In-Situ Sensors for the Chemical Industry- Final Report

Project Title: Development of In Situ Analysis for the Chemical Industry

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Project Objective: This project will develop two platforms for robust, in or at-line, process measurements that operate at or near real time. The two process analytical platforms will be; **(1) Laser Based Sensors and (2) Solid State Sensors**. These systems will be capable of operating at the required process conditions (pressure, temperature, etc.), allowing for the sensor to be placed in the process (in-line) or immediately adjacent to the process (at-line) , providing real time or near real time data, and significantly reducing the installation and operational cost when compared to the current market available products.

Background: The need for these platforms and the measurements they provide are driven by improvements in advanced process control (APC) systems and the need to "close the loop" in modern control systems. With few exceptions, current process analytical (PA) techniques are lacking in the speed of measurement, accuracy of measurement, sensitivity of measurement and the overall cost of providing the measurement.

Executive Summary

The project focused on *analytical techniques that can be applied in situ*. The innovative component of this project is the focus on achieving a significant breakthrough in two of the three primary Process Analytical (PA) fields. PA measurements can roughly be broken down into:

- Single component measurements,
- Multiple component measurements and
- Multiple component isomer analysis.

This project targeted single component measurements and multiple component measurements with two basic technologies, and to move these measurements to the process, achieving many of the process control needs.

During the project the following achievements were made:

- Development of a low cost Tunable Diode Laser (TDL) Analyzer system for measurement of 1) Oxygen in process and combustion applications, 2) part per million (ppm) H₂O impurities in aggressive service, 3) ppm CO in large scale combustion systems. This product is now commercially available
- Development of a process pathlength enhanced (high sensitivity) Laser Based Analyzer for measurement of product impurities. This product is now commercially available.
- Development of signal processing methods to eliminate measurement errors in complex and changing backgrounds (critical to chemical industry measurements). This development is incorporated into 2 commercially available products.
- Development of signal processing methods to allow multi-component measurements in complex chemical streams. This development is incorporated into 2 commercially available products.
- Development of process interface designs to allow in-situ application of TDL technology in aggressive (corrosive, high temperature, high pressure) commonly found in chemical processes. This development is incorporated in the commercially available ASI TDL analyzer.
- Field proving of 3 laser-based analyzer systems in process control and combustion applications at Dow Chemical.

Laser based analyzers have been available for >5yrs, however significant product price/performance issues have minimized their applicability in the chemical industry. In order to take advantage of the promise of this technology a number of technology advances were required, within price limits for market acceptance.

This project significantly advanced the state of TDL technology for application in chemical industry applications. With these advances a commercially available product

now exists that has already achieved market success and is installed in critical applications. The ability to make fast, sensitive and accurate measurements inside the chemical processes is now delivering improved process control, energy efficiency and emissions control within the U.S. Chemical Industry.

Despite the success we enjoyed for the laser-based sensors, there were significant technical barriers for the solid-state sensors. With exception of a generic close-coupled extractive housing and electronics interface, there were significant issues with all of the solid-state sensor devices we sought to develop and test. Ultimately, these issues were roadblocks that prevented further development and testing.

The fundamental limitations of available sensor materials that we identified, formulated and tested were overwhelming. This situation forced our team to cancel these portions of the project and focus our resources on laser-based sensor techniques. The barriers of material compatibility, sensitivity, speed of response, chemical interferences, etc. are surmountable in the field of solid-state sensors. Inability to address any single one of these attributes will prevent wide-implementation into this market. This situation is plainly evident by the lack of such devices in the online analyzer market (for petrochemicals).

The Goals and Objectives for this project were divided into two areas; 1) Laser Based Sensors, and 2) Solid State Sensors.

The following sections will discuss the original project goals/objectives and compare these with actual accomplishments.

I. Laser Based Sensors

Project Task	Objective	Application
1-Laser Sensor Platform	Develop sensor platform to handle aggressive service, temperature, pressure, corrosives	Oxygen in combustion service, incinerators, thermal oxidizers, corrosive service, etc. Moisture in aggressive service
	Signal processing and modeling to remove background effects (collisional broadening)	HCl analysis in VCM manufacturing, oxygen in ethylene oxide reactor loop
2-Sensitivity Enhancement	Pathlength enhancement for sensitivity improvement (ppm to ppb for impurities)	Acetylene in ethylene cracked gas and finished product
3-Multi-variate Analysis	Multivariate analysis using widely tunable NIR source	Severity index measurement for ethylene cracking
4-Mid-Infrared Analysis	Implement mid infrared QC lasers, room temperature operation, expand possible measurements	CO for combustion control
5-Identify Additional Applications	Develop high resolution infrared database for application development	All

A. Task 1 – Laser Sensor Platform Development (a) Develop sensor platform to handle aggressive service, temperature, pressure, corrosives

Original Hypothesis. Typical Process Analyzers require expensive (\$40-80,000 per analyzer) infrastructure, including sample transport, sample conditioning and analyzer houses to protect from ambient conditions. In order to reduce the installation costs for process measurements (allowing more measurements and improved process control) an analyzer must be able to be installed at or on the process itself, reducing installation costs from \$80-120,000 per analyzer to \$30-50,000 per analyzer.

While in theory TDL analyzers have the ability to meet these conditions, commercially available TDL (tunable diode laser) products have been designed for emissions monitoring or ambient air analysis. In order to be adapted for process applications, a TDL system must be able to measure under a different set of conditions including:

- Corrosive and lethal service. Of particular importance is the ability to seal to the process, eliminating potential product leaks (releases). In addition materials of construction must be suited for the process.
- High pressure process gases. In many applications process pressures can reach or exceed 20 bar. The process interface must be capable of meeting pipe specifications for the process.
- High temperature process gases. Especially important for combustion applications where the gas temperature can exceed 1200C. Also important is the combination of pressure/temperature (higher temperatures will reduce the process interface pressure rating)
- Process fouling. In many processes particulate, liquid or polymerizing compounds may be present, the optical process interface must be protected from window coating and fouling.

This project resulted in a Process TDL analyzer design to address the conditions above, while also meeting end-user requirement including:

- Ability to adjust analyzer alignment
- Fast and simple removal of the analyzer from the process for window cleaning and analyzer calibration
- On-line validation (dynamic spiking) for positive proof of operation
- Operation in hazardous area environments (NEC Class 1, Div 1/2)
- Unprotected (no analyzer shelter) installation from -20C to +50C, weather resistant (NEMA 4X)
- Full diagnostics capture and storage with local and networked analyzer access and data transfer
- Simple user interface for analyzer settings and control, including calibration/validation

Approaches Used

Process Interface and Alignment Mechanism. Common practice for existing TDL analyzers is to use an o-ring in between the process flange and the analyzer flange to both seal the process gas and also to provide a method of aligning the laser beam. To adjust alignment bolts are tightened or loosened to gimbal the analyzer on the o-ring. This results in one or more sections of the o-ring having higher compression than other sections. For high pressure, corrosive or lethal service this alignment/seal mechanism is not acceptable since the practice of alignment compromises the process seal, allowing process gas to escape to the atmosphere, or if the process is sub-atmospheric pressure, allowing ambient air to ingress.

For this project a number of methods were discussed and evaluated to eliminate this problem. Ultimately a welded metal bellows was selected as the alignment mechanism, installed behind and completely separated from the process seal. By adjusting the bolts surrounding the bellow, alignment can be adjusted with no effect on the process seal.

Conventional TDL	Project Final Design

Analyzer Quick Connect. With in-situ installation the analyzer must be periodically removed for cleaning of the process windows or analyzer calibration. This must be easily achieved without requiring re-alignment of the analyzer when returned to service. To achieve this the platform was designed with a “quick connect” located behind the alignment bellows. By removing 3 screws the analyzer can be disconnected from the process without any change in alignment when reconnected.

Dynamic Spiking. With full calibration required every 6-24 months a method is needed to “validate” the measurement without removing the analyzer from the process. This validation needs to be fully automated and provide a positive indication of operation and response factor.

The project platform design used a sealed cell in between the laser and process gas. This in-line validation cell is normally filled with nitrogen which has no effect on the reading. For validation a calibration gas is used to fill the in-line cell, providing a spike in the reading (calibration gas concentration + process gas concentration).

This approach was modeled after the recommended procedure in EPA PPS-001 (provisional performance specification 001) designed for in-situ ammonia emissions monitors.

Analyzer Enclosures, Electronics Design & Area Classification. For process applications equipment must be designed to operate in full ambient temperature conditions (typically - 20C to 50C) as well as meet NEC Class 1, Division 1 / 2, Groups B,C,D.

The project prototypes were designed with this in mind, incorporating the appropriate weather protection, purging systems and electronics to meet ambient and area classification requirements. Subsequently the commercialized product has received ATEX and CE certification for these conditions.

User Interface, Data Storage, Diagnostics, Communications. For both ultimate applicability in process applications as well as to speed up field testing a number of software and hardware features were required:

- User interface was designed to allow easy access to analyzer set up parameters, calibration/validation routines, spectral analysis and trending of data.
- Data storage was designed for 14 days of full measurement and diagnostics capture/storage for every measurement (2-5seconds). In addition automatic spectra capture routines were built in based on; a) time, b) high/low concentrations, c) alarm warning or fault conditions
- In order to transfer data and access the analyzer software both wired (local and network via Ethernet) and wireless (802.11 + Bluetooth) communications were built into the project test platforms

In particular, the ease of data capture and transfer was extremely valuable to the development process. Signal processing routines could be evaluated and quickly adjusted based on field performance. It was also found that the analyzer ability to store spectra for review allowed the measurements to be “proven” when they differed from the

existing analyzer (old technology) installed on the process. In many cases the speed and accuracy of the TDL analyzer resulted in process changes being seen that had not been seen before, having historical diagnostic data and spectra allowed the team to validate the TDL data.

Problems & Departure from planned methodology

During this stage of the project no major problems or changes in methodology were encountered.

B. Task 1 – Laser Sensor Platform Development (b) Signal processing and modeling to remove background effects (collisional broadening)

Original Hypothesis. One of the most significant issues limiting the applicability of TDL technology in process applications is the ability to deal with simultaneous changes of pressure, temperature and background gas changes (PTB). This is an absolute requirement since unlike emissions monitoring and ambient air analysis, most process samples will have changes in these conditions.

All existing commercially available products use a second harmonic (2f) method for analysis. This method is commonly used to reduce the measurement noise resulting from high frequency laser power fluctuations (1/f noise). 2f systems are generally limited to a peak height measurement, in limited applications a peak width measurement is used to approximate the peak area. Peak height and width are both affected by process gas pressure, temperature and background gases. While pressure and temperature can be measured to use for compensation, a full background gas measurement is not available for compensation. In addition both the gas temperature and pressure effects are non-linear for 2f peak height methods, making live compensation difficult or impossible.

In order to make an accurate measurement under process conditions, peak area integration is required. With peak area measurement background gas changes (foreign gas broadening), while changing the peak height and width (peak shape) does not affect the integrated peak area.

Direct absorption techniques preserve the peak shape.

Issues are:

- Laser (1/f) noise
- Baseline sensitive
- Temperature sensitive (area sees more reduction with temperature than peak height)

Noise suppression techniques and baseline treatment is required to reach 10^{-6} sensitivity.

Second harmonic (2f) techniques filter much of the laser noise through lock-in amplifier. Also, it is a “zero baseline” technique where much of the laser ramp and curvature is flattened.

This allows very sensitive detection.

Issues are:

- Peak shape is not preserved. Area integration not possible
- Pressure and foreign gas broadening introduce non-linear effects

Path length is constant... Gas pressure can be measured... Gas temperature can be measured... Background gases are typically unknown or changing

	Peak Height	Peak Area	Compensation possible
Concentration	Linear	Linear	NA
Path Length	Linear	Linear	NA
Gas pressure	Non-linear	Linear	Yes
Background gases	Non-linear	NONE	No
Gas Temperature	Non-linear	Non-linear	Yes
	3 NON LINEAR	1 NON LINEAR	

The difficulty with peak area integration in the past has been achieving the required sensitivity (dealing with 1f noise) and minimizing drift caused by baseline changes.

Approaches Used. One approach has been to use a balanced detector circuit such as developed by IBM (Hobbs), where a reference detector is used to cancel common mode noise (primarily laser noise).

Initially this project planned on using the Balanced Ratiometric Detector, or BRD (under license) approach in order to provide a peak area measurement at desired sensitivity and drift limits.

Problems & Departure from planned methodology. Early testing of the BRD system exposed a number of potential problems for our applications. The two most significant were:

1. Operation during changes in laser light transmission. In many processes particulate is present and particulate loading changes. The BRD circuit requires an ~2.2:1 measure detector/reference detector ratio of laser power. This is achieved by splitting the laser light using a beamsplitter before the light transmits across the process. During process particulate changes the amount of laser power at the measure detector can constantly fluctuate, changing the measure/reference detector power ratio. This has direct and significant effects on the noise cancellation efficiency. The only possible solution we found for this was to use a variable optical amplifier to change the laser power during particulate changes. This was found to be cost prohibitive.
2. Ambient temperature induced measurement drift was also observed during environmental cycling of the circuit. As one of the primary goals for this platform was at or on-line installation under full ambient conditions, the BRD circuit was deemed unsuitable.

In order to address these issues and provide the integrated peak area measurement the project team implemented a high speed data acquisition strategy. By modulating the laser and sampling the detector signal at extremely high frequency (>50mHz) we found that the laser noise could be reduced to allow sensitivities matching those of 2f systems and acceptable for our measurement targets. A custom circuit employing high speed DAQ with FPGA processing was developed at Analytical Specialties, Inc. for this project. This was required since commercially available DAQ systems were cost prohibitive.

Additionally a number of signal processing strategies (proprietary) were developed in order to deal with baseline fluctuations, resulting in measurement drift at or below the application requirements.

Impact on Project Results. Since the problems with the planned approach (BRD) were identified early in the project, subsequent development of the signal processing system at Analytical Specialties had no impact on the project timing or budget.

Extensive pre-field testing (below) supported the peak area concept, providing a vastly superior measurement when compared to commercially available 2f TDL platforms.

TEST SUMMARY

TEST	Comments	ASI TDL Analyzer		2f TDL system		Conditions
		Result	Units	Result	Units	
MDL 2min	3x stdev.	0.0155	% oxygen	0.0076	% oxygen	STP O ₂ /N ₂
MDL 10min	3x stdev.	0.0185	% oxygen	0.0124	% oxygen	STP O ₂ /N ₂
Linearity	0.1, 1.2, 5, 5.0, 10.0, 25% Oxygen	0.999994	R squared	0.99994	R squared	STP O ₂ /N ₂
Accuracy	1.1, 2.5, 5, 9, 10.0, 25% Oxygen	<2%	Relative	<2%	Relative	STP O ₂ /N ₂
Precision	1.1, 2.5, 5, 9, 10.0, 25% Oxygen	<2%	Relative	<2%	Relative	STP O ₂ /N ₂
Elevated Ambient Temp.	50C	<2%	Relative	4.3%	Relative	STP O ₂ /N ₂
Reduced Ambient Temp.	0C	<2%	Relative	<2%	Relative	STP O ₂ /N ₂
Gas Temperature	25-300C	2.1%	Relative	11.1%	Relative	Ambient P, 10% O ₂ /N ₂
Gas Pressure Cycling	0.5 – 2.0 bara	<2%	Relative	61.8%	Relative	Ambient T, 10% O ₂ /N ₂
Gas Pressure Change*	0.5 – 2.0 bara	<2%	Relative	3.9%	Relative	Ambient T, 10% O ₂ /N ₂
Gas Composition Change	10% O ₂ in He & CO ₂	<2%	Relative	2.4%	Relative	STP
Gas Pressure & Composition Change*	10% O ₂ in He & CO ₂ ↔ 0.5-2.0 bara	<2%	Relative	76.3%	Relative	
Gas Pressure & Concentration Change*	2.5/10/25 % O ₂ ↔ 0.5-2.0 bara	3.2%**	Relative	122.4%	Relative	
Gas Temperature, Pressure, Background Change	Interactive pressure, temperature, background tests	2.11%	Relative	17.57%	Relative	77, 300, 575F – 1.2 BarA, He, CO ₂ , N ₂ Background

Results within 2% relative error listed as <2%

* ASI analyzer tested to 4 bara, data based on 0.5-2.0 bara for comparison to 2f TDL

** Largest error at 2.5% oxygen (10% of range), error % FSD is <1%, relative error would be reduced with analyzer range reduced closer to measurement point.. checking gas standard

Pressure/Temperature/Background Variations - Summary

Run	Test Temp (F)	Test Press. (barA)	Background Gas	ASI TDL Analyzer		2f TDL Analyzer		Gas Cylinder %O ₂	
				Reading	Error %RSD	Reading	Error %RSD		
1	77	3	N ₂	9.93%	0.70%	9.78%	-2.20%	10.00%	*
2	77	3	CO ₂	9.93%	0.30%	8.81%	-11.55%	9.96%	*
3	77	1	CO ₂	9.95%	0.10%	9.88%	-0.80%	9.96%	
4	77	3	He	9.95%	0.50%	11.88%	18.80%	10.00%	*
5	77	1	He	9.99%	0.10%	9.97%	-0.30%	10.00%	
6	77	2	He	9.96%	0.10%	9.96%	-0.10%	9.97%	
7	77	2	CO ₂	9.94%	0.20%	9.74%	-2.21%	9.96%	
8	77	1	N ₂	9.98%	0.20%	9.93%	-0.70%	10.00%	
9	77	2	N ₂	9.91%	0.90%	9.89%	-1.10%	10.00%	
10	575	2	He	9.90%	1.00%	8.99%	-10.10%	10.00%	
11	575	2	N ₂	9.95%	0.50%	8.57%	-14.30%	10.00%	
12	575	1	He	10.14%	-1.40%	8.72%	-12.80%	10.00%	
13	575	3	N ₂	9.82%	1.80%	8.28%	-17.20%	10.00%	*
14	575	2	CO ₂	9.98%	-0.20%	8.21%	-17.57%	9.96%	
15	575	3	He	9.96%	0.40%	8.83%	-11.70%	10.00%	*
16	575	1	N ₂	9.99%	0.10%	8.41%	-15.90%	10.00%	
17	575	3	CO ₂	9.86%	1.00%	7.80%	-21.69%	9.96%	*
18	575	1	CO ₂	9.92%	0.40%	8.38%	-15.86%	9.96%	
19	270	3	He	10.12%	-1.20%	9.74%	-2.60%	10.00%	*
20	270	1	N ₂	10.19%	-1.90%	9.46%	-5.40%	10.00%	
21	270	3	N ₂	10.10%	-1.00%	9.42%	-5.80%	10.00%	*
22	270	1	CO ₂	10.17%	-2.11%	9.28%	-6.83%	9.96%	
23	270	3	CO ₂	10.16%	-2.01%	9.17%	-7.93%	9.96%	*
24	270	2	CO ₂	10.05%	-0.90%	9.25%	-7.13%	9.96%	
25	270	1	He	10.16%	-1.60%	9.28%	-7.20%	10.00%	
26	270	2	N ₂	10.15%	-1.50%	9.34%	-6.60%	10.00%	
27	270	2	He	10.11%	-1.10%	9.42%	-5.80%	10.00%	

The results of the pre-field testing were well within limits to pass the go/no-go point and proceed to field testing.

Field tests were performed at Dow Chemical in two applications; 1) oxygen measurement in an incineration system with comparison to existing zirconia and 2f TDL sensors, and 2) part per million moisture measurement in a chlorine plant.

Oxygen in a Waste Incinerator. This is the most difficult application for combustion oxygen measurement at Dow Chemical (and for most chemical facilities). Due to

chemical attack on zirconium oxide sensors (ZrO₂), facilities either operate with extremely high maintenance costs (up to \$110,000 per year) or do not install any oxygen measurement at all. The poor reliability of available oxygen analyzers or the lack of an oxygen measurement results

in compromised efficiency and energy waste. This application was chosen as the initial test for the developed TDL analyzer due to the difficulty, with the theory that if this

measurement was successful, most if not all combustion and process oxygen measurements within a chemical plant would be possible.

During the 6 month trial the TDL analyzer had no failures and required no maintenance. This combined with improved performance over the ZrO_2 analyzers has resulted in Dow naming TDL as the most effective technology (MET) for incineration measurements. In addition since the project was completed Dow has ordered/installed 23 Analytical Specialties, oxygen TDL analyzers.

Moisture in Chlorine Production. Moisture in Cl_2 is a critical measurement due to the impact of moisture on process quality and system corrosion. Due to the aggressive nature of the process most moisture measurement systems are not suitable. The industry standard has been electrochemical P_2O_5 sensors.

In addition to high installation and maintenance costs, P_2O_5 sensors are very slow to respond to moisture and recover from moisture exposure. This results in long periods of undetected moisture contamination which results in off-spec product (wasted energy in processing) and system corrosion (wasted energy in producing new process piping and components).

TDL technology offers two major benefits for this measurement; 1) speed of response and recovery is typically <10seconds, and 2) installation and maintenance costs are reduced, allowing for more measurements and improved process control.

This measurement was chosen as a test site for the TDL H_2O measurement again due to the aggressive nature of the process as well as the potential energy and efficiency savings.

During the pre-field testing (data below) and 6 month field trial the TDL analyzer proved the ability to detect moisture breakthroughs that were not seen by the existing analyzers. In addition during the 6 month trial and subsequent >8 months of process operation no maintenance has been required for the TDL system. As a result Dow has ordered the

commercial version of this system from ASI and has named the Analytical Specialties TDL as the MET for moisture in chlorine measurements.

The stated measurement need from the customer was that any moisture analyzer must

respond to 5ppm assault within 5 minutes. The graph shown here illustrates one of the key benefits of TDL for this analysis.

For the test, both the P2O5 analyzer and ASI TDL

analyzer were measuring a 0.7ppm standard. At 12:04 a 4.91ppm (cylinder value) standard was applied to both the P2O5 and TDL analyzers for one hour.

- The ASI TDL T50 response was 30seconds, T90 response was 60seconds.
- The P2O5 reached T50 in ~55 minutes. T90 response was not reached within the hour of gas exposure

At the end of the one hour run with 4.91ppm both analyzers were exposed to 8.2ppm for one minute.

- The ASI TDL reached T90 response within the one minute exposure
- The P2O5 sensor showed no response at all.

Both analyzers were then returned to the 0.7ppm standard for one hour:

- The ASI TDL recovered to T10 (3.8ppm drop in reading) in 4 minutes.
- The P2O5 sensor had only dropped in reading by 0.6ppm after one hour, additional test data from the customer has shown that full recovery from moisture assault can take hours for <10ppm and 1 or more days for >100ppm assaults.

C. Task 2 – Sensitivity Enhancement

Original Hypothesis. In order to achieve sensitivities required for impurity analysis in many chemical processes, sub-part per million (ppm) detection limits must be possible. To date the majority of these measurements are performed by gas chromatographs (GC). With GCs the typical response time for a sub ppm measurement is >5 minutes, this results in no measurement of transient process events, or in-accurate measurements of longer lasting events. The result is that off-spec product is missed during processing and not identified until final product measurements. Off-spec product either has to be recycled through the process (wasting energy used for processing), or in most cases sent to flare for disposal (feedstock energy and processing energy wasted).

For improved process control and energy efficiency a faster measurement time is needed.

Approaches Used. For technology development the application chosen was measurement of acetylene (an impurity in ethylene) at the hydrogenation reactor.

Acetylene Converter Flow Diagram

For this application the requirement is to accurately measure acetylene in a complex background gas mixture (with spectral overlap) with sub-ppm detection limits in less than 10 seconds.

The technology chosen to develop and test was ICOS (integrated cavity output spectroscopy), developed by Los Gatos Research, Inc. The optical bench (below) was supplied by Los Gatos and incorporated into a Process Analyzer package by Analytical Specialties.

The ICOS technology uses a tunable diode laser which is coupled to a gas flow cell that contains highly reflective mirrors. The laser beam reflects hundreds or thousands of times within the flow cell to provide up to 1000's of meters of pathlength. This provides pathlength and sensitivity enhancement orders of magnitude higher than standard TDL analyzers.

Off-Axis Integrated Cavity Output Spectroscopy

ASI integrated the ICOS into a package suitable for field installation (area classification, ambient conditions, etc.). The electronics package and software platform from the TDL portion of this project was adapted for use in the ICOS analyzer after having proved reliability and functionality in TDL field testing (Task 1)

Pre-Field Testing. Prior to field testing, extensive evaluation was performed. One of the most significant issues was to test the mirrors used in the ICOS system to determine if they would survive process gas exposure, of concern was if fouling would occur and the effect on the measurement. A “dummy” sample cell was created to hold the mirrors and installed in the field with process gas supplied by a typical GC sample system. The mirrors were removed after 1 week, 1 month and 6 months of gas exposure, tested, and without cleaning re-installed on the process. After a total of 7 months + 1 week of gas exposure the mirror loss increased from 140ppm per pass to 143ppm per pass, this was well within requirements and met the go/no-go requirement for full analyzer field testing.

APPLICATION FEASIBILITY STUDY

POTENTIAL MIRROR FOULING TEST

DOW

Parameter	Value
Mirror Loss Before	140ppm/pass
Test Duration Periods	1week, 1month, 6 Months
Mirror Loss After	143ppm/pass

In addition, extensive drift, linearity and sensitivity tests were performed at ASI and Dow to compare results to the current GC technology used.

PROTOTYPE OFF-AXIS ICOS

LAB PERFORMANCE VALIDATION

DOW

GC Vs OFF-AXIS ICOS**MEASUREMENT SPECIFICATIONS**

Acetylene (Sep 5-20, 04)					
BOC Reported (ppm)	ICOS Ave. (ppm)	Precision @ 95% RSD (± ppm)		Accuracy/Bias (± ppm)	
		ICOS	* Expected GC Spec.	ICOS	* Expected GC Spec.
0.50	0.49	0.03	0.06	0.01	0.08
0.96	0.88	0.07	0.06	0.08	0.08
0.99	1.02	0.04	0.06	0.03	0.08
1.48	1.51	0.07	0.14	0.03	0.20
2.86	2.58	0.06	0.14	0.28	0.20
8.00	7.74	0.14	0.14	0.26	0.20

Methylacetylene (Sep 5-20, 04)			
BOC Reported (ppm)	ICOS Ave. (ppm)	Precision @ 95% RSD (ppm)	Accuracy/Bias (± ppm)
1017	1020.9	5.8	3.9
1021	1021.1	13.9	0.1
3022	3082.3	63.0	60.3
5349	5144.0	130.7	205.2

As can be seen the precision and accuracy of the ICOS analyzer was as good or improved over the GC. This met the second go/no-go requirement for field installation and testing.

Field Testing. The analyzer supplied by ASI was installed for a 6 month field trial side by side with the existing GC with data fed to the plant control system for comparison. Below are trends of the two analyzers with a description of the trends.

As seen the ICOS analyzer measured the acetylene excursion above the process limit

GC Vs OFF-AXIS ICOS**RAPID ANALYSIS ALLOWS CONTROL**

of 1.5ppm >10 minutes prior to the GC.

In addition, since the GC does not provide a continuous update but rather one measurement every 5 minutes it only recorded one measurement above the process limit, before a second measurement could be made the process had recovered and the acetylene level was below limits.

For most process control systems at least 2 and often 3

measurements are required for a control change. In this case no action was taken since the GC (used for control) did not record two consecutive readings above 1.5ppm. With no control system change the excursion went through the process un-corrected.

If the ICOS analyzer had been used as the control input the excursion would have been measured >10 minutes prior to the GC with a second confirming measurement 7 seconds later, allowing control and reducing off-spec product.

Accuracy of the measurement is also improved significantly with near real time analysis. In this example the ICOS analyzer also recorded a transient methyl-acetylene spike while it was occurring where the GC did not respond until after the methyl-acetylene had already recovered to normal levels.

Another benefit if a near real time measurement is avoidance of feedback loops in the control system.

Problems & Departure from planned methodology - Impact on Project Results.
NONE

D. Task 3 – Multi-variate Analysis

Original Hypothesis. In order to widely apply laser based sensors into the chemical industry the analyzer must be capable of dealing with direct spectral interferences, and in some applications measuring multiple components. Commercially available laser sensors do not have the software or processing capability to apply chemometrics to allow these functions.

Approaches Used. The acetylene hydrogenation reactor measurement (using ICOS) was used as the test application to perform multi-variate analysis in an extremely complex background stream composition with multiple direct spectral interferences. In this application the analyzer measured both acetylene and methyl-acetylene (MA).

As can be seen, the acetylene (red) and MA (green) absorbance spectra is in a region that has significant absorbances from other hydrocarbons in the stream.

In order to deal with the interferences a chemometrics model was developed and integrated into the ASI ICOS and TDL software platform for this application and future applications

where modeling is required.

Since the hydrocarbon spectra resulted in broadband interferences the ICOS measurement was performed at sub atmospheric pressures. The hydrocarbon absorbances are then resolved, allowing the analyzer to measure them and apply the chemometrics model to compensate for their presence and changes in concentration.

The model was built using parent spectra for the interfering absorbers and subsequently

tested with varying compositions to prove the ability of the model to eliminate measurement errors from interfering background gases.

PROCESS OFF-AXIS ICOS

ON-LINE CHEMOMETRIC MODEL

Problems & Departure from planned methodology - Impact on Project Results -
NONE

E. Task 4 – Mid-Infrared Analysis

Original Hypothesis. At the time of the project initiation no commercially available lasers were available at 2300nm for the measurement of CO in combustion systems. The original plan was to employ mid-infrared lasers (quantum cascade) at 4.6 micron for this measurement.

The measurement target is large scale combustion systems such as process heaters and processing furnaces. Current practice is to install zirconia sensors to measure oxygen and

Rough control can be achieved using only an oxygen measurement. The "IDEAL" oxygen level can vary due to:

- > Load
- > Air quality (temperature, humidity)
- > Burner characteristics
- > Tramp air (erroneous reading)

to assign a best estimate setpoint based on excess oxygen. In order to truly determine the ideal excess oxygen set point a CO measurement is required (trim control) since the O2/CO cross over point can be effected by:

- Ambient air temperature and humidity
- Burner ageing
- Burner firing rate
- Burner ageing

In order to determine the optimum setpoint a sensitive (low-ppm) fast response, cross system measurement of CO near the combustion zone is required. This measurement will determine the lowest excess air operating point by measuring CO breakthrough.

Current technologies such as NDIR and thick film sensors do not have the required sensitivity (1-2ppm) or the ability to be installed in the combustion zone.

Laser based sensors are a good candidate for this measurement since they have 5-10 second response time, low-sub ppm detection limits and can be applied in a measurement across the entire combustion system, near the combustion zone.

Approaches Used. For this application the Tunable Diode Laser platform developed in Task 1 can be applied. With commercially available 2.3micron lasers from Nanoplus available there is no requirement to adapt for mid-infrared analysis.

Problems & Departure from planned methodology & Impact on Project Results.

Prior to actual work on the adaptation of the mid-infrared quantum cascade laser to the ASI TDL platform, we were informed by Nanoplus that 2.3micron near infrared DFB lasers would be available. It was decided to install the ASI developed TDL platform on an ethylene furnace in order to deal with the TDL platform issues while we waited for the availability of the 2.3micron lasers. The objective of the 6 month field trial at Dow's LHC8 ethylene furnace was:

1. Develop and test optical design to enable measurement across a 20 meter pathlength
2. Test the system mechanical and alignment stability during furnace de-coke operations (largest furnace temperature swing)
3. Develop and test optics to allow measurement of the laser in a highly radiant environment (firebox)

All 3 objectives were met with one loss of measurement during a tropical storm due to analyzer alignment shift. Post test the analyzer alignment mechanism was adapted to allow larger detect side aperture as well as larger diameter locking bolts for the alignment mechanism.

The analyzer is currently being fitted with the 2.3micron DFB laser for re-installation on the ethylene furnace and completion of field tests. These tests are being carried out with funding from Dow and ASI.

F. Task 5 – Identify Additional Applications

Original Hypothesis. With a properly developed platform for both TDL and ICOS techniques it was anticipated that a number of additional applications would be well suited for these technologies.

As the largest Chemical company and the largest user of on-line process analyzers, Dow Chemical is well suited to review applications, especially those with energy savings opportunities, and determine which would benefit from these developed technologies.

The laser sensor technologies are also well suited for adaptation to new applications since in most cases only a change in laser wavelength is required to measure different gases. Also, oxygen, moisture and carbon monoxide (three of the tested applications) are the most commonly measured gases in most chemical processes with large energy savings potential beyond the goals of this project.

Approaches Used. In order to evaluate further applications, Dow used existing survey data from global operations. This data included the process type, gas measured, application details and current technology used for the measurement.

Within Dow, globally a total of 779 (551 in US) potential applications have been identified for the TDL and ICOS technologies developed under this project. Additional applications are still under review and the target list is expected to grow.

Dow has also performed additional field trials outside of this project where the TDL technology has been successfully tested.

Analytical Specialties has also met with >30 separate chemical facilities to find applications outside of Dow processes. From this data the following are the Chemical Industry targets for further application of the technologies developed in this project:

- ICOS measurement of ethylene impurities in final product (H₂O, CO, CO₂, NH₃, C₂H₂) to reduce off spec product recycling and destruction
- TDL measurement of oxygen in formaldehyde manufacturing for reactor control (inlet and outlet)
- TDL measurement of oxygen for reactor control in acetonitrile manufacturing
- TDL measurement of oxygen for process control in TiO₂ manufacturing
- ICOS measurement of H₂O in (proprietary) rubber manufacturing

Also a number of measurement outside of the Chemical Industry have been identified (gasoline refining in particular).

In addition to application identification and testing a collection of high resolution spectra has been performed for measurements in the Vinyl Chloride process. Additional high resolution spectra is currently being gathered for further application evaluation.

Problems & Departure from planned methodology & Impact on Project Results -
NONE

II. Solid State Sensors

Project Task	Objective	Application
1-Solid State Sensor Platform	In line and at line sensor platform to handle aggressive service, temperature, corrosives	NO _x for combustion control NH ₃ for SCR control Hydrogen for chlorine streams Lambda sensor for air-fuel ratio
	Signal processing and electronics to meet cost objective and to allow future multivariate analysis	All
2-Sensor Design	Sensor chemistry to modify existing sensor designs for Chemical Industry process and combustion measurements (designed for ambient analysis, medical, automotive, etc.).	NO _x for combustion control NH ₃ for SCR control Hydrogen for chlorine streams Lambda sensor for air-fuel

Tasks 1 & 2: Solid State Sensor Platform Development

Original Hypothesis

Reproducible product quality during thermal processing depends on the ability to effectively measure, monitor, and control process heating operations, thus minimizing product variability. This level of control requires reliable and affordable sensors and control systems that can withstand harsh environments without recalibration for a certain minimum time (on the order of one year). Better, low-cost sensors are needed to monitor important process parameters such as material property uniformity, temperature, heat flux, air/fuel ratio, process atmospheres (oxidizing and reducing), emissions, and shop floor infiltration, as well as to control burning and detect flames and flame stability. Some of the actions include optimizing process air-fuel ratios to reduce emissions, providing intelligent responses to process variability, and providing control actions to meet desired or predicted outcomes.

Key Barriers

- *Few direct process measurement sensors*
- *Few low-cost sensors that are rugged, accurate, non-intrusive, and easy-to-use maintain*
- *Excessive failures and inaccuracies of thermocouples and other sensors*
- *Inability to reliably monitor and control critical product parameters (temperature, chemistry, pressure)*

- *Inability to reliably control processes*
- *Lack of smart controls*
- *Lack of cost-effective flow control devices (e.g., air/fuel ratio control)¹*

With the exception of ZrO₂ sensors, solid state sensors are not available in the marketplace. The technical limitations preventing wide implementation are; (1) lack of process knowledge, by the solid state sensor companies, specifically application chemistry, (2) lack of sensor formulations to take existing measurements to the field, (3) lack of suitable design (form factor) that can be applied in-situ.

Our approach can be compared to that of zirconia oxide (ZrO₂) oxygen sensors. Before the early 70's, measurements of excess oxygen in combustion processes were made with spot checks, or using extractive paramagnetic or electrochemical oxygen sensors. The existing measurement technology was not suitable for in-situ analysis and suffered from slow response (inadequate for proper control), questionable measurement quality, and high costs per measurement. As a result many combustion systems (particularly smaller capacity) did not continuously measure oxygen and use it as a control input. In the early 70's, Westinghouse introduced the first in-situ ZrO₂ sensor for combustion applications. From 1973 to 1990, Westinghouse sold in excess of 80,000 analyzers, and ZrO₂ analyzers have become the industry standard for oxygen measurement in combustion processes. This in-line or at-line measurement technique offered improvements in measurement quality, speed, reliability, and low long-term cost of ownership.

The O₂-% measurement is an example of how a disruptive technology, that is in-situ with near real time response, has resulted in an enormous commercial success (market now estimated at \$90,000,000 per year) with an incredible impact on industry energy savings and process optimization. It is also an example of how the pre-existing O₂ analyzer market suppliers (Servomex, Teledyne) refused to implement a disruptive technology. It took Servomex more than 10 years to fully enter the market with a ZrO₂ sensor and Teledyne never has.

An important element of success is that these sensors must be integrated into form factors suitable for in situ analysis in demanding Chemical Industry applications. In addition to the form factor, it is also important to test the devices in controlled conditions that mimic real process conditions. To enable the testing and development of such sensors requires extensive laboratory facilities, designed experiments and field testing under conditions typically encountered in harsh industrial manufacturing of chemicals. Both of these elements were primary objectives in the development of solid-state sensors proposed here.

Technical hurdles include the development of sensors for several important analytes, including NO_x, NH₃, hydrogen, and air-fuel ratio. Other hurdles are the development of appropriate sensor chemistries for corrosive service, and the integration of sensors into a

form suitable for in situ process analysis. The fundamental issues are the development of appropriate sensor chemistry and integration into an in situ analyzer package.

Approaches Used

Our goal was to incorporate solid-state sensors in an analytical package that is close coupled to or directly inserted in the process. This approach is a standard practice for some combustion related measurements such as oxygen (using zirconium oxide sensors) and CO (using solid-state sensors). However, solid-state sensors, while becoming available, are not currently suitable for many of the PA needs. The primary limitations are in the areas of material compatibility and packaging into a rugged field grade instrument. The work breakdown structure for this approach is summarized in the table below.

Action	Target	Description	Go/No Go
Develop in-line and at-line sensor platform to handle aggressive service, temperature, corrosives	Robust, high temperature physical platform, software for signal processing, data transfer	This design will be the basic platform for all solid state sensors. Mechanical layout, process interface, signal processing, user interface, communications	The major decision will be in two areas; ruggedness and estimated future production costs
Hydrogen sensor	Design sensor for process conditions	H ₂ measurement in chlorine	Corrosion resistance, no interference from background
NO _x sensor	Design sensor for process conditions	NO _x in combustion gases, control input for combustion optimization and SCR control	Sensitivity (0.2 ppm), selectivity, robustness
NH ₃ sensor	Design sensor for process conditions	NH ₃ slippage from SCR systems	Sensitivity (1.0 ppm), selectivity, robustness
H ₂ O sensor	Design sensor for process conditions	Moisture in non corrosive gases	Sensitivity (0.2 ppm), selectivity, robustness
Lambda sensor	Design sensor for process conditions	Air fuel ratio	Estimated system cost

ASI developed a CCE (close-coupled extractive) system complete with internal heat distribution to enable the integration of sensor devices to be placed in-situ for process measurements. A multi-function sensor interface board was been designed and built and tested. An off line test protocol was compiled and distributed for review within Dow and Synkera. A meeting was held at Dow (Plaquemine), in early December 2004, with Dow, ASI, and Synkera in attendance. This meeting further defined the needs of the program, in regards to Synkera's sensor development and ASI's incorporation of those sensors into instrumentation. The majority of the time was devoted to the NO_x sensor; however, ammonia, hydrogen and humidity sensors were also discussed.

Using the Synkera NO_x sensors, it was determined that the CCE system performed well (both mechanically and electronically). However, the Synkera sensor elements did not provide the level of performance required to meet the present measurement needs. Some materials received from Ohio State University (OSU) were tested that allegedly overcame the drawbacks of the Synkera NO_x sensors. Dow assigned an engineer to perform further

work using the CCE system and ASI test facilities such that some initial OSU sensor testing was performed.

- Development of sensors for multiple analytes including NO_x, Oxygen, NH₃, Hydrogen, Air fuel ratio.
- Development of appropriate sensor chemistries for corrosive service.
- Integration of sensors into a form factor suitable for in situ process analysis.

The key issues were developing the appropriate sensor chemistry and integration into in situ analyzer package. Dow / Synkera developed and tested the suitable sensor chemistry, while ASI designed an acceptable form factor.

Hydrogen Solid-State Sensors. Initial H₂ sensors were formulated by Synkera. Dow completed initial tests in non-corrosive service. As anticipated, there are issues with the sensor's ability to withstand installation in an elevated temperature, corrosive environment. Under testing conditions, it was observed that the sensors suffered from:

- a. severe corrosion of the sensor's material of construction
- b. an oxygen dependency:
- c. a reaction with chlorine which destroyed the metal oxide matrix.

To counter these behaviors, all of the corrosion prone materials were replaced with Teflon[®] or gold, the metal oxide matrix which depended on a stable oxide-oxygen interface was replaced with a reversible palladium red-ox reaction between hydrogen and chlorine, and all of the electro-active components were protected by integrating the palladium into a novel in situ palladium-organic polymer. Applying these modifications, the original metal oxide semi-conductor high impedance chemi-resistive devices were transformed into low impedance amperometric devices.

However, the formulation proved to be incompatible with Cl₂ (the target application). Dow re-formulated and tested the Synkera H₂ sensors. Synkera, Inc. supplied hydrogen sensors based on Dow formulation for testing. The packaging for the hydrogen sensor was designed by ASI. Initial prototype sensors were fabricated, modified and then sent to Dow for inspection and testing.

One of the modified samples is shown in Figure 1.

Figure 1: Redesigned H₂ sensor for Cl₂ stream.

Dow/ASI completed initial tests in non corrosive service. Previously, field testing of the hydrogen sensors was initiated to determine lifetime, operating constraints, sensor performance under varying cell conditions, and calibration issues under field conditions. The electroactive film, interdigitated electrodes, and the other sensor head components held up well under cell conditions. However, it was discovered that there were issues with the electrical connections from the sensor to the transmitter leads.

The sensor's electrodes have printed gold pads which were attached via resistive welds to ¼" long gold ribbons. The other ends of the gold ribbons were resistively welded to 0.1 mm diameter gold wire which in turn was soldered to electrical leads which were attached to the electronic transmission board for signal detection. After only a few days, the resistive welds between the gold ribbons and wires lost integrity. It was also apparent that the fragility of the gold ribbon would become a long term issue. Any twisting of the wire during installation resulted in severing or breaking the very thin gold ribbon. Therefore, alternative methods for maintaining electrical connect were investigated. To address these issues, the following modifications were investigated:

1. Repeated attempts to improve the resistive welding technique between the ribbon and wire were unsuccessful.
2. Attempts to improve the anchoring of the gold wires to the Teflon[®] body by improving the epoxy technique failed.
3. Because the resistive welds between the gold pad and the gold ribbon appeared to be good, the weld, causing the concern, between the ribbon and wire was removed by extending the length of the ribbon and inserting it through a ceramic rod with four prefabricated holes. The ends of the ribbon were then crimped into an electrical lead, secured in PVC shrink tubing and anchored in place with epoxy. This eliminated the need for the Teflon[®] support body, minimized twisting issues and increased the durability of the ribbon. However, these improvements led to another problem.
4. Under chlorine operating conditions with high relative humidity and sensor temperatures above 125° C, water still condensed on the surface of the ceramic due to rapid heat loss from a heat sink effect. Chlorine dissolved in the water which had a higher conductivity than the film on the sensor. Therefore, where ever the gold ribbon touched the ceramic it contacted the thin water layer. Because a potential was applied to the sensor, the gold ribbon which was exposed to a positive potential dissolved and the electrical connection was severed. The sensor operating temperature for optimal electroactive film performance was determined to be between 125 and 150° C. Due to heat sink effects, this temperature is not enough to prevent water condensation on the ceramic rod.

5. To counter this, the gold ribbon was insulated from the ceramic using paraffin wax which was inserted into the ceramic around the ribbon and heated to form a barrier between the ribbon and the ceramic. This modification is now being evaluated in the chlorine cell lab. An additional improvement of inserting the gold ribbon into PVC shrink tubing and then inserting that into the ceramic prefabricated holes is also be evaluated.

From longevity tests using these modified sensors, it was found that part of the gold ribbon was still susceptible to electrochemical corrosion from condensables present in the wet chlorine stream. The sensor's heater was not powerful enough to heat the entire sensing tip. Therefore, PVC shrink tubing was placed around each gold ribbon and any exposed gold was covered with high temperature epoxy. Epoxy may not last long term, but it was felt that the concept may be tested while a more long term solution was found. In addition, a porous, semi-permeable TFE membrane was placed and mechanically anchored to the top of the sensing tip. Four of these re-modified sensors were tested under realistic conditions with the same chlorine stream. Each of the four sensors was tested using different heater temperatures, film thickness, applied potential or permeable membrane or not using experimental design procedures.

In addition, an attempt was made to prepare the electro-active polymeric film without using the tin oxide semi-conductor matrix as either catalytic or stoichiometric agent for polymerization. It was discovered that using a saturated solution of palladium dichloride in acetone in the presence of dilute aqueous hydrogen peroxide would also produce the electro-active polymeric film. Utilizing this method may expand the use of this type of film for other applications.

We tested the hydrogen sensor under plant operating conditions for about 3 months.

NOx Solid-State Sensors. We tested two different NOx sensor formulations, one from Synkera LLC (formerly Nanomaterials Research Inc.) and one from Ohio State University. The Synkera NOx sensor sensitivity is well below desired level (15-20x lower than any other commercial solid state sensor).

However, some issues for the Synkera sensor existed:

1. Relatively long response/recovery times;
2. Lack of recovery to baseline values (memory effect);
3. Temperature and pressure including flow rate effects;
4. RF electrical interference effects which include high noise to signal levels;
5. Sensitivity/reproducibility differences from sensor to sensor.

To understand these issues and off-line protocol was devised to evaluate the sensors under a number of variables to:

1. Simulate a realistic application environment
2. Electronically isolate the equipment/sensor

3. Implement/develop an interactive spreadsheet for fast/timely condition changes
4. Vary NO and NO₂ concentrations to establish limit-of-detection, etc.
5. Evaluate humidity and flow rate effects
6. Determine the minimum concentration of oxygen to insure long term and steady sensor performance

In order to carry out the test protocol, a testing facility was built which included a gas pre-heater, a humidifier with heater, a close-couple extractive cell to house the sensor, a series of mass flow controllers to insure adequate and constant flows for mixing and delivering the desired amounts of NO_x gas and pressurized gas standards, and computer control with data logging capabilities.

The NO_x sensors supplied by Synkera were tested for performance issues. Sensor characterization including surface area, particle and pore size determinations, and electrochemical properties was completed. Electronics issues including RF and other electrical interferences and static charge effects from flowing gases were addressed. Further testing to determine NO/NO₂ responsivity at various sensor temperatures, operating voltages, ambient humidity, flow rate effects, and interference from other gases present in the sample was also investigated. Six sensors were evaluated using the testing protocol in concert with an electronic and signal processing package which mimics a real installation.

Previously, NO and NO₂ showed unequal responses for similar concentrations. The presence of humidity remedied this for the most part. An alternate method to handle this inequity would be to pass the gas through a catalyst bed converting the NO to NO₂. However, the issue of long response/recovery times has lingered. Increasing the sensor's temperature led to improvements, but the best times were approximately 3 - 5 minutes at best which is still too slow. A time of 1 or possibly 2 minutes is preferred. In addition, it was observed that at these elevated temperatures, the semiconductor material lost its performance and structural integrity.

Faster establishment of the adsorption/desorption equilibrium between the NO_x and the active sites on the WO₃ is accomplished at higher temperatures in the presence of oxygen. During sensor fabrication, nanoparticle sized WO₃ is used to prepare a paste which is applied to the interdigitated gold electrodes on an inert substrate. This procedure may alter the size of the WO₃ particles by forming aggregates, etc. Under higher temperatures, one possible explanation is that the WO₃ matrix has changed enough to invoke faster equilibrium, or that more sites are now available. However, under these higher temperatures, the resistive heater could not maintain its integrity and failed after a few days. The following surface modifications to the matrix were investigated in an attempt to allow faster establishment of equilibrium without invoking these high temperatures:

1. Attempts with mechanical abrasive techniques to alter the matrix surface are very delicate procedures and have failed.

2. Surface modifications involving doping the matrix with an organo-tungsten complex solution followed by electrolytic oxidation in air was investigated. By oxidizing the tungsten complex in air may allow the formation of extremely small particles of WO_3 . The formation of these small particles may allow more active sites for the adsorption and desorption of NO_x without the application of high temperatures. The results were mixed and not conclusive. The baseline noise levels are very high but with the presence of NO_x , the noise is minimized.
3. Surface modifications involving doping the matrix with dilute hydrogen peroxide solutions were also studied. The idea was to refurbish the WO_3 matrix by chemically oxidization. So far, this has yielded the best results. The response times under ambient conditions and normal sensor temperatures have improved to approximately one minute, however the recovery times are longer- and not acceptable.

NO_x Sensor from Ohio State University (OSU). We completed testing a NO_x sensor from OSU. The form factor for this sensor is much less developed (it exists as a powder). Dow assisted ASI in packaging and testing of this sensor. An apparatus to house the powder and perform tests was completed. initial tests with the Ohio State sensor were as follows:

- oxygen dependency from 0-21%
- NO/NO_2 response ratios (not important here as a converter will be used)
- Test humidity dependence from 5-15% H_2O in sample
- Response/recovery times at 1,3,6,10,20,50 ppm NO_x
- Sample - ambient air - sample response
- Sample (typical combustion mix) - dry calibration gas - sample response
- Short term stability/linearity/accuracy (48 hours)
- Long term stability/linearity/accuracy (1 month-3 months)

NH₃ Solid-State Sensors. The goal here was an ammonia sensor with a lower detection limit of 1 ppm. Two sensors were provided to ASI for evaluation alongside the NO_x sensors in the CCE system. Initial NH_3 sensors developed by Synkera did not achieve the sub ppm sensitivity required. Our team addressed reliability issues related to thick-film sensing materials. Completed evaluation of modified sensor and finished reproducibility runs.

Lambda Sensors. The target application was measuring air-to-fuel ratio in important combustion processes (furnaces, boilers, fired-heaters, etc.). Synkera performed tests on a Ga_2O_3 based sensor for air-to-fuel ratio (Lambda sensor).

- *General Response to Combustion Gases.* The following measurements were made for increasing levels of combustibles and CO in air(21% O_2). These measurements were made using a sensor power of 1.8W. Note that the selectivity of the sensor can be changed by adjusting the sensor temperature (power input). It has been seen, and reported in the literature, that the response to CO is greater at lower temperatures and the response to CH_4 is greater at higher temperatures. This data was taken on the most recent sensors (produced under the DOE-OIT program) that have been packaged in what should be a more reliable manner than

the previous sensors (from DOE Phase II). Note that only a few measurements were made with these sensors as we were mainly interested in determining issues related to packaging. As such, this is preliminary data for the sensor and there are still packaging improvements to be made, application specific testing to be performed, and optimization of operating conditions to be determined.

Sensor Response in Air (1.8W, dry)

- Pre-Combustion Measurements. These measurements were made with the same sensors as above. Varying air-to-fuel ratios were tested. Measurements were made at two different temperatures (powers) and also in dry and humid gas. The source gases were air and methane. The sensor resistance in air is noted on each plot.

- *Response Time.* The response times below have been calculated from the same data sets used to create the above plots. The testing segments used to perform the calculations are provided for reference.

Pre/Post Combustion	Power	Gas	Step	T ₉₀ (sec)	T ₅₀ (sec)
Pre	2.0 W	CH ₄	$\lambda = 1.1$ to 1.0	60	15
Post	1.8 W	CH ₄	1000 ppm to 5000 ppm	60	20

Problems & Departure from planned methodology.

With exception of a generic close-coupled extractive housing and electronics interface, there were significant issues with all of the solid-state sensor devices we sought to

develop and test. Ultimately, these issues were roadblocks that prevented further development and testing. These are summarized in the table below.

Action	Description	Technical Road Block
Hydrogen sensor	H ₂ measurement in chlorine	inability to eliminate chlorine interference with the hydrogen sensor
NO _x sensor	NO _x in combustion gases, control input for combustion optimization and SCR control	Inadequate response and recovery times
NH ₃ sensor	NH ₃ slippage from SCR systems	Poor sensitivity, and was a “sister” measurement to NO _x (i.e. not useful without NO _x measurement).
H ₂ O sensor	Moisture in non corrosive gases	Poor sensitivity, selectivity, drift
Lambda sensor	Air fuel ratio	Complicated packaging issues (requires high temperature heater which poses safety issues in target application)

These problems forced us to cancel further work for each of the original solid-state sensor targets (H₂, NO_x, NH₃ and Lambda).

Impact on Project Results.

The fundamental limitations of available sensor materials that we identified, formulated and tested were overwhelming. This situation forced our team to cancel these portions of the project and focus our resources on laser-based sensor techniques. The barriers of material compatibility, sensitivity, speed of response, chemical interferences, etc. are surmountable in the field of solid-state sensors. Inability to address any single one of these attributes will prevent wide-implementation into this market. This situation is plainly evident by the lack of such devices in the online analyzer market (for petrochemicals).

Publications.

Three conference presentations have been made based on the results of this project:

Papers presented at 2006 IFPAC conference

- Practical Application of TDL Analysis In Aggressive Applications
Trevor Knittel, Alan Cowie, Jie Zhu, Don Wyatt, Analytical Specialties, Inc., Houston, TX and J.D. Tate, Dow Chemical, Freeport, TX
- Rapid Online Analysis of Acetylene in Hydrocarbon Streams
Linh Le, J.D. Tate, Dow Chemical, Freeport, TX, Trevor Knittel, Alan Cowie, Jie Zhu, Analytical Specialties, Inc., Houston, TX

Paper presented at AIChE Ethylene Producers Conference, 2006

- Rapid Online Analysis of Acetylene for Improved Optimization of Hydrogenation Reactors
Linh D. Le, J.D. Tate, Mary Beth Seasholtz, Manish Gupta, Doug Baer, Trevor Knittel, Alan Cowie, Jie Zhu

Web site or other Internet sites that reflect the results of this project;

Detailed descriptions of the technologies commercialized as a result of this program can be found at www.analyzer.com, Analytical Specialties, Inc. website.

Information is available on the commercialized TDL and ICOS laser based sensor platforms.

Also available is the Dow paper presented at the Ethylene Producers Conference
http://www.analyzer.com/viewPDF.aspx?file=/assets/PDF/presentations/Paper_Presented_by_Dow_Chemical-New_Tech_Advances_In_Vibrational_Spectroscopy_for_Process_Analytical.pdf

Networks or collaborations fostered;

Los Gatos Research collaborated in the development of the ICOS laser based sensor. They are also extensively involved in current commercialization efforts and development of further applications for the technology.

Rice University Laser Sensor Group (Prof. Frank Tittel et al) are also actively involved with Dow and ASI in further development of laser based sensor projects

Technologies/Techniques Developed;

The most significant impact of this project is the development and subsequent commercialization of two new laser based sensors.

The TDL platform developed and subsequently commercialized by Analytical Specialties (tradename TruePeak TDL) has already achieved significant commercial success with >60 units built and sold to date (less than one year post project). Orders have been received from Dow, BP, Innovene, Kerr McGee, Hunstman Chemical and others. For the first time a commercially available TDL analyzer is available that can be applied widespread within the Chemical industry. Key to the success of this product/technology has been the development of the laser platform for aggressive service as well as the ability to perform peak area integration in complex applications.

The ICOS platform developed under this program has also been commercialized with the first production version analyzers shipped to Dow Chemical. ASI has received application request from 9 chemical companies representing >15 additional applications that are being evaluated for the ICOS platform.

Inventions/Patent Applications and Licensing Agreements

Two patents have been filed during the contract and notification to DOE office has been made. The titles are: Spectroscopic Analysis and Control; and Excess Air Control for Cracker Furnace Burners. A patent certification has been filed with the DOE.

This intellectual property is being licensed to Analytical Specialties Inc., a sub-contractor on this contract.