The Application of Differential Absorption Lidar (DIAL) for Pollutant Emissions Monitoring

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Jan 2015

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Outline of Presentation

- Introduction and brief background
- Fugitive emissions – requirement for monitoring
- The Differential Absorption Lidar (DIAL) Technique
- Examples of Measurement and Applications
About the National Physical Laboratory

The UK’s national standards laboratory

- Founded in 1900
- World leading National Measurement Institute
- 600+ specialists in Measurement Science
- State-of-the-art standards facilities
- The heart of the UK’s National Measurement System to support business and society

36,000 m² national laboratory

Most sophisticated measurement science building in the world
Magna Carta - 1215

“There is to be one measure of wine and ale and corn within the realm, namely the London quarter, and one breadth of cloth, and it is to be the same with weights.”
The invention of Radar 1935
Environmental Measurements Group

- Measurements of pollutants and Greenhouse Gases in ambient air, point source and fugitive emissions
- Data management, QA/QC and consultancy services for industry, government and universities
- Underpinned by UK National Measurement System research on the metrology of gases and particulates
- All our measurements are directly traceable to NPL gas standards
What are Fugitive Emissions?

- Fugitive emissions are those emissions which are not controlled
  Generally leaks from seals, valves, or other components
- Emissions estimated from leak detection and repair programmes
  99% of emissions from 0.1 % leaks
  Methods require ~ 10-20 % of components to be assessed

Models
- Landfill model – GasSim
- AP 42 - TANKS – based on emissions factors

- Regulations are currently based on modelled and calculated emissions
- Various studies have shown measured total-site emissions from refineries could be as much as a factor of 10 higher than calculated
- There have also been observed mismatches between ambient concentrations and source terms
Refinery Emissions

Data from A. Cuclis, HARC, 2008

Typical Estimated Emission
12 barrels
per 100,000
Studies in Houston – TEXAQS 2000, TEXAQS II have shown predicted Non Methane Volatile Hydrocarbon concentrations (NMVOC) were an order of magnitude too low

- Ozone formation critical issue
- Benzene ambient levels also exceeding limits

Improved measurements required to identify sources of VOCs and benzene

“The latest available emission inventories underestimate ethene emissions by approximately an order of magnitude”

Final Rapid Science Synthesis Report: Findings from the Second Texas Air Quality Study (TexAQS II)
European regulations

- European Directives define emission limits and monitoring requirements – Industrial emissions directive
- Best Available Technique Reference (BREF) documents define sector specific BAT
- Refining BREF includes fugitive emissions

- BAT conclusions (legal summary) published last year
  - LDAR and OGI for control
  - DIAL and SOF for measurement
- Refineries will have 4 years to implement BAT
European Standard Development

- Development of European standard to cover methods in refinery BREF
- Determine Fugitive and Diffuse emissions
  - DIAL, SOF, OGI, Tracer, Sniffing (EN 15446), Flux box, Calculations
- Standard currently being developed
  - I am chairing this committee (TC 264, WG38)
  - Intention is to validate the standard with 2 field campaigns
- Structure is a framework enabling user to select correct measurement tool and methods/ QA/QC to carry out each technique

DIAL will be validated and standardised as a method for fugitive VOC measurement
Basis of open-path Spectroscopic Measurement Methods

Direct Absorption Spectroscopy

![Diagram of Direct Absorption Spectroscopy]

Beer's Law

\[ I(\lambda) = I_0(\lambda) \exp(-\alpha(\lambda)NL) \]

where

- \( I \) = measured intensity
- \( I_0 \) = incident intensity
- \( N \) = concentration
- \( L \) = pathlength
- \( \alpha \) = absorption coefficient, at wavelength \( \lambda \)

\[ N = -\frac{1}{\alpha(\lambda)L} \log\left(\frac{I(\lambda)}{I_0(\lambda)}\right) \]
The Differential Absorption Lidar Principle

Pulsed lasers

Detector

Telescope

Electronics

Computer

Return signal

Distance

Concentration

Time delay

Off line

On line
NPL Differential Absorption LIDAR (DIAL)

- Optical Radar
- Range resolved concentration
- Able to measure wide range of species
  - VOCs including methane, ethene, methanol, and general hydrocarbons
  - SO$_2$, NO$_2$, NO, Hg, HCl
  - Benzene, Toluene, Xylenes
- Spatial resolution <8 metres
- Range up to 3 km
- Measurement sensitivity typically 50 ppb
Development of DIAL

- Extension of lidar to Differential Absorption – allows measurement of concentrations of gases
- NPL developed the source and detection systems to enable IR DIAL in mid/late 1980’s
- Commercial system built for BP late 1980’s
- Was spun out from BP as Spectrasyne
- Commercial system built for British Gas/Shell/Siemens 1995
- This system now operated by NPL, refurbished with new lasers, detection system, software
- Developed DIAL as a routine measurement service
- In 2013/2014 NPL developed a new DIAL system, with new lasers, detectors and software
- Launched in 2014
Timeline

1980
- Development of IR DIAL NPL/BP – enabling measurement of VOCs
- BP system later spun out as Spectrasyne
- Initial development of NPL UV DIAL

1990
- Development of IR DIAL NPL/BP

2000
- Commercialisation of DIAL NPL/Siemens build ‘Shell’ DIAL

2010
- Improved detection and analysis
- Standardisation of technique
- New mini DIAL

2020
- Development of New NPL DIAL, 2014
- NPL DIAL first used in US 2007
- Refurbishment of system with new lasers
- Use of system in commercial services and research
New NPL DIAL

- Launched 2014
- Twin DIAL (UV and IR)
- Improved lasers, detection systems
- New software
- Analysis algorithms
- Many other improvements to usability/performance
- And it looks nice and shiny 😊
Two DIALs
## Typical NPL DIAL Performance (older system)

<table>
<thead>
<tr>
<th>Species</th>
<th>Sensitivity (1)</th>
<th>Flux Uncertainty (2)</th>
<th>Maximum range (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric oxide</td>
<td>5 ppbv</td>
<td>7.0%</td>
<td>500 m</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>10 ppbv</td>
<td>7.2%</td>
<td>3 km</td>
</tr>
<tr>
<td>Ozone</td>
<td>5 ppbv</td>
<td>7.0%</td>
<td>2 km</td>
</tr>
<tr>
<td>Benzene</td>
<td>10 ppbv</td>
<td>7.2%</td>
<td>800 m</td>
</tr>
<tr>
<td>Toluene</td>
<td>10 ppbv</td>
<td>7.2%</td>
<td>800 m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>Sensitivity (1)</th>
<th>Flux Uncertainty (2)</th>
<th>Maximum range (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>50 ppbv</td>
<td>12.3%</td>
<td>1 km</td>
</tr>
<tr>
<td>Ethane</td>
<td>20 ppbv</td>
<td>8.0%</td>
<td>800 m</td>
</tr>
<tr>
<td>Ethene</td>
<td>10 ppbv</td>
<td>7.2%</td>
<td>800 m</td>
</tr>
<tr>
<td>Ethyne</td>
<td>40 ppbv</td>
<td>10.7%</td>
<td>800 m</td>
</tr>
<tr>
<td>General hydrocarbons</td>
<td>40 ppbv</td>
<td>10.7%</td>
<td>800 m</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>20 ppbv</td>
<td>8.0%</td>
<td>1 km</td>
</tr>
<tr>
<td>Methanol</td>
<td>200 ppbv</td>
<td>41.4%</td>
<td>500 m</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>100 ppbv</td>
<td>21.5%</td>
<td>800 m</td>
</tr>
</tbody>
</table>

- **Note 1.** 50m wide plume, 200m from DIAL
- **Note 2.** Expanded uncertainty, based on typical sensitivity, with an assigned flux of 50 kg/hr, wind speed of 4 m/s with an uncertainty of 1% and wind direction uncertainty of 5 degrees
- **Note 3.** The range value represents the typical working maximum range for the NPL DIAL system.
Examples of Field Validation Measurements

- Repeated DIAL measurements downwind of a source of a known flux of methane agreed to within +/- 10% of emitted value
- Comparison with a line of pumped absorption tube samplers inside chemical plant agreed with DIAL measurements of:
  - aliphatic hydrocarbons to within +/- 12%
  - toluene to within +/- 15%.
- VOC emission measurements from a petro-chemical storage facility made by DIAL and standard point sampling methods agreed to within +/- 8%.
- Recent validation work as part of US studies 2007 –
  Comparison against DOAS open path system (Benzene)
  Comparison with point samples
- Two validation studies at landfill sites
  Comparison of different techniques
Windowless Cell for ‘Free-space’ Calibration

- 10 m long x 1 m diameter
- External calibration of open-path instruments
- No reflections from windows
- On-line monitoring of internal conditions
- Dynamic operation
- Also provides range-resolution data for lidar-type instruments
DIAL Measurement Configuration for Emission Rate (Flux) Measurement

- Vertical scans enable plume mapping and flux calculation
- Combine integrated concentration with simple wind field to give flux
- Can measure away from source
Flux calculation

- Concentration profile measured in vertical plane
- Wind speed and direction measured on mast at two heights (11m and 3m) plus portable (tripod) and DIAL sensors
- Wind averaged over period of DIAL scan (vector average)
- Vertical wind profile determined from simple neutral condition model \( u(z) = a \ln(z) - b \)
- Component of wind normal to measurement plane used and calculated at each ‘cell’ (3.75m x 3.75m)
- Flux determined for each cell (conc * perpendicular wind)
- Total flux determined from sum all cells
Typical DIAL measurement

Scan 49; NC02

Elevation from DIAL (m) vs. Range from DIAL (m)

benzene ppm
DIAL Can Identify and Quantify Emissions from an Industrial Plant
DIAL Can Identify and Quantify Emissions from an Industrial Plant
## NPL experience with DIAL

### Industrial measurements include

<table>
<thead>
<tr>
<th>Count</th>
<th>Description</th>
<th>Measured quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Natural gas distribution and storage sites</td>
<td>Methane emissions fluxes</td>
</tr>
<tr>
<td>&gt;30 campaigns</td>
<td>At petrochemical process plants and oil refineries, including process plant, crude and product storage, water &amp; waste treatment and distribution</td>
<td>VOC emission fluxes, benzene emissions fluxes, toluene fluxes, methane fluxes, SO$_2$ fluxes</td>
</tr>
<tr>
<td>&gt;10</td>
<td>Flare measurements (stack and ground)</td>
<td>Unburnt VOC, methane fluxes</td>
</tr>
<tr>
<td>5</td>
<td>Road-loading terminals</td>
<td>VOC fluxes</td>
</tr>
<tr>
<td>1</td>
<td>Crude oil gathering-station</td>
<td>VOC and benzene fluxes</td>
</tr>
<tr>
<td>3</td>
<td>Independent tank farms</td>
<td>VOC and benzene fluxes</td>
</tr>
<tr>
<td>3</td>
<td>Coke batteries</td>
<td>VOC and benzene fluxes</td>
</tr>
<tr>
<td>3</td>
<td>Chemical plants</td>
<td>Siloxane fluxes, Ethylene fluxes, VOC fluxes, HCl fluxes</td>
</tr>
<tr>
<td>4</td>
<td>Ship loading</td>
<td>VOC fluxes, benzene fluxes</td>
</tr>
<tr>
<td>2</td>
<td>Petroleum retail garages, including a study of vapour recovery system efficiency</td>
<td>VOC fluxes, Benzene fluxes, Gasoline mass fluxes</td>
</tr>
<tr>
<td>4</td>
<td>Power stations, including plume dispersion</td>
<td>SO$_2$ fluxes, NO/NO$_2$ ratios</td>
</tr>
<tr>
<td>32 weeks</td>
<td>Plume dispersion modelling studies</td>
<td>Methane fluxes and plume profiles</td>
</tr>
<tr>
<td>3</td>
<td>Mixed industrial / urban area studies</td>
<td>NO, NO$_2$ concentration map studies</td>
</tr>
<tr>
<td>3</td>
<td>Rail loading terminals</td>
<td>VOC and benzene fluxes</td>
</tr>
<tr>
<td>1</td>
<td>On-shore oil well head</td>
<td>Methane fluxes</td>
</tr>
<tr>
<td>&gt;32</td>
<td>Landfill sites</td>
<td>Methane fluxes</td>
</tr>
</tbody>
</table>
Area source simulator

- Development of a portable facility to test and validate techniques used for fugitive emissions monitoring
- Will be able to reproduce a wide range of emission characteristics
  - Range of pure or mixed ratio gases
  - Traceable emission rates up to 55 kg/hr
  - Different emission nodes (line, point, area sources) can be combined
- Developing validation protocols
  - Including a specific project on shale gas
EXAMPLES OF NPL DIAL MEASUREMENTS
Sulphur Dioxide Plumes Measured 2.1 km Downwind of Source
Sulphur Dioxide Plumes Measured 2.3 km Downwind of Source
Plume Tracking
Plume Tracking
Plume Tracking
Plume Tracking
Plume Tracking

Plume grounding
Measuring Driver Exposure when Filling Petrol

- Loss 0.3 – 0.15 %
- Vapour recovery reduced this by 63%
DIAL in the USA

- Major studies carried out using the NPL DIAL in USA
- 2007
  - Large study of refinery and tank farm
    Carried out for State Regulator
- 2010
  - Study for City of Houston of refinery
- Other measurements
  - Refineries, coke works, tank farms, landfills
- Demonstrator projects to show capabilities of DIAL
- Aim to assess emissions from specific sources within the refinery and compare with expected emissions
- VOC’s, methane and benzene
Texas DIAL study 2007

- Looked at specific sources for comparison with emissions estimates
- Day and night time measurements
- Comparisons made with FLIR imaging infrared camera
  EPA Open path DOAS system for benzene concentration
Examples of VOC scans at a Texas Refinery

- Un-burnt hydrocarbons from a flare stack
- VOC plume from storage tank
Comparison Between DIAL and UV-DOAS

- **DIAL**
  1.6 ppb to 26.3 ppbv

- **UV-DOAS**
  5 ppb to 10 ppbv

- **Tube and canister**
  1.44 ppb to 20.52 ppbv

UV-DOAS data courtesy of Cary Secrest EPA.
Initial Conclusions from Texas Study

- **Tanks**
  - Day and night time measurements gave similar emissions
  - Crude oil and heated oil tank emissions measured by DIAL were 5-10 times higher than estimated by TANKS
  - Gasoline tank emissions measured by DIAL were similar to those estimated by TANKS

- **Flares**
  - Temporary flare gave efficiency ~ 99.7 %
  - Ultra cracker unit (ULC) process flare gave efficiencies < 85%
Comparison Between DIAL and UV-DOAS

UV-DOAS data courtesy of Cary Secrest EPA.
Recent work in Europe

- Regulatory monitoring of onshore gas in Norway
- ‘Routine’ monitoring
- Process, storage, flares
- Periodic monitoring
- Enables check and control of fugitive emissions
- Results generally consistent with previous measurements (undertaken by Spectrasyne)
Fume project

- Research project to develop measurement techniques to monitor methane emissions from
  - Waste water treatment plant
  - Gas transmission plant
  - Shale gas sites

- Combining
  - DIAL - detailed understanding of emissions
  - Low cost sensor networks and models to give long term monitoring
  - Open path TDL integrated
Onshore oil well

- Measurement of emissions from (conventional) well
- Carried out from outside facility
- Demonstrator of capability to find and quantify leaks from small sources
  
  Only one measurement location from access road
  Small site – expected low emissions

- Showed we could locate and quantify emissions
Benzene measurements in Netherlands

- We carried out measurements of benzene at three facilities near Port of Rotterdam
- DCMR (regulatory authority) suspected emissions due to enhanced ambient levels
- Monitored benzene from specific areas of sites
- DIAL was able to remotely measure all areas of sites very efficiently.
Results of benzene study

- Identified significant benzene emissions
- DIAL able to show where plume was, and quantify emission
- Led to further investigations
- Significant leaks identified
Measurement of Methane

- Methane is an important greenhouse gas
  28 times greater effect than CO$_2$
  IPCC fifth assessment

- Major source in UK GHG emissions inventory
  Total CH$_4$  50 Mt CO$_2$ equivalent
  ~10% of CO$_2$

- Landfill is an important source
  ~20 Mt CO$_2$ equivalent
Measurements of methane from landfill

- Recent measurement campaigns in UK, France (6) and USA (2) have demonstrated use of DIAL for measurement of methane emissions from landfill
- Intercomparison study in France identified DIAL as most appropriate technique
- Able to map methane emissions and identify ‘hotspots’ by scanning horizontally across the site.
- Provide quantified measurement of emissions flux
- Measured levels of emissions from ‘active’ areas and from capped areas
Landfill Studies
Measure Downwind Emissions from Area Sources
Finding methane leaks
Future development of DIAL at NPL

- **Improved ‘NPL DIAL’**
  Better sensitivity – new components
  Extension to CO\(_2\) and other GHGs
  Field demonstration at power plant

- **Current research programme investigating development of compact DIAL**
  Less flexible than current DIAL
  Different systems focussed on specific roles

- **Method development**
  Improved analysis algorithms
  Meteorology
  Uncertainty determination
  Flux measurement in complex environment
Summary

- NPL IR-UV DIAL provides a method to identify fugitive emissions
- Can perform a ‘whole site’ survey and identify leaks
- Often identify unknown emissions
- One of the most direct methods to quantify fugitive emissions flux
- Can work in most conditions - Non intrusive
- Commercial service since 1990
- Active programme to develop technology

Development of CO$_2$ measurement capability based on NPL DIAL

- This is a world first remote measurement of CO$_2$ from an industrial source
  
  Other research groups are working on this eg NIST

- Next slides will present what was needed to be done to achieve the measurements
  
  Choice of wavelength region
  Modifications to system
    • Source
    • Detector
    • Diagnostics

- Field measurement demonstration
  
  Objective to see if we can observe a CO$_2$ plume from a power station under real conditions
Summary of CO$_2$ measurements

- We have shown that DIAL is capable of making measurements of CO$_2$ emissions from power stations.
- To best of our knowledge this is *first time* remote emission measurements have been made of an individual facility.
  
  Could do this from outside facility.
- Paper currently being submitted to Atmospheric Environment on this work.

Average plume observed by DIAL

Scans 10-17
LOS 2

CO₂ ppm
Thank You
Any Questions?
OTHER SLIDES
UK Landfill Study

- Study at a UK landfill for Environment Agency
- Compared
  - DIAL
  - FID point measurement
  - Aircraft based short wavelength IR passive technique
  - GasSim – monte carlo based model
  - Flux box survey
Landfill study

[Diagram of landfill area with labels for Portable Mast, Fixed Mast, LOS1, and LOS2.]
## Results

<table>
<thead>
<tr>
<th>Method</th>
<th>Equivalent methane flux Kg/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metered flow</td>
<td>280</td>
</tr>
<tr>
<td>Model - GasSim</td>
<td>520 ± 130</td>
</tr>
<tr>
<td>DIAL</td>
<td>163 ± 41</td>
</tr>
<tr>
<td>Flux Box survey</td>
<td>45</td>
</tr>
<tr>
<td>Airborne SWIR</td>
<td>No results</td>
</tr>
</tbody>
</table>

- Dial agreed with FID point measurement concentrations
- Flux box could not survey slopes or other difficult areas of terrain
- Measured emissions lower than captured is expected
  - Oxidation
  - Active capture
Horizontal Scan Across Tipping Zone

- Can identify leaks points and hot spots
First results

- 47 measurements made over two days
- No influence from background
- No interference from steam plume
- Comparison to calculated emission
- Measurements remarkably close to calculated emissions (2700 tonne/hr)
- Particularly as campaign was not designed to measure fluxes