SOURCES

There have been various methods, of significantly differing complexity, to estimate point source diffuse emissions. One of the least complex is to use average emission factors determined for different component types (e.g. valves, pump seals, etc) and in different service (i.e. vapour and volatile 'light' liquid). This method is relatively simple, but generates conservatively high estimates as every similar component is considered to be leaking at the same rate. In reality, work by the API has shown that in a typical US refinery over 90% of the point emissions come from only about 0.13% of the components [21].

To improve the accuracy of the estimate, leak detection surveys can be undertaken. Historically these have required every accessible component to be 'sniffed' with a conventional hydrocarbon detector to determine the concentration of any NMVOC emissions emanating from it. Correlations can then be used to relate the concentration to emission flux.

The great advantage of leak detection surveys is that they can identify the few 'significant emitters' which are the major contributors to the total emissions, thus permitting focussed maintenance. The main disadvantages of these conventional surveys are the length of time required to cover an entire refinery and the consequent high cost. The method is inefficient as all accessible components must be physically sniffed, but only a few are responsible for the majority of the mass flux. In addition, not all sources can be monitored; typically 15-25% of components are inaccessible or hidden, for example by lagging.

The use of the newly developed optical gas imaging technologies has significant advantages over conventional leak detection 'sniffing' surveys. Hand-held cameras can provide a visual image of a vapour plume emanating from a component. Thus by scanning all components, including those which are not accessible with conventional instrumentation, the 'significant emitters' can be readily detected. This technique can reportedly speed up the leak detection process by a factor of 30. The leak detection threshold with the latest camera technologies has been shown to be sufficiently low to demonstrate that they are a robust alternative to sniffing with conventional detectors. The US EPA are, therefore, currently considering permitting their use as an 'alternative work procedure'.

7.2. AREA SOURCES

As the emissions from area sources cannot be deduced using conventional instrumentation, historically they have been quantified using algorithms. For floating roof tanks the API has invested significant effort into the derivation of methodologies suitable for estimation of annual emissions as required by regulators both in the US and Europe.

These methodologies have been proven to be robust where the user has applied the appropriate algorithms and the tanks are properly maintained.

However, as with point sources, even at a well maintained refinery there may be 'significant emitters' for which the application of the API methodologies is not appropriate.

Optical techniques have been developed and used in industrial facilities to provide short term measurements of emission fluxes from area sources. The two most commonly used are differential absorption LIDAR (DIAL) and solar occultation flux (SOF). Both of these use the fact that hydrocarbons absorb light at certain wavelengths; DIAL uses a laser whereas SOF uses solar radiation as the light source. Both also only measure the concentration of the vapour plume downwind of the source. To determine the flux, the concentration must be multiplied by the wind speed.

SOF is the least complex of the two techniques, but with consequent restrictions in its applicability. It can only be used when there is adequate solar radiation and it generates the average concentration along the entire path from the detector to the sun. Emissions from individual area sources are determined by moving the device around a site so that the detected solar light beam passes through the plumes. DIAL is more complex; using a laser beam scanned across a facility it provides range-resolved concentration measurements.

Both techniques have disadvantages, the most significant of which is that they can only measure in the short term. Emissions from area sources at refineries can be very variable (e.g. wind and solar radiation effects on tank emissions) and regulators require average annual estimates. A comparison study has shown that short term measurements can be 4 times greater than the average, even over a relatively medium-term period of a few days.

Although both techniques can be used to identify those area sources which are the 'significant emitters', the cost to employ them is high; over 10k EUR per day for a DIAL refinery survey which typically lasts ten days.

It has been shown that the optical gas imaging cameras can detect vapour leaks from fittings and seals on floating-roof tanks. A study has shown that where there were either no vapour leaks, or only a small number, observed with such a camera, the API emission estimations were comparable to measurements made with tracer gas. Optical gas imaging, therefore, can also be used to detect 'significant emitters' within refinery storage tank farms.

The capability to identify those tanks which are 'significant emitters' permits maintenance to be undertaken on faulty emission control equipment, such as roof seals, and thus enables the tanks to be returned to within the bounds of operation for which the robust emission estimation algorithms are valid.

This is directly comparable to the situation regarding emission estimation for the largest source of man-made VOCs – road transport. Emission estimation algorithms have been developed over a number of years for automobiles, which assume that their emission control systems are operating within certain limits. Automobiles are tested at regular intervals and those operating outside of the bounds are repaired to ensure that the algorithms remain valid for all vehicles over the long-term. Correspondingly, emission estimation is considered fully acceptable for this source and direct measurements of VOCs are not required.

8. CONCLUSIONS

This report discusses techniques for estimating diffuse emissions in refineries. For the two types of sources the following conclusions are drawn:

8.1. POINT SOURCES

The major point sources of fugitive emissions are pressurised equipment components installed on process plant.

Emission estimates based on average component emission factors give conservatively high values as all similar components are considered to be leaking and all at the same rate. In practice, the majority of emissions are due to a few 'significant emitters': data from the US indicate 90% of fugitives originate from just over 0.1% of point sources.

There is a standard method for the detection of fugitive emission point sources using conventional VOC instrumentation. Measured point source concentrations can be converted to annual average emissions using well established correlations.

This method requires physical access to equipment components. This is a time consuming, costly and inefficient procedure as the majority of emissions emanate from only a very small percentage of the components that have to be monitored. In addition, access constraints result in a significant number of components not being checked for leaks.

To obtain measurements of the total diffuse point source emissions from refinery process plant, two complex techniques have been used: DIAL and SOF. There are significant challenges with both techniques. The most important are that:

- they require accurate wind field data within the plume line to calculate emission fluxes, which is very difficult in the complex topography of refineries;
- upwind source emissions can only be inferred from non-simultaneous measurements;
- the systems are costly, and require specialist operators.

These complex systems can provide a measure of total emission flux from all equipment components on a plant, but cannot identify the 'significant emitters' amongst the components. SOF can only provide an average plume concentration downwind of the plant, and DIAL has range resolution constraints.

Recently developed optical gas imaging (OGI) techniques permit remote leak detection with hand held, relatively simple to use, cameras. All components can be scanned and surveys can be completed at a much faster rate. An OGI leak detection survey can identify the 'significant emitters' permitting focused equipment maintenance and subsequent emission reductions.

The use of OGI cameras has been demonstrated to be a viable alternative to sniffing with conventional detectors. The US EPA is currently considering permitting their use as an 'alternative work procedure'.

Emission factors have been developed so that average annual emissions for all point source fugitive emissions can be determined from OGI leak detection surveys.

8.2. AREA SOURCES

The emissions from area sources (e.g. storage tanks, uncovered oil-water separators, process plants, etc) are very variable, being dependent for example on meteorological conditions, process operations, etc.

The two complex techniques (DIAL and SOF) have also been used to determine emissions from oil refinery area diffuse sources.

Both provide values for emission flux only over short term scan periods. Although this permits the identification of the 'significant emitters', extrapolation to provide annual average emissions results in large errors.

It has been proven that the well established API algorithms for the quantification of annual average emissions from storage are robust, but only if the tanks are properly maintained. However, a tank may be a 'significant emitter' for which the application of the API methodologies is not appropriate. Emissions from floating roof storage tanks result from point sources e.g. leaks from the seals on roof fittings and against the tank shell. It has been demonstrated that OGI techniques can detect these leak sources, which are otherwise non-identifiable.

If a tank is a 'significant emitter' it can be identified using either a complex optical technique (DIAL or SOF) or a more cost-effective relatively simple OGI leak detection survey of tank fittings. The latter also has the advantage that it can identify the precise location of the emission sources (e.g. leaking fittings and/or components) which are causing the tank to be a 'significant emitter'.

Subsequent maintenance of the emission sources results in reduced emissions and, importantly, returns the tank to a condition that permits the application of the API algorithms to provide robust annual average emission estimates.

Emissions from waste water collection and treatment can be estimated using simple factors related to throughput. These, however, result in conservatively high emission estimates as the factors have been derived from worst case examples.

Because of the high variability in the amount and volatility of entrained oil, more accurate evaporative emission quantification requires regular sampling and analyses of the waste water. This permits the use of established algorithms.

8.3. OVERALL CONCLUSIONS

- The use of emission factor methodologies is very effective in combination with a procedure to detect 'significant emitters' amongst the diffuse sources in a refinery.
- Relatively simple OGI equipment can scan all fugitive emission point sources on a process plant, which is not possible using conventional hydrocarbon leak detection instruments. The use of complex optical techniques to determine the total emissions from point emitters (e.g. equipment components) is then not necessary.

- The use of complex optical techniques to determine the emissions from diffuse area sources (e.g. tanks) provides only short term flux data. Extrapolation of these data to provide annual emission estimates results in large errors. Moreover, although these techniques can identify a tank with significant emissions, they cannot pinpoint the equipment components causing them.
- The use of OGI tank surveys is an alternative, reliable, relatively simple and cost-effective method to identify tank equipment in need of maintenance. Subsequent maintenance enables a tank to be returned to within the bounds of operation for which robust emission estimation algorithms are valid.

9. ACRONYMS

The following provides the meaning of the acronyms used in this report.

API	American Petroleum Institute
AWP	Alternative Work Practice
BREF	Best Available Techniques Reference Document
BTEX	Benzene + Toluene + Ethyl benzene + Toluene
CEN	Comité Européen de Normalisation
CLRTAP	Convention for the Long Range Transport of Air Pollution
CWP	Current Work Practice
DIAL	Differential Absorption LIDAR
DOAS	Differential Optical Absorption Spectroscopy
EFRT	External Floating Roof Tank
EPA	Environmental Protection Agency
EPER	European Pollutant Emissions Register
FID	Flame Ionisation Detector
FRT	Fixed Roof Tank
FTIR	Fourier Transform Infrared
IFRT	Internal Floating Roof Tank
LDAR	Leak Detection and Repair
LIDAR	Light Detection and Ranging
NEC	National Electrical Code
NMVOC	Non-Methane Volatile Organic Compound
NPL	National Physical Laboratory
OGI	Optical Gas Imaging
PID	Photo-Ionisation Detector
PRTR (E-PRTR)	(European) Pollutant Release and Transfer Register
RADAR	Radio Detection and Ranging
SOCMI	Synthetic Organic Chemical Manufacturing Industries
SOF	Solar Occultation Flux
TCT	Time Correlation Tracer
TDLAS	Tunable Diode Laser Absorption Spectroscopy
TOC	Total Organic Compounds
VOC	Volatile Organic Compounds

10. REFERENCES

1. EIPPCB (2003) BAT Reference document on the general principles of monitoring. Sevilla: European IPPC Bureau (<http://eippcb.jrc.es/pages/FActivities.htm>)
2. CEN (2008) Fugitive and diffuse emissions of common concern to industry sectors – measurement of fugitive emission of vapours generating from equipment and piping leaks. Standard No. EN 15446:2008. Brussels: Comité Européen de Normalisation
3. CONCAWE (2007) Air pollutant emission estimation methods for E-PRTR reporting by refineries. Report No. 3/07. Brussels: CONCAWE
4. EPA (1995) AP 42, fifth edition: Compilation of air pollutant emission factors. Vol 1: Stationary point and area sources. Chapter 5: Petroleum industry. Research Triangle Park, NC: US Environmental Protection Agency
5. API (2003) Manual of petroleum measurement standards. Chapter 19: Evaporative loss measurement, Section 2: Evaporative loss from floating-roof tanks. Washington DC: American Petroleum Institute
6. API (2005) Manual of petroleum measurement standards. Chapter 19: Evaporative loss measurement, Section 1: Evaporative loss from fixed-roof tanks. Washington DC: American Petroleum Institute
7. EPA (1995) Protocol for Equipment Leak Emission Estimates. Report No. EPA-453/R-95-017. Research Triangle Park: US Environmental Protection Agency
8. The County Administration of Västra Götaland (2003) Fugitive VOC-emissions measured at oil refineries in the Province of Västra Götaland in South West Sweden – a success story. Report No. 2003:56. Göteborg: The County Administration of Västra Götaland
9. EIPPCB (2003) BAT Reference document on Best Available Techniques for mineral oil and gas refineries. Sevilla: European IPPC Bureau (<http://eippcb.jrc.es/pages/FActivities.htm>)
10. EIPPCB (2005) BAT Reference document on Best Available Techniques on emissions from storage. Sevilla: European IPPC Bureau (<http://eippcb.jrc.es/pages/FActivities.htm>)
11. EPA (1999) Code of Federal Regulations Standard Test Method 21: Determination of volatile organic compound leaks. 40CFR Part 60, Appendix A. Research Triangle Park, NC: US Environmental Protection Agency
12. McRae, T.G. (2006) Backscatter absorption gas imaging: past, present and future. Paper No. 06-A-48 presented at the A&WMA's 99th Annual Conference, June 21-23, New Orleans LA
13. Kulp, T.J. et al (2006) Development and evaluation of a portable mid-IR active imaging system to image hydrocarbon vapors for Smart Leak Detection and Repair (LDAR) operations. Paper No. 06-A-528 presented at the A&WMA's 99th Annual Conference, June 21-23, New Orleans LA

14. Benson, R. et al (2006) Standoff passive optical leak detection of volatile organic compound using a cooled InSb based infrared imager. Paper No. 06-A-131 presented at the A&WMA's 99th Annual Conference, June 21-23, New Orleans LA
15. Hinrichs, M. et al (2006) Infrared gas imaging and quantification camera for LDAR applications. Paper No. 06-A-210 presented at the A&WMA's 99th Annual Conference, June 21-23, New Orleans LA
16. Panek, J. et al (2006) Controlled laboratory sensitivity and performance evaluation of optical leak imaging infrared cameras for identifying alkane, alkene, and aromatic compounds. Paper No. 06-A-159 presented at the A&WMA's 99th Annual Conference, June 21-23, New Orleans LA
17. Furry, D.W. et al (2007) Evaluation of instrument leak detection capabilities for Smart LDAR application: Chemical plant testing. *Environmental Progress* 26, 2, 197-205
18. Robinson, R. et al (2007) Review of the use of remote optical techniques for emissions monitoring. EMPA: CEM 2007 8th International Conference on Emissions Monitoring, September 5–6, Zürich, Switzerland
19. Mellqvist, J. et al (2007) Measurements of industrial emissions of VOCs, NH₃, NO₂ and SO₂ in Texas using the Solar Occultation Flux method and mobile DOAS. HARC Project H-53. Houston TX: Texas Environmental Research Consortium (<http://www.tercairquality.org/AQR/Projects/H053.2005>)
20. API (1997) Analysis of refinery screening data. API Publication No. 310. Washington DC: American Petroleum Institute
21. Taback, H.J. et al (1997) Los Angeles refinery emissions, have they changed after six years of LDAR? Paper presented at the A&WMA/EPA Specialty Conference, The Emissions Inventory: Planning for the Future, October 1997, Research Triangle Park NC
22. EPA (1999) Monte Carlo simulation approach for evaluating alternative work practices for equipment leaks. Office of Air Quality Planning and Standards, Draft Report. Durham NC: US Environmental Protection Agency
23. Epperson, D. et al (2007) Equivalent leak definitions for Smart LDAR (leak detection and repair) when using optical imaging technology. *J Air Waste Manag Assoc* 57, 9, 1050-1060
24. Lev-On, M. et al (2007) Derivation of new emission factors for quantification of mass emissions when using optical gas imaging for detecting leaks. *J Air Waste Manag Assoc* 57, 9, 1061-1070
25. Reese, D. et al (2007) Smart LDAR: pipe dream or potential reality? A&WMA Fall Conference, October 29-30, Baton Rouge LA
26. API (2005) Evaporative loss from storage tank floating roof landings. Technical Report 2567. Washington DC: American Petroleum Institute
27. EPA (2006) AP 42, fifth edition: Compilation of air pollutant emission factors. Vol. 1: Stationary point and area sources. Chapter 7: Liquid storage tanks. Research Triangle Park NC: US Environmental Protection Agency

28. CONCAWE (1995) VOC emissions from external floating roof tanks: comparison of remote measurements by laser with calculation methods. Report No. 95/52. Brussels: CONCAWE
29. API (2006) Atmospheric hydrocarbon emissions from marine vessel transfer operations. Publication 2514A. Second edition 1981, reaffirmed 2006. Washington DC: American Petroleum Institute
30. Litchfield, D.K. (1971) Controlling odors and vapors from API separators. Oil & Gas Journal, November 1, 60-62
31. EPA (1994) Air emissions models for waste and wastewater. Report EPA-453/R-94-080A. Research Triangle Park, NC: US Environmental Protection Agency
32. CPPI (2005) Code of practice for developing an emission inventory for refineries and terminals, Rev. 9. Ottawa: Canadian Petroleum Products Institute
33. Mellqvist, J. et al (2000) Extinction of infrared light by liquid aerosols and effects on DIAL measurements. Göteborg: Chalmers University of Technology

APPENDIX 1 COMPARISON OF MEASUREMENTS USING DIAL, SOF, TRACER AND CONVENTIONAL TECHNIQUES FOR A BITUMEN VAPOUR VENT

A1.1 INTRODUCTION

Three comprehensive VOC emission surveys were carried out at AB Nynäs Petroleum's refinery in Nynäshamn, Sweden in August 2000, late autumn 2000 and June/July 2005. The Nynäshamn refinery is a simple refinery, producing mainly naphthenic speciality oils and bitumen and has, therefore, significantly different emissions to a conventional fuel-orientated refinery. The refinery has a crude oil throughput of about one million tonnes per annum, this being mostly heavy Venezuelan.

The first survey was undertaken using a DIAL system. For the survey the site was sub-divided into eight separate areas; six where emissions were continuous and two, ship loading and road tanker loading, where the emissions were discontinuous. In each area the DIAL system measured simultaneously both a cocktail of C2+ non-aromatic species and benzene. Sorption tube samples were also taken in some areas which provided additional speciation information enabling mass emission data for other aromatics to be derived from the measured benzene emissions.

The estimate of the annual VOC emissions from the refinery extrapolated from the DIAL survey data was 4576 te (tonne equivalent). This total was considered unrealistically high, especially the contribution from storage and handling of hot products (bitumen & crude oil). Correspondingly, a second comprehensive VOC survey was carried out a few months later. In this survey a variety of different methods were used e.g. concentration and flow measurements were made on open ventilated tanks and API calculations were undertaken for floating roof tanks. The estimate for the refinery annual VOC emissions determined by this survey was 284 te.

In June/July 2005, a third VOC survey was carried out at the refinery using two independent IR methods. One of the methods was SOF, the other method being a tracer gas technique using an FTIR called Time Correlation Tracer (TCT). In addition, concentration measurements were made on some sources using a conventional monitor utilising a flame ionisation detector (FID). This survey estimated the annual emissions from the refinery to be 432 te.

This case study focuses on the measurements made on one well defined channelled emissions source at the refinery: a common ventilation pipe from ten bitumen storage tanks. The emissions from this source were measured explicitly in all the three surveys. The results of the third survey enable the variation in vent vapour concentration with flow to be plotted. Hence, although the three surveys were carried out at different times under different flow conditions, a comparison can be made of the values of vent vapour concentration determined by each technique used.

A1.2 EMISSION SOURCE DESCRIPTION

The emission source is a common ventilation pipe, connected to ten hot bitumen storage tanks. There are normally no breathing losses from the tank farm, since the tanks are equipped with pressure/vacuum (P/V) valves.

- The 10 tanks have a total tank volume of 100,000 m³
- The tank farm ventilation system is piped into a common vent pipe
- The vapour space is pressurised with nitrogen (over pressure of 30–60 mm of water)
- There is only ventilation from the vent pipe if pressure exceeds 60 mm of water pressure

- In-flow to the bitumen tank farm is mainly from the vacuum distillation unit
- Out-flow is to the ship and/or truck loading facilities

A1.3 SURVEY 1: EMISSIONS FROM VENT PIPE MEASURED WITH DIAL TECHNIQUE

Emissions from the bitumen tanks vent pipe were measured with the DIAL technique for about 2 hours. The in-flow of bitumen into the tank farm during the measurements was 105 te/h at 166°C. With a bitumen density at 166 °C of approximately 0.95 kg/m³, and with no discharge from the tanks, the vent flow was calculated to be 68.7 Nm³/h.

The average hydrocarbon emission was reported to be 26.5 kg/hr. ‘Hydrocarbons’ in the DIAL report are referred to as ‘all non-methane, non-aromatic, non-cyclic, non-ethylene hydrocarbons’. The benzene flux from the vent pipe was also measured with DIAL technique as 0.20 kg/hr. Sorption tube measurements were not carried out on the vapours emitted from the vent pipe. However, an estimation of the BTEX emission was made by assuming that the ratio of BTEX components in the vent pipe is equal to the average BTEX ratio measured in the bitumen storage area. By making this assumption the total BTEX emissions in **Table A1.1** were calculated.

Table A1.1 BTEX Emission Fluxes Determined during DIAL Survey

	Benzene	Toluene	Ethyl benzene	Xylenes	Σ BTEX
Average emissions in bitumen storage area	0.67 kg/h (18%)	1.02 kg/h (27%)	0.41 kg/h (11%)	1.62 kg/h (44%)	3.72 kg/h (100%)
Vent Pipe	0.20 kg/h ⁽¹⁾	0.30 kg/h ⁽²⁾	0.091 kg/h ⁽²⁾	0.49 kg/h ⁽²⁾	1.11 kg/h ⁽²⁾

Notes:

1 – Measured value

2 – Estimated value using BTEX component data for bitumen storage area.

The ‘total’ VOC in the DIAL report is defined as the VOCs measured by DIAL plus those aromatics (toluene, xylenes & ethyl-benzene) derived from the sorption tube samples by relating to the measured benzene flux.

The total VOC emission from the vent pipe was thus determined to equal 26.5 + 1.11 = 27.6 kg/h.

Note that the DIAL result does not include cyclic and ethylene compounds. The crude being processed during the survey was heavy naphthenic crude which by nature contain some molecules of cyclic nature.

A1.4 SURVEY 2: VENT PIPE VAPOUR CONCENTRATION DETERMINED BY CONVENTIONAL TECHNIQUES

During filling of the bitumen tanks, the VOC concentration in the vent pipe was measured with an instrument designed to measure total organic compounds (TOC) equipped with a flame ionisation detector (FID). At the same time, vapour samples were taken on adsorption tubes and in gas pipettes for quantification by gas chromatography. Both measuring techniques gave the same VOC vent concentration of 4.38 mg/Nm³.

The composition of the vent vapour was determined from the GC analysis to be:

- C1-C4 (from gas pipette sample) = 64.3% m/m (of which C1 = 24% m/m)
- C5-C10 (from charcoal adsorption tube) = 34.7% m/m
- C11-C35 (from XAD2 type adsorption tube) = 0.01% m/m

As DIAL measures non-methane VOCs, the concentration of VOCs measured above was adjusted to permit comparison with DIAL. The calculated value of NMVOCs was 3349 mg/Nm³.

The in-flow of bitumen into the tank farm during the measurements was 49.4 te/h at 166°C. With a bitumen density at 166°C of approximately 0.95 kg/m³, and with no discharge from the tanks, the vent flow was calculated to be 32.3 Nm³/h.

A1.5 SURVEY 3: EMISSIONS FROM VENT PIPE MEASURED WITH FID, TRACER AND SOF TECHNIQUES

In June/July 2005 the third VOC survey was carried out at the Nynäshamn refinery using SOF, TCT (mobile FTIR plus tracer) and a flame ionisation detector type TOC monitor. Vapour flows in the vent pipe were estimated from a knowledge of the bitumen in-flow rates and temperatures. The outcome of the measurements on the vent pipe is compiled in **Table A1.2**.

The data indicate that there is an increase in the vent concentration with bitumen in-flow, possibly due to increased turbulence in the stored product. From the table it can be seen that the tracer and FID techniques had good agreement at an in-flow of 108 te/h bitumen and similarly with the SOF and tracer method at an in-flow of 107 te/h from production plus 221 te/h from ship. At an inflow of 109 te/h from production plus 315 te/h import from ship the spread in the measured VOC concentrations in the vent pipe for the three methods ranged from 22-43 g/Nm³.

Table A1.2 Comparison of Concentration Measurements of Vent Vapour by Tracer, SOF and Conventional Techniques

Technique	Survey No. Date Time	In-flow of bitumen to tank farm te/h	Estimated flow in vent pipe Nm ³ /h	Vent VOC mass flux kg/h	Vent Concentration g/Nm ³
Mobile FTIR plus tracer (TCT)	3.1 01-06-2005 9:50-11:20	108	70.7	0.7	9.9
FID	3.1 01-06-2005 9:50-11:20	108	70.7	0.7	9.9
Mobile FTIR plus tracer (TCT)	3.1 01-06-2005 14:55-15:30	108	70.7	0.6	8.5
FID	3.1 01-06-2005 14:55-15:30	108	70.7	0.8	11
Mobile FTIR plus tracer (TCT)	3.2 23-06-2005 19:00-20:00	107 te/hr from production 221 te/hr from ship	215	4.3	20
SOF	3.2 23-06-2005 18:00-19:00	107 te/hr from production 221 te/hr from ship	215	3.9	18
Mobile FTIR plus tracer (TCT)	3.3 04-07-2005 16:45-17:15	109 te/h from production 315 te/hr from ship	278	6	22
FID	3.3 04-07-2005 16:45-17:15	109 te/h from production 315 te/hr from ship	278	12	43
SOF	3.3 04-07-2005 14:00-15:40	109 te/h from production 315 te/hr from ship	278	8.7	31

A1.6 COMPARISON OF RESULTS FROM THE VENT PIPE CONCENTRATION MEASUREMENTS

Table A1.3 provides a comparison between the vent pipe vapour concentrations measured in the three surveys. The results are plotted in **Figure A1.1**.

Table A1.3 Comparison Between Concentration Measurement Method Results

	Survey	Flow in vent pipe [Nm ³ /h]	Concentration [g/Nm ³]
DIAL	1	68.7	402
Sampling + GC	2	32.3	3.35
FID	2	32.3	3.35
FID	3.1	70.7	10.45 ⁽¹⁾
FID	3.3	278	43
Mobile FTIR plus tracer	3.1	70.7	9.2 ⁽¹⁾
Mobile FTIR plus tracer	3.2	215	20
Mobile FTIR plus tracer	3.3	278	22
SOF	3.2	215	18
SOF	3.3	278	31

Notes:

1.- Average from the two tests conducted during survey 3 with the same flow conditions

Figure A1.1 Plot of concentration data measured by 4 different techniques

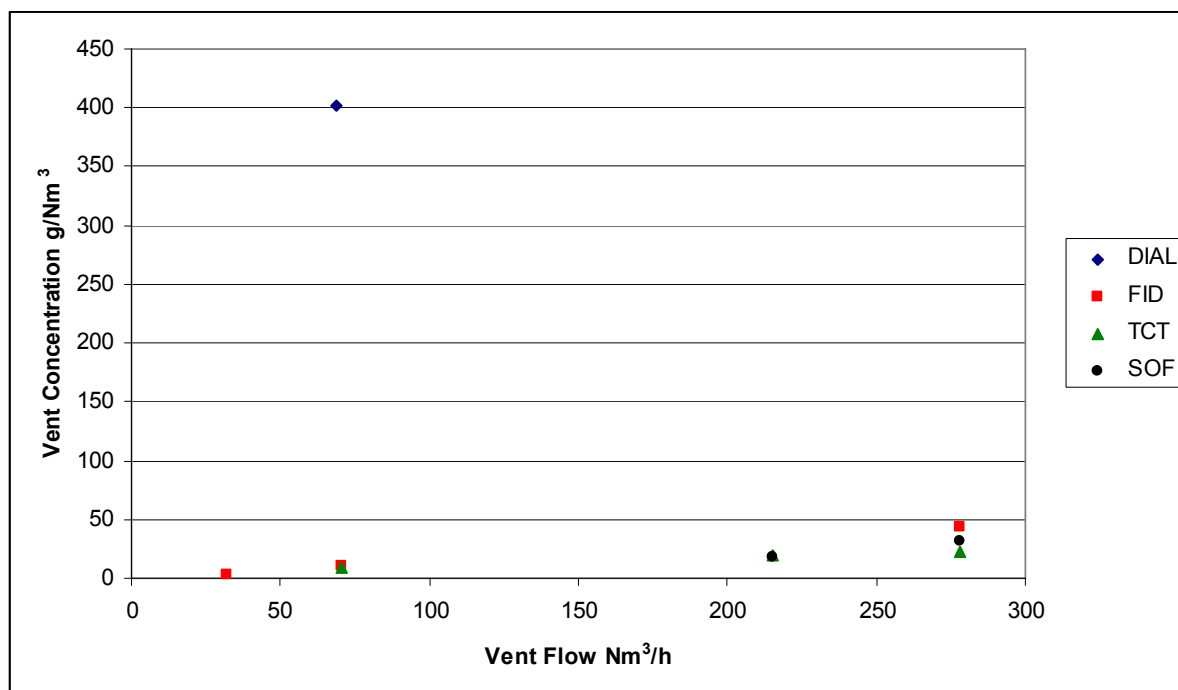


Figure A1.1 indicates that three techniques, FID, tracer (TCT) and SOF give similar results. The DIAL gives a significantly greater reading (approximately 40 times) the FID and TCT values at approximately the same vent flow rate.

There are significant overlaps in the absorption spectra of the different hydrocarbons that may be detected by a DIAL system. To simplify operations, DIAL facilities tend to use the absorption frequency that provides strong signals for the mix of typical hydrocarbons found at a conventional refinery, and it is possible that during the survey this was used for all sources. An incorrect IR spectra could, therefore, have been used for the hot bitumen tank vent vapour

There is also the possibility that the vent vapour contains entrained aerosols as the hot bitumen vapour cools. Limited tests have been conducted on the impact of aerosols [33] on IR absorption which identified significant spectral differences. In addition, there would be an impact on the scattering properties affecting DIAL measurements. These would cause an apparent increase in the VOC measured.

APPENDIX 2 COMPARISON OF DIAL MEASUREMENTS WITH THE API STORAGE TANK ESTIMATION METHODOLOGY

In the early 1990s some reports compared extrapolated DIAL measurements against annual average emissions from storage tanks calculated using the API algorithms [5] [6]. The result was that the values derived from DIAL measurements were greater than those calculated by industry, leading to the conclusion that the API methods under-estimated tank emissions.

In response, CONCAWE undertook an exercise in 1994 [28] to compare the API algorithms with DIAL measurements. Recognising that the API methods were developed for long-term emission estimates, the project was planned to measure continuously the emissions from five external floating roof gasoline tanks using DIAL over a period of several days; normal DIAL practice involves maximum periods of measurement of a few hours per scan location.

Checks on the tanks established that using the API algorithms was appropriate, in particular that the roof seals were in good order. During the test the contents of one tank were almost fully turned over, ensuring that any variations in emissions between high and low levels of the floating roof would be included over the measurement period.

A log was maintained over the entire test period showing tank movements, receipt and loading information and details of operational events around the terminal which may have resulted in emissions from sources other than the tanks being studied.

Over the four day period a total of 116 DIAL scans were completed with an average scan time of about 30 minutes. 16 of these scans were subsequently rejected, for example because of up-wind site operations causing large short-term emissions which could not be satisfactorily subtracted from down-wind measurements or because of atmospheric conditions such as heavy rain. To measure up-wind conditions 27 scans were undertaken, which is about a quarter of the total. This resulted in a total of 73 valid DIAL scans which were used for emissions analysis.

Over the test period the emissions from the five tanks were estimated on an hourly basis using the API algorithms for external floating roof tanks [5] to permit comparison with the DIAL measurements.

The individual DIAL scan data are plotted in **Figure A2.1** which also shows the running average of the DIAL data and the emission estimate using the API methodology over the same period.

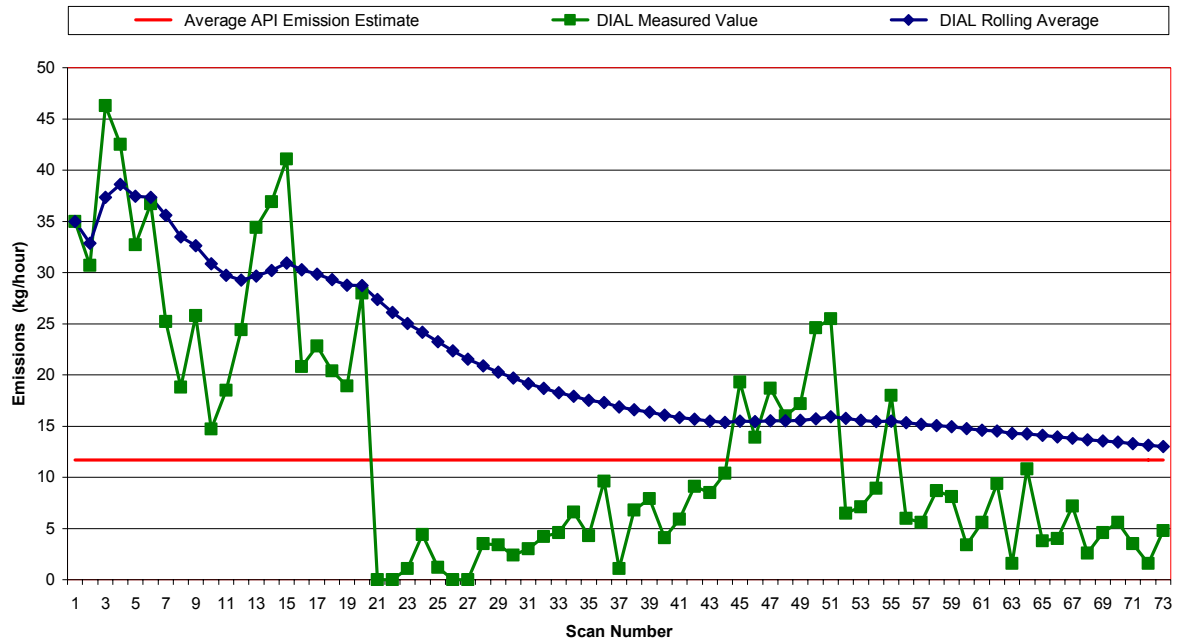
The maximum value of the emission flux from the five tanks determined using the DIAL system was 46.3 kg/hour and the minimum value was < 0.1 kg/hour. The average of the DIAL measurements was 13.0 kg/hour. The API estimated value of the average tank emissions was 11.7 kg/hour over the period of the valid DIAL scans.

The average of the DIAL remote measurements was, therefore, within 10% of the value of the tank emissions calculated using the API algorithms. It should be noted that the rolling average of the DIAL measurements is converging with the estimated emissions value.

This demonstrates that DIAL measurements and the API estimation method provide similar values for emissions over the medium to long-term.

However, it can be seen that the DIAL measurements on a scan by scan basis were up to 3.6 times the average value of the valid scan data, demonstrating the potential errors in extrapolating short-term data to provide long-term emission values.

Figure A2.1 DIAL measurement compared to emission estimation



APPENDIX 3 COMPARISON OF TRACER GAS MEASUREMENTS WITH THE API STORAGE TANK ESTIMATION METHODOLOGIES

Following measurements on the tanks at Shell Gothenburg refinery in 2006 using the SOF system, three external floating roof tanks (EFRT) storing crude oil were identified as being in need of roof maintenance.

Repeat measurements were undertaken in June 2007 to establish that repair work had effectively reduced emissions. It was planned to use the SOF system again and to complement this with tracer gas tests to permit validation of the SOF measurements. In addition, an infra-red OGI camera was to be used to identify sources of emissions from the equipment on the floating roofs and the peripheral seals.

Due to the cloudy weather conditions on the day of the measurements it was not possible to use the SOF system as this method relies on solar radiation (see **Section 4.4**).

Measurements were still undertaken using a tracer gas which was released at a known rate within the shell of the tank under study and gas samples taken at a number of locations downwind of the tank and analysed. The ratio of the tracer gas to the crude vapour concentrations permits leakage rates to be calculated.

In addition to the three crude tanks, measurements were also undertaken on two other tanks. These were a fixed roof tank (FRT) fitted with pressure/vacuum valves containing fuel oil and an internal floating roof tank (IFRT) containing reformat.

The OGI camera identified a number of pinhole leaks on the roofs of the three crude tanks between the seal and the tank shell. On two of these tanks there were also leaks where the seal system is bolted to the roof and, in addition, the vacuum breakers were seen to be leaking while in the 'closed' position. A summary of the number and locations of identified leaks is in **Table A3.1**.

Table A3.1 Number and location of *emission leaks observed with OGI camera*

Tank	Contents	Tank Type	Leaks detected using OGI camera	Leak locations
T-105	Crude oil	EFRT with secondary seal	1	Between roof seal and tank shell.
T-107	Crude oil	EFRT with secondary seal	4	Two between roof seal and tank shell, one where seal bolted to roof and one from vacuum breaker
T-108	Crude oil	EFRT with secondary seal	22	16 between roof seal and tank shell, five where seal bolted to roof and one from vacuum breaker
T-304	Reformate	IFRT with secondary seal	0	None identified
T-325	Fuel Oil	FRT with P/V valves	0	None identified

For all five tanks the API storage tank algorithms [5] [6] were used to estimate annual emissions. These were compared to the tracer gas test data measured in kg/hour (extrapolated to t/a). The comparative results are provided in **Table A3.2**.

Table A3.2 Tracer gas measurement compared to API algorithm

Tank	Leaks detected using OGI camera	Emissions estimated using API algorithm t/a	Emissions measured with tracer gas technique t/a
T-105	1	3	4
T-107	4	4	35
T-108	22	4	120
T-304	0	0.2	0
T-325	0	1	0

Although the use of extrapolated short-term measurements can provide significant errors, these data show acceptable comparison between the tracer gas measurements and the API estimation methodologies for tanks 105, 304 and 325. This demonstrates that the API estimation methodologies are robust where the tank fittings are in good condition i.e. there are minimal leaks seen using the OGI camera.