

ATTACHMENT A

to

City's Petition to EPA
Challenging Emission Factors

July 9, 2008

**Refinery Demonstration of Optical Technologies for
Measurement of Fugitive Emissions and for Leak Detection**

prepared for:

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Preface

Over the last 4 years, Environment Canada has worked with industry (primarily the Canadian Association of Petroleum Producers) in demonstrating and promoting the application of a laser-based technology called DIAL (Differential Absorption Light Detection and Ranging) for the direct measurement of fugitive emissions (leaks) from the upstream oil and gas industrial sector over the period 2003 through 2005. The technology has been effectively used to quantify fugitive emissions from storage tanks and process facilities and to focus the work of closing serious leaks, significantly reducing the loss of valuable volatile products at upstream oil and gas facilities and reducing air pollution related emissions. The upstream oil and gas sector has accepted the value of direct DIAL measurement.

In addition, Environment Canada, Ontario Ministry of Environment and Alberta Environment recognize that:

- more accurate measurement and inventory numbers are essential for assessing emissions trends and performance; and
- current inventory estimates are based on emission factors with inherent uncertainty and direct measurement will improve accuracy and demonstrate important new technology to industry and government.

More accurate, direct measurement of emissions to air is an important initiative. Indeed, the March 22, 2006 report of the United States Environmental Protection Agency's Office of Inspector General recognizes and concurs with the Agency "shifting toward more direct, continuous monitoring and measurement of emissions from all major sources" in the U.S.

Environment Canada, Ontario Ministry of Environment and Alberta Environment co-funded the work reported herein to demonstrate the application of the optical technologies at a Canadian refinery to obtain direct measurements of fugitive emissions. The purpose of this work was to:

1. facilitate improved emissions measurement and leak detection technologies at a refinery through the application of DIAL technology as well as Infra Red Imaging gas leak visualization technology;
2. analyze the refinery plume for volatile organic compounds, methane and benzene;
3. identify the potential for emission reductions from Canadian refineries predicated on the demonstration work at the refinery; and
4. ultimately improve the emission estimates, and emission inventories and reporting for selected key air pollutants and greenhouse gases released from refineries.

The work demonstrated the efficient location of leaks using Infra Red Imaging camera technology and the quantification of refinery fugitive emissions using the DIAL technology. Emission losses were significant. Recommendations were developed to assist the refiner to:

1. reduce fugitive emissions, focusing on the most significant sources;
2. better characterize emissions; and
3. improve tracking and location of leaks.

The report also recommends further work to formalize methods for performing future DIAL surveys. To achieve this recommendation, Environment Canada, Ontario Ministry of Environment and Alberta Environment have:

1. engaged in discussions with industry and other governments to collaborate in further DIAL measurement studies; and
2. suggested collaboration with the United States EPA to identify sites for more demonstration projects specifically aimed at formalizing methods and protocols for the application of DIAL measurement techniques at facilities in Canada and the United States.

In addition, to facilitate analysis of the information presented in this report, Environment Canada commissioned the preparation of a literature review to document experience in the application of DIAL technology, both in Europe (including the European IPPC Bureau's Integrated Pollution Prevention and Control Reference Document on Best Available Techniques on Emissions from Storage) and in Canada. This review document will be available through the following link: <ftp://public:access@ts.clearstone.ca>

Environment Canada, Ontario Ministry of Environment and Alberta Environment encourage the ongoing assessment of various technologies that can aid in effectively measuring leak detection and dispersion.

Executive Summary

Refinery Demonstration of Optical Technologies for Measurement of Fugitive Emissions and for Leak Detection

Refineries and other hydrocarbon processing facilities are a potential source of hydrocarbon emissions to the atmosphere. Emissions from leaking equipment and uncontained vents or unknown sources, generally known as fugitive emissions, are difficult to measure. The current practice for most industrial sites is to estimate fugitive emissions based on standard emission factors. Established methods for finding sources of fugitive emissions are labour intensive and difficult to use in areas that are inaccessible or unsafe for personnel.

This project demonstrated two new optical methods, one for direct measurement of the quantity of fugitive emissions and one for locating sources of fugitive emissions. Differential Absorption Lidar (DIAL) is a laser-based method that can remotely measure concentration profiles of hydrocarbons and other gases in the atmosphere at distances up to several hundred meters. When combined with wind speed measurements, this data can be used to calculate mass fluxes of the measured gas and to locate large leak sources. Recently developed gas leak imaging cameras are modified infrared video cameras that visually indicate hydrocarbon plumes from leaking equipment. With these cameras, leaks can quickly be identified and a video record made of the leaks.

A survey of fugitive emissions was completed over a period of ten days at an Alberta refinery with the DIAL method to quantify fugitive emissions of methane, C₂₊ hydrocarbons (alkane hydrocarbons ethane and larger) and benzene. The survey apportioned the hydrocarbon emissions to the various areas of the refinery. A gas leak imaging survey was also completed over a five day period, coinciding with the DIAL survey, to locate leaking equipment.

The total fugitive emissions from the refinery as measured with the DIAL were 1,240 kg/h of C₂₊ hydrocarbons, 300 kg/h of methane and 5.0 kg/h of benzene. The emissions of C₂₊ hydrocarbons amounted to 0.17% on a mass basis of the hydrocarbon throughput of the refinery, representing lost product with a value in the order of \$3.2 million per year (assuming \$40/bbl). Emissions from storage tanks accounted for over 50% of the total site fugitive emissions of both C₂₊ hydrocarbons and benzene. The coker area and the cooling towers were the main sources of hydrocarbon emissions in the process plant area. When compared to emissions factor estimates, the DIAL measurements of hydrocarbon emissions gave a different perspective on both the total losses of hydrocarbons due to fugitive emissions and on the ranking of which areas of the refinery had the highest emissions. Fugitive emissions of methane contribute less than 5% to the total greenhouse gas emissions from the refinery.

The gas leak imaging camera was simple to use and required minimal training. The camera was an effective method for locating leaks of hydrocarbon gases to the atmosphere. The camera located both indoor and outdoor leaks and also remotely located leaks in high or inaccessible equipment. Since the completion of this project, the refinery has purchased a gas leak imaging camera for routine use at the site.

Based on the results of this project, the following is recommended:

1. Efforts to reduce fugitive emissions at this refinery should focus on the coker area, the cooling towers, the crude feed tanks and the final product tanks. These areas were the major sources of fugitive emissions.
2. Gas leak imaging cameras are recommended as an alternative or complement to current leak detection equipment and should be used to expand leak surveys to include equipment currently exempted from EPA Method 21 leak surveys.
3. Periodic direct measurement of fugitive emissions from refineries is recommended to improve the efficiency and effectiveness of leak repair and to quantify reductions in fugitive emissions achieved as a result of improved leak detection and repair.
4. 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. This would lead to improved tank emissions estimation procedures and a better understanding of methods to reduce tank emissions.
5. Based on the significant level of hydrocarbon emissions from this refinery's cooling towers, new methods and/or instrumentation should be developed to improve the tracking and location of heat exchanger leaks.
6. Measurement of fugitive emissions over a longer period of time and range of refinery conditions is recommended to better understand the variability of fugitive emissions and the difference between direct measurements and estimated emissions and to develop methods to calculate annual emissions based on short term measurements.
7. Further measurements are recommended to better understand fugitive emissions of hydrocarbons from sources that are currently not accounted for in the CCME VOC Code of Practice, such as coker emissions and emissions from cooling towers.
8. A program of measurements, data analysis and atmospheric modeling is recommended to better understand the relationship between hydrocarbon emissions from this refinery and other industries in the area and the hydrocarbon concentration data from the surrounding ambient air monitoring network. This should include a comparison with PrAIRie 2005 results.
9. Formalized protocols should be developed for performing DIAL surveys and calculating fugitive emissions from the results. Guidelines for recommended length and extent of surveys should also be developed.

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Refinery Demonstration of Optical Technology for Fugitive Emissions Survey and Leak Detection

1. Background

Refineries and other hydrocarbon processing facilities are a potential source of hydrocarbon emissions to the atmosphere. Emissions of methane are a concern due to greenhouse gas potential while hydrocarbons larger than ethane are a concern for their potential to contribute to smog and ozone formation. Certain hydrocarbons, such as benzene, are also considered toxic and/or carcinogenic. These concerns are reflected in government requirements to annually report site emissions of methane, Volatile Organic Hydrocarbons (VOCs) and Criteria Air Contaminants (CACs).

Emissions can occur from point sources, such as stacks or vents, or from widely dispersed sources, such as leaking valves and fittings. The quantity of emissions from point sources can often be measured with in-stack concentration and flow rate instrumentation. Emissions from leaking equipment and uncontained vents or unknown sources, generally known as fugitive emissions, are difficult to measure and the current practice for most industrial sites is to estimate fugitive emissions.

1.1 Estimating Fugitive Emissions

Currently fugitive emissions of methane and VOCs are often 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 and operating parameters and a standard emission factor for the equipment. As an example, the VOC emissions from a tank are estimated from emissions factors based on tank size, seal type, material in the tank and the rate of material transfer through the tank. Fugitive emissions due to leaking valves and other equipment may be estimated from measurements using EPA Method 21 and correlation equations developed to estimate leaks rates from the Method 21 screening value measurements.

The Canadian Petroleum Products Institute (CPPI) has developed a code of practice that refineries in Canada follow to estimate fugitive emissions (www.cppi.ca/tech/COPREI.pdf). Emissions of VOCs and CACs are reported to the National Pollutant Release Inventory (NPRI) (www.ec.gc.ca/pdb/npri/npri_home_e.cfm) with the resulting information publicly available on the NPRI website.

The operating permit for the refinery of this study requires an annual submission of measured (or estimated emissions if measurements are not available or possible) emissions of VOCs and other CACs. The refinery is also required to conduct continuous in-stack measurement of CACs such as SO₂, CO and particulate matter (opacity) and this monitoring is complemented with periodic stack surveys on major sources. The results of the continuous in-stack and stack survey monitoring are required to be submitted to Alberta Environment on a monthly basis. The refinery is 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 regulations. The refinery also follows the Environmental Guidelines for Controlling Emissions of Volatile Organic Compounds from Aboveground Storage Tanks, also published by the CCME.

Requirements for reporting and maintaining inventories of Greenhouse Gas (GHG) emissions, including emissions of methane, are more recent. Canadian facilities emitting over 100,000 tonnes/y of GHG were first required to report their emissions in 2004. Fugitive emissions of methane are one component of a facility's GHG emissions. The data is being collected by Statistics Canada and will be available in the near future on their website (www.ec.gc.ca/pdb/ghg/ghg_home_e.cfm).

1.2 Measuring Fugitive Emissions

Differential absorption Lidar (DIAL) is a unique, laser-based method that can directly measure fugitive emissions. DIAL can remotely measure concentration profiles of hydrocarbons and other gases in the atmosphere at distances up to several hundred meters from the instrument. With the DIAL method, two dimensional gas concentration profiles can be measured downwind of the equipment of interest. When combined with wind speed measurements, this data can be used to calculate mass fluxes of the gas compounds through the measurement plane. In addition, the location of significant emission sources can often be identified.

Spectrasyne Ltd., UK, (www.spectrasyne.ltd.uk) has commercially operated a mobile DIAL system for over 15 years, primarily used for emissions surveys at oil and gas facilities in Europe (Frisch, 2003). Spectrasyne has demonstrated DIAL to be an effective method to measure fugitive emissions of hydrocarbons from oil and gas processing and storage facilities, combustion efficiency of flares, hydrocarbon emissions from airports, benzene emissions from petrochemical facilities and NO_x emissions from flares. Spectrasyne has also operated their DIAL unit in North America for the measurement of fugitive emissions from several gas processing plants in Alberta during 2003 and 2004 (Chambers, 2003; Chambers, 2004). The DIAL method was very effective at quantifying the mass emissions of methane and other hydrocarbons from the gas processing plants.

1.3 Locating Sources of Fugitive Emissions

Several methods exist for locating leaks in equipment and fittings. A widely used method employs a portable total hydrocarbon detector that measures the total concentration of hydrocarbons at the probe tip where gas is sampled. This requires an operator to hold the probe next to each fitting or valve and look for an indication of hydrocarbons. U.S. EPA Method 21 was developed to estimate leak rates based on the measurement of hydrocarbon concentration at a point near the equipment, such as a flange or valve. Current methods are time consuming and require access to the equipment to be measured. About 20% of potential leak sources as defined in the CCME VOC Code of Practice are not routinely assessed with these methods at a typical refinery due to lack of resources, difficulty of access to the equipment or for safety reasons.

Recently developed modified infra-red cameras can provide a video image of hydrocarbon gas leaks. Although these cameras cannot currently discriminate hydrocarbon species or measure a mass flux rate, they are an effective method to locate leaks. These cameras have the potential to

improve the efficiency and effectiveness of locating leaking equipment in a large industrial site such as a refinery. They also improve coverage of areas of the plant that are difficult or unsafe to access with current leak detection methods. A prototype gas leak imaging camera was demonstrated at two gas processing plants in Alberta during previous studies by the Alberta Research Council (Chambers, 2004).

2. Objective

Remote optical methods such as DIAL and gas leak imaging could lead to a better understanding of fugitive emissions from refinery operations and more effective and efficient methods to quantify and locate fugitive emissions sources.

The objective of this project was to:

- use the DIAL method to measure the mass emissions of methane, C₂₊ hydrocarbons and benzene from a Canadian refinery,
- apportion the measured fugitive emissions to various areas of the plant,
- demonstrate the use of gas leak imaging cameras to locate hydrocarbon gas leaks, and
- compare the DIAL measured rate of fugitive emissions with the emission rates calculated using estimation methods.

3. Measurement Protocols for the Refinery Survey

The following summarizes the measurement protocols used during the refinery survey of fugitive emissions.

3.1 DIAL measurements

The protocols for the DIAL measurements require the location of the DIAL truck in a position, optimally about 50 metres from the closest area to be measured and approximately orthogonal to the wind direction. The laser beams are then directed along a plane downwind of the target areas and scanned upwards to encompass completely the emission plume from the target area. The measured concentration profiles throughout the plume and the plume area are combined with wind speed and direction information, relayed from meteorological stations on the scan plane, to give a mass emission figure for the scan. **Figure 1** is a schematic drawing of the DIAL method measuring hydrocarbon emissions from a set of tanks.

Emissions from areas of oil and gas industry plants can vary significantly from day to day and even hour to hour in response to operational or meteorological changes. For this reason the measurement procedure normally adopted by Spectrasynce is to measure each target area for two or three hours and to return to the area on at least one other occasion on a different day. This provides an indication of the emission stability of an area and the impact of operational and meteorological changes. Based on the concentration and wind speed measurements of each DIAL scan and the time between repeat scans, a time-weighted mean flux rate is calculated from the repeat scan data.

An important component of the DIAL measurements is the subtraction of background concentrations or upwind sources when present. For methane measurements, the background concentration of methane is subtracted from the scan data when calculating mass fluxes.

Background concentration of methane is determined by measuring in 'clean air' either above the scan line or to the upwind side. The column content of methane (mg/m^2) in this measurement is then used as a baseline for the in-scan measurements. A constant background concentration of methane is indicated by a continuous rise in column content with distance from the DIAL unit. If changes of slope are seen in the baseline measurement line, the record is not used as a background reading. Background readings are taken at the end of the first scan at each new location of the DIAL unit and intermittently during the time at that location.

Depending on wind direction, there were potential upwind hydrocarbon sources outside of the refinery. In these situations, DIAL measurements both upwind and downwind of the area of interest were required to determine emissions from the targeted part of the refinery. Further details on the Spectrasyne DIAL measurement method are contained in Appendix A.

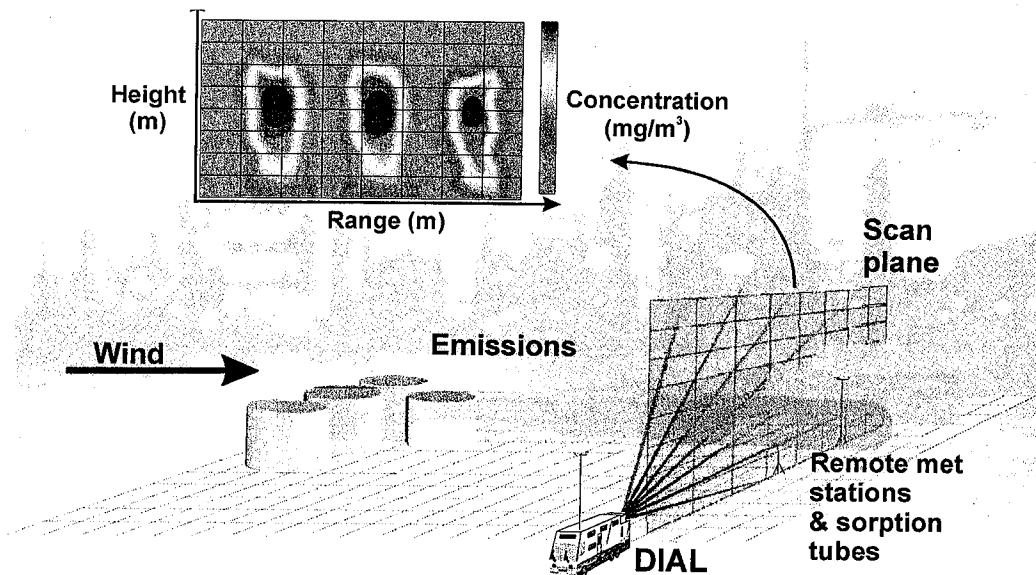


Figure 1: Schematic of DIAL System Measuring Emissions
(figure courtesy of Spectrasyne Ltd., UK)

3.1.1 Validation of the DIAL Method

The DIAL method contains several sources of potential error, including errors in the DIAL concentration measurement, wind speed and direction measurement, assumptions used for wind variation with elevation, subtraction of background sources and the average molecular weight used for converting concentration to mass. The relative contribution of these error sources may also differ from survey site to survey site. The best demonstration of the relative accuracy of the method is DIAL measurements of a known emission source.

The DIAL method of measuring mass emissions has been validated in several studies in Europe and two studies in Alberta. DIAL mass flux measurements in the European validation studies ranged from 3 to 12% below the known emissions source. Smithers, 1995, reported an independent validation study based on hydrocarbon emissions from a barge while loading gasoline. DIAL scans were collected 36 m downwind of the barge over a four hour period. The DIAL measured emissions were 390 kg as compared to 435 kg determined from the gas displaced and gas concentration measurements in the tank vent, a difference of 10%.

There have been two validation studies 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 sulphur dioxide (SO₂) plume from a tail gas incinerator stack at a gas processing facility (Chambers, 2003) while the other was a nitric oxide (NO) plume from a gas turbine power plant (confidential client report). In these two studies, the DIAL measured flux rate was within -11% to +1% of the flux rate determined by in-stack monitoring.

Table 1: Comparison of DIAL Measured Mass Flux with Stack Monitoring

Source	Stack Monitor (kg/h)	DIAL (kg/h)	difference (%)
SO ₂ plume from tail gas incinerator	340	304	-11
NO plume from a gas turbine power plant	66.5	67.1	+1

The information in Table 1 demonstrates the accuracy of the DIAL method when measuring a relatively constant source. As discussed above, fugitive emissions from a refinery can vary significantly with time due to process changes, upsets or short term events. This must be considered when projecting average yearly emissions based on the DIAL measurements that were collected over a relatively short period of time.

Currently refineries often estimate fugitive emissions by a survey of leaking components using Method 21 and correlation equations to estimate component leak rates based on the screening value measurements. However the variability of this technique is high, with tests demonstrating that actual mass emissions can vary by several orders of magnitude from the mass emission calculated from the Method 21 screening value (ICF Consulting, 2004). The validated DIAL method relative accuracy of -3 to -12% is significantly better.

3.2 Meteorological Measurements

Wind speed measurements were required to calculate a mass emissions rate from the two dimensional DIAL concentrations profiles. The DIAL truck was equipped with a telescopic met mast that normally operates at a height of 14.5 meters and measures the free air wind speed, direction and temperature. In complex areas, meteorological measurements were also collected from portable remote met stations placed near the scan plane and operated at a height of six or

eight meters. The accuracy of wind measurements is an important component of the calculation of emission mass fluxes from the DIAL measurements of concentrations.

3.3 Gas Sampling and Analysis

To collect detailed information on the species present and relative distribution of hydrocarbons in the emission plume, gas samples from the plume were collected and analysed where possible. Two sampling methods were used in this study. One method collected gas samples over a one hour period in evacuated Silco steel lined canisters (EPA Method TO-15). These were analyzed at Alberta Research Council's Vegreville location. The analysis method used a gas chromatograph to measure concentrations of light hydrocarbon gases (C1 to C4) and reduced sulphur compounds and a gas chromatograph/mass spectrometer to measure concentrations of VOC's (equivalent to EPA Method TO-15). Appendix B contains further details on the canister sampling and analysis method.

The second method used sorption tubes to collect hydrocarbon samples from the plume over a three hour period. Spectrasyne Ltd. used the detailed analysis of the hydrocarbon distribution in the sorption tubes to provide information on the identity and relative amounts of hydrocarbon species in the emissions plume. This information enables calculation of an average molecular weight of the C₂₊ hydrocarbons present in the plume that are measured with the DIAL. This average molecular weight combined with DIAL measurements of C₂₊ concentration information was used to calculate mass emissions rates of C₂₊ in the plume.

3.4 Gas Leak Imaging Camera

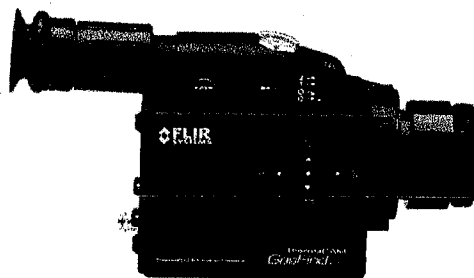
New methods have been developed to detect hydrocarbon gas leaks in oil and gas processing facilities, refineries and pipelines. Much of this research and development was driven by the American refinery industry and the natural gas pipeline industry to improve the reliability and to reduce the cost of current Leak Detection and Repair (LDAR) surveys using EPA Method 21. Gas leak imaging cameras could potentially reduce these costs by more quickly identifying leaks and focusing repair efforts on areas with the highest number of leaks.

Infra-red (IR) cameras were originally developed for thermal imaging inspection of equipment. Methane and other hydrocarbon gases absorb in a wavelength within the range of modern infrared cameras. With filters in the appropriate wavelengths, an infrared camera can be modified to produce an image of hydrocarbon gas plumes. Although these cameras cannot discriminate between hydrocarbon species or measure the mass emissions of the leak, they can be used to efficiently locate leaks.

Leak Surveys Inc., Texas, (www.leaksurveysinc.com) has developed a commercial prototype and is offering a leak survey service using their camera. Figure 2(a) is a photograph of the prototype Hawk camera in use. The result of the leak camera survey is a video record with hydrocarbon leaks visible as light or dark clouds in the video. The technology was repackaged by FLIR, a commercial manufacturer of infrared cameras, into a compact video camera sized unit, shown in Figure 2(b).



(a)



(b)

Figure 2: Hawk Leak Imaging Camera
(from www.leaksurveysinc.com and www.flir.com)

The minimum size of leak that can be detected by a gas leak imaging camera will depend on many factors such as type of hydrocarbon, distance from the leak, light levels, wind speed and operator. One field project at a petrochemical plant environment determined that the Hawk camera was able to view leaks with a mass emission rate as low as 1.4 g/h (ENVIRON, 2005).

The utility of gas leak imaging cameras was demonstrated during a study at a gas processing plant in Alberta. Over thirty leaking components were identified by an imaging camera survey conducted with the Hawk camera. A focused leak repair was completed and the follow up camera survey only identified seven leaks. DIAL measurement of the fugitive emissions from the processing area before and after the camera survey and leak repair measured a 50% reduction in methane emissions and over a 90% reduction in C₂₊ hydrocarbon emissions (Chambers, 2004).

4. Overview of Field Test Program

The testing program took place at a refinery in Alberta. Some characteristics of the refinery site relevant to the study included:

- capacity of about 140,000 bbl/day (throughput was within 3% of capacity throughout the DIAL survey),
- produces a variety of products, such as gasoline, diesel and jet fuel,
- three major separate areas of tank storage for liquid products,
- area for storage of propane and butane,
- on-site delayed coker,
- processing areas for fractionation and upgrading,

- most hydrocarbon contaminated waste water was deep well injected, with only minimal waste water treatment facilities on-site,
- waste gases collected and recompressed for use as fuel gas on the site, minimizing the use of the process flare for disposal of waste gas,
- 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,
- the refinery operated at full capacity during the test period.

The Spectrasynce Ltd. team performed DIAL surveys at the refinery site over two periods during 2005, from August 25 to September 1 and from September 13 to September 15. The Alberta Research Council collected and analyzed ambient air samples at select locations to determine details of the hydrocarbon species present. The gas leak imaging survey was performed from September 12 to September 16 by Leak Surveys Inc., Texas. Table 2 summarizes the DIAL measurements and gas sampling completed. The gas leak imaging survey essentially covered all areas of the site during the five days of the leak imaging survey. A portion of the refinery testing coincided with the Prairie2005 Edmonton area air monitoring program performed as a separate project by Environment Canada.

During the survey period the wind was primarily from the northwest or the west, with some days of wind from the south or east. This narrow range of wind directions limited the amount of segregation possible in some areas of the plant. During the survey period, evening lows ranged from 6°C to 19°C while daytime highs ranged from 8°C to 28°C with a mix of sunny and rainy days.

Table 2: Measurements Completed During the DIAL Refinery Survey

Area	CH ₄ DIAL	C ₂₊ DIAL	Benzene DIAL	Canister Sample	Sorption Tube Sample
Coker/Vacuum Unit/Pond	X	X	X		X
New Process Plant	X	X	X		
Old Process Plant	X	X	X	XX	X
Cooling Towers	X	X			
Bullets & Spheres		X			
Tanks - crude oil	X	X	X		
Tanks – intermediate products		X	X		
Tanks – final products		X	X	X	X
Tanks – new tank farm	X	X	X		

Emissions from flares and water treatment systems were two areas not covered by this DIAL survey. Flares and waste water treatment may be important sources of hydrocarbon emissions at other refineries. The refinery of this study disposed of hydrocarbon-contaminated water by deep

well injection, with little on-site water treatment. The waste gas recovery system at the refinery resulted in minimal flare use and, given the restricted time available in the survey, measuring emissions from the flare was given low priority.

A portion of the DIAL survey at the refinery corresponded with PrAIRie 2005, an atmospheric sampling project operated by Environment Canada. This study combined both ground and air based mobile sampling equipment to examine hydrocarbon, ozone and particulate concentrations in the vicinity of Edmonton. A future study should examine relationships between the results of the DIAL study and measurements and analysis from the PrAIRie 2005 study.

5. Results of the DIAL Measurement of Emissions

The following summarizes the results of the DIAL measurements of emissions of CH₄, C₂₊ hydrocarbons and benzene at the refinery. The DIAL survey of emissions from the refinery did not include any measurements to determine emissions from combustion source stacks or flare stacks. The upper level of DIAL scans included in mass flux calculations was indicated by a decrease in significant emissions above the physical height of the process plant or tanks being surveyed. Possible 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 survey at this refinery was performed over a period of ten survey days. For a refinery of this size, a survey of 14 to 24 days would be recommended for a thorough assessment of fugitive emissions (Frisch, 2003).

5.1 Emissions of C₂₊ Hydrocarbons

For measurement of general hydrocarbons other than CH₄, Spectrasyne uses an infrared range wavelength that is absorbed by straight-chain alkane hydrocarbons ethane and larger. In the report this measured quantity is referred to as C₂₊ hydrocarbons.

The DIAL measurement of C₂₊ does not directly correspond to the Canadian Environmental Protection Act definition of VOCs, defined as volatile organic compounds that participate in atmospheric photochemical reactions. VOCs do not include ethane, a species that is measured with the DIAL C₂₊ wavelength, but do include alkenes and cyclic hydrocarbons, species that are not measured with the DIAL C₂₊ wavelength. The gas samples collected from hydrocarbon emissions plumes at the refinery gave information on the relative difference between VOCs and the C₂₊ measurement. The compounds included in the DIAL C₂₊ hydrocarbons measurement included from 55 to 85% by weight of the total hydrocarbons that relate to VOCs. The results of both the canister samples and the sorption tube samples are included as Appendix C.

The results of the C₂₊ hydrocarbon emissions measurements are summarized in Table 3. DIAL measurements outside of the measurement scan plane were collected to check for background concentrations of C₂₊ hydrocarbons (see Section 3.1). When significant background levels of C₂₊ were measured during the background scans, they were large and variable, indicating an

upwind source of hydrocarbons. Further measurements under a different wind direction and/or upwind DIAL scans were completed in those cases.

Total site emissions of C₂₊ hydrocarbons measured with the DIAL were 1237 kg/h. The areas of the refinery with highest emissions of C₂₊ were:

- final product tanks (22.4% of total C₂₊ emissions),
- coker area including vacuum unit and coker water pond (17.1%), and
- cooling towers (13.3%).

As a group, tankage at the refinery was the source of about 50% of the fugitive emissions of C₂₊ hydrocarbons. The cooling towers, an unexpected source of hydrocarbon emissions, were the source of 13.3% of the total site C₂₊ emissions.

Table 3: Summary of Refinery Site Emissions of C₂₊ Hydrocarbons

Area	C ₂₊ Emissions (kg/h)	% of total site emissions
coker + vacuum unit	211 ⁽¹⁾	17.1
new process area	68.3	5.5
old process area north	105	8.5
old process area south	56.8	4.6
cooling towers	164	13.3
tanks - crude feed	141	11.4
tanks - intermediate product	68.7	5.6
tanks - final product	277	22.4
new tank farm	137	11.1
bullets and spheres	7.4	0.6
Site total	1237	

1) coker area emissions are average of drilling and non-drilling emissions

5.2 Emissions of Methane

The results of the CH₄ emissions measurements are summarized in Table 4. The reported CH₄ emissions have been adjusted for a background methane concentration of about 2.4 ppm. Background readings were measured with the DIAL directed either above or upwind of the measurement scan plane at the beginning of scanning at each measurement location and intermittently during the measurements (see Section 3.1). The column content of methane

(mg/m²) from these background measurements was used as a baseline for calculations of methane mass flux from the scan plane measurements.

Total site emissions of CH₄ measured with the DIAL were 300 kg/h. The areas of the refinery with highest emissions of CH₄ were:

- coker area, including vacuum unit and coker water pond (41.7% of the total CH₄ emissions),
- north section of the old process area (15.8%), and
- new process area.

The single largest source of CH₄ emissions was from the delayed coker area. Any efforts to reduce emissions of CH₄ should focus on this area. The second highest source of CH₄ was the process plant area.

Table 4 Summary of Refinery Site Emissions of CH₄

Area	CH ₄ Emissions (kg/h)	% of total site emissions
coker + vacuum unit	125	41.7
new process area	44.8	14.9
old process area north	47.3	15.8
old process area south	17.9	6.0
cooling towers	26.1	8.7
tanks - crude feed	18.4	6.1
tanks – intermediate and final products	not measured	not measured
new tank farm	20.6	6.9
bullets and spheres	not measured	not measured
Site total	300	

Figure 3 and Figure 4 are example DIAL scans of methane emissions from the old process area north. This is an example of varying emissions from an area of the plant. An apparent intermittent methane leak resulted in higher emissions in Figure 4. The additional variable methane emission of about 40 kg/h appeared to be in the Saturated Gas Plant at an elevation of about 25 m.

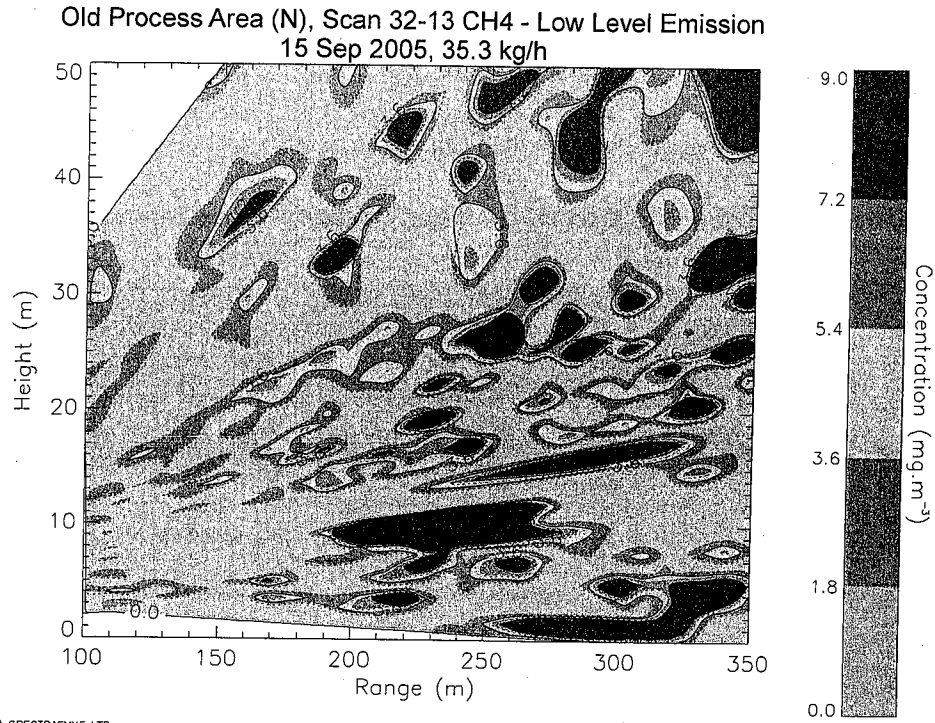


Figure 3: Methane Concentrations – North Process Area, Low Emission

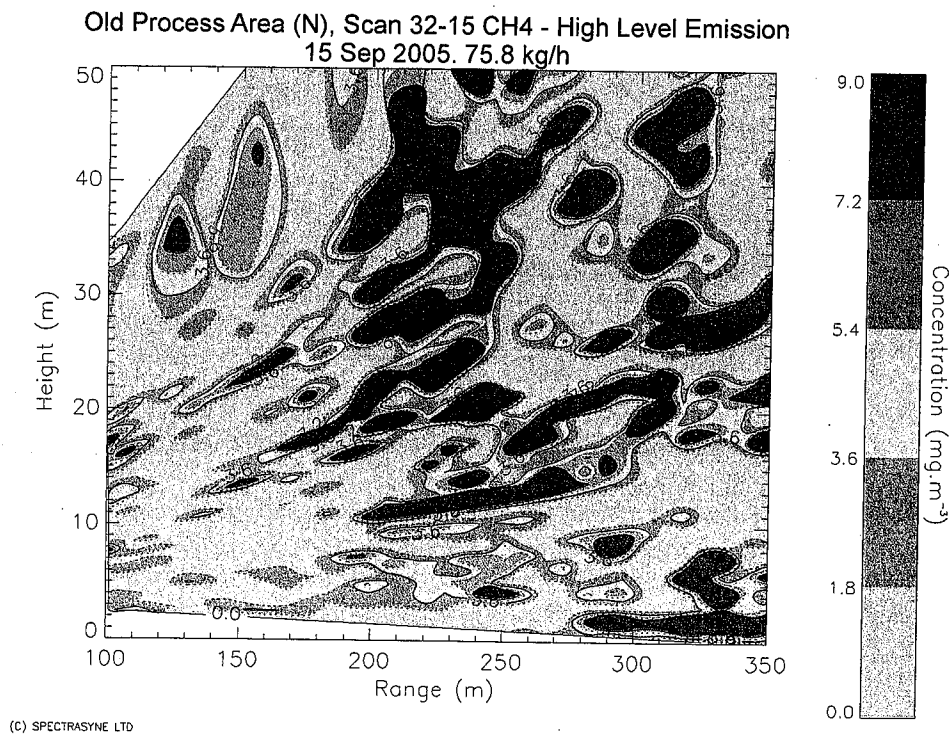


Figure 4: Methane Concentrations – North Process Area, High Emission

5.3 Emissions of Benzene

The results of the benzene emissions measurements are summarized in Table 5. DIAL measurements outside of the measurement scan plane were also collected to check for background concentrations of benzene (see Section 3.1). Measured background levels of benzene were insignificant.

Total site emissions of benzene measured with the DIAL were 5.0 kg/h. The areas of the refinery with highest emissions of benzene were:

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

The single largest source of benzene emissions was the delayed coker area, with the final product tanks emitting a similar amount. Efforts to reduce emissions of benzene should focus on the coker area and the final product tanks. On a whole, tankage was the source of 64% of the benzene emissions from the site while process plant areas, other than the coker area, were the source of less than 10% of the benzene emissions.

Table 5: Summary of Refinery Site Emissions of Benzene

Area	Benzene Emissions (kg/h)	% of total site emissions
coker + vacuum unit	1.3	26
new process area	0.3	6
old process area north	0.1	2
old process area south	0.1	2
cooling towers	not measured	not measured
tanks - crude feed	0.7	14
tanks - intermediate product	0.6	12
tanks - final product	1.3	26
new tank farm	0.6	12
Site total	5.0	

5.4 Example of Varying Emissions from the Delayed Coker Area

The coker area was the largest source of CH₄ and benzene emissions and one of the largest sources of C₂₊ emissions. The coker area DIAL measurements were broken into three main components, the delayed coker, the holding pond containing discharge water from the coker and a vacuum unit. The delayed coker unit consisted of two parallel units that alternated between an operation cycle and a discharge cycle. During the discharge cycle, the coke was removed from the unit by drilling with water jets and the coke was discharged directly into rail cars for transportation off site. Water was separated into a holding pond for cleaning and re-use.

Emissions of C₂₊ were measured with the DIAL during both the coke discharge phase and during the steam purge phase after the coker had been re-sealed. During the measurements, one coker was sealed and in operation. Table 6 summarizes the time weighted mean emissions of C₂₊ from the delayed cokers and the associated water pond. The emissions from the coker and water pond were 298 kg/h during drilling while coke was being dumped as compared with 114 kg/h when the coker was sealed for operation. This is an example of a refinery process that has emissions that vary significantly during normal operation.

Table 6: Emissions of C₂₊ from the Delayed Coker

	Coker C₂₊ Emission (kg/h)	Coker Pond C₂₊ Emissions (kg/h)	Vacuum Unit Emissions (kg/h)	Total C₂₊ Emissions (kg/h)
during drilling	134	164	7.0	305
during steam purging	64.2	50.2	4.2	118
average				211

5.5 Emissions from Tanks

Based on the DIAL measurements, the tanks at the refinery were the source of about 50% of the C₂₊ emissions and over 60% of the benzene emissions. 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 has a significant effect on tank emissions, particularly for floating roof tanks. Emissions increase with increasing wind speed based on measurements performed in Europe by Spectrasyne Ltd., as discussed further in Section 5.7. Table 7 summarizes the effect of wind speed on DIAL measured hydrocarbon emissions on eleven tanks that were located together in the final products tank farm at the Alberta refinery. With an increase in wind speed from 10 km/h to 30 km/h the total emissions increased by a factor of four times. The difference in emissions may not all be attributed to wind speed but may also include effects such as different tank levels and tank level movements.

Table 7: Effect of Wind Speed on Emissions from a Group of Eleven Tanks

Wind Speed	C₂₊ Emissions (kg/h)	Benzene Emission (kg/h)
low wind (10 km/h)	71.6	0.3
high wind (30 km/h)	284	1.3

The data in Table 7 highlights a caution required when estimating yearly hydrocarbon emissions from the tanks using the relatively short term DIAL measurements over a limited range of wind speeds for each tank. The average historical annual wind speed for the refinery location is 12.1 km/h (3.36 m/s). During the DIAL measurements of tanks at the refinery wind speeds covered a wide range, from 5.8 to 34 k/h (1.6 to 9.5 m/s). However there was insufficient survey time available to measure all of the tanks under different wind speed conditions and different conditions of tank levels and tank level movement. The average wind speeds during C₂₊ emissions measurements of the tanks were:

- 17 km/h for conventional crude feed tanks and 8.8 km/h for syncrude tank
- 8 km/h for intermediate product tanks (other than feed tanks)
- 10 km/h to 30 km/h for final product tanks
- 17 km/h for the new tank farm

The DIAL measurements of the tanks were a mix of measurements below and above the annual average wind speed. Tank emissions will also vary due to tank level, fill and empty cycles and other factors. Without further DIAL measurements for a range of tank conditions it is difficult to estimate what the variability of tank emissions are at the refinery and how the measured emissions during this test program relate to total annual emissions from the tanks.

5.6 Comparison of DIAL Measured Fugitives and Emission Factor Estimates

One objective of this project was to compare the DIAL measured hydrocarbon emissions to the estimated hydrocarbon emissions to the air as submitted for NPRI reporting. The following section will discuss the assumptions made to estimate annual emissions from the DIAL measurements collected over a ten day period and how these compared to the estimated annual emissions reported to NPRI for 2004. Calculating annual emission rates from the DIAL measurements could be improved with more frequent and extended DIAL measurements to assess the variability of emissions and to develop protocols to address any variability. To estimate annual emissions, the refinery followed the code of practice developed by the Canadian Petroleum Products Institute (CPPI) (www.cppi.ca/tech/COPREI.pdf). Fugitive emissions estimates from the process area were developed from EPA Method 21 measurements and correlation equations to estimate leak rates from screening value measurements. A portion of the difference identified between the DIAL results and normal emissions estimating procedures may be due to the methods used and simplifying assumptions made to calculate annual emissions from short term measurements.

The DIAL survey did not include any measurements to determine emissions from combustion source stacks or flare stacks. The upper level of DIAL scans included in mass flux calculations was indicated by a decrease in significant emissions above the physical height of the process plant or tanks being surveyed.

Possible 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.

5.6.1 Assumptions Used to Calculate Annual Emissions from DIAL Measurements

The estimates of VOC and benzene emissions submitted to the NPRI for 2004 were estimates of total annual emissions for the refinery calculated using emission factor methods. DIAL measurements of fugitive emissions at each section of the refinery were typically a time weighted average of at least one hour of DIAL scans. During the period of the DIAL measurements the plant was operating at full throughput. There were no significant upsets in the plant operation or hydrocarbon spills during the survey.

Recognizing the variation in fugitive emissions due to normal process changes and wind variation, the annual emissions for the refinery were calculated from the relatively short term DIAL emissions. To do these calculations, several important assumptions were made, including:

- DIAL short term measurements represent annual average emissions,
- refinery operation continuously at full throughput for 48 weeks of the year (8,064 hours),
- C₂₊ emissions represent VOC emissions,
- no refinery upsets or venting during the DIAL measurement period that would have affected emissions,
- DIAL tank measurements represent annual average wind speed conditions, tank levels and tank level changes for the refinery,
- average of coker emissions while drilling and not drilling represent average full year coker area emissions.

These assumptions and their potential impact on calculated total annual emissions based on the DIAL measurements must be kept in mind when comparing the DIAL measurements with estimated emissions.

NPRI requires reporting of air emissions of VOCs to be sub-totaled into five categories. 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 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 as per the CCME VOC Code of Practice (CCME-EPC-73E).
4. spills – calculated volumes of inadvertent or accidental releases
5. other non-point releases – no emissions were reported in this category.

5.6.2 Comparison of C₂₊ Emissions Measurement and Estimates

Table 8 compares the DIAL measurements of C₂₊ fugitive emissions from the process plant and storage tank areas with the estimated emissions reported to the NPRI for 2004. Emissions from point sources, such as flares or stacks from combustion equipment, or spills were not part of the DIAL survey. Emissions from combustion system stacks are well characterized and, based on the NPRI reported data, contribute less than 15% of the site VOC emissions. If the DIAL scans included some portion of these stack gases, the total measured mass flux attributed to fugitive releases would not change significantly. Possible 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, instrumentation vents, emissions from contaminated water sewers and event related emissions, such as coke removal from the delayed coker.

The C₂₊ emissions measured with the DIAL method were significantly higher than the estimated emissions and the relative proportions of various areas of the plant were different than the estimates. Based on the DIAL measurements, the storage tanks were about 50% of storage plus fugitive releases of C₂₊ hydrocarbons at the site as compared to the estimation methods results that the storage tanks emissions were about 27% of storage plus fugitive releases.

The DIAL measurements suggest that the value of product lost due to storage tank and process plant fugitive emissions is an order of 15 fold higher than that indicated by the emissions estimation procedures. Assuming a value of \$40/bbl (\$314/tonne), the annual fugitive losses of C₂₊ hydrocarbons as measured during the DIAL survey have a value in the order of \$3.1 million per year. The C₂₊ hydrocarbon emissions from the cooling towers alone represent about \$530,000 per year of lost product.

Table 8: Comparison of VOC Estimates and DIAL Measurements

	NPRI Report 2004 (tonnes/y)	DIAL C₂₊ Measurements (tonnes/y)
stack or point release	98.69	not measured
storage or handling	153.0	5,090 ¹
fugitive releases	407.1	4,880
spills	11.5	not measured
Total	670.4	9,970

1) emissions from tanks vary with wind speed and other factors

5.6.3 Comparison of Benzene Emissions Measurements and Estimates

Table 9 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. Emissions from point sources, such as flares or stacks from combustion equipment, or spills were not part of the DIAL survey and were not measured.

Table 9: Comparison of Estimated and Measured Benzene Emissions

	NPRI Report 2004 (tonnes/y)	DIAL Measurements (tonnes/y)
stack or point release	0.039	not measured
storage or handling	0.265	25.4 ¹
fugitive releases	1.850	14.7
spills	0.061	not measured
Total	2.215	40.1

¹⁾ emissions from tanks vary with wind speed and other factors

The benzene emissions measured with the DIAL method were significantly higher than the estimated emissions. The DIAL measurements also indicated that the storage tanks were the source of about 63% of storage plus fugitive releases of benzene as compared to 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 could be significantly different than the DIAL measurements.

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 ug/m³) 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 one hour average concentration of 9 ppb.

Emissions estimation procedures currently used to estimate fugitive emissions are based on equipment installed and standard emission factors for the equipment. The DIAL method directly measures hydrocarbon emissions from the equipment at the time of the measurements. The actual hydrocarbon emission measurements gave a different perspective on the total losses of hydrocarbons due to fugitive emissions from the tanks and process equipment as well as a different ranking of which portions of the refinery had the highest emissions. Direct

measurements of emissions could be used 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.

5.6.4 Comparison of Methane 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 CO₂, CH₄, N₂O and HFCs with contributions estimated from three main sources, namely stationary fuel combustion, industrial process, 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 methane measured by the DIAL were compared with total methane emissions reported by the refinery.

The reported methane emissions were estimated by the refinery based on total fuel consumption multiplied by a factor that estimated methane emissions resulting from fuel combustion. The refinery did not estimate fugitive emissions of methane as they were assumed to be negligible relative to other greenhouse gas emissions.

To calculate the annual amount of fugitive emissions of methane from the DIAL measurements, the measured hourly methane fugitive emission of 300 kg/h was multiplied by 8,064 hours of operation during 2004. The DIAL measurements of methane did not include potential contributions from stacks or flares.

The overall estimated methane emissions reported by the refinery for 2004 were 258 tonnes CH₄/year. Fugitive methane emissions as measured by the DIAL method were equivalent to 2,400 tonnes CH₄/year. The DIAL measured fugitive emissions of methane were about nine times the estimate of total methane emissions from all sources as reported by the refinery, with the exception of flare emissions which were not included in the estimated or measured emissions.

According to current estimation methodologies, fugitive emissions of methane are typically not considered to be a major source of GHG emissions in a refinery operation. Based on the DIAL measurements of methane emissions, the fugitive emissions of methane were a much larger contributor to GHG emissions than reported by the refinery.

5.7 Comparison with European Refineries

This project was the first DIAL fugitive emissions survey performed by Spectrasyne on a refinery in North America. Spectrasyne Ltd. has performed DIAL measurement of refinery fugitive emissions for over 15 years in Europe and some of these refineries have been revisited several times for repeat surveys. Figure 5 is a summary of several refinery surveys, with fugitive emissions expressed as a percentage of refinery throughput on a weight basis. Some of the surveys with relatively low emissions were repeat surveys at refineries that have benefited from previous DIAL surveys followed by focused leak reduction efforts.

On a mass basis, the measured fugitive emissions of C_{2+} hydrocarbons from the Alberta refinery were equivalent to 0.17% of plant throughput at the time of the emissions measurements. This falls near the median of the range of emissions from 0.05% to 0.7% of throughput that Spectrasyne has measured in Europe.

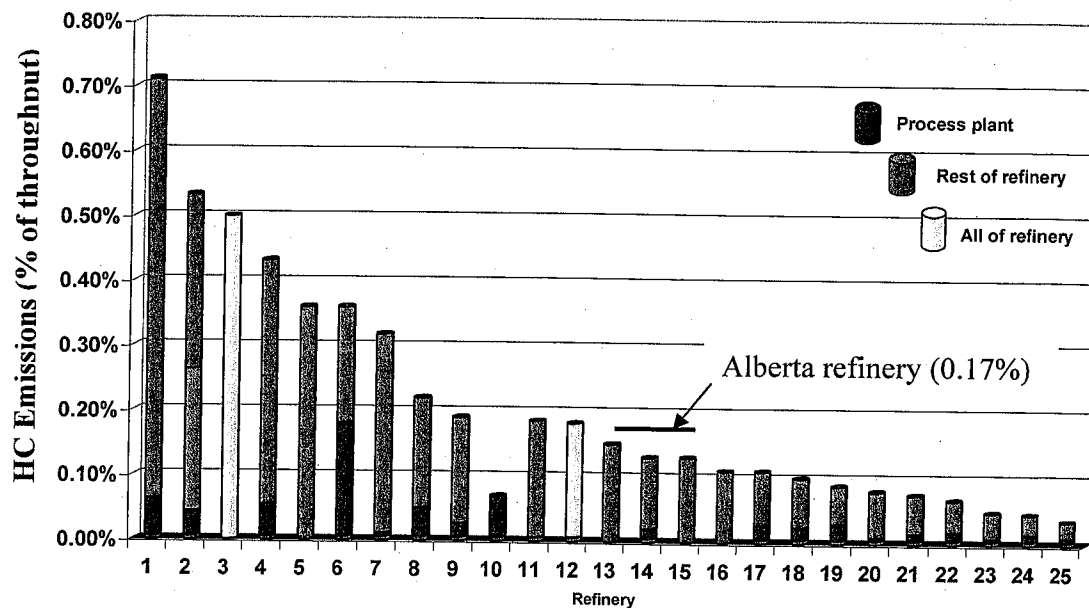


Figure 5: Comparison of AB Refinery with Spectrasyne's Refinery Surveys in Europe (figure courtesy of Spectrasyne Ltd., UK)

Spectrasyne has also performed numerous DIAL measurements of hydrocarbon emissions from storage tanks at refineries and transfer facilities in Europe. Figure 6 includes some of the data from this work and demonstrates the large range of emissions measured from single tanks. The highest hydrocarbon emission from any single tank at the Alberta refinery was 92 kg/h. The other tanks at the refinery had emissions below 40 kg/h. The majority of the tanks at the Alberta refinery had emissions below the median of the tanks shown in Figure 6. Also illustrated in Figure 6 is the significant effect of wind speed on emissions from floating roof tanks, with emissions increasing with increasing wind speed.

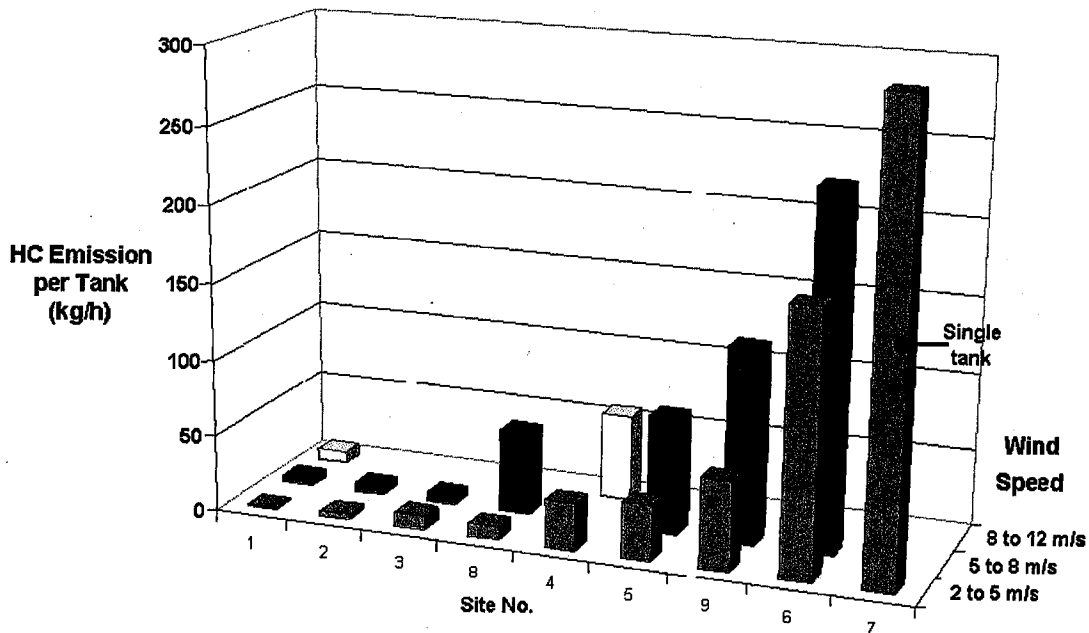


Figure 6: Emissions from Light Distillate Floating Roof Tanks in Europe (figure courtesy of Spectrasyne Ltd., UK)

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. Figure 7 shows hydrocarbon emissions (not including methane) at the Preem refinery in Sweden as measured with the DIAL method from 1988 to 1999 (Frisch, 2003). In the first survey of 1988, the majority of emissions were from the process area which accounted for 57% of total hydrocarbon emissions. Tank emissions were a source of 40% of the emissions. 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%. Some of the improvements at the Preem refinery that resulted in reduced emissions included:

- secondary seals on all tanks with outer floating roofs
- switched blanket gas on naphtha tanks from reformer off gas to nitrogen
- covered sumps for oil pumps
- installed new roof drainage system on crude oil tanks
- all control valves on refinery equipped with live-load packing
- safety relief valves led to flare
- upgrade of piston rod seals on piston compressors
- all flanges handling light hydrocarbons were equipped with expanding graphite seals.

Fritsch, 2003, details further results from measurements of emissions and the measures taken to reduce emissions from refineries in Sweden.

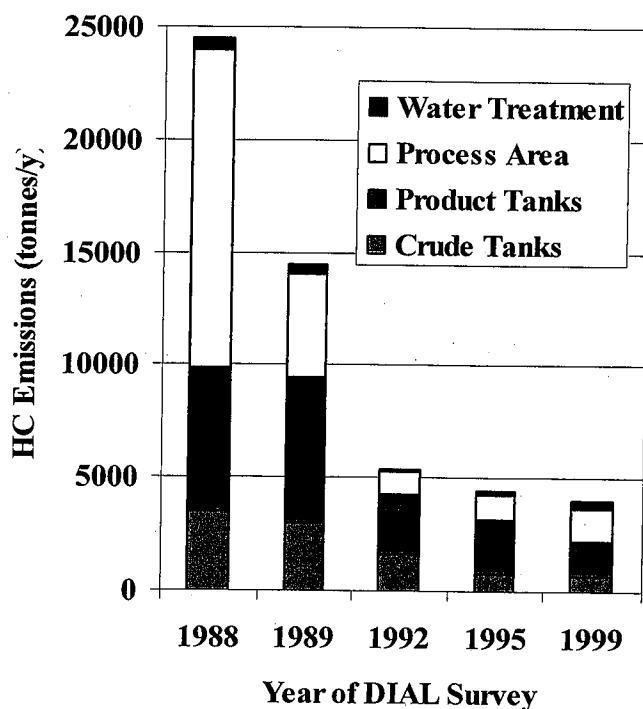


Figure 7: Reducing Emissions at the Preem Refinery in Sweden (data from Frisch, 2003)

Figure 9 is an example of leak detection from a distance. In this instance the hydrocarbon emission is seen as a white plume from a pressure relief valve vent at the top of a tower. The camera was operated from ground level, about 40 meters from the leak. This demonstrated the leak camera's utility for accessing locations that would be difficult or dangerous to access with conventional leak detection equipment.

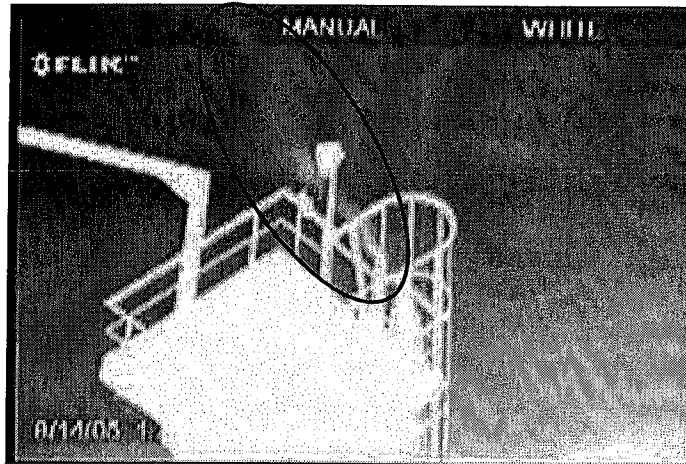


Figure 9: Leak at Top of Tower Detected from Ground Level

Figure 10 is an example of hydrocarbons emitted from a compressor packing vent. These vents collect gases that leak through high pressure seals, typically around rotating shafts, and direct the gases to a safe location for venting.

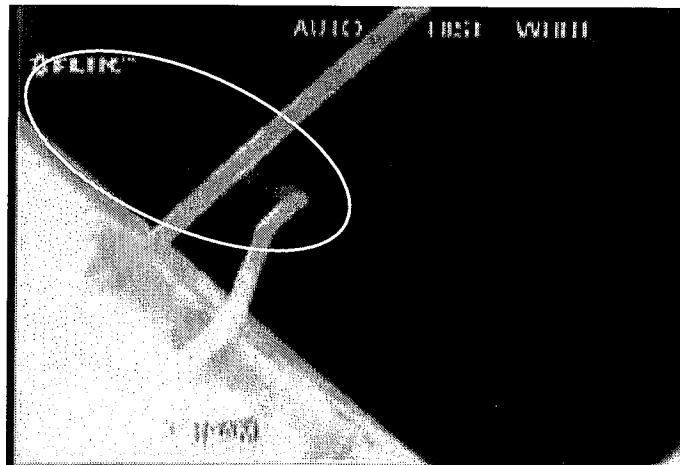


Figure 10: Example of Leak from Compressor Packing Vent

The gas leak imaging camera was an effective method for locating hydrocarbon leaks for both in-door and out-door equipment. The camera was easy to use and required only minimal training for effective use. The camera performance for outdoor leak detection was improved on clear, sunny days. As different lenses were available for use with the camera, significant leaks could be determined at distances at least 100 meters from the camera. The current design of the camera could not be used to discriminate different hydrocarbon species or to determine the size of the leak.

Gas leak imaging cameras will likely provide a more economical, safe and effective method to locate hydrocarbon leaks than current techniques, such as total hydrocarbon analyzers. Other applications for the cameras that could improve operations at the refinery include:

- leak survey of specific equipment after repair or overhaul,
- locating leaks in combination with EPA Method 21 methods to estimate leak size,
- identifying leaks in equipment exempted from EPA Method 21, such as valves smaller than $\frac{3}{4}$ inch,
- remote leak survey of an area with high hydrocarbons alarm to quickly and safely locate the hydrocarbon source.

Since this project was completed, the refinery has purchased a gas leak imaging camera for routine use at the site.

7. Conclusions

The following conclusions are based on the results of the demonstration at an Alberta refinery of Differential Absorption Lidar (DIAL) for quantifying fugitive emissions and a gas leak imaging camera for locating leaks:

1. The total fugitive emissions from the refinery as measured with DIAL were 1,240 kg/h of C₂₊ hydrocarbons (alkane hydrocarbons ethane and larger), 300 kg/h of methane and 5.0 kg/h of benzene. When expressed as a percentage of the refinery throughput during the test period, the emissions of C₂₊ hydrocarbons represented 0.166% of throughput by weight and the CH₄ emissions represented 0.04% of throughput.
2. Emissions from storage tanks accounted for over 50% of the total site fugitive emissions of both C₂₊ hydrocarbons and benzene. The final product tanks area was a large contributor to the total site emissions of C₂₊ hydrocarbons. These emissions were primarily from floating roof tanks and would be dependent on wind speed.
3. The coker area was responsible for over 40% of the site emissions of CH₄ and was also a significant source of both C₂₊ hydrocarbons and benzene emissions. The cooling towers accounted for about 13% of the site's emissions of C₂₊ hydrocarbons.
4. The gas leak imaging camera was easy to use and an effective method for locating leaks of hydrocarbon gases to the atmosphere. The camera located both indoor and outdoor leaks and also remotely located leaks in high or inaccessible equipment.
5. The measured fugitive emissions fell in the middle of the range of emissions measured by Spectrasyne for refineries in Europe when expressed as a percentage of throughput.
6. The DIAL measurements of fugitive hydrocarbon emission, when compared to estimates based on emission factors, gave a different picture of both the total loss of hydrocarbon product due to fugitive emissions and the relative proportion of fugitive losses from various areas of the refinery.
7. Actual measurements of fugitive emissions better represent the value of product loss due to equipment leaks, tank vents and other fugitive losses. Based on the DIAL measurements, fugitive emissions losses of methane and C₂₊ hydrocarbons from the refinery surveyed represent lost revenue in the order of \$3.2 million per year (assuming a product value of \$40/bbl).
8. Based on the DIAL measurement of methane emissions, fugitive methane accounts for less than 5% of the refinery's total greenhouse gas emissions.

8. Recommendations

The following is recommended based on the results of this project:

1. Based on the DIAL measurements, efforts to reduce fugitive emissions at this refinery should focus on the coker area, the cooling towers, the crude feed tanks and the final product tanks. To address emissions from the tanks and cooling towers, the refinery plans to review their tank seal integrity program and to enhance their heat exchanger monitoring and repair.
2. The gas leak imaging camera is a recommended method to efficiently locate hydrocarbon gas leaks in a refinery operation.
3. Direct measurements of emissions are recommended 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. The frequency of direct measurements should allow sufficient time for leak repair and emissions reduction procedures based on the refineries operation and turn-around schedules.
4. 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. This would lead to improved tank emissions estimation procedures and a better understanding of methods to reduce tank emissions.
5. Based on the significant level of hydrocarbon emissions from this refinery's cooling towers, the development of methods and/or instrumentation to improve the tracking and location of heat exchanger leaks is recommended.
6. Measurement of fugitive emissions over a longer period of time and range of refinery conditions is recommended to better understand the variability of fugitive emissions, the difference between direct measurements and estimated emissions and methods to calculate annual emissions based on short term measurements.
7. Further measurements are recommended to better understand fugitive emissions of hydrocarbons from sources that are currently not accounted for in the CCME VOC Code of Practice, such as coker emissions and emissions from cooling towers.
8. A program of measurements, data analysis and atmospheric modeling is recommended to better understand the relationship between hydrocarbon emissions from this refinery and other industries in the area and the measured hydrocarbon concentrations from the surrounding ambient air monitoring network. The results of this study should also be analyzed in conjunction with the results of the PrAIRie 2005 study performed by Environment Canada.
9. Formalized protocols should be developed for performing DIAL surveys, calculating fugitive emissions from DIAL survey results and establishing the uncertainty in the results. These protocols should include recommended length and extent of survey based on the site size and complexity and a set of procedures for quality assurance and control.

Glossary

API	American Petroleum Institute
CAC	Criteria air contaminants
C ₂₊ Hydrocarbons	straight chain alkane hydrocarbons ethane and larger
CCME	Canadian Council of Ministers of the Environment
CH ₄	methane
CPPI	Canadian Petroleum Products Institute
DIAL	Differential Absorption Lidar (Light Detection and Ranging)
NPRI	National Pollutant Release Inventory (www.ec.gc.ca/pdb/npri/)
US EPA	United States Environmental Protection Agency
VOCs	Volatile Organic Compounds as defined in the <i>Proposed Order Adding Toxic Substances to Schedule 1 to the Canadian Environmental Protection Act, 1999</i> , published in the <i>Canada Gazette Part I</i> , Vol. 136, No. 30 (Ottawa, July 27, 2002). (www.ec.gc.ca/CEPARegistry/subs_list/Toxicupdate.cfm)

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Appendix A DIAL Background

Spectrasyne Ltd., UK

History

Light/laser based technology systems for the remote monitoring of gaseous species in the atmosphere has been under development for the past decade and a half. The flagship of these developments is a Differential Absorption LIDAR or DIAL system. DIAL is a development of LIDAR, a light based range-finding system similar to RADAR. If a laser is used as the LIDAR light source, the collimated, coherent light emitted can be used to define the range of specific small objects with great precision. A tuneable laser source can give LIDAR an additional spectroscopic capability as the source laser can alternately be tuned onto then off an absorption feature in the known 'spectral fingerprint' of a specific gas. The concentration of gas in the path length between the laser and the detector is determined by comparing the energies in the two return signals.

Until 1986 the DIAL development programme had concentrated on the UV and visible spectral regions where gases such as sulphur dioxide, nitric oxide, nitrogen dioxide and ozone have specific absorption features. Many other gases including the majority of the hydrocarbons have strong absorption features in the infrared region. The significance and potential of a system that could operate in the infrared was realised by all concerned and a further research programme was established to enable the technology development for DIAL hydrocarbon species monitoring. This programme involved a number of British companies, a laser manufacturer and the creation of a unique infrared source assembly, which with the customised laser system, provided tuneable infrared laser radiation. During the prototype testing phase, and subsequently, a more commercially orientated DIAL system was designed and constructed. This system was built on the experience of the prototype and incorporated many recent technological improvements in optics, laser equipment, fast data transfer and communications hardware. Two parallel laser systems were installed to enable simultaneous measurement in the UV, visible, and IR spectral regions. The acquisition software was improved, and fast data handling programs were designed to speed up the processing of the vast amount of data generated by the system. This data processing development is continuing to provide, ultimately, a real-time read-out capability.

The construction of the new, commercial DIAL was completed, installed in the 12 metre mobile Environmental Surveying System (ESS, Figure right), in September 1990, 6 months ahead of the original schedule. The ESS (which was the basis of a management buyout by Spectrasyne from BP Research in 1992) also houses a unique in-stack, emissions monitoring system, which



along with its current Spectrasyne operating team has been engaged by a number of national authorities to make emission measurements from various refinery sources. Throughout the 1980s and early 90s, at various critical development stages, validation and correlation work was carried out with the DIAL. This work ranged from making measurements through gas cells, which had been filled with gravimetric standard gas mixtures to correlation exercises between DIAL concentration measurements and stack gas analyses collected using conventional gas analysers and gas chromatography equipment. Concentration correlations at ambient/ environmental levels against accredited thermal sorption tube data were also undertaken. In all cases the DIAL measured concentrations were within 10-15% of the standard or the data generated by the more conventional technologies. However, since 1988, DIAL concentration data has been used with wind speed and direction to produce mass emission fluxes (kg/h) and some further validation work on the production of mass emission fluxes was considered necessary. A number of mass emission correlation exercises between the SPECTRASYN DIAL and other measurement techniques have been carried out during recent years. The other methods include SF₆, calibrated releases of methane from a point source and marine tanker vent measurements. In all of these exercises the maximum divergence from the DIAL measurements recorded was 15%.

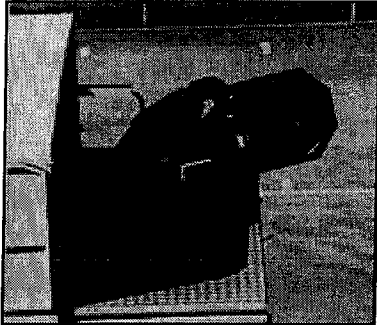
One of the most significant correlation exercises was carried out with personnel from the European oil industries association, CONCAWE. The correlation exercise was carried out during one complete loading schedule of a river barge loading motor spirit as this represented a discrete emission source. The CONCAWE team calculated the mass hydrocarbon emission levels throughout the loading from the tank vent measurements and knowledge of the loading rate and thus vapours displacement rate. The Spectrasyne DIAL measurements were made some distance downwind of the barge. The sequential measurement data derived from the two methods were integrated over the loading period to provide total mass emission figures for each measurement technique. The resultant correlation was within 12%.

DIAL Equipment

The Spectrasyne DIAL is based on two high energy (1.4J), 10Hz pulsed Nd:YAG pumped dye lasers. Tuneable ultraviolet and visible radiation is generated in one of the laser sets by selective use of frequency doubling and tripling crystals. The second laser set, which has an injection seeded Nd:YAG, is used to generate tuneable infrared radiation by means of the unique infrared source assembly. The DIAL is single ended and its output beam is directed by means of a mirror steering system which rotates in two planes. The backscattered light, which returns along the same path, is collected in a cassegrain-type receiving telescope and delivered to the appropriate detector through a multi-dichroic, beam splitting, collimating and focusing system. In order to collect, store, handle and process the DIAL signals a sophisticated, high speed data communication network has been developed in parallel with a unique PC based software package.

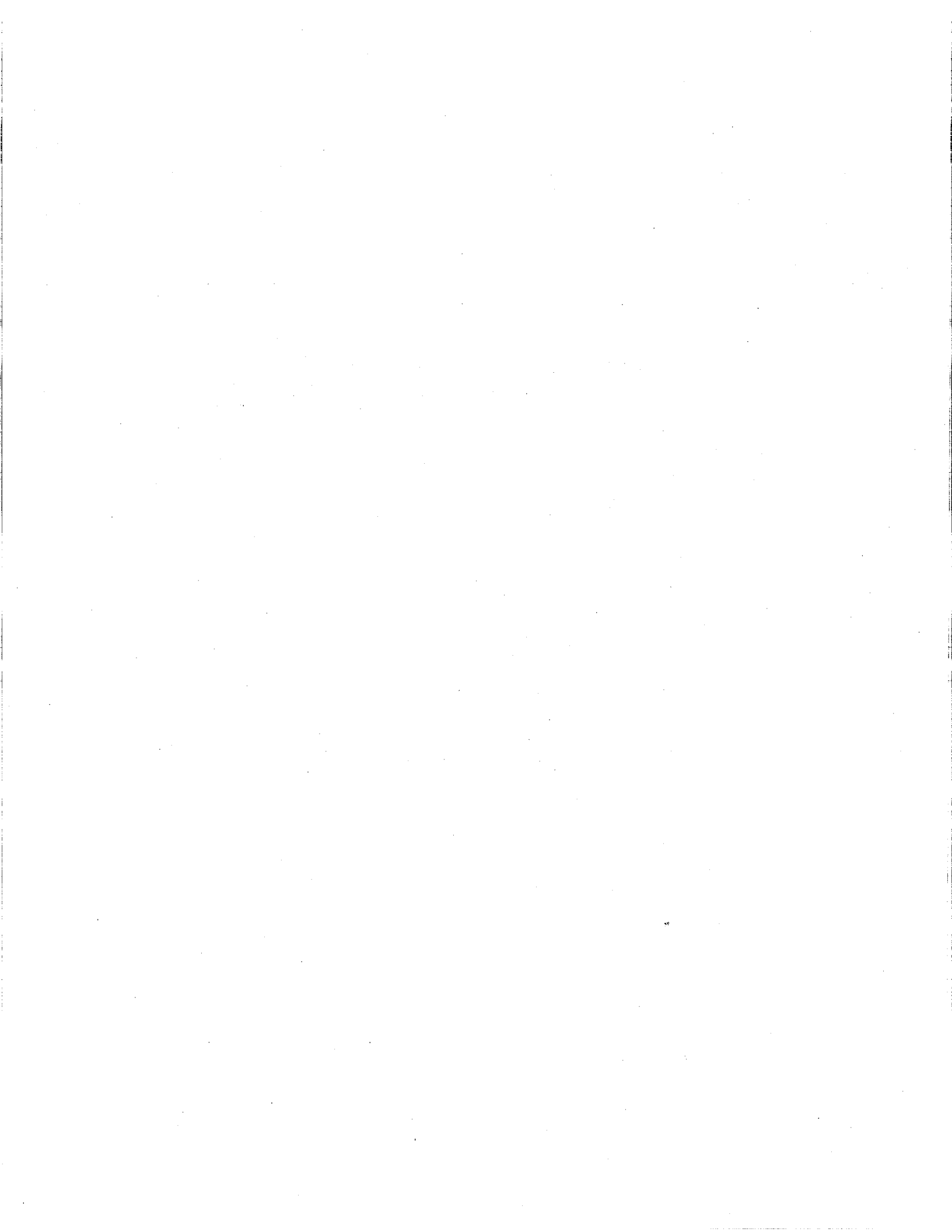
PCs are also used to perform a number of ancillary control functions and to store essential spectroscopic and other databases. The vehicle is also equipped with an extendible meteorological mast and a number of portable telemetric stations, which

are used along the DIAL scan lines to measure wind speed and direction, temperature and humidity. These data are displayed in real time and digitally logged for subsequent use with DIAL concentration data to produce mass emission fluxes. A sophisticated 3D computational fluid dynamics (CFD) model can also be



connected to the processing system and can be used to provide interpolation between measured wind speed data points for flux calculation and to assist in the definition of suitable measurement positions where the wind fields are complex.

Telephoto and wide-angle TV cameras are used on the steering system to facilitate beam pointing, the wide angle image is recorded on a time-lapse video recorder to be used if necessary to identify problems visually during subsequent data analysis.



Appendix B Canister Analysis Method

The canister sample system preparation and gas analysis was performed by the Environmental Monitoring Unit of the Alberta Research Council, Vegreville.

The sampling method used for the detailed identification of hydrocarbon and sulphur compounds consisted of drawing ambient air samples into evacuated silco steel lined canisters as specified in the EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Method TO-15). The canisters were equipped with fixed orifices to collect the air samples over a one-hour period. Initial results from the DIAL measurements were used to determine optimal positioning of the samplers. Sufficient air samples were collected to allow subsequent analyses for the light hydrocarbon gases, for volatile organic compounds and for sulphur containing compounds. The following is a description of these analyses.

C1 to C4 Section of the Analysis

Direct injection into a GC/FID system is used to analyse gas samples. Typically methane through butane components are reported from this system. No sample concentration is performed in this scan. The typical minimum detection limit for this group of compounds is 50 ppbv.

C5 through C12 are typically reported with the VOC section of the analysis as described below.

Reduced Sulphur Compound Section of the Analysis

Reduced sulphur compounds are analysed by GC/SCD (sulphur chemiluminescence detector). H₂S, COS, CS₂, sulphides, mercaptans, and thiophenes are routinely analysed. The calibration mixtures contain approximately 20 components and the minimum detection limits for these compounds is ~3 to 5 ppbv.

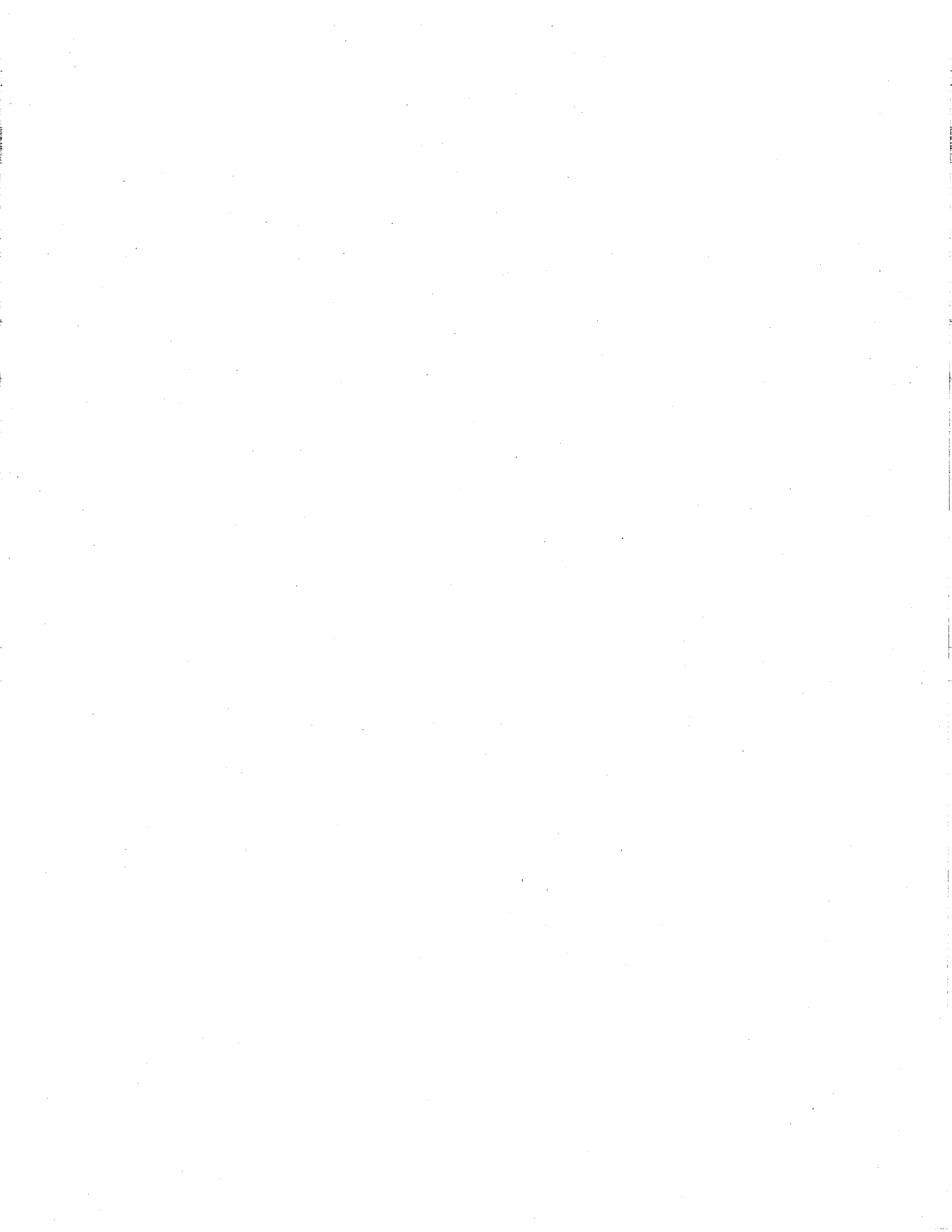
VOC Section of the Analysis

The VOC scan is equivalent to EPA method TO-15. A Tekmar Autocan system is used to concentrate the sample on a chemical trap. The trap is then back flushed and cryo focused prior to GC/MS full scan analysis.

Calibration of this analytical system is achieved with the commercially available ozone precursor and TO-14 calibration mixtures. These compounds (approximately 80) are treated as calibrated target compounds.

The minimum detection limit for these components is 0.5 ppbv or less.

Any other non-target components eluting in the chromatographic run are identified by their mass spectral data via a library search. The match quality data is reported. These tentatively identified compounds (tic) are quantified against an appropriate internal standard assuming a 1:1 response factor.



APPENDIX C: CANISTER GAS SAMPLE ANALYSIS

			Product Tanks	Old Process South	Old Process North
NAME	Formula	MW	(ug/m ³)		
C1 TO C4 COMPOUNDS					
Methane	CH ₄	16	1367	1858	4854
Ethane	C ₂ H ₆	30	0.00	0.00	452.6
Propane	C ₃ H ₈	44	0.00	97.14	0.00
REDUCED SULPHUR COMPOUNDS					
Carbonyl sulphide	COS	60	2.99	1.67	4.91
Carbon disulphide	CS ₂	76	2.73	0.50	0.00
Dimethyl disulphide	C ₂ H ₆ S ₂	94	0.00	1.88	0.00
VOC ANALYSIS					
Formaldehyde	CH ₂ O	30	56.42	8.59	72.24
Isobutane	C ₄ H ₁₀	58	9.15	8.42	3.37
1-Butene	C ₄ H ₈	56	1.64	1.97	0.27
Acetaldehyde	C ₂ H ₄ O	44	39.57	11.87	0.00
Butane	C ₄ H ₁₀	58	83.47	20.53	4.70
Methanol	CH ₄ O	32	0.00	0.00	0.00
trans-2-Butene	C ₄ H ₈	56	3.91	1.48	0.00
cis-2-Butene	C ₄ H ₈	56	4.46	1.26	0.13
3-Methyl-1-butene	C ₅ H ₁₀	70	0.98	0.00	0.00
Isopentane	C ₅ H ₁₂	72	70.94	11.27	6.00
1-Pentene	C ₅ H ₁₀	70	4.15	0.25	0.00
Acetone	C ₃ H ₆ O	58	9.25	3.68	1.71
Pentane	C ₅ H ₁₂	72	18.69	16.60	7.74
Isoprene	C ₅ H ₈	68	1.25	0.00	0.11
trans-2-Pentene	C ₅ H ₁₀	70	9.22	0.25	0.10
cis-2-Pentene	C ₅ H ₁₀	70	5.07	0.17	0.00
2-Methyl-2-butene	C ₅ H ₁₀	70	13.71	0.30	0.13
2,2-Dimethylbutane	C ₆ H ₁₄	86	1.40	0.07	0.32
Cyclopentene	C ₅ H ₈	68	1.26	0.00	0.00
4-Methyl-1-pentene	C ₆ H ₁₂	84	0.68	0.00	0.00
2,3-Dimethylbutane	C ₆ H ₁₄	86	4.18	0.30	0.58
Cyclopentane	C ₅ H ₁₀	70	2.00	0.64	0.62
2-Methylpentane	C ₆ H ₁₄	86	20.15	3.80	3.80
3-Methylpentane	C ₆ H ₁₄	86	12.06	2.08	2.33
2-Methyl-1-pentene	C ₆ H ₁₂	84	1.30	0.00	0.00
Hexane	C ₆ H ₁₄	86	3.55	3.97	3.97
Methyl ethyl ketone	C ₄ H ₈ O	72	0.00	0.00	0.00
cis-2-Hexene	C ₆ H ₁₂	84	1.14	0.10	0.00
trans-2-Hexene	C ₆ H ₁₂	84	0.68	0.00	0.00
2,4-Dimethylpentane	C ₇ H ₁₆	100	0.00	0.00	0.57
Methylcyclopentane	C ₆ H ₁₂	84	5.53	1.36	1.69

VOC ANALYSIS (continued)			Product Tanks	Old Process South	Old Process North
NAME	Formula	MW	(ug/m ³)		
Cyclohexane	C6H12	84	1.48	0.69	0.98
Benzene	C6H6	78	4.72	1.18	3.57
2-Methylhexane	C7H16	100	2.35	0.70	0.85
2,3-Dimethylpentane	C7H16	100	4.58	0.73	0.00
3-Methylhexane	C7H16	100	3.45	1.27	1.17
2,2,4-Trimethylpentane	C8H18	114	3.84	0.73	0.67
Heptane	C7H16	100	2.26	1.57	1.80
Methylcyclohexane	C7H14	98	2.28	1.67	1.48
2,3,4-Trimethylpentane	C8H18	114	0.62	0.14	0.28
2-Methylheptane	C8H18	114	0.00	0.67	0.88
Toluene	C7H8	92	5.98	2.50	14.29
3-Methylheptane	C8H18	114	0.00	0.44	0.52
Octane	C8H18	114	0.73	1.46	1.40
Ethyl benzene	C8H10	106	0.62	0.81	1.23
m,p-Xylene	C8H10	106	2.04	2.99	9.23
Styrene	C8H8	104	0.00	0.23	0.37
Nonane	C9H20	128	0.33	0.72	0.76
o-Xylene	C8H10	106	0.70	0.98	3.54
Isopropylbenzene	C9H12	120	0.00	0.14	0.20
n-Propylbenzene	C9H12	120	0.00	0.19	0.45
1,3,5-Trimethylbenzene	C9H12	120	0.00	0.26	0.85
Decane	C10H22	142	0.56	0.39	0.15
1,2,4-Trimethylbenzene	C9H12	120	1.84	0.70	2.31
Undecane	C11H24	156	0.20	0.21	0.11
Dodecane	C12H26	170	0.00	0.13	0.28
Naphthalene	C10H8	128	0.00	0.00	0.21
Naphthalene, 2-methyl	C11H10	142	0.00	0.00	1.06
2-Pentene, 3-methyl-, (E)-	C6H12	84	1.55	0.00	0.00
Cyclopentane, 1,3-dimethyl-	C7H14	98	2.57	0.00	0.00
Isopropylcyclobutane	C7H14	98	1.74	0.00	0.00
Bicyclo[2.2.1]heptane, 7,7-dimethyl-2-me	C10H16	136	2.54	0.00	0.00
Camphene	C10H16	136	13.84	0.00	0.00
1-Heptene	C7H14	98	0.00	0.75	0.00
Cyclohexane, 1,4-dimethyl-	C8H16	112	0.00	0.97	0.00
Heptane, 1,1'-oxybis-	C14H30	214	0.00	1.02	0.00
Benzene, (1-methylethyl)-	C9H12	120	0.00	0.60	0.00
Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethy	C10H16	136	0.00	0.00	0.72
Bicyclo[2.2.1]heptane, 7,7-dimethyl-2-me	C10H16	136	0.00	0.00	1.25
Benzene, 1-ethyl-3-methyl-	C9H12	120	0.00	0.00	0.77
pentadecane	C15H32	212	0.00	0.00	1.20
Total			1819	2083	5474

Sorption Tubes			
	Coker ug/m ³	Tanks ug/m ³	Old Process South ug/m ³
Methane			
Ethylene	0.5	0.3	4.4
Ethane	3.1	0.9	15.2
Propane	13.1	12.4	32.0
Propene	1.6	1.9	7.6
i-Butane	16.7	31.2	35.6
n-Butane	0.9	41.2	19.0
1-Butene		2.2	2.1
cis-2-Butene		26.1	1.8
2-Butene / n-Butane			
i-Pentane	4.9	101.6	18.5
2-Methyl-butene-1		7.0	
n-Pentane		13.0	14.1
3-Methylpentane			
1-Pentene		4.7	
cis-2-Pentene		7.2	
Cyclopentene			
Other Cyclics			
2,3-Dimethylbutane		8.4	
2-Methylpentane		21.6	
4-Methyl-2-pentene			28.0
3-Methylpentane	9.1	24.2	16.5
n-Hexane		3.3	9.1
Methylcyclopentane		6.6	4.0
Benzene	1.4	3.7	3.7
Cyclohexane			169.4
n-Heptane			
2-Methylhexane			3.2
2,3-Dimethylpentane		3.0	3.1
3-Methylhexane			4.5
2,2,4-Trimethylpentane	1.5	5.1	2.9
n-Heptane	2.7	4.6	8.1
Methylcyclohexane	2.2		9.2
Toluene	2.0	6.5	39.6
2-Methylheptane			7.3
Cycloheptane			2.6
n-Octane	1.9		12.8
Ethylbenzene		10.3	13.1
m/p-Xylene		3.7	41.8
Styrene			5.7
o-Xylene		8.9	15.8
n-Nonane		7.7	16.4
i-Propylbenzene			2.5
Cyclooctane			1.9
n-Propylbenzene			17.2
Ethyltoluene	1.4	2.9	24.9
1,3,5-Trimethylbenzene			2.6
1,2,4-Trimethylbenzene			9.5
n-Decane			15.3
1,2,3-Trimethylbenzene			4.1
1,2,3,5-Tetramethylbenzene			2.9
n-Undecane			9.4
n-Dodecane			12.3
Naphthalene		9.5	
n-Tridecane	1.8	4.6	5.8
Total Hydrocarbons	119	460	1091