

# Direct Measurement of Fugitive Emissions of Hydrocarbons from a Refinery

Allan K. Chambers and Melvin Strosher

*Alberta Research Council Inc., Edmonton, Alberta, Canada*

Tony Wootton, Jan Moncrieff, and Philip McCready

*Spectrasyne Ltd., Hampshire, United Kingdom*

## ABSTRACT

Refineries are a source of emissions of volatile hydrocarbons that contribute to the formation of smog and ozone. Fugitive emissions of hydrocarbons are difficult to measure and quantify. Currently these emissions are estimated based on standard emission factors for the type and use of equipment installed. Differential absorption light detection and ranging (DIAL) can remotely measure concentration profiles of hydrocarbons in the atmosphere up to several hundred meters from the instrument. When combined with wind speed and direction, downwind vertical DIAL scans can be used to calculate mass fluxes of the measured gas leaving the site. Using a mobile DIAL unit, a survey was completed at a Canadian refinery to quantify fugitive emissions of methane, C<sub>2+</sub> hydrocarbons, and benzene and to apportion the hydrocarbon emissions to the various areas of the refinery. Refinery fugitive emissions as measured with DIAL during this demonstration study were 1240 kg/hr of C<sub>2+</sub> hydrocarbons, 300 kg/hr of methane, and 5 kg/hr of benzene. Storage tanks accounted for over 50% of the total emissions of C<sub>2+</sub> hydrocarbons and benzene. The coker area and cooling towers were also significant sources. The C<sub>2+</sub> hydrocarbon emissions measured during the demonstration amounted to 0.17% of the mass of the refinery hydrocarbon throughput for that period. If the same loss were repeated throughout the year, the lost product would represent a value of US\$3.1 million/yr (assuming US\$40/bbl). The DIAL-measured hourly emissions of C<sub>2+</sub> hydrocarbons were 15 times higher than the emission factor estimates and gave a different perspective on which areas of the

refinery were the main source of emissions. Methods, such as DIAL, that can directly measure fugitive emissions would improve the effectiveness of efforts to reduce emissions, quantify the reduction in emissions, and improve the accuracy of emissions data that are reported to regulators and the public.

## INTRODUCTION

Refineries and other hydrocarbon processing facilities are a potential source of hydrocarbon emissions to the atmosphere. Emissions of methane (CH<sub>4</sub>) are a concern because of a greenhouse gas potential 21 times that of carbon dioxide. Emissions of hydrocarbons larger than ethane are a concern for their potential to contribute to smog and ozone formation. Certain volatile hydrocarbons, such as benzene, are genotoxic and carcinogenic.<sup>1,2</sup> These concerns are reflected in Canadian government requirements to annually report site emissions of CH<sub>4</sub>, volatile organic hydrocarbons, and criteria air contaminants (CACs).

Emissions can occur from point sources, such as stacks or vents, or from widely dispersed sources such as drains, leaking valves, and fittings. Emissions from point sources can often be quantified with in-stack concentration and flow rate instrumentation. Emissions from leaking equipment and uncontained vents or unknown sources, generally known as fugitive emissions, have been difficult or impractical to measure. The current practice for most refineries is to estimate fugitive emissions.

Fugitive emissions of VOCs from refineries are estimated using emission factor methods developed by the American Petroleum Institute (API) and the U.S. Environmental Protection Agency (EPA). Emissions are estimated based on installed equipment, operating parameters, and a standard emission factor for the equipment. As an example, the volatile organic compound (VOC) emissions from a tank are estimated from emissions factors on the basis of tank size, seal type, material in the tank, the rate of material transfer through the tank, and other parameters. Fugitive emissions from leaking valves, flanges, and pipe fittings are often estimated from "sniffing" measurements using EPA Method 21 and correlation equations developed to estimate leak rates from the Method 21 screening value measurements.<sup>3</sup> The variability of Method 21 results is high, with tests demonstrating that

## IMPLICATIONS

DIAL technology can be used to map and quantify fugitive emissions of hydrocarbons from large industrial sites. Direct measurement provides a more realistic view than emission factor estimates of the amount and value of product lost to fugitive emissions and provides information to improve the focus and effectiveness of emissions reduction efforts. Direct measurement of fugitive emissions would lead to improved accuracy of reporting to regulators, improved assessment of efforts to reduce fugitive emissions of hydrocarbons and their impacts on air quality, and more accurate database information for air quality model development.

the mass emission calculated from the Method 21 screening value for a leak can vary by several orders of magnitude from the actual mass emissions.<sup>4</sup> In a large, complex refinery, the application of Method 21 can be labor intensive and costly. A significant number of potential leak sources may be difficult or unsafe to access and will not be included in the Method 21 survey.

Government regulators in Canada recognize that more accurate inventory numbers are essential for assessing emission trends and performance and that direct measurement would improve accuracy of fugitive emission data. Along with other methods, Environment Canada has worked with industry to demonstrate the use of differential absorption light detection and ranging (DIAL) as one method to directly measure fugitive emissions. The DIAL method was used in previous studies in Canada from 2003 to 2005 to measure fugitive emissions of hydrocarbons from natural gas processing facilities and to measure the combustion efficiency of three flares.<sup>5,6</sup>

### OBJECTIVE OF THIS PROJECT

The objectives of this project were:

- (1) To evaluate DIAL as a method to directly measure the quantity of fugitive emissions of CH<sub>4</sub>, C<sub>2+</sub> hydrocarbons, and benzene from a Canadian refinery;
- (2) To apportion the measured fugitive emissions to various areas of the plant; and
- (3) To compare the DIAL-measured rate of fugitive emissions with the emission rates calculated using estimation methods.

To perform this project, a mobile DIAL unit owned and operated by Spectrasyne Ltd., U.K., was shipped to Canada during the summer of 2005. The following describes the DIAL method for measuring fugitive emissions and the results of the refinery survey.

### EXPERIMENTAL METHOD DIAL

DIAL is a laser-based optical method that can measure the concentration of a gas species at a remote point in the atmosphere. One configuration of the DIAL method uses a pulsed tunable laser operating at two discrete wavelengths, one strongly absorbed by the gas species of interest and one weakly absorbed. A system of mirrors and lenses is used to direct the laser pulses toward the target gas volume and to collect light backscattered from particles and aerosols in the atmosphere. The pulse time and light absorption information from the return signals enables calculation of a gas concentration distribution along the length of the light path. This DIAL configuration is unique and different from other open-path optical methods in its ability to measure the changes in gas concentration along the length of the line of sight and in its lack of a requirement for a remote reflector or solid target. Because the DIAL method has its own light source, measurements can be collected day or night and in a wide range of weather conditions. The unique capabilities of the DIAL method enable a detailed mapping of air pollutant emissions from industrial sites.<sup>7</sup>

### The Spectrasyne Mobile DIAL Unit

Spectrasyne Ltd., U.K., has operated a mobile DIAL unit for the purpose of fugitive emissions surveys at oil and chemical facilities since 1988 (as part of BP Research) and since 1992 as an independent company. During the period from 1978 to 1988, the Spectrasyne team (then BP Research) was part of a collaborative United Kingdom Department of Trade and Industry/Oil Industry program to design, develop, and commercialize DIAL technology. Commercialization was achieved in 1992 when the BP Research commercial DIAL system was sold via a management buyout to Spectrasyne Ltd. The Spectrasyne DIAL comprises two DIAL laser sets, along with the required power generation and cooling, all contained in a 12-m long mobile unit. Once set up at a site, the mobile DIAL unit can be easily moved around the site, with approximately 15 min of setup time required after a move.

The Spectrasyne mobile DIAL consists of two parallel systems based on two high-energy (1.4 J), 10-Hz pulsed Nd:YAG pumped dye lasers. Tunable ultraviolet (UV) and visible radiation is generated in one of the laser sets by selective use of frequency doubling and tripling crystals. Tunable infrared (IR) radiation is generated in the second laser with an injection seeded Nd:YAG by means of a unique IR source assembly. The output beams from both laser systems are directed by means of a mirror steering system that rotates in two planes. The return signal consists of light backscattered from aerosols and particulates in the atmosphere. This light, which returns along the same path as the outgoing laser pulses, is collected in a Cassegrain-type receiving telescope and delivered to the appropriate detector through a multidichroic, beam splitting, collimating and focusing system.

To collect, store, handle, and process the DIAL signals from the two parallel DIAL systems, a high-speed data communication network was developed that now runs in parallel with a unique PC-based software package. Using the data analysis suite of the package, preliminary concentration profiles and mass emission results can be produced in near real time by the DIAL operators with immediate feedback to plant personnel. On several occasions in European surveys, this has enabled rapid location of leaks and other problems that were dealt with in very short time frames, followed by additional DIAL measurements to confirm the effectiveness of repairs.

For each gas to be analyzed, the selection of appropriate wavelengths for both the absorbing and nonabsorbing features is critical to avoid interference from other gases, such as water vapor, and to provide sufficient sensitivity. Some gases of interest that have been measured with the Spectrasyne DIAL system include CH<sub>4</sub>, ethane, benzene, 1,3-butadiene, sulfur dioxide (SO<sub>2</sub>), toluene, xylenes, and nitric oxide. The range, sensitivity, and detection limit vary depending on gas species and atmospheric conditions. For example, concentrations of benzene down to 0.5 parts per billion (ppb) and concentrations of CH<sub>4</sub> and alkanes down to 50 ppb can often be measured several hundred meters remote from the DIAL unit.

For this project, the mobile DIAL unit was set up to measure CH<sub>4</sub> and C<sub>2+</sub> hydrocarbons in the IR range and benzene in the UV range. The concentration of CH<sub>4</sub> and benzene were measured directly, with a known molecular

weight used to calculate mass per unit volume from the volume concentration output of the DIAL. The wavelength used for the  $C_{2+}$  measurements is a "mixed" wavelength that is absorbed by several low-molecular-weight alkane hydrocarbons from ethane ( $C_2$ ) upwards. The content of the mix of hydrocarbons was determined by collection and analysis of a gas sample from the emissions plume. After initial DIAL scans to locate the plume, sorbent tube sampling sets were deployed at an appropriate distance and height above ground in the DIAL scan plane to collect 3-hr average gas samples in the emission plume. These gas samples were later analyzed by gas chromatograph-flame ionization detection (GC-FID) to determine the identity and relative amounts of hydrocarbon species in the emissions plume to characterize the  $C_{2+}$  hydrocarbon mix. In the remainder of this paper, this mixed compound measured quantity is referred to as  $C_{2+}$  hydrocarbons.

Wind speed and direction measurements are required to derive a mass emissions rate from the two-dimensional DIAL concentration profiles. The Spectrasyne DIAL unit was equipped with a telescopic meteorological mast operated at a height of 14.5 m to record the free air wind speed, direction, humidity, and temperature during each DIAL scan. Further meteorological measurements were also collected from portable remote meteorological stations placed near the scan plane and operated at various heights. The accuracy of wind measurements is an important component in the derivation of emission mass fluxes from the DIAL measurements of concentrations.

### Using the DIAL Method for Fugitive Emissions Surveys

The protocols for the DIAL measurements required the DIAL truck to be located approximately 50 m from the closest area to be measured and approximately orthogonal to the wind direction. The laser beams were then directed along a plane downwind of the target areas and scanned upwards to encompass the complete emission plume from the target area. The measured concentration profiles throughout the plume, the wind speed and direction information, and the molecular weight of the gas measured were combined to calculate a mass emission rate for each scan. A typical vertical scan of gas concentration profiles in a plane 500 m long by 50 m high required 5–7 min of data collection time. For most scans, the IR and UV DIAL systems were operated simultaneously to collect data on two gas species or mixtures during each scan. Figure 1 is a schematic illustrating how the DIAL method would be applied to measure hydrocarbon emissions from a set of tanks.

Previous DIAL surveys performed by Spectrasyne Ltd. in Europe have demonstrated that emissions from areas of oil and gas industry plants can vary in response to operational and/or meteorological changes. For this reason, the procedure adopted by Spectrasyne was to measure each target area for 2 or 3 hr and to return to the area on at least one other occasion on a different day. This provided an indication of the emission stability of an area and the impact of operational and meteorological changes. On the basis of the concentration and wind speed measurements of each DIAL scan and the time

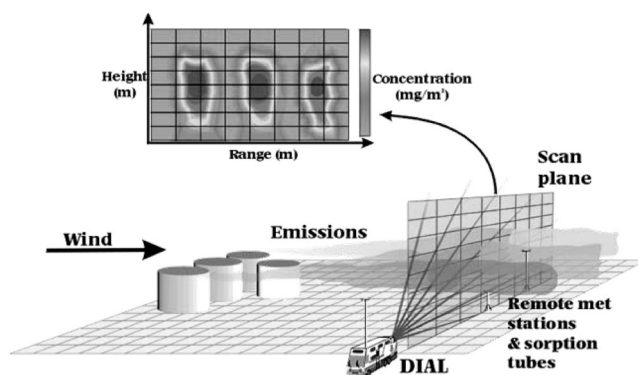


Figure 1. Schematic of DIAL system measuring emissions.

between repeat scans, a time-weighted mean flux rate was calculated from the repeat scan data, as in eq 1.

$$\text{Time Weighted Mean} = \frac{\sum_{i=1}^k (t_i \times f_i)}{\sum_{i=1}^k t_i} \quad (1)$$

where  $t_i$  is the length of scan in minutes,  $f_i$  is the corresponding flux calculated for each scan, and  $k$  is the number of scans.

An important component of the DIAL measurements is the subtraction of background concentrations or upwind sources if present. Background concentration of  $CH_4$  was determined at the site by measuring in "clean air" either above the scan line or to the upwind side. A constant background concentration of  $CH_4$  was indicated by a continuous rise in column content with distance from the DIAL unit. The column content of  $CH_4$  in this measurement was then used as a baseline for the in-scan measurements. Background readings were taken at the end of the first scan at each new location of the DIAL unit and intermittently during the time at that location. In addition, the portion before and after the  $CH_4$  plume was analyzed to determine the background for each scan line, with  $CH_4$  increases above that background used for the calculation of  $CH_4$  emissions. At locations without upwind sources, the DIAL measured background  $CH_4$  concentration over the entire 2-week survey had a mean of 2.84 parts per million (ppm) with a standard deviation of 0.34 ppm.

Depending on wind direction, there were potential upwind hydrocarbon sources outside of the refinery surveyed. In these situations, DIAL measurements both upwind and downwind of the area of interest were collected to determine emissions from the targeted part of the refinery. Upwind measurements were collected within 2 hr of the time of the downwind measurements to minimize the possible effect of wind changes.

### Validation of the DIAL Method of Measuring Mass Flux

The Spectrasyne DIAL method for measuring mass emissions has been validated using sources of known mass flux in several studies in Europe and two studies in Alberta. DIAL mass flux measurements in the European validation studies ranged from +5 to -15% compared with the known emissions source. In independent validation

study, monitored by the Conservation of Clean Air and Water in Europe, Spectrasyne collected DIAL scans of hydrocarbon emissions over a 4-hr period 36 m downwind of a barge loading gasoline. The DIAL measurements of total emissions over the 4-hr period were 390 kg, as compared with 435 kg determined from the gas displaced and gas composition measurements in the tank vent, a difference of 10%.<sup>8</sup>

Two validation studies were completed in Alberta that compared the mass flux of a gas as determined from DIAL measurements to the mass flux determined from in-stack measurements of gas concentration and flow rate. One source was a SO<sub>2</sub> plume from a tail gas incinerator stack at a gas processing facility<sup>5</sup> whereas the other was a nitric oxide (NO) plume from a gas turbine power plant.<sup>9</sup> Table 1 summarizes the results of these two studies. The DIAL measured flux rate was within -11 to +1% of the flux rate determined by in-stack monitoring, demonstrating the accuracy of the DIAL method for measuring emissions mass flux.

### OVERVIEW OF FIELD TEST PROGRAM

The Canadian refinery selected for the DIAL survey of fugitive emissions produces a variety of products, including gasoline, diesel, and jet fuel. During the period of the survey, the refinery operated near a full capacity of approximately 140,000 bbl/day. Most hydrocarbon-contaminated wastewater was collected and deep-well injected for disposal, with only minimal wastewater treatment on-site. Waste process gases were collected and recompressed for use as fuel gas on the site, minimizing the use of the process flare. Neither the wastewater treatment area nor the process flare was included in this DIAL survey. These two areas could be significant sources of hydrocarbon emissions at other refineries and DIAL is capable of measuring emissions from these types of sources.

The Spectrasyne Ltd. team performed a total of 10 days of DIAL surveys at the refinery site over two periods in late August and mid-September of 2005. During the survey, the DIAL unit operated from 32 different positions to optimize the coverage of the refinery and the ability to allocate emissions to separate areas in the refinery. The location of the DIAL unit was often selected based on wind direction to minimize sources upwind of the area being surveyed. Complex areas, such as multiple-tank storage areas, were visited several times to perform surveys under different wind directions and speeds. Major areas surveyed to determine fugitive emissions included:

- Four major separate areas of tank storage for crude feed and liquid products;
- An area for storage of propane and butane in pressurized tanks;

**Table 1.** Comparison of DIAL-measured mass flux with stack monitoring.

Species	Stack Monitor (kg/hr)	DIAL (kg/hr)	Difference (%)
SO <sub>2</sub> (plume from a Claus plant tail gas incinerator)	340	304	-11
NO (plume from a natural gas turbine power plant)	66.5	67.1	+1

- An on-site delayed coker, a coker black water storage pond, and a vacuum unit;
- Cooling towers; and
- Three separate processing areas for fractionation and upgrading.

Adjacent to the site but not part of the refinery operation were other potential sources of hydrocarbons, such as storage tanks and product transfer facilities.

During the survey period, the wind was primarily from the northwest or the west, with some days of wind from the south or east. Evening lows ranged from 6 to 19 °C, whereas daytime highs ranged from 8 to 28 °C with a mix of sunny and rainy days. Wind speeds ranged from 4 to 34 km/hr during the survey.

### RESULTS OF DIAL REFINERY SURVEY

The following summarizes the results of the DIAL measurements of emissions of CH<sub>4</sub>, C<sub>2+</sub> hydrocarbons, and benzene at the refinery. The upper limit of DIAL scans included in mass flux calculations was indicated by a decrease in emissions to below the detection limit above the physical height of the process plant or tanks being surveyed. Sources of emissions that were included in the DIAL scans include leaking valves and fittings, pressure relief valves venting to atmosphere, compressor packing vents, tank vents, cooling towers, instrumentation vents, and emissions from contaminated water sewers. The DIAL scans at this refinery did not include any measurements to determine emissions from combustion source stacks or flare stacks.

On the basis of previous validation studies of DIAL surveys on known sources, the reported time weighted mean average emissions have an estimated error of +5 to -15% of actual emissions at the time of measurement.

#### Emissions of CH<sub>4</sub>

The results of the CH<sub>4</sub> emissions measurements are summarized in Table 2. The reported CH<sub>4</sub> emissions were adjusted online to remove the contribution of a background CH<sub>4</sub> concentration around the plant.

Total site emissions of CH<sub>4</sub> measured with the DIAL were 300 kg/hr. The areas of the refinery with the highest emissions of CH<sub>4</sub> were:

- The coker area, including the vacuum unit and the coker water pond (41.7% of the total CH<sub>4</sub> emissions);
- Process area A (15.8%); and
- Process area C (14.9%).

The single largest source of CH<sub>4</sub> emissions was from the delayed coker area. Any efforts to reduce emissions of CH<sub>4</sub> should focus on this area. The second highest source of CH<sub>4</sub> was the process plant area.

Figures 2 and 3 are example DIAL scans of CH<sub>4</sub> emissions from process area A where a variable emission source was located. The CH<sub>4</sub> emissions shown in Figure 3 are approximately 40 kg/hr higher than the emissions from the scan in Figure 2. The source of this variable CH<sub>4</sub> emission appeared to be located in the saturated gas plant area at approximately 25 m above ground level.

**Table 2.** Summary of refinery site emissions of CH<sub>4</sub>.

Area	Range of Individual Scans (kg/hr)	CH <sub>4</sub> Emissions Time-Weighted Mean (kg/hr)	Portion of Total Site Emissions (%)
Coker + vacuum unit	50.7–196	125 <sup>a</sup>	41.7
Process area A	22.9–75.8	47.3	15.8
Process area B	9.5–27.6	17.9	6.0
Process area C	22.8–60	44.8	14.9
Cooling towers	15.1–29.1	26.1	8.7
Tanks—crude feed	16.6–21.4	18.4	6.1
Tanks—intermediate and final products	–	Not measured	Not measured
New tank farm	16.4–34.9	20.6	6.9
Propane, butane storage	–	Not measured	Not measured
Site total		300	

Notes: <sup>a</sup>Coker area emissions are average of drilling and nondrilling emissions.

### Emissions of C<sub>2+</sub> Hydrocarbons

The results of the C<sub>2+</sub> hydrocarbon emissions measurements are summarized in Table 3. DIAL measurements beyond and above the measurement scan plane were checked for background concentrations of C<sub>2+</sub> hydrocarbons. Where significant surrounding background levels of C<sub>2+</sub> were measured, either upwind DIAL scans were made to quantify the upwind source or the area was resurveyed during a wind direction that avoided the upwind source.

Total site emissions of C<sub>2+</sub> hydrocarbons measured with the DIAL were 1240 kg/hr. The areas of the refinery with highest emissions of C<sub>2+</sub> hydrocarbons were:

- The final product tanks (22.4% of total C<sub>2+</sub> emissions);
- The coker area, including the vacuum unit and the coker water pond (17.1%); and
- The cooling towers (13.3%).

As a group, tankage at the refinery was the source of approximately 50% of the fugitive emissions of C<sub>2+</sub> hydrocarbons. The cooling towers, an unexpected source of hydrocarbon emissions, were the source of 13.3% of the total site C<sub>2+</sub> emissions. All three major process areas combined were responsible for 18.6% of C<sub>2+</sub> emissions.

Gas sampling and analysis from the emission plumes were completed to examine the hydrocarbons present in

the plume and to determine a representative molecular weight of the C<sub>2+</sub> hydrocarbons measured by the DIAL. The C<sub>2+</sub> hydrocarbons present varied from different areas around the site. The mean molecular weight was generally in the C<sub>4</sub> to C<sub>6</sub> carbon number range.

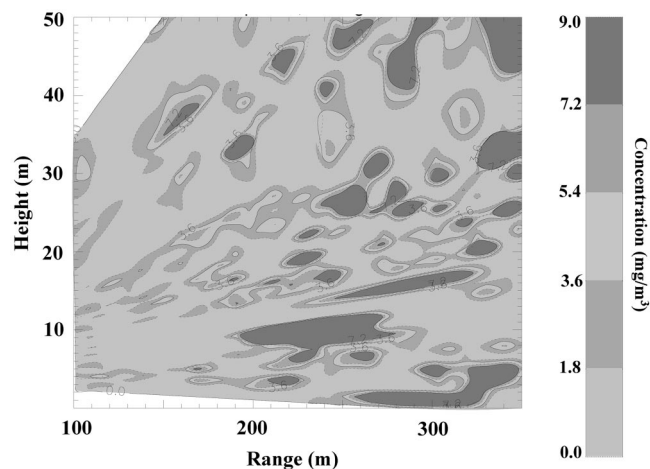
### Emissions of Benzene

The results of the benzene emissions measurements are summarized in Table 4. DIAL measurements around and above the main measurement scan plane were collected to check for upwind/background concentrations of benzene. In all cases these were found to be insignificant, indicating no notable upwind benzene sources during the measurements.

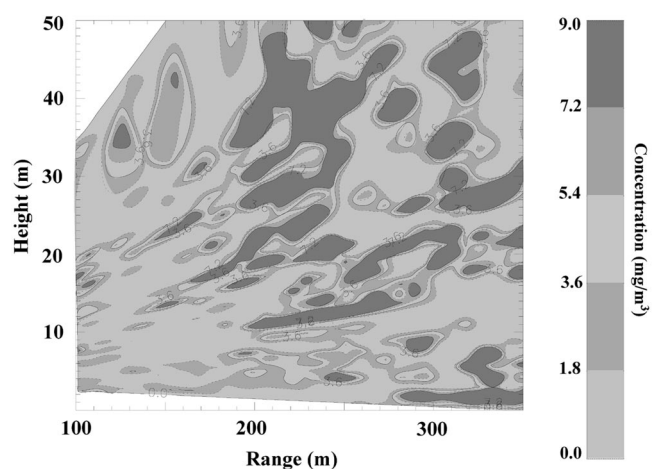
Total site emissions of benzene measured with the DIAL were 5 kg/hr. The areas of the refinery with the highest emissions of benzene were:

- The coker area, including the vacuum unit and coker water pond (26% of total benzene emissions);
- The final product tanks (26%); and
- The crude feed tanks (14%).

The single largest source of benzene emissions was the delayed coker area, with the final product tanks, as a group, emitting a similar amount. Efforts to reduce emissions of benzene should focus on the coker area and the



**Figure 2.** CH<sub>4</sub> concentrations—process area A, low emission (35.3 kg/hr).



**Figure 3.** CH<sub>4</sub> concentrations—process area A, high emission (75.8 kg/hr).

**Table 3.** Summary of refinery site emissions of C<sub>2+</sub> hydrocarbons.

Area	Range of Individual Scans (kg/hr)	C <sub>2+</sub> Emissions Time-Weighted Mean (kg/hr)	Portion of Total Site Emissions (%)
Coker + vacuum unit	77.4–369	211 <sup>a</sup>	17.1
Process area A	25.3–224	105	8.5
Process area B	20.6–94.7	57	4.6
Process area C	36.3–111	68	5.5
Cooling towers	57.0–220	164	13.3
Tanks—crude feed	115–170	141	11.4
Tanks—intermediate product	32.8–80.9	69	5.6
Tanks—final product	98.5–516	277	22.4
New tank farm	46.3–150	137	11.1
Propane, butane storage	5.4–9.1	7	0.6
Site total		1236	

Notes: <sup>a</sup>Coker area emissions are average of drilling and nondrilling emissions.

final product tanks. On a whole, tankage was the source of 64% of the benzene emissions from the site whereas process plant areas, other than the coker area, were the source of less than 10% of the benzene emissions.

#### Varying Emissions from the Delayed Coker Area

The coker area was the largest source of CH<sub>4</sub> and benzene emissions and one of the largest sources of C<sub>2+</sub> emissions. The coker area DIAL measurements were broken into three main component sections: the delayed coker, the holding pond containing discharge water from the coker, and a vacuum unit. The delayed coker consisted of two parallel units that alternated between an operation cycle and a discharge cycle. During the discharge cycle, the coke was removed from one of the units by drilling with water jets. The coke was discharged directly into rail cars for transportation off-site. Water was separated into an open holding pond for cleaning and reuse.

Emissions of C<sub>2+</sub> hydrocarbons were measured with the DIAL during both the coke discharge phase and during the steam purge phase after the discharged coker had been resealed. Throughout the measurements, one coker was sealed and in operation. Table 5 summarizes the difference in time-weighted mean emissions of C<sub>2+</sub> from the delayed cokers and the associated water pond while one coker is being drilled and after this unit was sealed and undergoing steam purging. The C<sub>2+</sub> emissions from

the coker and water pond were 298 kg/hr during drilling while coke was being dumped, as compared with 114 kg/hr when the coker was sealed for operation. Variations in emissions from cokers may be linked to the various operations within the coker cycle.

#### Emissions from Storage Tanks

On the basis of the DIAL measurements, the storage tanks at the refinery were the source of approximately 50% of the C<sub>2+</sub> emissions and over 60% of the benzene emissions from the refinery. Spectrasyne's DIAL measurements of tanks in Europe indicate that emissions from tanks can vary significantly based on tank size and design, liquid properties, tank maintenance, tank level, wind speed, and whether the tank is filling, stable, or emptying.

Wind speed can have a significant effect on tank emissions, particularly for floating roof tanks. Table 6 summarizes the effect of wind speed on the DIAL-measured C<sub>2+</sub> hydrocarbon emissions on 11 tanks that were located together in the final products tank farm at the Canadian refinery. With an increase in wind speed, from a range during measurements of 7–15 km/hr to a range of 24–34 km/hr, the total emissions from this set of tanks increased by a factor of 4. This difference in emissions may not all be attributed to wind speed but may also include effects such as differing tank levels and level movements. In this DIAL demonstration project, there

**Table 4.** Summary of refinery site emissions of benzene.

Area	Range of Individual Scans (kg/hr)	Benzene Emissions Time-Weighted Mean (kg/hr)	Portion of Total Site Emissions (%)
Coker + vacuum unit	0.33–1.72	1.3 <sup>a</sup>	26
Process area A	0.01–0.41	0.1	2
Process area B	0.01–0.37	0.1	2
Process area C	0.12–0.53	0.3	6
Cooling towers	–	Not measured	Not measured
Tanks—crude feed	0.58–0.81	0.7	14
Tanks—intermediate product	0.4–0.67	0.6	12
Tanks—final product	0.36–3.06	1.3	26
New tank farm	0.42–0.66	0.6	12
Site total		5.0	

Notes: <sup>a</sup>Coker area emissions are average of drilling and nondrilling emissions.

**Table 5.** Emissions of C<sub>2+</sub> hydrocarbons from the delayed coker area.

	Coker C <sub>2+</sub> Emission (kg/hr)	Coker Pond C <sub>2+</sub> Emissions (kg/hr)	Vacuum Unit Emissions (kg/hr)	Total C <sub>2+</sub> Emissions (kg/hr)
During drilling (range of individual scans)	134 (60.8–230)	164 (87.7–235)	7.0 (0.7–18.4)	305 (136–369)
During steam purging (range of individual scans)	64.2 (37.2–112)	50.2 (35.7–77)	4.2 (0.6–8.6)	118 (77.4–198)
Average				211

was insufficient survey time available to measure all of the tanks under different wind speed conditions and different conditions of tank levels and level movement. In Europe, the protocol for Spectrasyne DIAL measurements is that all areas should be visited at least two to three times on different days and under different conditions (where appropriate) so that the range of emissions from each area can be gauged. In many cases where emission variations are seen (e.g., from crude storage tanks) separate, complete tank filling and emptying cycles are characterized with DIAL and measurements are taken under different wind speed regimes, preferably bracketing the annual average wind speed for the site, to provide a fuller emissions picture.

The data in Table 6 highlights a caution required when estimating yearly hydrocarbon emissions from the tanks using the relatively short term measurements of emissions over a limited range of wind speeds for each tank. The average historical annual wind speed for the Canadian refinery location was 12.1 km/hr (3.36 m/sec). During the DIAL measurements of tanks at the refinery, wind speeds covered a wide range, from 5.8 to 34 km/hr (1.6–9.5 m/sec). Without a full DIAL survey covering a range of wind and tank operating conditions it would be difficult to gauge the variability of tank emissions likely to be encountered over the year at the refinery.

Spectrasyne has performed around 57 DIAL measurement surveys of hydrocarbon emissions from storage tanks at refineries, chemical plants, and transfer facilities in Europe and seven detailed cycle and wind effect studies of individual tanks or small groups of tanks. Figure 4 includes some of the data from the European studies. Emissions from single tanks ranged from under 10 kg/hr to over 250 kg/hr in these studies. The highest hydrocarbon emission from any single tank at the Canadian refinery was 92 kg/hr. The majority of the tanks at the Canadian refinery had emissions below 40 kg/hr, less than the median of the tanks shown in Figure 4. Also illustrated in Figure 4 is the significant effect of wind speed on emissions from floating roof tanks, with emissions increasing with increasing wind speed.

**Table 6.** Effect of wind speed on emissions from a group of 11 tanks.

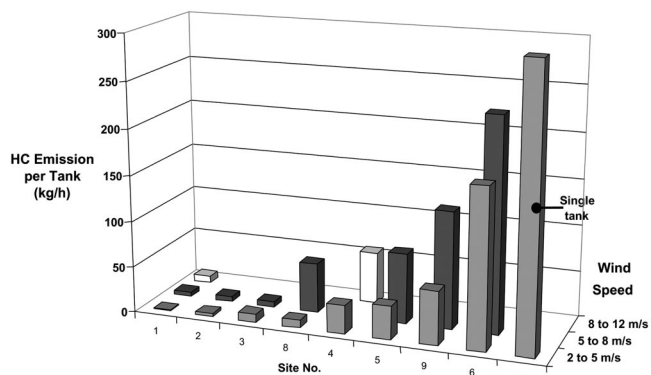
Wind Speed	C <sub>2+</sub> Emissions (kg/hr)	Benzene Emission (kg/hr)
Low wind (7–15 km/hr)	71.6	0.3
High wind (24–34 km/hr)	284	1.3

### COMPARISON OF DIAL-MEASURED FUGITIVES AND EMISSION FACTOR ESTIMATES

The refinery chosen for this demonstration DIAL survey was required to measure and control fugitive emissions in accordance with the “Environmental Code of Practice for the Measurement and Control of Fugitive VOC Emissions from Equipment Leaks,” published by the Canadian Council of Ministers of the Environment (CCME). This code includes leak measurement and control practices based on EPA Method 21. The refinery also followed the “Environmental Guidelines for Controlling Emissions of Volatile Organic Compounds from Aboveground Storage Tanks,” also published by the CCME. The refinery was required to annually submit measured emissions of VOCs and other CACs or estimated emissions if measurements were not available or possible.

To estimate its annual fugitive emissions of VOCs and benzene, the refinery followed the code of practice developed by the Canadian Petroleum Products Institute (CPPI). Fugitive emissions estimates from the process area were developed using EPA Method 21 measurements and correlation equations to estimate leak rates from screening value measurements and using emission factor estimates for inaccessible equipment. Emissions from the storage tanks were estimated using EPA TANKS software. These methods were the basis of the refinery’s estimate of VOCs and benzene emissions as reported to the Canadian National Pollutant Release Inventory (NPRI).

The estimates of fugitive emissions of VOCs and benzene submitted to the NPRI for 2004 were estimates of total annual emissions for the refinery calculated using emission factor methods. DIAL demonstration measurements of fugitive emissions at each section of the refinery were typically a time-weighted average of at least 1 hr of DIAL scans. To make some comparison between the DIAL-measured hourly fugitive emissions and the estimated

**Figure 4.** Variation of emissions from light distillate floating roof tanks in Europe.

annual total fugitive emissions as submitted to the NPRI, the NPRI figures were divided by the number of operational hours in a year using the following assumptions:

- The refinery operated continuously at full throughput for 48 weeks of the year (8064 hr);
- C<sub>2+</sub> hydrocarbon emissions as measured by DIAL represent VOC emissions as defined by NPRI;
- There were no refinery upsets or venting during the DIAL measurement period that would have affected emissions;
- DIAL demonstration tank emission measurements represent annual average wind speed conditions, tank levels, and tank level changes for the refinery; and
- The average of coker emissions during DIAL measurements while drilling and not drilling represent average annual coker area emissions.

During the period of the DIAL measurements the refinery was operating at full throughput and there were no significant upsets in the plant operation or hydrocarbon spills.

A detailed breakdown of the emissions estimates by refinery area was not available for this study so the emissions estimates and DIAL measurements were compared based on the broad groupings required for NPRI reporting. The categories and the methods used by the refinery to develop emissions values were as follows:

- (1) Stack or point release: combination of direct measurements with in-stack monitors, periodic stack measurement, and emission factors suitable for combustion sources.
- (2) Storage or handling: emissions estimates from storage tanks based on the EPA TANKS procedures as recommended by CPPI.
- (3) Fugitive releases: based on EPA Method 21 plant specific leak rate screening value correlation equations, applied per the CCME VOC Code of Practice.<sup>10</sup>
- (4) Spills: calculated volumes of inadvertent or accidental releases.
- (5) Other nonpoint releases: no emissions were reported in this category.

Emissions from point sources, such as flares or stacks from combustion equipment, or spills were not measured during the DIAL survey.

### Comparison of C<sub>2+</sub> Emissions Measurement and Estimates

Table 7 compares the DIAL measurements of C<sub>2+</sub> hydrocarbon fugitive emissions from the process plant and storage tank areas with the estimated VOC emissions reported to the NPRI for 2004. The DIAL measurement of C<sub>2+</sub> hydrocarbons does not directly correspond to the Canadian Environmental Protection Act definition of VOCs, defined as VOCs that participate in atmospheric photochemical reactions. The gas samples collected from hydrocarbon emission plumes at the refinery gave information on the relative difference between VOCs and the DIAL C<sub>2+</sub> measurement. The compounds included in the DIAL C<sub>2+</sub> hydrocarbons measurement did not include all of the species defined as VOCs by NPRI.

**Table 7.** Comparison of VOC estimates and DIAL measurements.

	Emission Estimates Based on NPRI Report 2004 <sup>a</sup> (kg/hr)	DIAL C <sub>2+</sub> Measurements (kg/hr)
Stack or point release	12	Not measured
Storage or handling	19	631 <sup>b</sup>
Fugitive releases	50.5	605
Spills	1.4	Not measured
Total	82.9	1236

Notes: <sup>a</sup>Annual emissions estimates divided by 8064 operating hours; <sup>b</sup>Tank emissions may vary with wind speed and other factors.

Using the assumptions detailed above, the C<sub>2+</sub> emissions measured with the DIAL method were approximately 15 times the amount of estimated VOC emissions and the relative proportions of various areas of the plant were different from the estimates. On the basis of the DIAL measurements, the storage tanks were the source of approximately 50% of storage and fugitive emission releases of C<sub>2+</sub> hydrocarbons at the site. This compares to the estimation method results that the storage tanks emissions were approximately 27% of storage plus fugitive releases.

Assuming a value of US\$40/bbl (US\$314/t), the annual fugitive losses of C<sub>2+</sub> hydrocarbons as measured during the demonstration DIAL survey represented a value on the order of US\$3.1 million/yr.

### Comparison of Benzene Emissions Measurements and Estimates

Table 8 compares the DIAL measurements of benzene fugitive emissions from the process plant and storage areas with the estimated emissions reported to the NPRI for 2004.

The benzene emissions measured with the DIAL method were approximately 19 times the amount estimated using emission factor methods. The DIAL measurements indicated that the storage tanks were the source of approximately 63% of storage plus fugitive releases of benzene as compared with the estimation method results that the tanks were a source of only 12.5% of storage plus fugitive releases. The emissions from the storage tanks would vary with wind speed and other factors. Thus, the annual emissions of benzene from storage tanks may be significantly different from the levels measured during the DIAL demonstration survey.

**Table 8.** Comparison of estimated and measured benzene emissions.

	Emission Estimates Based on NPRI Report 2004 <sup>a</sup> (kg/hr)	DIAL Benzene Measurements (kg/hr)
Stack or point release	0.005	Not measured
Storage or handling	0.0328	3.2 <sup>b</sup>
Fugitive releases	0.229	1.8
Spills	0.0076	Not measured
Total	0.2747	5.0

Notes: <sup>a</sup>Annual emissions estimates divided by 8064 operating hours; <sup>b</sup>Tank emissions may vary with wind speed and other factors.



Although the measured emissions of benzene were significantly higher than the estimates, the ambient concentrations measured from gas samples collected at the refinery during this study were well below Alberta ambient air quality guidelines. The highest benzene concentration measured was 1.48 ppb ( $4.7 \text{ ug/m}^3$ ) for an air sample collected from the hydrocarbon plume coming from the final product tanks. The Alberta ambient air quality guideline for benzene is a 1-hr average concentration of 9 ppb.

### Comparison of CH<sub>4</sub> Emission Measurement and Estimates

The refinery reported estimated 2004 greenhouse gas (GHG) emissions to Environment Canada under GHG reporting by major emitters. The reported GHG compounds included carbon dioxide (CO<sub>2</sub>), CH<sub>4</sub>, nitrous oxide (N<sub>2</sub>O), and hydrofluorocarbons (HFCs) with contributions estimated from three main sources: stationary fuel combustion, industrial processes, and fugitive emissions. In the public report of GHG emissions for 2004, a breakdown of GHG contribution by compounds was given but no information on sources was included. Thus the fugitive emissions of CH<sub>4</sub> measured by DIAL were compared with total CH<sub>4</sub> emissions from all sources as reported by the refinery.

The reported CH<sub>4</sub> emissions were estimated by the refinery on the basis of total fuel consumption multiplied by a factor that estimated CH<sub>4</sub> emissions resulting from fuel combustion. The refinery did not estimate fugitive emissions of CH<sub>4</sub> because they were assumed to be negligible relative to other GHG emissions.

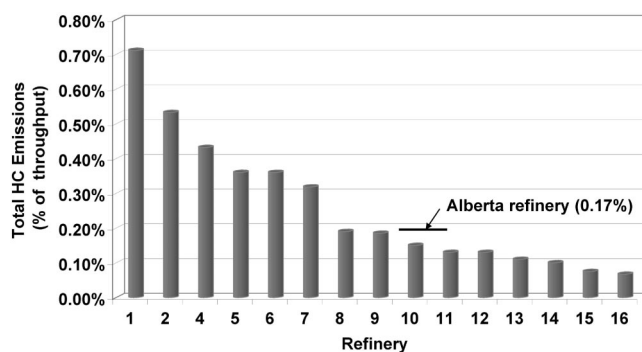
The overall estimated CH<sub>4</sub> emissions reported by the refinery for 2004 were 258 t CH<sub>4</sub>/yr or approximately 32 kg/hr. Fugitive CH<sub>4</sub> emissions as measured by the DIAL method were equivalent to 300 kg/hr, or about 9 times the estimate of total CH<sub>4</sub> emissions from all sources as reported by the refinery.

According to current estimation methodologies, fugitive emissions of CH<sub>4</sub> are typically not considered to be a major source of GHG emissions in a refinery operation. On the basis of the DIAL measurements of CH<sub>4</sub> emissions, the GHG equivalent CO<sub>2</sub> emissions due to fugitive emissions of CH<sub>4</sub> were a much larger contributor to GHG emissions than reported by the refinery, but were still less than 5% of the total GHG emissions for the refinery. The major source of GHG emissions at this refinery was CO<sub>2</sub> emissions from combustion equipment on the site.

### Comparing Canadian Refinery Emissions with European Refineries

To the authors' knowledge, this project was the first DIAL fugitive emissions survey performed on a refinery in North America. Spectrasyne Ltd. (and pre-1992 as BP Research) has performed a commercial DIAL service including measurement of refinery fugitive emissions for over 19 yr in Europe. Figure 5 is a summary of the results of the initial DIAL survey at 16 European refineries. In Figure 5, fugitive emissions of C<sub>2+</sub> hydrocarbons are expressed as a percentage of refinery throughput on a mass basis.

On a mass basis, the measured fugitive emissions of C<sub>2+</sub> hydrocarbons from the Canadian refinery were



**Figure 5.** Canadian refinery emissions relative to DIAL refinery surveys in Europe.

equivalent to 0.17% of plant throughput at the time of the emissions measurements. This falls near the median of the range of C<sub>2+</sub> hydrocarbon emissions from 0.05 to 0.7% of throughput that was measured at the refineries in Europe.

Several refineries in Europe have had successive DIAL surveys of fugitive emissions over a period of years. The information available from these surveys has enabled the refineries to focus emissions reduction in the areas with the largest potential impact. One example that is in the public domain is the Preem refinery in Sweden, with DIAL surveys of emissions in 1988, 1989, 1992, 1995, and 1999.<sup>11</sup> In the first survey of 1988, hydrocarbon emissions equivalent to 0.36% of throughput were measured, with approximately 57% from the process area and 40% from the tanks. By focusing leak reduction efforts on the process area, the refinery reduced hydrocarbon emissions by 40% between 1988 and 1989. From 1989 on, emissions from the feed and product tanks were also reduced. By the 1999 DIAL survey, the improvements in the refinery had reduced hydrocarbon emissions by 84% from the initial DIAL survey in 1988. The impetus for these improvements came largely from the initial DIAL measurements that indicated actual losses of hydrocarbon were several times the emissions estimated using emission factor methods.

### CONCLUSIONS AND RECOMMENDATIONS

The mobile DIAL unit, as operated by Spectrasyne Ltd., was an effective method for quantifying fugitive emissions of hydrocarbons from the Canadian refinery and for apportioning these emissions to various areas of the refinery. The total fugitive emissions as measured with DIAL during a 10-day survey period were 1240 kg/hr of C<sub>2+</sub> hydrocarbons (nonaromatic hydrocarbons ethane and larger), 300 kg/hr of CH<sub>4</sub>, and 5 kg/hr of benzene. The fugitive emissions of C<sub>2+</sub> hydrocarbons were equivalent to 0.17% of refinery throughput by mass during the DIAL demonstration measurement period. Assuming that these emissions continued at the same rate for a 12-month period, lost revenue attributable to these emissions could be on the order of \$3.2 million/yr. Emissions from storage tanks accounted for over 50% of the total site fugitive emissions of both C<sub>2+</sub> hydrocarbons and benzene. Other large sources of emissions included the delayed coker area and the cooling towers.

The DIAL measurements enabled a more realistic evaluation of the main sources of fugitive emissions than the information from the emission factor estimation methods typically used by industry. For this refinery, on the basis of the DIAL demonstration period measurements, the measured emissions of  $C_{2+}$  hydrocarbons were 15 times the amount of VOC emissions estimated using emission factor methods. The DIAL measurements also gave a different perspective on the relative contribution to emissions of the various areas within the refinery. On the basis of the DIAL measurements, efforts to reduce fugitive emissions at the Canadian refinery should focus on the coker area, the crude feed tanks, and the final product tanks.

Direct measurement of fugitive emissions is recommended as a way to improve the efficiency and effectiveness of leak repair and to quantify reductions in fugitive emissions as a result of improved leak detection and repair. A program of measurements is recommended to better understand storage tank emissions and how they vary with wind speed, material stored, tank level, and other factors. Measurement of fugitive emissions over a longer period of time and a range of refinery conditions would help to better understand the variability of fugitive emissions, the difference between direct measurements and emission factor estimates, and methods to calculate annual refinery emissions from short-term emissions measurement data. Direct measurement of fugitive emissions would also lead to improved accuracy of reporting to regulators, improved assessment of efforts to reduce fugitive emissions of hydrocarbons and their impacts on air quality, and more accurate database information for air quality model development.

#### ACKNOWLEDGMENTS

This project was jointly funded by Environment Canada, the Ontario Ministry of the Environment, and Alberta Environment. The authors also acknowledge the assistance of refinery staff during the planning and performance of the DIAL survey and during the interpretation and reporting of the results.

#### REFERENCES

1. *Priority Substances List Assessment Report—Benzene*; Canadian Environmental Protection Act; Environment Canada: Ottawa, Ontario, Canada, 1993.
2. *Integrated Risk Information System (IRIS) on Benzene*; U.S. Environmental Protection Agency; National Center for Environmental Assessment; Office of Research and Development: Washington, DC, 2002.
3. *EPA Method 21: Determination of Volatile Organic Compound Leaks*; U.S. Environmental Protection Agency; Emissions Measurement Center; available at <http://www.epa.gov/ttn/emc/methods/method21.html> (accessed 2007).
4. ICF Consulting, Inc. *Smart Leak Detection and Repair (LDAR) for Control of Fugitive Emissions*; American Petroleum Institute: Washington, DC, 2004.
5. Chambers, A.K. *Well Test Flare Plume Monitoring Phase II: DIAL Testing in Alberta*; CEM 7454-2003; Alberta Research Council: Edmonton, Alberta, Canada, 2003.
6. Chambers, A.K. *Optical Measurement Technology for Fugitive Emissions from Upstream Oil and Gas Facilities*; CEM-P004.03; Alberta Research Council: Edmonton, Alberta, Canada, 2004.
7. Fredriksson, K.A. In *Laser Remote Chemical Analysis*; Measures, R.M., Ed.; Vol. 94 of Wiley InterScience Series on Chemical Analysis; John Wiley & Sons: New York, 1988; Vol. 94, pp 273-332.
8. Smithers, B.; McKay, J.; Van Ophem, G.; Van Parijs, K.; White, L. *VOC Emissions from External Floating Roof Tanks: Comparison of Remote Measurements by Laser with Calculation Methods*; Report No. 95/52. Prepared for Conservation of Clean Air and Water in Europe Air Quality Management Group: Brussels, Belgium, 1995.
9. Chambers, A.K. Confidential Project Report, 2005.
10. *Environmental Code of Practice for the Measurement and Control of Fugitive VOC Emissions from Equipment Leaks*; CCME-EPC-73E; Canadian Council of Ministers of the Environment: Ottawa, Ontario, Canada, 1993.
11. Frisch, L. *Fugitive VOC-Emissions Measured at Oil Refineries in the Province of Vastra Gotaland in South West Sweden*; Publication No. 2003:56; Goteborgs Lanstryckeri: Goteborg, Sweden, 2003.

#### About the Authors

Allan Chambers and Melvin Strosher are senior research scientists with the Carbon and Energy Management Business Unit of the Alberta Research Council Inc., an applied research and development corporation. Tony Wootton, Jan Moncrieff, and Phil McCready are directors of Spectrasyne Ltd., U.K., a company specializing in DIAL-based environmental surveying for oil and chemical industries. Please address correspondence to: Allan Chambers, Alberta Research Council Inc., 250 Karl Clark Road, Edmonton, Alberta, Canada T6N 1E4; phone: +780-450-5122; fax: +780-450-5083; e-mail: chambers@arc.ab.ca.