

Remote Sensing Feasibility Study of Refinery Fenceline Emissions

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ABSTRACT

This report reviews the state of the art of optical remote sensing (ORS) technology and examines the potential use of ORS systems combined with ancillary measurements such as meteorological and tracer gas release data to determine fugitive emission rates. With the need to track the effectiveness of controls of fugitive emission sources and to conduct downwind health risk assessments for refineries, ORS technology appears to be an attractive tool for characterizing an entire facility's emissions. The American Petroleum Institute (API) sponsored this technical review effort as part of its planning for a refinery emissions field study in which ORS methods might be used. The report concludes that under some special conditions, ORS systems can document the fugitive emissions and that no prior studies preclude the need for API to carry out an evaluation of the general concept. The report highlights some issues to consider in planning such a study and clarifies the attendant tradeoffs for issues such as: selection of appropriate ORS systems, consideration of detection limits and beam placement, choice of dispersion models, use of tracer gas releases, time scale and timing of field studies and the requisite meteorological measurements. Finally, the report emphasizes that the uses of ORS instrumentation for the determination of aromatic emissions is perhaps the most difficult and challenging of the possible use of the ORS at refineries. When compared to the current point sampling methods, however, the current ORS systems have the potential for integrating the multiple small sources that comprise the overall fugitive emission plume.

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EXECUTIVE SUMMARY

Under Title III of the Clean Air Act amendments of 1990, the U.S. Environmental Protection Agency (EPA) is required to promulgate Maximum Achievable Control Technology (MACT) regulations for emissions of hazardous air pollutants (air toxics) from various industrial sources including refineries. Once the control technology is in place, EPA must develop information on the residual risks associated with exposure to low-level air toxics downwind of major industrial sources. It is anticipated that the EPA will require industry to use actual emission measurements or emission estimates derived from emission factors and dispersion modeling to estimate the risks. Recent studies, however, have shown that EPA dispersion models may significantly overestimate ambient concentrations of low-level air toxics for areas less than one kilometer from the source (near field). In addition, at the time this study was initiated, EPA and several state agencies were considering requiring industry to use open-path optical remote sensing (ORS) technology to establish concentrations of low level air toxics downwind of industrial sources.

For these reasons, the American Petroleum Institute (API) considered conducting a comprehensive field study at a refinery to assess whether upwind and downwind ORS measurements, combined with ancillary measurements such as meteorological and tracer gas release data, could be used to calculate emission rates of air toxics from a refinery. A secondary objective was to develop better information on the near-field dispersion of air toxic emissions from refineries for the purposes of improving existing dispersion models.

Before embarking on a costly field study, API sponsored this study to review the state of the art of optical remote sensing technology and to provide answers to several questions which arose concerning the feasibility of achieving the field study objectives.

STUDY APPROACH

The feasibility study was conducted by performing two major tasks. The first task was to conduct a comprehensive review of studies related to the use of optical remote sensing for the

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measurement of emissions of refinery-related compounds both in refinery settings and non-refinery settings. In addition, conventional sampling studies for emission rate estimates were reviewed. In the second task, the reviewed information was synthesized and key technical issues such as detection limits, light beam placement, dispersion modeling, tracer gas releases, and time interval for measurements were summarized. Based on the review, the questions posed by API were answered and technical considerations for design of a refinery emissions study using ORS were developed.

SUMMARY OF FINDINGS

The findings of this study can best be summarized in the context of the answers to the feasibility questions posed by API and the design considerations that were developed.

Is the amount of information collected from other, recent studies of a similar nature sufficient to accomplish the objectives of the proposed field study thereby negating the necessity for the field study?

None of the reported studies addressed detection limits and transport parameters in sufficient detail to provide technically defensible emission rate data, especially for the benzene, toluene, ethylbenzene, xylenes (BTEX) compounds and, specifically, benzene. There are indications that progress has been made in the past four to five years in obtaining emission rates for these compounds but more work is still needed. Hence, there is not sufficient data at present to rule out the need for a field study.

Most of the experience in using ORS for fugitive emissions estimates at refineries has been gained from two studies at Swedish refineries in the late 1980s. The reports (mainly internal and not peer-reviewed) from these studies were reviewed for the apparent successes and problems with this application. No specific studies have been completed with a focus on benzene. The Swedish studies involved total non-methane hydrocarbon estimates as well as toluene and p-xylene. Several suggestions regarding use of vertically-scanning laser-based

systems and the time scale for measurements emerged from these programs. There seem to be no hard numbers evaluating the emissions determinations from these studies.

The refinery experience in the United States has been predominantly a series of measurement demonstrations with no published attempts to estimate fugitive emissions. While many successful measurement efforts are reported using both infrared and ultraviolet systems, none have been carried out with sufficient meteorological support data and measurement strategy to allow computation of emission rates.

Several ORS studies have looked at downward concentrations of benzene, toluene, ethylbenzene, and the xylenes emitted from refinery process areas such as land farms and impoundments, but not from entire facilities. For the simpler geometry of these area sources having surface releases, emission rate estimates have been made and compared to tracer releases and modeling predictions with some success.

Will it be possible to separate a refinery's contribution from the background contribution for low-level concentrations measured along the fenceline and further downwind from a refinery?

Adequate detection limits are important to be able to separate a refinery's contribution from background contributions of air toxics downwind of a refinery. The ultraviolet (UV) ORS systems have lower detection limits for the aromatic compounds of most concern to the petroleum industry; however, the one commercially available system had not been tested reliably in fenceline studies as of the end of 1992. The versatility of the open-path Fourier Transform Infrared (OP-FTIR) ORS systems in being able to detect a large number of organic and inorganic vapors is offset by their relatively poor sensitivity for aromatic compounds caused by water vapor interference in the regions of strong absorption. A number of factors affect the actual detection limits attained at a particular site, at a particular time. These include the presence of interfering compounds, the path length, meteorological conditions, the time interval of sampling, and the detector in the particular instrument being used. These factors need to be considered in the design of a field study.

For refineries in isolated locations, it should be possible to separate the contributions due to the refinery from the background provided that a UV-based ORS system is used for the BTEX compounds. Of course, if the refinery emits low concentrations of air toxics even those isolated downwind levels may be below currently achievable minimum detection limits (MDLs). No information on the actual contribution from the refinery would be gained if both the upwind and downwind concentrations are below the MDLs.

For non-BTEX air toxics unique to refineries, it should also be possible to separate the contribution due to the refinery from the background by either a UV or FTIR system even in a more complex industrial setting, again with certain MDL caveats.

For BTEX compounds at refineries in an urban or industrial setting, it will probably not be possible to separate the contribution due to the refinery from the background with the currently available systems due in part to the complex source pattern and present MDLs for these compounds. This qualification recognizes that the presence of BTEX, especially benzene, in the ambient air comes from the cars and trucks in parking lots as well as the nearby highways (Stevens and Vossler, 1991) and other nearby industrial sources and, thus, must be compensated for. The concentrations from these non-refinery sources may be significantly higher than those from the refinery itself. For such complex settings, monitoring close to the various process areas at the refinery may make it possible to determine emissions rates for each process area since the ambient concentrations due to the process area will be significantly higher near the process area (source) than at the fenceline, thus, reducing the importance of the upwind concentrations.

Is the state of the technology of optical remote sensing (and required ancillary measurements) sufficiently refined to provide technically defensible data for the calculation of air toxics emission rates due to a refinery complex located in either an isolated setting or in a complex industrial area?

To address the issue of the technical defensibility of the calculated refinery specific emission rates, one must address not only the defensibility of the path-integrated concentration

measurements but also the defensibility of the contribution due to the refinery determined from these measurements and the defensibility of the models and/or tracer data which combine the meteorological data with the concentration data to produce emission rates.

With respect to ORS path-integrated or path-average concentrations, ORS instrumentation and field techniques have been improving rapidly in recent years and have compared well with conventional sampling methods in several field intercomparison studies. In addition two draft guidance documents have been prepared by the EPA to provide guidance on quality assurance and quality control measures to ensure that path-average concentrations determined with the FTIR are technically defensible. Thus, the ORS systems are sufficiently refined to provide technically defensible **path-integrated or path-average concentrations**. These technically defensible data may consist of statements that the concentrations are below the MDL.

To determine the contribution due to the refinery, the technical defensibility depends on having sufficiently low MDLs and, thus, sufficient sensitivity to determine the difference between the upwind and downwind concentrations as discussed in the answer to the second question. While the individual upwind and downwind path-integrated concentrations may be technically defensible, if these path-integrated concentrations are similar to each other or both are below the MDL, it may not be possible to determine the refinery's contribution to the downwind concentration field outside the overall uncertainties of the measurements. When more sensitive instruments are available to provide lower detection limits and reduced uncertainties in the path-averaged concentrations, the separation of a refinery's contribution will be possible for refineries in complex settings.

To determine the refinery specific emission rates, the technical defensibility depends on the defensibility of the modeling, meteorological data and possible tracer data in addition to the path-average concentration and refinery specific contribution discussed above. In order to determine the emission rate, the upwind and downwind path-average concentrations or MDLs must be used to determine the refinery's contribution which then must be combined with either tracer gas release data or a dispersion model. Although there have been wind tunnel

studies with models of refineries with different surface roughness, very little field verification data similar to the ORS intercomparison studies exist to technically defend the modeling of turbulent transport conditions in a physically complex setting or the use of tracer gas releases for the determination of emission rates from such complex settings. Thus, it would be very useful to combine a dispersion model and tracer gas release evaluation program with an ORS field study/evaluation.

In summary, the state of the technology of ORS systems is sufficiently refined to provide technically defensible path-average concentrations which could be used for the calculation of emission rates. There is somewhat less certainty about determining the contribution due to the refinery at the fence line or about the technical defensibility of the emission rates calculated from these path-average concentrations using dispersion models and/or tracer gas releases with meteorological data.

DESIGN CONSIDERATIONS

With refinements and incorporation of a broader understanding of the issues as discussed in this report, a field study can be designed that meets both of the objectives stated by API. The fact that a refinery has elevated releases and buoyant plumes in addition to near-surface releases requires consideration of what ORS observation path(s) are adequate and in what settings. Thus, the vertical and downwind placement of the ORS beams need to be considered along with the air dispersion modeling implications for interpreting the data. The physical and meteorological complexity of a refinery setting must be considered, not only in gathering an adequate data set during a field study, but also in using the appropriate models for interpreting the ORS and supporting measurements.

Section 1

INTRODUCTION

Under Title III of the Clean Air Act amendments of 1990, the U.S. Environmental Protection Agency (EPA) is required to promulgate Maximum Achievable Control Technology (MACT) regulations for emissions of hazardous air pollutants (air toxics) from various industrial sources including refineries. Once the control technology is in place, EPA must develop information on the residual risks associated with exposure to low-level air toxics downwind of major industrial sources. It is anticipated that the EPA will require industry to use actual emission measurements or emission estimates derived from emission factors and dispersion modeling to estimate the risks. Recent studies, however, have shown that EPA dispersion models may significantly overestimate ambient concentrations of low-level air toxics for areas less than one kilometer from the source (near field). In addition, at the time this study was initiated, EPA and several state agencies were considering requiring industry to use open-path optical remote sensing (ORS) technology to establish concentrations of low level air toxics downwind of industrial sources.

For these reasons, the American Petroleum Institute (API) considered conducting a comprehensive field study at a refinery to assess whether upwind and downwind ORS measurements, combined with ancillary measurements such as meteorological and tracer gas release data, could be used to calculate emission rates of air toxics from a refinery. A secondary objective was to develop better information on the near-field dispersion of air toxic emissions from refineries for the purposes of improving existing dispersion models.

Before embarking on a costly field study, API sponsored this study to provide answers to the following questions which arose concerning the feasibility of achieving the field study objectives:

1. Is the amount of information collected from other, recent studies of a similar nature sufficient to accomplish the objectives of the proposed field study thereby negating the necessity for the field study?
2. Will it be possible to separate a refinery's contribution from the background contribution for low-level concentrations measured along the fenceline and further downwind from a refinery?
3. Is the state of the technology of optical remote sensing (and required ancillary measurements) sufficiently refined to provide technically defensible data for the calculation of air toxics emission rates from a refinery complex located in either an isolated setting or in a complex industrial area?

API proposed using two versions of ORS technology, infrared (IR) and ultraviolet (UV) absorption, to measure the path-integrated or path-average concentrations of aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes--also designated as BTEX) along the fenceline of a petroleum refinery. For comparative purposes, point sampling of aromatic hydrocarbons would also be conducted along the fenceline using wind-directional whole air canisters. Additionally, a non-toxic, non-reactive tracer gas (e.g., sulfur hexafluoride) would be released from a large source of emissions within the refinery and traced to and beyond the downwind fenceline using a tracer monitoring system. On-site meteorological data would be collected to calculate more accurately the emission rates from the refinery.

At this point it should be noted that there is an important distinction between measurements of concentration of air toxics along a fenceline and determinations of emission rates for the same air toxics from a facility. Concentrations of air toxics can be measured by a number of presently available point samplers/monitors at discrete points and by ORS systems along the path of the beam. Determination of emission rates requires knowledge of concentrations upwind of the facility and at the fenceline as well as dispersion information gained from ancillary data such as simultaneous meteorological measurements, simultaneous tracer gas release data and/or dispersion modeling. The problems and uncertainties related to determining emission rates using such ancillary data are similar whether concentrations are

measured by point samplers/monitors or by open-path ORS systems. Hence, emission rate determinations are more complicated than concentration measurements.

The primary focus of the proposed field study was directed at BTEX compounds, with special focus on benzene. The monitoring of other air toxics was also of interest. Since ORS systems can monitor multiple species simultaneously, there is the possibility that the concentrations of benzene as well as other gases might be measured using a single measurement system. Thus, attention was given to the experienced minimum detection limits (MDLs) for the refinery emissions of interest but with an emphasis on the BTEX compounds.

This report presents a review of previously conducted ORS field studies and a review of traditional methods of determining emissions rates. The feasibility of the proposed field study is presented along with design considerations for conducting such a study. Technical advancements are occurring rapidly in ORS technology; thus, it must be kept in mind that the perspective of the present report is limited to the general state of the technology at the end of 1992.

This feasibility study was conducted by a technical team organized by Remote Sensing=Air, Inc. (RS=A). The team was managed and coordinated by RS=A with Dr. William M. Vaughan as Project Manager. Formal input came from the University of Denver group under Dr. Donald H. Stedman, the Kansas State University group under Dr. William G. Fateley, MDA Scientific, Inc., and Ogden Environmental and Energy Services, Inc. Informal input was received from Dr. Peter T. Woods of the National Physical Laboratory in the United Kingdom and Dr. Konradin Weber, formerly of the VDI (Din Deutsches Institut für Normung e.v. Verein Deutscher Ingenieure) in Germany (See Figure 1-1).

The team examined existing ORS studies of emissions at petroleum refineries and petrochemical plants. Non-petroleum industry ORS monitoring programs conducted at facilities where BTEX compounds were measured and emission calculations carried out were also reviewed.

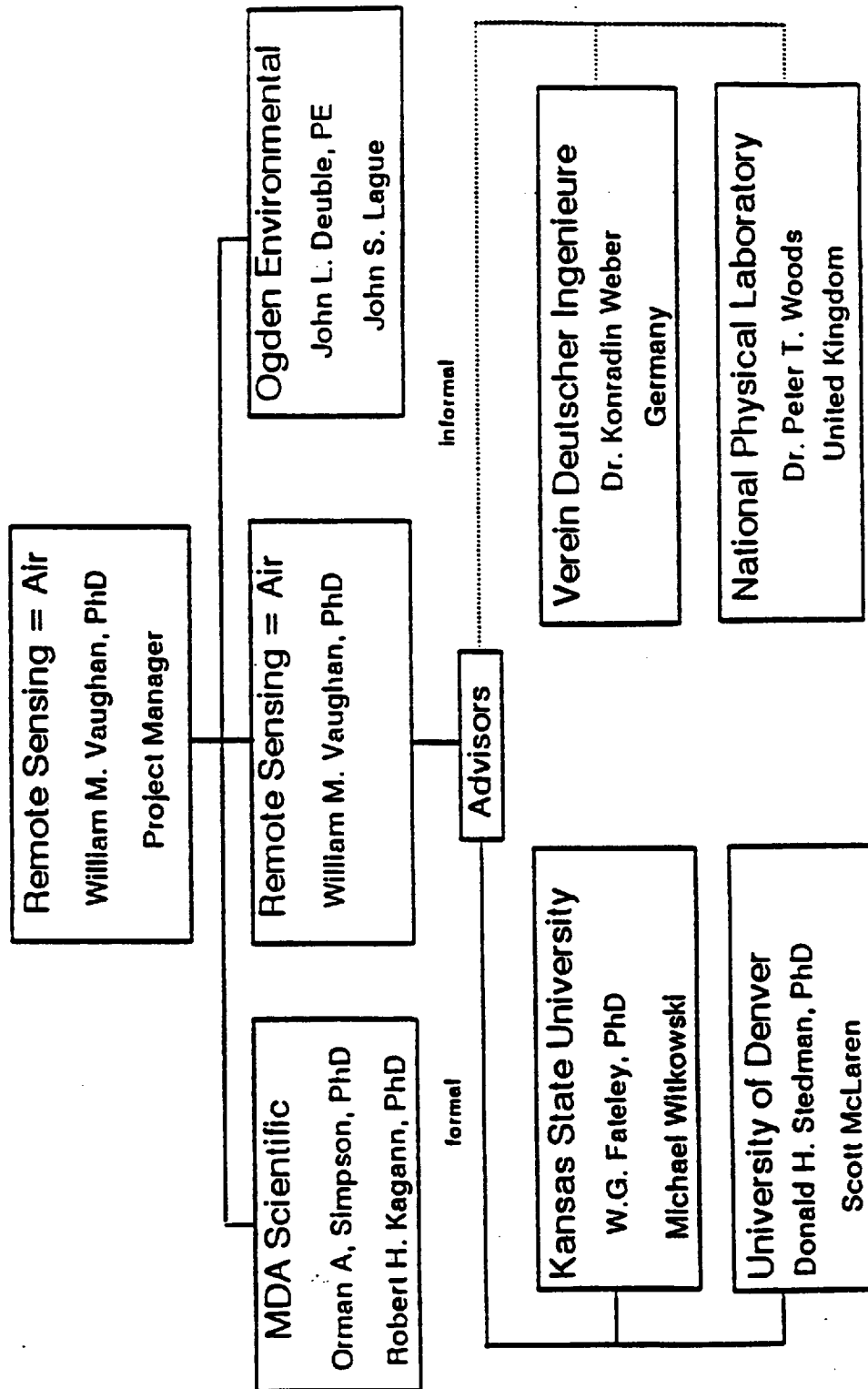


Figure 1-1. Project Organization Chart.

Traditional emissions estimates were reviewed also to provide insights on process areas where ORS techniques might be tested. These traditional methods of determining fugitive emissions include (1) using EPA's stationary source emission factors (AP-42) for specific operations; (2) making an inventory of any leaking equipment components such as valves, fittings, or seals using EPA Method 21 and applying emission factors to those components; and (3) releasing tracer gases at known flow rates while conducting grab and time-averaged sampling of both tracer gas and chemical compounds to establish approximate emission rates of chemical compounds by ratio techniques.

The project team provided design and research recommendations to enhance the proposed field study. Appendix A is a glossary of the acronyms and terminology used throughout this report. Appendix B is a copy of "Remote Sensing Terminology" (Vaughan, 1991) that will assist the reader in understanding specific remote sensing terminology.

Section 2

STATE-OF-TECHNOLOGY OF OPTICAL REMOTE SENSING

The several optical remote sensing (ORS) systems used in the studies discussed in this report are summarized below. There is no attempt to discuss in detail the theory behind ORS systems as this is provided in several recent review articles (Grant, *et al.*, 1992; Skippon, 1992b; Weber, 1992). Each of these ORS systems determines the total molecular content per unit of beam area and the results are generally reported as the product of concentration times the path length for a beam of electromagnetic radiation (UV or IR) between a source and a detector.

The **Fourier Transform Infrared (FTIR)** systems discussed in this study are open-path systems. Extractive instruments are also referred to as FTIR since they use the same basic instrumentation and principles for analysis of the spectra. The FTIR uses an IR source, an interferometer, and a detector to produce an interferogram for a range of wavelengths. The interferogram is transformed into an absorption spectrum using computer algorithms, and the resulting spectrum is compared to the library of available spectra to provide path-integrated concentration data. At present there are about 130 compounds available in the spectral libraries of the commercially available systems. The system is capable of determining unknown compounds and compensating for known interferences. There are several open-path systems in use which are sometimes termed long-path IR (LPIR) or open-path FTIR (OP-FTIR). FTIR open-path systems have been used at refinery and petrochemical sites as well as industrial, urban and Superfund sites in the United States. The Kansas Intercomparison study (Carter *et al.*, 1992) indicated that the two commercial instruments and one research instrument studied were comparable; thus, the study does not refer to the manufacturers of the open-path FTIR systems. FTIR will be used as the general term for the open-path technique.

The **Differential Absorption Lidar (DIAL)** system manufactured by the National Physical Laboratory of the United Kingdom (NPL) was used in the studies reviewed. A DIAL instrument uses a pulsed laser whose selected wavelengths (IR, visible or UV) are

backscattered by the atmosphere and collected by the detector (IR, visible or UV). One wavelength is selected from a region of the spectrum which is expected to absorb radiation due to the compound being measured while the other is selected from a region where no absorption is expected from the compound of interest or interfering compounds. The laser is tuned to evaluate one pair of wavelengths at a time and, thus, can determine the concentration of only one compound or class of compounds (e.g., total hydrocarbons using the C-H stretch spectral region) at a time. If, in addition to the specific wavelength radiation, a short duration pulse is transmitted, the backscattered radiation can be measured as a function of time to provide the range resolved profile of a plume directly. This system has been used in refinery settings in Europe in both its IR and UV modes as well as in Superfund studies in the United States.

The **Differential Optical Absorption Spectrometer (DOAS)** manufactured by Opsis in Sweden, uses broad band visible and ultraviolet (UV) light, usually from a high pressure lamp housed at one end of the path. The spectral pattern received at the detector at the other end of the path is compared with stored spectra of a gas-specific spectral band. At present there are about 30 compounds available in the spectral library. The spectra obtained are compared to library spectra for determining the path-averaged concentrations. Path lengths for this system range from 1 meter to 2,000 meters. This system has been used in studies at refinery settings in Europe and the United States as well as other industrial and urban settings.

The **long path UV (LPUV)** refers to the system from the University of Denver which is more properly known as an open-path UV (OPUV) to indicate that the path is open to the free flow of air rather than an enclosed cell in which the beam is folded by multiple reflections to achieve a long path measurement. OPUV systems use a high pressure lamp but incorporate the lamp into the main instrument to transmit a beam of UV light along the measurement path to a retroreflector. The resulting beam is projected onto an array of photodetectors (or diodes) so that a spectrum is built up from many individual detectors, each representing a small wavelength window. Like the other UV systems, the OPUV system can detect some compounds that FTIR cannot, as well as detect some compounds with greater sensitivity;

however, its spectral library is not nearly so large as that of the FTIR. To date, path lengths have ranged up to 500 meters. This system has been used in refinery and Superfund sites in the United States but is not commercially available at the time of this writing. ;

This report focuses on the feasibility of using ORS systems to provide accurate data on refinery air toxics concentrations at the fenceline with emphasis on the use of the ORS data in the calculation of emission rates. To determine emission rates, the path-averaged concentration data supplied by the ORS system needs to be coordinated with meteorological data as well as dispersion modeling and/or tracer gas releases at known rates. This section presents a summary of ORS measurement experience as of the end of 1992 along with the issues and tradeoffs for improving detection limits and the representativeness of ORS measurements.

SUMMARY OF ORS MEASUREMENT EXPERIENCE

A number of studies that have used ORS systems were reviewed in depth to prepare this report and are summarized below. A detailed presentation can be found in Appendix C.

Since the late 1980s, a number of studies using ORS systems to determine petroleum-related compound emissions have been conducted at refinery and petrochemical facilities as well as at other sites both in Europe and the United States. A summary of the ORS systems used at refineries or petrochemical facilities is presented in Table 2-1. The two most ambitious studies were performed in the Hisingen district of Sweden in 1988 and 1989 (Indic, 1988; Woods, 1992a). The results of these studies are available only as un-reviewed reports and do not clearly state minimum detection limits (MDLs) or comparisons between the conventional and ORS methods for determining the concentration of the same compounds. The goal of each study was to determine the hydrocarbon emission rates.

Table 2-1. ORS Systems Used in Studies in Refinery or Petrochemical Settings

STUDY	DATE OF STUDY	ORS SYSTEM(S)	EMISSIONS CALCULATIONS
Hisingen (Indic, 1988)	1988	DOAS	Yes
Gothenburg (Woods, 1992a)	1988, 1989	IR-DIAL	Yes
Wastewater Impoundments (Indaco, Inc., 1990)	1989	FTIR and OPUV	Yes
Land Farm (Lupo, <i>et al.</i> , 1991)	1991	FTIR and OPUV	No
Tank Truck Loading Area (Milton, <i>et al.</i> , 1992)	1991	UV-DIAL	No
Exxon Chemical Americas (Spellicy, <i>et al.</i> , 1992)	1991	FTIR and DOAS	No
Shell Deer Park (Thomas, <i>et al.</i> , 1992)	1992	FTIR	No

Indic and Opsi (Indic, 1988) attempted to determine emission rates of hydrocarbons from both the Shell and British Petroleum (BP) refineries using the DOAS system and various methods of calculating the emissions rates, but were successful in calculating emission rates for only toluene (using DOAS data) and p-xylene (using conventional sorbent tube concentration data) at the Shell refinery. Indic's limited 1988 efforts do not seem to have been duplicated in more recent published reports although Indic has indicated plans for the implementation of an upgraded approach for a new refinery in Chile (Gidhagen, 1992a). The NPL study at the BP refinery (Woods, 1992a) was successful in determining plume profiles as well as non-methane hydrocarbon and toluene emission rates from discrete process areas at the refinery using the IR-DIAL. The system had problems measuring toluene (used as a surrogate to determine aromatics). Later refinery studies with this instrument are not reported; however, a 1991 study (Milton, *et al.*, 1992) indicates that the UV-DIAL system is preferable to the IR-DIAL for determining toluene concentrations. The 1991 study presents

measurements of toluene concentration profiles using a UV-DIAL system and calculation of the total flux by combining the concentration data with simultaneous wind speed data.

To date, the most ambitious U.S. study of refinery-related emissions using ORS systems reported was conducted by the University of Denver and Indaco. BTEX emission rates from a refinery's wastewater impoundment were determined (Indaco, Inc. 1990; McLaren and Stedman, 1990). This study was more complete than the NPL (Woods, 1992a) and Indic (Indic, 1988) studies in that tracer releases were used to simulate emissions and provide a methodological cross-check. In addition, Indaco and the University of Denver were able to evaluate the performance of the EPA CHEMDAT7 air emissions model against these field data. The study indicated that the OPUV system can measure concentrations of benzene at low levels which are comparable to SUMMA® canister results and that the variations in the OPUV signals could be correlated with site sources. The report also suggests that more work is needed to improve air emission models for use in refinery settings.

A study at a land farm to monitor concentrations of BTEX and hexane using OPUV, FTIR and conventional sorbent tube sampling (Lupo, *et al.*, 1991) suggested two advantages of the ORS systems over the conventional sampling. These advantages were the ability of the ORS samplers to determine temporal variations in the concentrations which could be linked to site activities and the fact that the ORS data were less costly and less labor intensive to gather.

The study at Exxon Chemical Americas (Radian, 1991b; Spellicy, *et al.*, 1992) demonstrated that the DOAS and FTIR systems could operate in a stand-alone mode for extended periods and that correlations could be made between temporal variations in the measured concentrations and meteorological and plant conditions. As expected, the reported MDL for benzene with the DOAS was lower (0.76 ppm-m) than that reported for the FTIR (12.5-15 ppm-m).

The Shell Deer Park study (Thomas, *et al.*, 1992) again demonstrated the ability of the FTIR to determine concentrations of compounds of interest and the ability to correlate temporal

variations with plant operations. It also confirmed the difficulty of using the FTIR to determine benzene at very low concentrations.

Several emission rate studies using ORS have been performed at Superfund sites for surface emission releases where conditions are simpler than at refineries or petrochemical plants, making evaluation less complicated. Usually these emission rate estimates have been determined using simultaneous tracer releases with known emission rates so they are related to empirical values rather than engineering estimates (Kricks, *et al.*, 1991; Scotto, *et al.*, 1992).

In discussing the ORS programs in Appendix C, some of the individual system limitations are presented such as stability of alignment, the inability to identify unknown compounds with the UV systems, the limited frequencies for the older DIAL systems, and the difficulty in attaining sufficiently low MDLs for benzene. Most of these "limitations" are related to the earlier stages of rapidly developing technologies. Some, such as attaining sufficiently low MDLs, are less an issue than they were 3 to 4 years ago due to recent improvements in system equipment design and processing software. For FTIR systems the ever-present issue of water vapor interference is being addressed by new measurement and data processing procedures.

In summary, most, if not all, of the measurement components required for determination of emissions rates from a refinery or process area have been conducted at one or more locations. Many recognized problems have been addressed to some extent, but not necessarily solved. Yet, no studies reported, to date, adequately answer the question, "Has the state-of-technology of ORS advanced far enough to provide technically defensible data of incremental air toxic emissions from an isolated or chemically complex refinery setting?" These studies, however, have raised several issues that would need to be addressed in planning a definitive refinery field study.

ISSUES AND TRADEOFFS

In considering the implementation of an emissions measurement program using ORS techniques with possible combinations of meteorological and tracer gas measurements and modeling, one must acknowledge that each site is different both physically and meteorologically. Specific measurement needs, such as configurations of light beams, timing of measurements and the presence of possible interfering compounds, may not be ascertainable until the site itself is known and observed. Some of the technical issues that are part of the planning and evaluation of an overall measurement strategy include: detection limits, light beam placement, dispersion modeling, tracer gas release, time intervals for measurements, and meteorological measurements.

Detection Limits

Detection limits for ORS systems are dependent on the type of compound being identified, the system to be used, the path length, and conditions that affect the signal-to-noise ratio such as the number of spectra coadded, the stability of the placement of the system, and the type of electrical generator being used. The lowest realistic MDLs are preferred for determining risks of exposure and for tracking of control emissions. The most desirable detection limit for a compound like benzene would be one near its "one-in-a-million" 70-year cancer risk level, ≈ 0.035 ppb [this concentration was calculated, assuming standard temperature and pressure, from the value of $0.12 \mu\text{g}/\text{m}^3$ reported in the IRIS Database which cited a 1985 Interim Quantitation from the Office of Health and Environmental Affairs (USEPA, 1985).] Measurements with such a low detection limit would support the validity of exposure assessments. However, at present no air monitoring system is able to meet these limits. Thus, assumptions must be made regarding whether the levels should be conservatively estimated at or below the actual detection limits. Of course, if an exposure assessment is based on a detection limit which is well above the actual level at which the compound is present, unnecessarily large projected exposures and risks will be predicted. Further complications arise when trying to show that combined cancer risks for all species of toxics are below the "one-in-a-million" level. Unless one species really dominates, actual MDLs must be even lower than the "one-in-a-million" risk level to preclude overpredicting exposures

based on poor MDLs. Progress in emissions control cannot be tracked by an analytical method if levels determined before controls were imposed were already below the detection limits of the systems. Therefore, it is important to attempt to attain the lowest detection limits possible but also to realize the real limitations of the present technology when setting requirements for detection limits.

Both laboratory-determined and field-determined detection limits for the BTEX compounds are presented in Tables 2-2a (as path-averaged concentrations in ppb units) and 2-2b (as path-integrated concentrations in ppm-m units) for the ORS systems described in this report. As can be seen, in most cases, the UV systems (OPUV, DOAS and UV-DIAL) have the lowest detection limits for these compounds. The FTIR limits are 2 to 100 times higher than the UV values. However, even the FTIR detection limits are well below the NIOSH and OSHA time weighted average (TWA) exposure limits of 100 ppm (100,000 ppb) for toluene, ethylbenzene and the xylenes and the OSHA 1 ppm (1,000 ppb) for benzene (NIOSH, 1990). The NIOSH TWA for benzene is 0.1 ppm (100 ppb) which is below some of the FTIR MDLs.

In the following paragraphs, some of the factors that affect the MDLs obtained with a specific system at a specific site are discussed. These factors include the absorbance bands used to determine the specific compounds of interest, the type of detector, the strength of the source, the size and focus of the optics, the time interval of the data collection, the meteorology, the path length, and the background/upwind spectra corrections.

Absorbance Bands. The ORS systems discussed in this report use light sources and detectors that operate in either the UV or IR regions of the electromagnetic radiation spectrum. Because aromatic compounds, which are the focus of this report, absorb most strongly in the UV region, their MDLs are lower for the UV systems than for the FTIR systems. It has been noted (Milton, *et al.*, 1992; Axelsson, *et al.*, 1991) that atmospheric oxygen and ozone absorb in the same uv regions as the aromatics in much the same way as water and carbon dioxide absorb in the infrared regions. However, careful background correction can be used to reduce their interference and allow the MDLs shown in Tables 2-2a and 2-2b even under field conditions.

Table 2-2a. Summary of BTEX Path-Averaged Detection Limits for ORS Systems

ORS Method (Path length, m)	Path-average Concentrations (ppb)				Source/ Reference
	Benzene	Toluene	Ethylbenzene	Xylenes	
FTIR (200) ^a	310	690	600	310, 640, 400	Kagann, 1992a
FTIR (200) ^b	34	34	34	1.5, 2.7, 1.4	Kagann, 1992b
FTIR (500) ^c	25-30	50	NR	20	Spellicy, <i>et al.</i> , 1992
FTIR (400) ^d	NR	~100	NR	NR	Carter, <i>et al.</i> , 1992
FTIR (300) ^e	177	291	54	49	Scotto, <i>et al.</i> , 1992
FTIR (200) ^f	10	30	NR	30	Thomas, <i>et al.</i> , 1992
OPUV (200) ^g	NR	NR	NR	<30	McLaren, <i>et al.</i> , 1992
OPUV (102) ^h	29	29	196	20-294	Indaco, Inc., 1990
DOAS (500) ⁱ	1.6	1.6	NR	1.6	Spellicy, <i>et al.</i> , 1992
DOAS (600) ^j	2.9	2.4	NR	NR	Lofgren & Ramnas, 1991
DOAS (1000+) ^k	<2.1	<3.4	NR	<0.9	Stevens and Vossler, 1991
DOAS (2000+) ^k	<2.4	<4.9	NR	<1.1	Stevens and Vossler, 1991
UV-DIAL (unknown) ^j	NR	10	NR	NR	Milton, <i>et al.</i> , 1992
UV-DIAL (500) ^j	1.5	2-20	NR	1-10	Woods, 1992b

NR No MDL reported for this compound.

Note: FTIR path lengths are twice the distance from the instrument to the retroreflector.

- a Determined by R. Kagann using the "visual estimation method"; xylenes are listed as meta, ortho, and para.
- b Optimized detection limits achieved with careful data acquisition and manipulation; xylene are listed as meta, ortho and para.
- c Using 0.5 cm⁻¹ resolution. Xylene is the meta isomer. MDL determined from spectra and long term time series plots.
- d Estimated from the fact that the FTIR systems could not detect the 30 ppb test but some could detect the 100 ppb test.
- e Average of daily MDLs calculated by Scotto; the ppm-m values have been converted to ppb using twice the background path length of 150 m. The MDLs were determined as twice the observed noise in the spectral region.
- f Using 20 inch optics. No method of MDL determination stated.
- g Based on the ability of the OPUV to determine the ~30 ppb release with good correlation with the conventional method.
- h Determined by adding the spectrum of each BTEX compound to the measured spectrum until peaks were observed above the noise. This concentration for each was termed the detection limit.
- i Detections observed and limits from time series plots are consistent with Opsis MDLs.
- j Method of MDL determination not stated.
- k Actual concentration determined in µg/m³; MDL assumed to be less than these values and calculated as ppb from µg/m³ MDLs assuming standard temperature and pressure during the measurement.

Table 2-2b. Summary of BTEX Path-Integrated Detection Limits for ORS Systems

ORS Method (Path length, m)	Path-integrated Concentrations (ppm-m)				Source/ Reference
	Benzene	Toluene	Ethylbenzene	Xylenes	
FTIR (200) ^a	62	138	120	62, 128, 80	Kagann, 1992a
FTIR (200) ^b	6.8	6.8	6.8	0.30,0.52,0.28	Kagann, 1992b
FTIR (500) ^c	12.5-15	25	NR	10	Spellicy, <i>et al.</i> , 1992
FTIR (400) ^d	NR	~40	NR	NR	Carter, <i>et al.</i> , 1992
FTIR (300) ^e	53	87	16	15	Scotto, <i>et al.</i> , 1992
FTIR (200) ^f	2	6	NR	6	Thomas, <i>et al.</i> , 1992
OPUV (200) ^g	NR	NR	NR	<6	McLaren, <i>et al.</i> , 1992
OPUV (102) ^h	3	3	20	2-30	Indaco, Inc., 1990
DOAS (500) ⁱ	0.8	0.8	NR	0.8	Spellicy, <i>et al.</i> , 1992
DOAS (600) ^j	1.7	1.4	NR	NR	Lofgren & Ramnas, 1991
DOAS (1000+) ^k	<2.1	<3.4	NR	<0.9	Stevens and Vossler, 1991
DOAS (2000+) ^k	<4.8	<9.8	NR	<2.2	Stevens and Vossler, 1991
UV-DIAL (unknown) ^j	NR	unk	NR	NR	Milton, <i>et al.</i> , 1992
UV-DIAL (500) ^j	0.75	1-10	NR	0.5-5	Woods, 1992b

NR No MDL reported for this compound.

- a Determined by R. Kagann using the "visual estimation method"; xylenes are listed as meta, ortho, and para.
- b Optimized detection limits achieved with careful data acquisition and manipulation; xylene are listed as meta, ortho and para.
- c Using 0.5 cm⁻¹ resolution. Xylene is the meta isomer. MDL determined from spectra and long term time series plots.
- d Estimated from the fact that the FTIR systems could not detect the 30 ppb test but some could detect the 100 ppb test.
- e Average of daily MDLs calculated by Scotto. The MDLs were determined as twice the observed noise in the spectral region.
- f Using 20 inch optics. No method of MDL determination stated.
- g Based on the ability of the OPUV to determine the ~30 ppb release with good correlation with the conventional method.
- h Determined by adding the spectrum of each BTEX compound to the measured spectrum until peaks were observed above the noise. This concentration for each was termed the detection limit.
- i Detections observed and limits from time series plots are consistent with Opsis MDLs.
- j Method of MDL determination not stated.
- k Actual concentration determined in µg/m³; MDL assumed to be less than these values and calculated as ppm-m from µg/m³ MDLs using the path length and assuming standard temperature and pressure during the measurement.

Chlorinated and fluorinated hydrocarbons exhibit strong infrared absorption bands in the 1400 to 650 cm^{-1} (wavenumber) region of the mid-infrared spectrum. Because of this strong infrared absorption, the ORS detection limits for these types of compounds using FTIR systems are low (≈ 5 to 20 ppb average concentration along a total beam of 100 m). While aromatic hydrocarbons like benzene and toluene are strong infrared absorbers, their strongest absorbance bands occur in the regions of the mid-infrared which include interferences from ubiquitous carbon dioxide and water vapor. The available alternative for obtaining lower MDLs for aromatic compounds using FTIR systems is to use the weaker absorbance bands for these compounds which are affected less by the carbon dioxide and water vapor bands. For example, the strongest absorption band for benzene is at 671 cm^{-1} (in the same region where carbon dioxide and water vapor absorb); however, benzene also has a much weaker band at 1038 cm^{-1} ($\approx 1/50^{\text{th}}$ the absorbance of that at 671 cm^{-1}) in a region relatively free of the interferences. If one could use the more intense 671 cm^{-1} region, an MDL of about 1 ppb over a 100 m path could be achieved for benzene; however, carbon dioxide will absorb nearly all the energy at 671 cm^{-1} leaving no signal for benzene to absorb. For the 1038 cm^{-1} region that is used to avoid the carbon dioxide interferences, the MDL is a couple orders of magnitude higher (or ≈ 310 ppb over 100 m for commercial units). If the analytical software can compensate for water vapor interferences in this region this MDL can be moved downward to about 70 to 100 ppb over 100 m and, with careful manual subtraction, an MDL of 34 ppb over 100 m has been obtained.

Detectors. There is the possibility that the FTIR MDL for benzene might be lowered if the detector were modified. The common commercial detector is a mercury cadmium telluride (MCT) crystal that can be "customized" (by altering the ratio of M, C and T) for different spectral ranges - wide, medium and narrow. Since the narrow band detector has somewhat greater response in the 900 to 1100 cm^{-1} region than the wide band detector, it might be more useful for detecting benzene. However, with its sharp cutoff at 800 cm^{-1} , the strong absorption bands for chlorinated compounds, such as 1,1,1-trichloroethane at 725 cm^{-1} , would not be available. Similarly one would lose the ability to observe the sharp 730 to 800 cm^{-1} bands of the xylene isomers. These tradeoffs might not be acceptable if the facility being