S5-1 Infrared Differential Absorption Lidar for Trace Gas Measurement

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1. INTRODUCTION

The differential absorption lidar (DIAL) technique allows the remote measurement of gaseous concentration profiles in the atmosphere. These measurements can be combined with wind field data to determine the mass emission rate from diffuse sources, such as large scale industrial plant. The combined infrared and ultraviolet capabilities of the mobile NPL DIAL system allows it to monitor many species of relevance to the industrial, regulatory and atmospheric science communities.

2. DESCRIPTION OF THE DIAL TECHNIQUE

2.1 Theory of DIAL

The DIAL technique involves the launching of a pulse of tunable laser radiation into the atmosphere[1]. A small fraction of the laser energy is scattered back towards the source, where it is collected by a telescope and measured using a fast detection system. Since the atmosphere acts as an extended scatterer, light is scattered from all distances along the transmitted beam. Therefore, if the amount of backscattered radiation is measured as a function of time, then the signal observed at a particular time after the pulse was transmitted results from backscattering at a specific distance from the source. The range-resolved concentration of a particular gas can then be measured by tuning the wavelength of the transmitted radiation on and off an absorption feature of that gas and measuring the difference in backscattered power of the on and off-resonant signals.

2.2 Description of the NPL DIAL system

The DIAL system operated by NPL[2] is housed in a mobile laboratory, shown in Figure 1. It can operate in the infrared, visible and ultraviolet spectral regions allowing coverage of a large number of atmospheric species, including CH_4, C_2H_4, C_2H_6, higher molecular weight alkanes and alkenes, aromatic species such as toluene and benzene, CO, HCl, N_2O and SO_2. A scanner system directs the output beam and detection optics, giving almost full coverage of the horizontal and vertical planes.

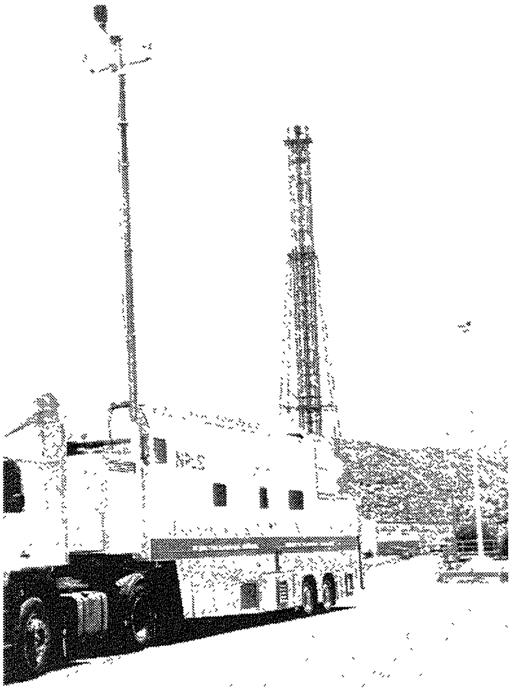

Figure 1. NPL Mobile DIAL System

The mobile laboratory also contains ancillary equipment for meteorological measurements, including an integral 14 m mast with wind speed and direction, temperature and humidity monitors. The system also contains point monitors for measuring NO_x, SO_x and total hydrocarbons, and solar flux monitors.

The system is powered by an on-board generator and has full air conditioning allowing operation in a range of ambient conditions.

The optical sources used in the DIAL system are shown schematically in Figure 2. The system employs two independent Nd-YAG pumped tunable dye lasers each with a repetition rate of 10 Hz. These systems allow two species to be monitored simultaneously. The output laser pulse length is ~10 ns. A small fraction of the output beam in each channel is split off by a beam splitter and measured by a pyroelectric detector to provide a value for the transmitted energy with which to normalise the measured backscatter return. It is also possible to transmit a separate YAG beam which allows a single wavelength lidar channel to be operated simultaneously with the DIAL channels. Various non-linear optical techniques are used in the infrared system to achieve the required output energy (~20 mJ), bandwidth (<0.1 cm^{-1}) and tunability (~2 - 4 μm).

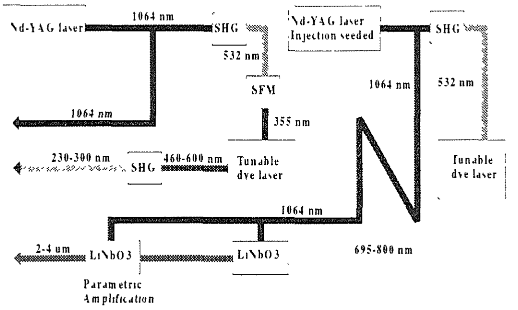

Figure 2. Schematic Diagram of UV and IR Sources in the NPL DIAL System

The returned atmospheric backscatter signal is collected by a scanning telescope. The collected light is then separated into the infrared, visible/ultraviolet and lidar detection channels. The returned light passes through band-pass filters relevant to each detection channel and is then focused onto the detection elements. Solid state cryogenically-cooled detectors are used in the infrared channels and photomultipliers in the ultraviolet.

After amplification the signals from the detectors are digitised using 20 MHz 10 bit digitisers. The digitisers are clocked using an external clock generator triggered by an optical detector in the transmission chain. This ensures the range gating is correctly synchronised to the laser pulse transmission. The signals from the pyroelectric detectors monitoring the transmitted power are also digitised and stored.

2.3 The application of DIAL to emission monitoring

A single measurement using the DIAL technique gives the concentration distribution of the selected gas as a function of range along the transmitted beam. The concentration distribution of the measured gas(es) can be measured by scanning the telescope. This can then be combined with measurements of the atmospheric wind speed and direction to calculate the mass flux of gas through the plane. An array of wind sensors is deployed for each measurement to determine the wind field.

An empirical model is used to calculate the variation of wind speed with height, as a function of various parameters (such as the roughness of the terrain). This is used to supplement the meteorological measurements and, where appropriate, these model results are combined with the measurements to improve the accuracy of the estimates of the wind field pattern.

The emitted flux is determined using an algorithm which calculates the product of the gas concentration measured with the DIAL technique at a given point in space, and the component of the wind velocity perpendicular to the DIAL measurement plane at the same location. This calculation is repeated at all points within the measured concentration profile, to form a two-dimensional array of data. The array is then integrated over the complete concentration profile to produce a value for the total emitted flux.

2.4 Calibration and Validation of the NPL DIAL system

The NPL DIAL system has several in-built calibration techniques and procedures. The most important are the in-line gas calibration cells. Part of the transmitted beam is split off to a pyroelectric detector in the same way as the beam for the transmitted energy monitors. This second beam passes through a gas cell before being detected. The gas cell is filled with a known concentration of the target species, using NPL standard gas mixtures which are traceable to national standards. This gives a direct measurement of the differential absorption of the DIAL wavelengths by the target gas. It is continuously monitored during the operation of the system to detect any drifts in the laser wavelengths. Calibration cells are also placed in the output beam to show the concentration response of the whole system is as expected.

NPL has also undertaken a number of comparisons to validate flux measurements made with the DIAL system :

i) Comparisons between DIAL and point sampling techniques have been carried out in the vicinity of chemical and petrochemical plants where a large number of different volatile organic species are present. In these comparisons, the DIAL beam was directed along the same line-of-sight as a line of point samplers. The results obtained for the total concentrations of VOCs measured by the point samplers and those measured by the infrared DIAL technique agreed within ± 15%. The concentrations of atmospheric toluene measured by the ultraviolet DIAL system agreed with those obtained by the point samplers to within ± 20%.

ii) The ultraviolet DIAL facility was used to monitor the fluxes and concentrations of sulphur dioxide, produced from combustion and emitted by industrial stacks. These stacks were instrumented with calibrated in-stack sampling instruments. The results of the two sets of measurements agreed to within ± 12%.

iii) The DIAL flux measurements agreed with the known, controlled, fluxes of methane emitted from a test stack to within ± 15%

The uncertainties in these tests depend largely upon the accuracy of the wind profiles used to calculate flux rates..

NPL have also developed and operate a large scale facility for the calibration of long path monitors including DIAL[3]. This consists of a 10m long window-less cell able to maintain a uniform concentration of gas along its length.

3. EXAMPLES OF MEASUREMENTS MADE WITH THE NPL DIAL SYSTEM

3.1 Typical Measurements of Diffuse Sources

NPL have carried out many successful studies of the emissions from diffuse sources using the DIAL technique. These have ranged from relatively small scale industrial plant to the distribution of air pollution over large urban areas. Examples include :

- VOC emission flux surveys of large oil refinery storage tank farms, some covering many square kilometres.
- Complete refinery loss studies including major UK, German and Greek refinery complexes.
- Tracking large plumes from industrial stacks for many kilometres downwind of the sources.
- Surveys of the distribution of NO_x in urban areas.

Many different species have been measured during these studies, and Table 1 below shows typical sensitivities (at a range of 200 metres) for a number of these species.

Table 1. Typical Detection Sensitivities Achieved with NPL DIAL System

IR DIAL System		UV DIAL System	
Species	**Sensitivity**	**Species**	**Sensitivity**
CH_4	50 ppb	NO	5 ppb
C_2H_2	40 ppb	NO2	10 ppb
C_2H_4	10 ppb	SO2	10 ppb
C_2H_6	20 ppb	O3	5 ppb
higher alkanes	40 ppb	Hg	0.5 ppb
HCl	20 ppb	Benzene	10 ppb
N_2O	100 ppb	Toluene	10 ppb
CH_3OH	200 ppb	Xylene	20 ppb

The system has also been used to provide data for use in the development of dispersion and atmospheric chemistry models[4].

3.2 Specific Measurement Examples

3.2.1 Oil Refinery Product Storage

The objectives of this study[5] were :

- to measure the total emissions of VOCs from storage tanks at a major refinery and petrochemical complex in the UK.
- to compare the fluxes measured by DIAL with those derived from industry standard estimation procedures.

Vertical profiles of VOC concentration were taken downwind of various areas containing storage tanks. These scans were repeated in order to average short-term fluctuations in the emitted concentrations. DIAL measurements were also made of the concentration profiles upwind of the tanks under study in order to determine the fluxes arising from upwind sources. Measurements of the wind field were made along each measurement plane.

The measured data were used to calculate the emitted fluxes during each scan, and averaged to produce approximate hourly mean values for the emitted VOC fluxes.

The emissions from a total of 56 storage tanks were investigated during the measurement period. These comprised fixed-roof tanks, ventilated fixed-roof tanks with internal floating roofs and external floating-roof tanks. Some of these external floating-roof tanks have single seals whilst others were also fitted with double seals.

Most of tanks studied contained motor gasoline, intermediate components or other finished high-volatility products. However, some of the DIAL scans included tanks containing products such as kerosine and gas oils from which significant VOC emissions would not normally be expected.

In parallel with these measurements the US American Petroleum Institute's (API) procedures[6] for estimating loss from storage tanks, were applied to the areas of tanks measured. These procedures provide a coherent way for industry to estimate the annual emission from storage tanks. They are based on measurements made, on a test rig in the US, of the effects on emissions of various components of tanks design. However it should be noted that they are designed to provide long-term average emission values and therefore there are inherent problems in using the procedures to estimate short-term emissions on the timescale of the DIAL measurements.

Figure 3 summarises all the data sets taken. It shows the comparisons of the VOC fluxes determined from the DIAL measurements with those calculated by the API procedures.

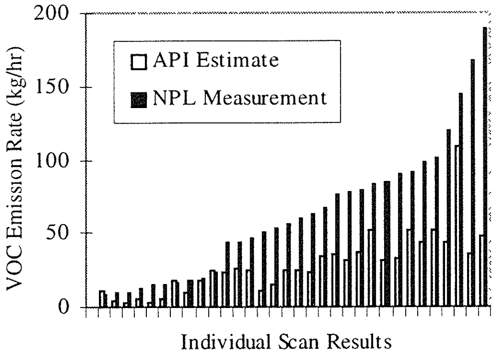

Figure 3. Comparison of NPL DIAL results and API estimated emissions

The NPL DIAL measurements are generally higher than the API calculations. There are several reasons for this. There are some errors within the API procedures as applied to this study which are known to cause underestimation. These have been corrected in a later release of the procedures, although these have not been applied to this data set. There are also concerns over using the procedures for short term loss estimations. For example, the rate of emission is dependant on the temperature of the stored material and the procedures assume that it is the bulk temperature that is the crucial factor over long time scales. In short term daytime measurements the difference between the bulk and surface temperature is significant, particularly with strong solar radiation, and this can lead to higher emissions than predicted. The measurements were undertaken during a relatively cold and overcast period which minimised this effect.

Even when these effects are included in the comparison, the total loss from the tanks is higher than estimated. There a several reasons why this might be expected. Firstly there are possible losses from drainage vents and other sources within the tankage which are not distinguishable from tankage losses. Secondly the emissions depend heavily on the state of repair of the tankage, and for example there is no ability for the user to input into the industry procedures, a state for the roof seals other than `average' or `good'.

3.2.2 Ethylene Production Plant

The objectives of this study were :

- to measure the fluxes of VOCs emitted to atmosphere from an industrial plant processing ethylene to polyethylene under normal operating conditions, with ethylene being the principal species emitted to atmosphere.
- to compare these measured fluxes with industry standard procedures developed by the Synthetic Organic Compound Manufacturers Industry (SOCMI) and the USEPA.

Measurements were carried out using the NPL DIAL facility for ten days at the petrochemical site[7].

Measurements were made of the vertical concentration profiles downwind of two adjacent polyethylene process units. The wind field was monitored along the DIAL measurement plane using ground based anemometers and wind vanes. A balloon sonde was used to provide information on the vertical profile up to 90 metres, well above the tallest structure.

The average measured ethylene emission from both polyethylene plants was 56 kg/hour, equivalent to an annual emission rate of 446 tonnes per year. The measured emissions were in the range 47-59 kg/hour, equivalent to 381-477 tonnes per annum. The annual losses for the new polyethylene unit are equivalent to 0.18% of throughput, compared with losses of 0.27% of throughput from the older unit.

The DIAL measurements of the emissions from one of the process units were then compared to the annual emissions estimated using a range of different techniques. These techniques gave a wide range of emission estimates, and the DIAL measurement of 212 tonnes per annum from the unit was of the order of six times the average estimated value. However, the DIAL measured flux contains emissions from high level vents and pressure release valves that were not included in the estimation work. By using knowledge of the vertical location of the valves it was possible to identify 23 tonnes per annum as attributable to the flanges and valves within the plant. The remaining emissions, although still significantly higher than the average estimated value, are within the 95% confidence limit value for the upper limit to the industry estimation procedure of 136 tonnes per annum.

There are several uncertainties within the estimation procedure. The data upon which the emission factors are based has a significant degree of scatter. Changes in screening instrumentation since the original work may also mean that the correlation between screening value and emission factor needs to be adjusted.

In this particular study the inaccessibility of many components led to a smaller screening population than was ideal. There is also an uncertainty introduced by estimating annual totals from the short term emissions measured by DIAL.

This study highlighted the range of values which it is possible to derive for the emissions of a complex plant using the SOCMI procedures. It shows that if care is taken when applying the factors the results are comparable to measured values. However more work on refining the procedures could improve this agreement.

3.2.3 Retail Petrol-filling Station

The objectives of this study[8] were to :

- Measure the total mass emissions to atmosphere of VOCs produced by the service station during normal vehicle filling operations. This information would be used to provide an estimate for the UK VOC inventory of emissions from petrol-vehicle retail-filling operations.
- Determine the effective reduction in emissions caused by operating an active vapour recovery system which had been installed in the fuel delivery system at the site.
- Measure the concentrations of total VOCs and benzene in the atmosphere within the filling station forecourt during normal vehicle-filling operations, and to monitor their spatial and temporal variations.

Measurements of the emissions from the filling station were made over a five day period.

The DIAL system was used to measure the vertical concentration distribution downwind of the filling station, with the vapour recovery system both on and off. These data were combined with meteorological measurements to determine the mass emissions and the effectiveness of the vapour recovery system.

Range-resolved measurements of the localised VOC and benzene concentrations were made by directing the beam across the fuel delivery pumps during vehicle-filling operations. The measured concentrations were therefore indicative of the levels of customer exposure whilst filling a vehicle petrol tank.

The mass emissions measured with the DIAL system were compared to the mass of petrol delivered in order to determine the percentage mass loss. The average VOC emission produced by retail vehicle-filling operations, as measured during this exercise, was 0.15% ±0.016% (95% confidence limit) by mass of petrol throughput, without the vapour recovery system in operation. The vapour recovery system was shown to reduce the level of emissions by 63% ±8%.

4. CONCLUSIONS

The DIAL system described in this paper has been successfully used for the measurement of the concentration distributions of a wide range of different gases from a variety of sources. Measurements have been made in both the ultraviolet and infrared regions, the later region being particularly important for the study of industrial emissions. The results of the measurements have been used to estimate the mass flux from industrial sources, validate dispersion models, and monitor the impact of pollution emissions on the local environment.

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