

**Innovations Deserving
Exploratory Analysis Programs**

IDEA

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High-Speed Rail IDEA Program

Continuous Locomotive Emissions Analyzer

Final Report for High-Speed Rail IDEA Project 29

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TRANSPORTATION RESEARCH BOARD
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INNOVATIONS DESERVING EXPLORATORY ANALYSIS (IDEA) PROGRAMS MANAGED BY THE TRANSPORTATION RESEARCH BOARD

This investigation was performed as part of the High-Speed Rail IDEA program supports innovative methods and technology in support of the Federal Railroad Administration's (FRA) next-generation high-speed rail technology development program.

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Continuous Locomotive Emissions Analyzer

IDEA Program Final Report

for the period December 2000 through January 2002

HSR-29

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TABLE OF CONTENTS

EXECUTIVE SUMMARY	6
IDEA PRODUCT	8
EXPLANATION OF PROJECT GOALS.....	9
EMD REQUIREMENTS FOR SENSORS INCLUDING OUR NO_x SENSOR.....	9
CHEMICAL SENSING TECHNIQUES CONSIDERED FOR DIESEL EMISSIONS TESTING....	10
IMS TECHNOLOGY - PRINCIPLES OF THE INNOVATION	11
ION MOBILITY SPECTROMETRY (IMS)	11
SOLID ELECTROLYTE	11
PROTON AND ELECTRON AFFINITY SCALES	13
MEMBRANE INLET	13
CHOICE OF AN IONIZATION SOURCE	14
HARDENING THE RADIOACTIVE SOURCE.....	15
MOLECULAR ANALYTICS IMS CELL USED IN THIS APPLICATION	15
MOLECULAR ANALYTICS ALGORITHM.....	15
MOLECULAR ANALYTICS IMS ANALYZER SPECIFICATIONS	16
UNIQUENESS OF THE IDEA PRODUCT (IMS NO_x SENSOR) FOR APPLICATION TO PRACTICE.....	16
INVESTIGATION	16
SUMMARY OF STAGE I WORK	17
STAGE II LABORATORY TESTING	19
SUMMARY OF METHOD AND EQUIPMENT.....	19
RESULTS.....	20
COMPARISON TO THE IMS	21
COMBINED RESULTS.....	22
DATA EXPLANATIONS	23
STAGE II NO CONVERTER TESTING.....	23
EXPERIMENTAL ANALYSIS AND RESULTS	25
STAGE III WORK.....	28
TEST SITE	28
EXPERIMENTAL SETUP	29
IMS CALIBRATION	30
CHEM I CALIBRATION	30
FIRST TEST SESSION	30
IMS DATA	30
COMPARISON TO CHEMILUMINESCENCE ANALYZER	32
DILUTION TEST	32
SECOND TEST SESSION	33

Executive Summary

The objective of this project was to evaluate the use of Ion Mobility Spectrometry (IMS) sensors to continuously monitor NO_x levels in the exhaust stream of diesel electric locomotives. The output signals from such sensors could potentially be used as input to a system that continuously controls injector settings to achieve an optimum balance between engine efficiency and exhaust emissions. The IMS-based system, shown in Figures 1 and 2, could adjust engine parameters to maximize engine efficiency while meeting EPA NO_x emission standards. Laboratory tests conducted during this project provided some preliminary indication that the IMS has potential for incorporation into this type of system. However, the results of full-scale testing of the sensors on a stationary 1500 horsepower diesel engine proved inconclusive due to problems with calibration procedures and data collection equipment.

This research was conducted as a result of new standards adopted by the Environmental Protection Agency (EPA) in 1997 in an effort to reduce diesel locomotive emissions. Included in these standards are regulations on NO_x emissions. Despite these EPA regulations, currently there are no continuous locomotive emissions monitors on the market. In addition to environmental concerns, fuel economy, which is a significant portion of operating expenses, is of great concern. A NO_x regulating system has the potential to help maintain or lower NO_x emissions while improving fuel efficiency.

IMS sensor technology is a reasonable option for consideration in locomotive engine emissions controls because of its applicable characteristics. It has a very fast response time, between 40 and 1000 milliseconds, and a reasonable limit of detection and dynamic range. It is also inexpensive and relatively small using resources readily available on a locomotive. Most importantly, IMS responds accurately to changes in overall NO_x concentration.

IMS sensors consist of a reaction tube and a drift tube, separated by a shutter grid (Figure 1). Exhaust gas entering the reaction tube is ionized, and the ions are gated into the drift tube through the shutter grid. The ions are drawn down the drift tube toward a Faraday cup where they impact a metal plate and transfer their charge, creating an electric current. This current is amplified and digitized, and the analysis of this signal can be translated into concentrations of NO_x.

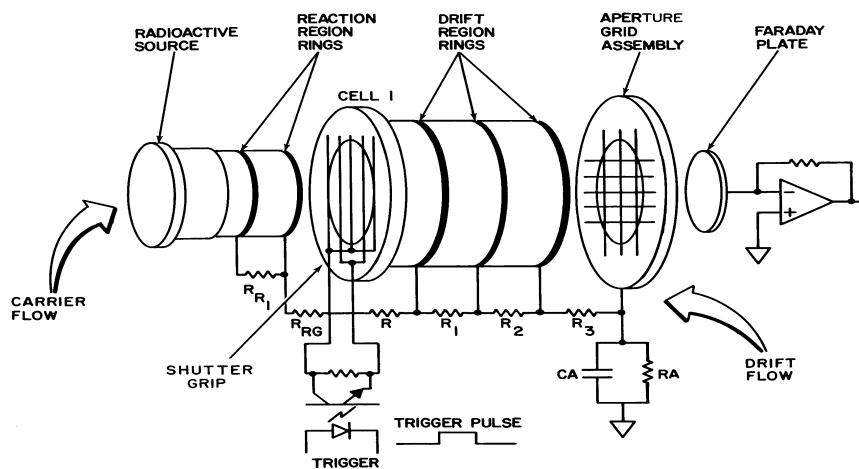


Figure 1 - Conventional IMS Cell

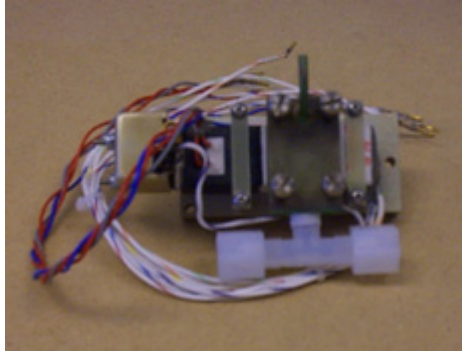


Figure 2 – Modern IMS Cell (Molecular Analytics)

Preliminary Findings and Recommendations

Preliminary laboratory investigations, though inconclusive, suggested that the characteristics and performance of IMS sensor technology show promise for instantaneous monitoring of diesel exhaust streams to determine concentrations of such constituents as NO_x. The results of the full-scale testing on a 1500 horsepower stationary diesel engine could not be properly interpreted due to problems with the calibration equipment and data recording equipment. Unfortunately, these problems were not discovered until after the tests were conducted, and remaining project funds would not permit a repeat of these tests. Based on the potential of IMS sensor technology for such applications, further testing and evaluation of this concept deserves consideration. Such testing should use the latest developments in IMS sensors, and a rigorous test protocol should be designed and followed. Such protocol should include comprehensive laboratory and Diesel engine test procedures that specify data to be collected, sample size, data collection and analysis procedures, and instrumentation calibration procedures.

IDEA Product

This IDEA project represents the first step in developing a control system for Diesel-electric locomotives. Scentzar Corporation and our teammates at HRL have the ultimate goal of developing the control system illustrated in Figure 3. The product of this is a preliminary assessment of a candidate sensor technology, Ion Mobility Spectrometry (IMS), for a Diesel engine control system. Major components that must be developed in order to implement the complete system and any progress made on each component in our phase I work are listed in table 1.

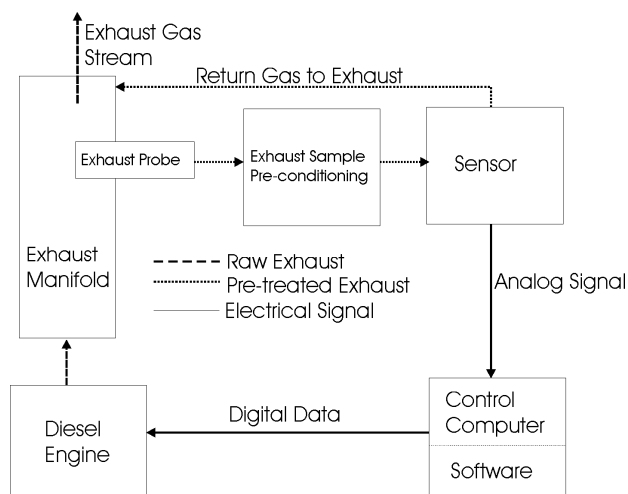


Figure 3 – NO_x Control System For Diesel Locomotives

Table 1 – Components that must be developed for the locomotive control system

Component	Description	Relevance of This Project
Gas Sampling System	The gas sampling system draws sample from the Diesel engine exhaust and pre-processes it prior to the NO _x sensor.	We began development of a gas sampling probe during this study.
NO _x Sensor	The NO _x sensor will measure NO _x concentration in the exhaust manifold in real time as input to the control system.	We evaluated IMS as the NO _x sensor.
Control Computer	The control computer will be a “black box” installed in the locomotive that collects sensor input, implements the control algorithm embedded in control software, and controls the actuators that adjust engine parameters through an electrical interface to the actuators.	We researched basic engine control strategies. Table 3 summarizes the engine variables that might be adjusted in the final system.
Control Software	Control software using a specialized control language will implement the control algorithm that continuously sets the actuators based on sensor data and control logic.	We gained valuable experience on the engine parameters and how we might vary them in the control system.
Actuators	Electro-mechanical actuators will be required to interface the computer output to Diesel engine electrical and mechanical components.	We did not address actuators during this project.

The product of this study was the development of a first concept, backed up with laboratory test data on a particular IMS sensor. When the final control system is implemented it will allow high-speed railroad operators to more cost-effectively operate their system while preserving the environment.

Explanation of Project Goals

A real-time control system can only function properly if its sensors are compatible with the requirements of the control system. The characteristics in Table 2 can be applied to a sensor or to the entire measurement element of a control system including gas processing and inlet. Measurements made to determine the characteristics of a sensor must be extrapolated to account for the entire measurement element. For example if the sensor consists of an infrared bench, which is very sensitive to water vapor, a drying step will be required prior to the sensor element. If the target chemical gets caught in the dryer the response time and clear down time of the measurement element will be significantly longer than that for the sensor.

We proposed using Ion Mobility Spectrometry (IMS) as our baseline sensor for this application because it has characteristics that make it a good choice as a real-time control system sensor. Figure 4 illustrates the characteristics of a typical sensor. Table 2 defines the characteristics and gives typical values for IMS.

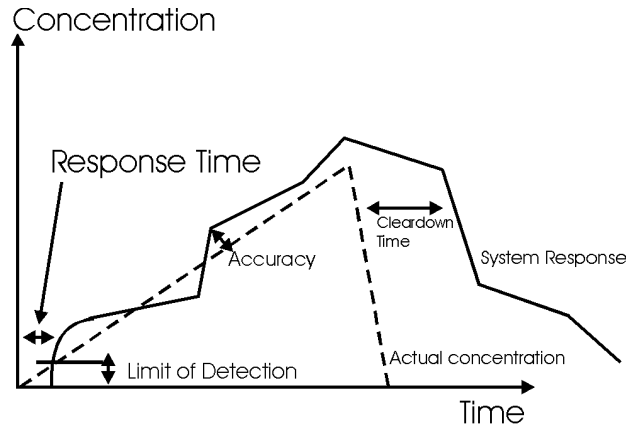


Figure 4 - Chemical Sensor Performance Characteristics

Table 2- Defining Sensor Performance Characteristics

Characteristic	Definition	Typical IMS
Response Time	The time it takes from the introduction of a step function of target gas until the sensor responds at a fixed percentage (say 90%) of the correct reading.	Between 40 milliseconds and 1 second
Limit of Detection	The smallest concentration of material to which the sensor will respond.	Potentially parts per billion.
Accuracy	The maximum deviation of any concentration point from the calibration curve or response curve.	2 %
Dynamic Range	Saturation concentration as a multiple of Limit of Detection	200
Cleardown Time	The time it takes the unit to return to a percentage (say 10%) of its zero once the sample gas stream has been removed from the inlet to the sensor.	1 second
Response to co-existing gases and humidity	Most sensors will have some response to other gases besides the target gas (NO _x in our case). These gases and the response must be known before a sensor can be applied to an application.	May respond to aldehydes

EMD Requirements for Sensors including our NO_x Sensor

This study, funded by the National Academy of Sciences as part of the IDEA program, is part of a larger effort by General Motors EMD and HRL LLC to evaluate several exhaust sensors for Diesel

locomotive application. Table 3 describes the sensor requirements initially presented to HRL and Scentczar by EMD prior to this study. These requirements have not been modified during the study.

Table 3 – Composite Locomotive Emissions Monitor Specifications including NO_x Analyzer

Specification	Requirement	Source
Performance		
Measure NO _x , particle emissions, carbon monoxide (CO), total hydrocarbons (HC), and opacity	Adjust engine to minimize fuel consumption while meeting requirement on locomotive emissions based on 40 CFR 92.	EPA (40 CFR 92)
Measured Variable	Mass of pollutants in grams/hour in order to demonstrate compliance with 40 CFR 92.	EPA (40 CFR 92)
Response Time	8-10 msec.	EMD
Environment		
Operating temperature	-40 ⁰ C to 700 ⁰ C	EMD
Sampling Stream Characteristics		
Pressure	Exhaust pressure up to 100 inches of mercury absolute	EMD
Anti-Fouling	1) Capable of operation after recovery from coating with lube oil from prolonged engine operation at high speed without load. 2) Capable of operation after cold start-up at idle. 3) Capable of operation after cold start-up at idle.	EMD
Mounting	Mounted on the interior of the exhaust manifold upstream of the engine turbocharger.	EMD
Reliability/Maintainability		
Lifetime	> 80,000 hours	EMD

This study only deals with measuring one of the control variables -NO_x. Future research should investigate other sensors for the other gases and particulates.

Chemical Sensing Techniques considered for Diesel Emissions Testing

Table 4 lists the technologies initially considered for Diesel locomotive emissions testing by HRL in conjunction with EMD and subsequent recommendations to EMD provided at the beginning of the work with the Transportation Research Board (TRB) IDEA program. Scentczar, a subcontractor to HRL on the EMD work, chose IMS because Scentczar employees had previous experience with the technology. Note that we have found that a simple dilution system can convert NO to NO₂.

Table 4 – Technologies chosen for Evaluation including IMS

Technology	Description	Applicability	Recommendations
Ion Mobility Spectrometry (IMS)	Uses a radioactive source or photoionization source to ionize sample at atmospheric pressure and then separate it in a drift tube.	Has the required response time. Must develop a pre-processing step to convert NO to NO ₂	Scenczar Corporation, an HRL subcontractor, has an HSR-IDEA contract to evaluate IMS for this application.
Chemiluminescence	Converts NO ₂ into NO and then counts photons as NO is converted back to NO ₂	Is the standard instrument for this measurement. Does not respond as quickly as IMS. Complex instrument requiring an ozone generator.	Literature search to evaluate existing instruments.
Near Infrared (NIR)	Uses Near Infrared Spectra of NO and NO ₂	May find reasonable NIR spectra for compounds in Diesel exhaust. May be possible to use as an in-situ device.	Perform tests with a NIR spectrometer at HRL.
Solid electrolyte	Uses electrochemical reaction across a solid membrane that produces a tiny electric current.	May be possible to insert small sensor in exhaust system. Electrochemical sensors tend to respond to co-existing gases such as carbon monoxide or sulfur dioxide.	HRL to evaluate this technology in the laboratory including the Horiba solid state sensor used for Diesel trucks.

Chemiluminescence analyzers and Infrared analyzers were dropped from the competition because it was felt that they could not be made cost-competitive with IMS and solid electrolyte sensors.

Preliminary Conclusions:

- Two technologies, IMS and solid electrolyte, appear promising after initial testing by Scenczar and HRL solid state sensor testing funded by EMD
- These technologies deserve further evaluation.

IMS Technology – Principles of the Innovation

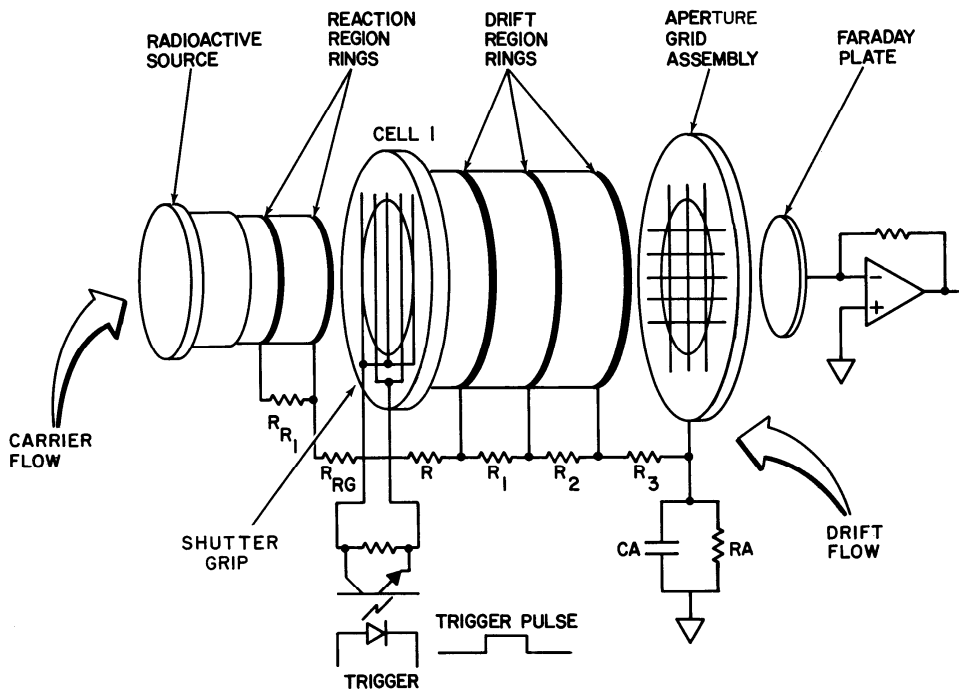


Figure 5 - Conventional IMS Cell

Figure 5 illustrates a conventional IMS cell. The IMS cell consists of two major components: 1) a reaction region, and 2) a drift tube. Sample gas enters the reaction region in the carrier flow and is ionized by the radioactive source. Ions formed from ion-molecule reactions are gated into the drift tube through a shutter grid. When ions enter the drift tube they are drawn down the tube toward a Faraday cup where they impact a metal plate and transfer their charge creating an electrical current. The electrical current is amplified and digitized to form an ionogram or simply a signature. Figure 6 illustrates two idealized IMS signatures: one in the positive mode in which positive ions drift down the drift tube, and one in the negative mode in which negative ions drift down the drift tube.

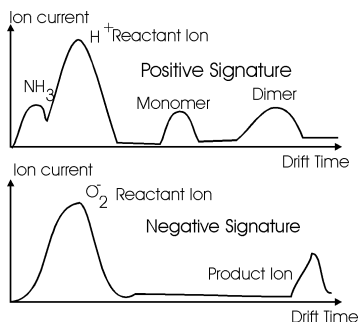


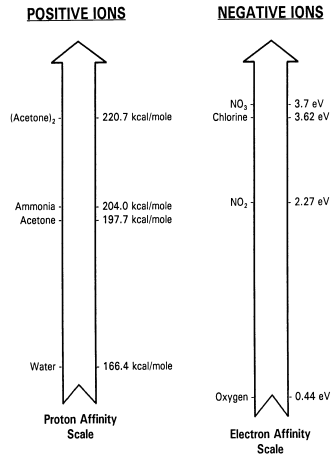
Figure 6 - Idealized Positive Mode and negative Mode Signature

Chemicals are separated in IMS in two ways: 1) by their proton and electron affinities, and 2) by their time of flight as they drift down the drift tube. Both of these mechanisms are important in achieving a satisfactory separation.

Proton and Electron Affinity Scales

Ions are created in the reaction region by undergoing ion-molecule reactions. When a radioactive source is used directly in air, for example, water molecules are first ionized forming the positive reactant ion H^+ and the negative reactant ion O_2^- . These reactant ions are illustrated in Figure 6. The water ions react with trace chemicals in the air stream transferring their charge to the molecules with the highest proton affinity in the positive mode and the highest electron affinity in the negative mode. The product ions form peaks that often consist of monomers and dimers in the positive mode and consist of single peaks in the negative mode. Figure 7 illustrates the proton and electron affinity scales. Note NO_2 is a negative ion. One of the issues raised by the panel for this project was that there could be safety concerns over the use of a radioactive source even though the source is well shielded in the IMS cell housing. Because the radioactive source may not be acceptable in the final product, future work may be required to modify the reaction region of our IMS cell to accommodate a photoionization source. This will change the reaction chemistry because a photoionization source is not as energetic as a radioactive source.

REACTION CHEMISTRIES



F
Figure 7 - Scales

Membrane Inlet

In air sampling applications and stack monitoring applications such as our Diesel-electric locomotive application a membrane inlet is used in front of the IMS cell. An IMS cell with a membrane inlet is illustrated in Figure 8.

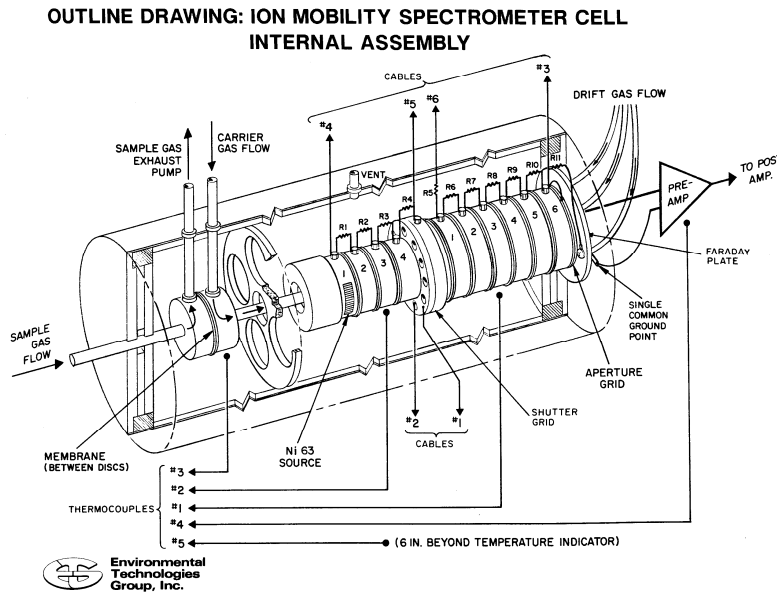


Figure 8 - IMS Cell with Membrane Holder in Front

Diesel engine exhaust enters as sample gas and passes over a membrane before being returned to the main exhaust stream. A separate airflow passes over the inside of the membrane and into the reaction

region. The advantage of the membrane inlet is that it controls the amount of humidity entering the IMS cell and blocks particulates. These two components of our sample gas stream will be important.

Choice of an Ionization Source

Ion Mobility Spectrometry (IMS) requires an ionization source to ionize molecules in the incoming sample gas stream commonly called the carrier gas. After ion-molecule reactions take place in the reaction region of the IMS cell, ions can be moved down the drift tube and separated because they carry either a positive or negative electric charge and can be easily move through an electrostatic field. The IMS detection strategy based on this phenomenon is illustrated in Figure 9. Typically, with a radioactive ionization source for example, water in the incoming carrier gas stream is ionized because of its prevalence and collision cross section. The water ions transfer their charge to dopant molecules injected into the gas stream to produce a new reactant ion with a carefully chosen characteristic. The characteristic is that the

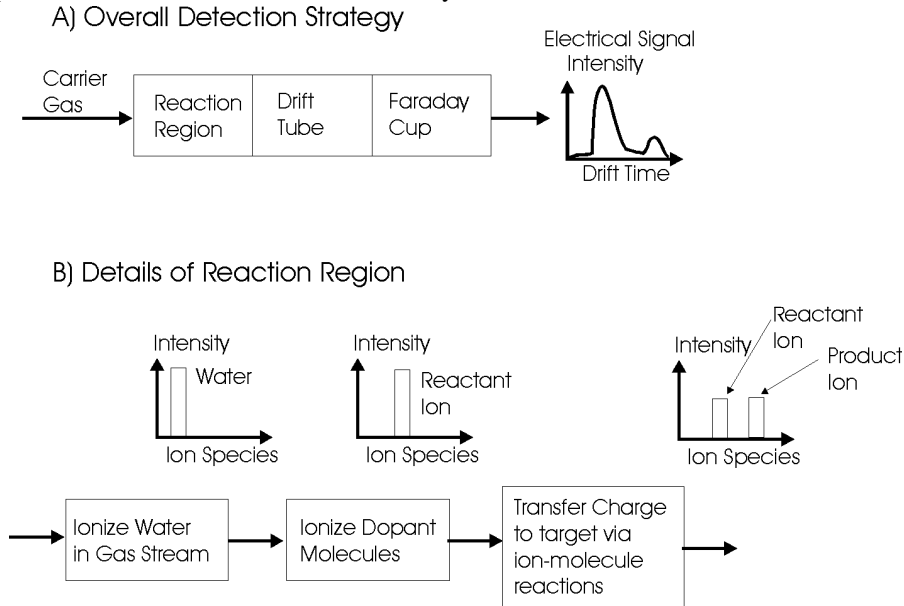


Figure 9 - Ion-Molecule Reactions are important to IMS operation

reactant ion will transfer its charge to a target molecule but to as few other molecules as possible. As the target gas, in this case NO_2 , enters the stream it will “steal” charge from the reactant ion reducing the number of reactant ion molecules and produce new product ion molecules at the expense of the reactant ion molecules. This situation is illustrated in Figure 9-B. The Molecular Analytics IMS algorithm uses the ratio between the reactant ion and product ion, as illustrated in Figure 9-B, to determine NO_2 concentration.

Any ionization source produces some ionizing radiation and has some health or safety risk associated with it. Ionizing radiation may be from nuclear radiation (alpha, beta, gamma, X-ray), ultraviolet light, or an intense electrostatic field (corona discharge). A radioactive source might produce actual and/or perceived health hazards. One of the items that will be required in any follow-on work will be to resolve this issue. There are two approaches to addressing the health hazard concern: 1) adapt a non-radioactive source to NO_x detection thus eliminating a radioactive source entirely, or 2) sufficiently harden the radioactive source so that it will require no tracking, special handling or labeling. Both approaches are technically feasible.

There are two commonly-used alternatives to radioactive source ionization: 1) a photoionization source using a photoionization lamp, and 2) a corona discharge source using a high voltage source with a specialized set of electrodes. These two approaches are illustrated in Figure 10 and Figure 11. Photoionization lamps are off-the-shelf devices that are sealed and can easily be used to ionize the gas in the reaction region. Corona discharge sources must be designed for a specific application but are simple devices with only two electrodes.

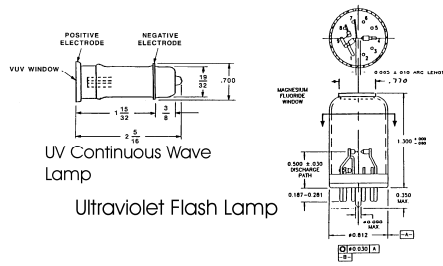


Figure 10 - Photoionization Lamps

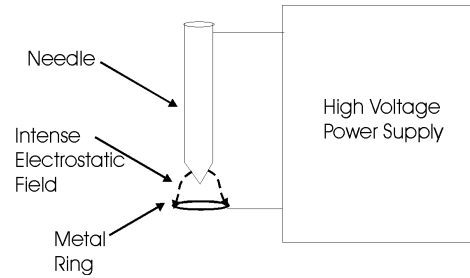


Figure 11 - Corona Discharge Source

Hardening the Radioactive Source

The alternative to developing a non-radioactive source is to harden the radioactive source enclosure and demonstrate to the Nuclear Regulatory Commission (NRC) that the source is hermetically sealed and will not leak radioactive material. Scentzar Corporation has had preliminary discussions with the NRC on this approach and is obtaining the required documents: “Consolidated Guidance about Materials Application for a Sealed Source and Device Evaluation and Registration” Volumes 3 and 8.

Molecular Analytics IMS Cell Used in this Application

Figure 12 is the Molecular Analytics cell that we are using in this application. The cell looks somewhat different from the classic design of Figure 5 but has all of the same characteristics.

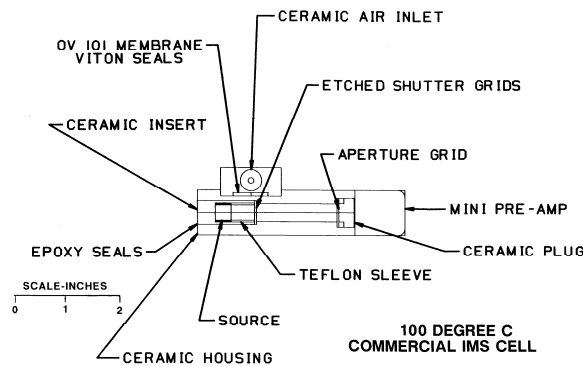


Figure 12 - M.A. IMS Cell for this application

Molecular Analytics Algorithm

Molecular Analytics programmed the algorithm used in this study. To get a reading on the IMS, the program compares the NO₂ peak to a reactant peak. The ratio of the amplitudes between these two peaks is compared to a standard calibration table also programmed into the instrument. These settings are specific to pure concentrations of NO₂.

Molecular Analytics IMS Analyzer Specifications

We used a modified Molecular Analytics Ion Mobility Spectrometer for our laboratory and Diesel engine test stand testing. The basic Molecular Analytics NO₂ analyzer has the published specifications listed in Table 5 column 2. Our analyzer was modified by changing the proprietary dopant material used in the carrier gas and by changing the proprietary membrane material to achieve a higher concentration range. During Molecular Analytics testing prior to delivery the Molecular Analytics test staff verified that our analyzer met the specifications listed in the third column of Table 5. Otherwise the analyzer and underlying technology remains the same. According to Molecular Analytics our analyzer should meet the specifications in column three below.

Table 5 – Molecular Analytics Standard Specifications and Changes for Our Project

Specification	Published for Standard Analyzer	Our Analyzer with Modifications
Detection Range	0 to 10 parts per billion (ppb)	0 to 100 parts per million (ppm)
Minimum Detectable Limit	0.5 ppb	0.5 ppm
Readout Resolution	0.1 ppb	0.5 ppm
Accuracy and Repeatability	10% of full scale	Same
Zero Drift	None	None
Span Drift	None	None
Over-range Limitation	None	None
Zero Shift After Over-range	None	None
Time to Alarm	Not specified	Not specified
Response Time	Not specified	Not specified

Uniqueness of the IDEA product (IMS NO_x Sensor) for application to practice

This IMS sensor system would be unique. We could find no evidence of a continuous locomotive emission monitoring or control system on the market or, to the best of our knowledge, in near term development. This was confirmed by the members of the project panel.

Investigation

This study was comprised of three technical stages.

Stage One

During stage one, a panel of user representatives (see acknowledgements) and technical experts were convened to review the project’s objectives. This panel included experts familiar with the specific needs of the railroad industry. An IMS prototype was adapted from an actual IMS system originally developed for the analysis of other gasses. Based on background research, a laboratory test apparatus, resembling EPA procedures and simulating engine conditions, was designed for use in the laboratory testing stage.

Stage Two

In stage two, the IMS was tested under laboratory conditions with controlled mixtures of purified air, NO and NO₂. IMS performance was also compared to an adapted EPA wet chemical method. In

preparation of stationary diesel engine testing, experiments were designed to evaluate IMS performance under “real” engine conditions. An NO to NO₂ converter was also tested during this stage. The system based on UV catalysis performed inadequately under our testing conditions. Further research conducted in stage three, showed that a converter may not be necessary since an IMS signal, using only NO₂, appears to follow overall NO_x concentration fairly well.

Stage Three

The effectiveness of the prototype IMS was tested with a stationary 1500 horsepower diesel engine. The IMS was setup alongside of a chemiluminescence analyzer, which was to be used as a standard comparison. Two test sessions were conducted. During the first session, we observed that the IMS did not appear to be overwhelmed by impurities in the exhaust stream. Tests were performed at three different load settings. Figure 36, in the body of the text, shows a summary of the results from the first test session as compared to the chemiluminescence analyzer.

Based on our findings in the first diesel engine test session, we designed new experiments for the second test session. A new dilution scheme was used and new engine operating techniques were incorporated. Two separate tests were run at two different dilutions to examine repeatability.

Summary of Stage I work

During Stage 1 we developed a laboratory apparatus including three main subsystems:

- Laboratory simulator that generates gas and humidity mixtures at a controlled temperature
- Analyzer prototype consisting of the NO → NO₂ converter and the Ion Mobility Spectrometer (IMS)
- Personnel computer data acquisition system that collects data from the IMS and controls the experiment

Figure 13 illustrates our test fixture for demonstrating the IMS and comparing it to a standard method. We left room in the test fixture for a number of gases. We originally intended to use the test fixture to compare IMS with a standard wet chemical method similar to the EPA wet chemical method used in field analysis. As can be seen from the diagram the test fixture consisted of three major components:

- The laboratory simulator that we used to mix gases
- The analyzer system
- The Personnel Computer data acquisition system

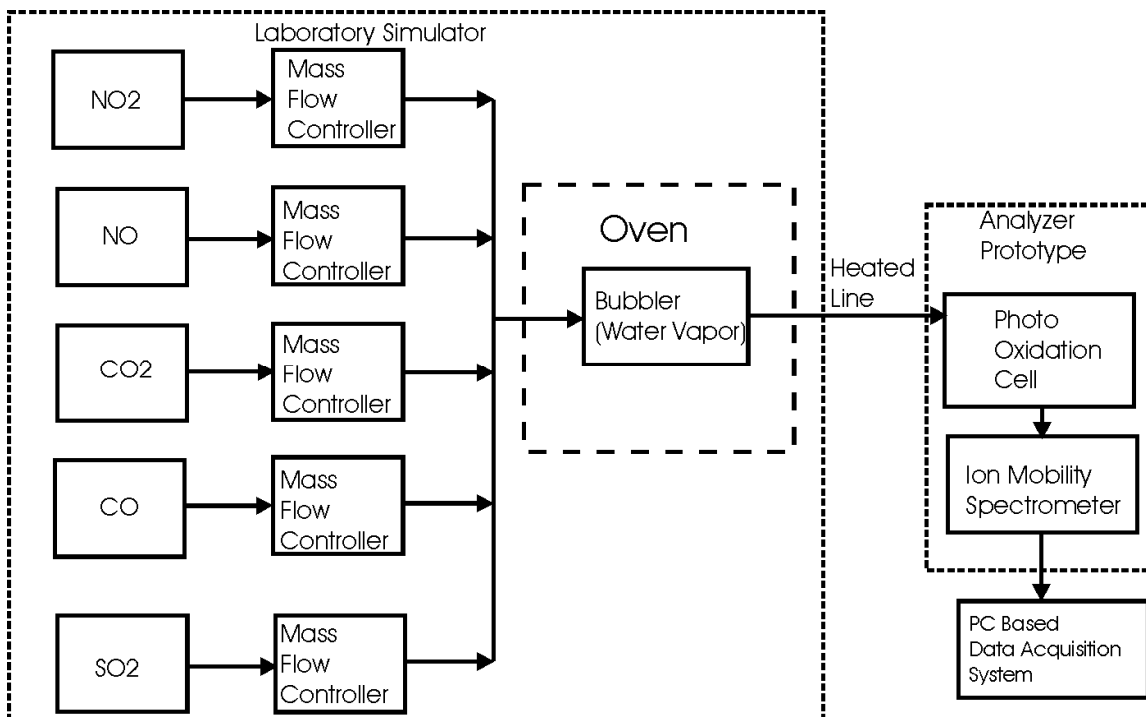


Figure 13 - Laboratory Test System

Table 6 describes the major components of our laboratory system and their significance to the end application.

Table 6 – Major components of test system

Test System Component	Function	Significance to the overall project
Various gas tanks	Provide gases for our laboratory testing with known composition in known concentrations.	Purchasing gases in tanks allowed us to simulate important portions of the Diesel exhaust stream without the expense of operating a Diesel engine.
Mass Flow Controllers	Mass Flow Controllers provide gas at a constant mass flow rate. Mixing and processing gases from the mass flow controllers allowed us to accurately estimate and control gas concentrations.	Mass Flow controllers were used in Stage I and Stage II to accurately meter out gas flows in order to determine NO and NO ₂ concentration and in Stage III to meter out dilution gas to bring the Diesel exhaust gas into the range of our IMS.
Oven/bubbler	Heat and humidify the gas stream prior to analysis.	Bring the simulator gas closer in physical state and composition to the expected exhaust gas in the actual end application.
Photoionization converter	Convert NO to NO ₂	IMS is sensitive to NO ₂ but not NO. The Diesel engine produces NO in its cylinders that spontaneously mixes with air and converts to NO ₂ . It may be required to measure both species in order to implement an effective control algorithm.
Ion Mobility Spectrometer	Measure NO ₂	We modified an existing IMS system for evaluation during our phase I study. Later work will require us to modify IMS by changing the radioactive source to a photoionization source and changing the concentration range to better match the Diesel exhaust stream.

Data Acquisition System	Hardware and personal computer used to collect IMS data.	The data acquisition system is the interface hardware and personal computer adapted to control the test system and acquire IMS signal data. The data acquisition system was used to collect laboratory data using a personal computer and later used to collect Diesel engine test stand data using a portable lap top computer.
LabView Software computer program	We programmed the data acquisition function for our experiments in the LabView language.	LabView allowed us to easily interface with the Data Acquisition System and modify the data acquisition technique as required. Our LabView data acquisition software will easily fit into larger programs designed to control the engine as work progresses.

Stage II Laboratory Testing

During Stage II we compared IMS with a wet chemical technique derived from an EPA method. IMS compared favorably with the wet chemical technique as can be seen from the following discussion. In addition, we used a Dräger electrochemical cell to conduct our laboratory evaluation of the NO converter. The following describes our laboratory work.

Summary of Method and Equipment

The wet chemical method was adapted from *Standard Methods of Chemical Analysis* and allowed us to use a solution to capture the NO₂ and to later quantify it. The set up included a complete gas aspirating system using mass flow controllers, a gas bubbler, and low-pressure vinyl tubing (Figure 14 and 15). Several tests were run at different flow rates and diffusion times to achieve specific NO₂ concentrations.

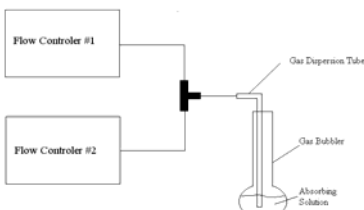


Figure 14 - Sampling using the Wet Chemical Method

The gas is introduced into an absorbing solution at a specified flow rate. Using two mass flow controllers, a specific mixture of air and NO₂ can be achieved and an expected amount of NO₂ in solution can be calculated. After a predetermined amount of time, the gas is removed from the solution. The solution is then mixed with other reagents and diluted to 50mL with water. At this point, solutions containing NO₂ will turn shades of pink depending on the concentration of NO₂ in the solution (Figure 16). Finally, these solutions are analyzed using a UV-Vis Spectrophotometer at 550nm and then compared to a standard dilution series.

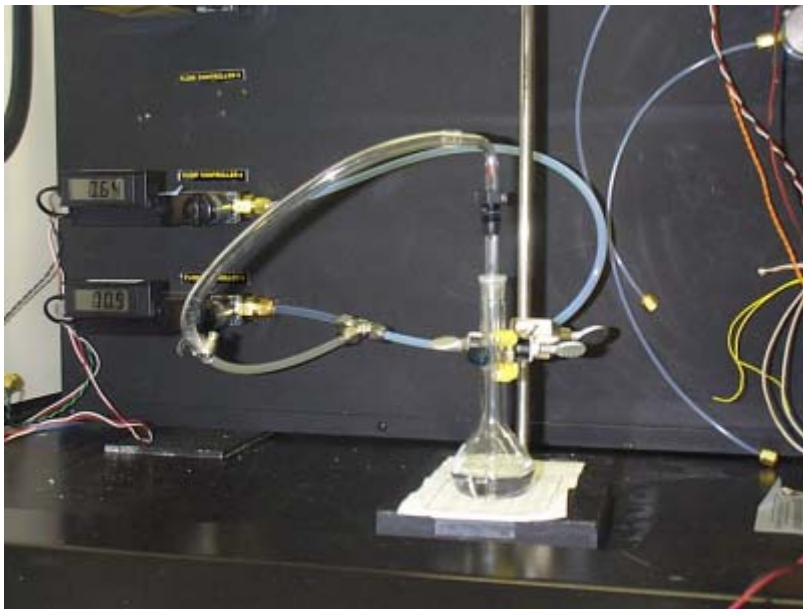


Figure 15 – Photo of Gas Aspirating System



Figure 16- Samples just before spectrometer analysis

Because the original method was intended for the *ultramicro* determination of NO_2 , the method needed to be adapted to higher concentrations of NO_2 . This was achieved by calculating the rate (by mass) at which NO_2 entered the solution and using those results to set the parameters of the testing system. This ensures that the intended results will stay within the detection limits of the spectrophotometer and the standard series.

Results

Once the absorbance in the samples and the standards were read, a standard curve was produced. A trend line was then fitted to the points, and the mass of NO_2 in the samples was found from the equation

of the trend line. The numerical results and the graphical comparison of the samples to the standards are shown in Table 7 and Figure 17.

Table 7 – Wet Chemical Method Data

Sample Number	Air : NO2 Flow Rates (L/min)	Actual PPM of NO2 In Final Mix	Actual Mass of NO2 in Solution (ug)	Observed Mass Of NO2 in Solution (ug)	Observed PPM of NO2 In Final Mix
3	0.0 : 0.05	100	5.73	3.41	59.56
4	0.074 : 0.3	79.98	6.87	4.06	17.53
5	0.4 : 0.4	49.63	4.58	3.92	42.48
6	0.3 : 0.1	24.72	5.7	2.95	34.34
7	0.5 : 0.56	9.94	6.41	3.04	4.71

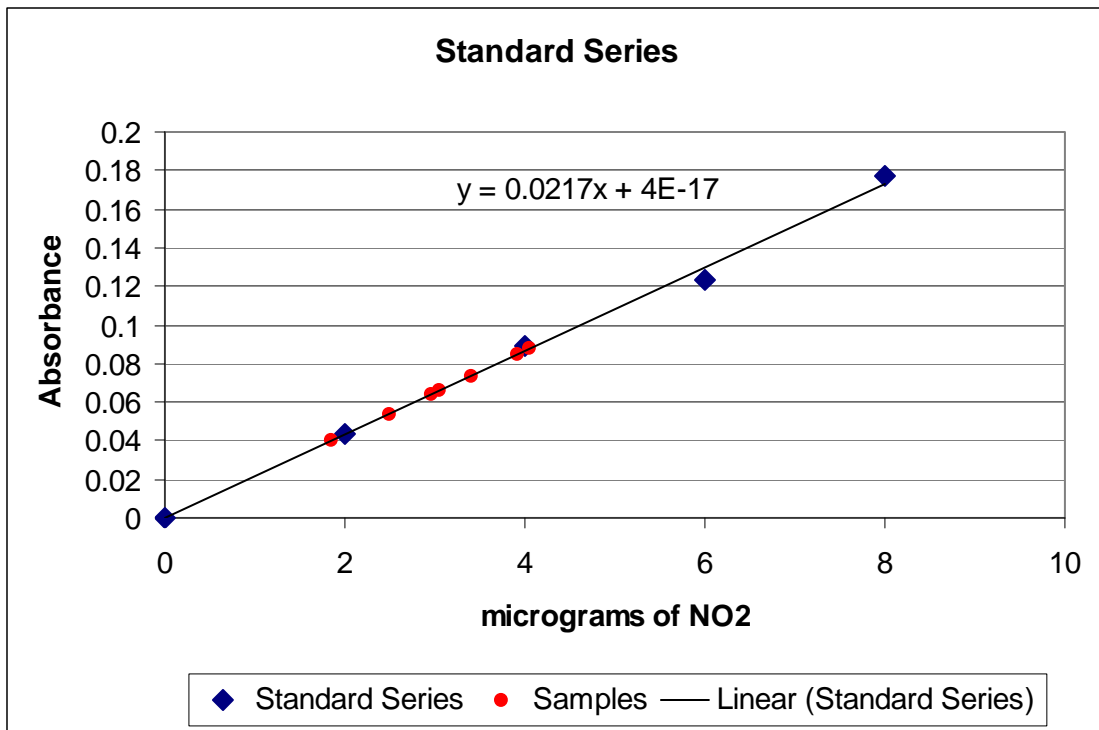


Figure 17 – Samples Compared to Standard Series

Comparison to the IMS

The ultimate goal of this project is to show that an Ion Mobility Spectrometer (IMS) can accurately and reliably measure changes in NO₂ concentration in exhaust gas. Our IMS was challenged with the same concentrations of NO₂ that were tested with the wet chemical method. Because the IMS requires that the flow rate of gas be higher than the flow rate needed for the wet chemical method, calculations were made to ensure the final concentration of NO₂ tested with the IMS were the same as those tested with the wet chemical method. The final IMS readings are summarized in Table 8.

Table 8 – IMS Data

Air : NO2 Flow Rates (L/min)	Actual PPM of NO2 In Final Mix	Observed IMS Reading Average Values (PPM)
0.0 : 2.4	100	37.75
0.6 : 2.4	80	31.5
1.8 : 1.8	50	22.25
2.25 : .75	25	16
5.0 : 0.5	10	10.5

Combined Results

The IMS displayed a more linear response to the changing NO₂ concentration than did the wet chemical method. These results are displayed in Figure 18.

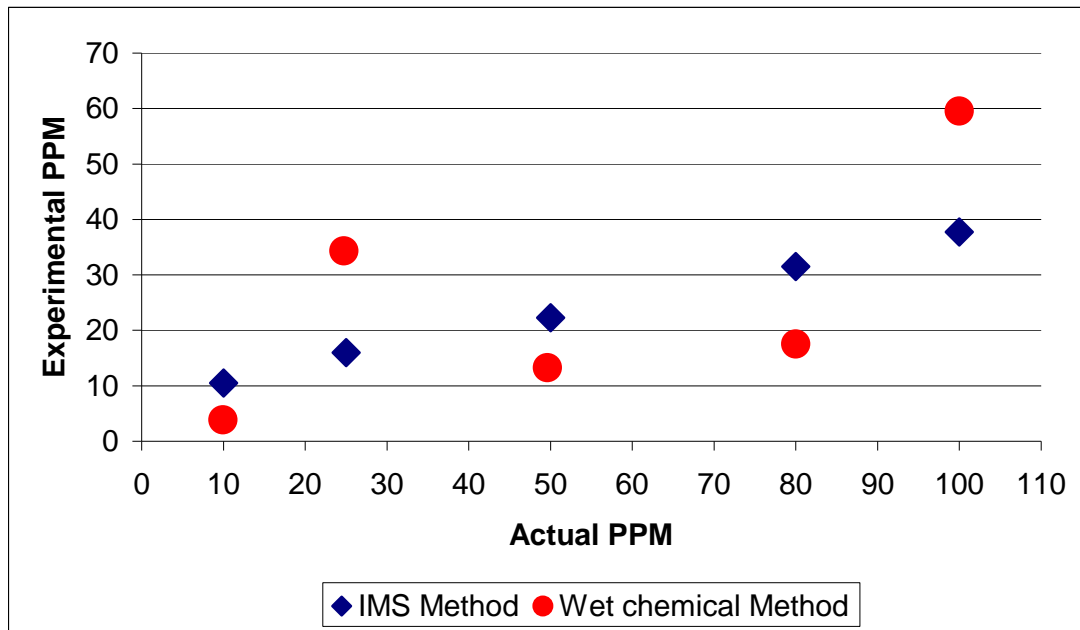


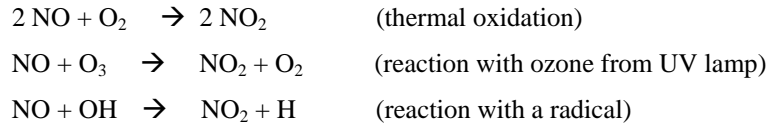
Figure 18 – IMS and Wet Chemical Methods Compared

Data Explanations

As shown in Figure 18, neither the wet chemical method nor the IMS method produced accurate results. For example, at 80 ppm actual NO₂ concentrations, the wet chemical method indicated only 17.5 ppm and the IMS method indicated only 31.5 ppm. There are a few theories that may help explain the observed behavior. First, the scale-up wet chemical method may not be as sensitive to small changes in NO₂ concentration. This could be due to the size of the bubbles that are introduced to the absorbing solution as well as the inaccuracy of the flow controllers at such low flow rates. This coupled with the short time intervals that the gas was bubbled through the absorbing solution could cause significant inaccuracies with the wet chemical method. Second, the IMS may be more sensitive to such small changes in concentrations since it was developed to take small samples from a gas stream and analyze them continuously. Also, IMS calibration will be rechecked before diesel test stand testing to ensure proper operation.

Stage II NO Converter Testing

The IMS sensor is intended to control the NO and NO₂ levels in diesel exhaust, however, the IMS instrument cannot detect NO. Two options are open: 1) assume a fixed ratio between NO and NO₂ at the sampling point and estimate the total concentration from the NO₂ measurement, or 2) develop a converter to convert the NO into NO₂. A small photochemical reactor was designed to experiment with (2). The reactor converts NO to NO₂ through the following three reactions:



The converter is composed of a plastic cylinder with a hole bored through the longitudinal axis and a UV lamp of a smaller diameter inside the hole. The empty space is the active reactor volume. The gas enters through a compression fitting on the top and flows around the UV lamp and out of another compression fitting on the top. The lamp is powered by a 12.5 V DC adapter. Ozone produced by the lamp drives the second reaction while energy from the lamp drives the first reaction. A schematic of the converter is found in Figure 19. The third reaction was not utilized at this stage of testing since dehydrated air was used, but will be implemented in later stage III.

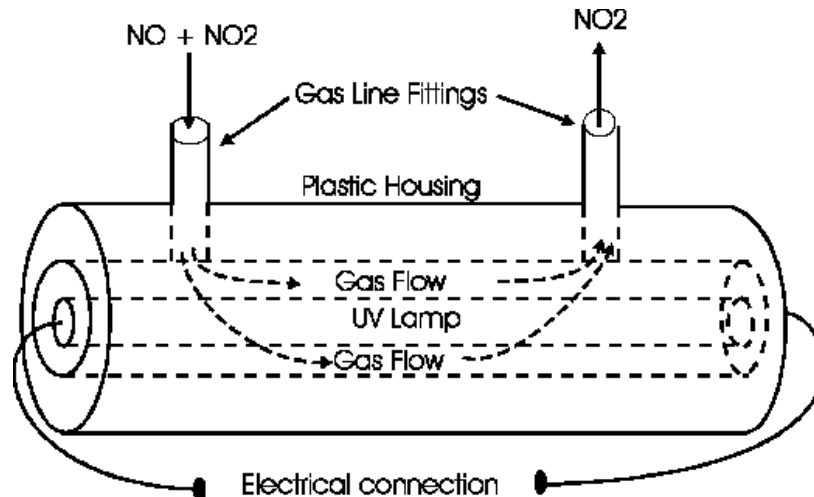


Figure 19 – NO Converter Schematic

Experimental Analysis and Results

The converter had not been tested previously, so experiments were designed to verify correct operation of the converter. In these experiments, we used a Dräger Miniwarn detector (Figure 20) which uses two electrochemical cells, one for the detection of NO and the other for the detection of NO₂. Normally, the Dräger detector is used for the detection of gaseous chemicals in the air, but with a special cap, a gas stream can be introduced directly into the detector's sensors. The detector then continuously gives a readout of NO and NO₂ (in ppm) simultaneously.

A gas mixture consisting of 10% O₂, 100 ppm NO, and the balance N₂ was fed through the converter and to the Dräger detector at different flowrates. The readout of the Dräger detector was recorded with the converter off and on for each trial. Mass flow controllers (MFCs) were used to control the flowrates. A schematic of the experimental setup is shown in Figure 21.



Figure 20 – Photo of Dräger Miniwarn Detector

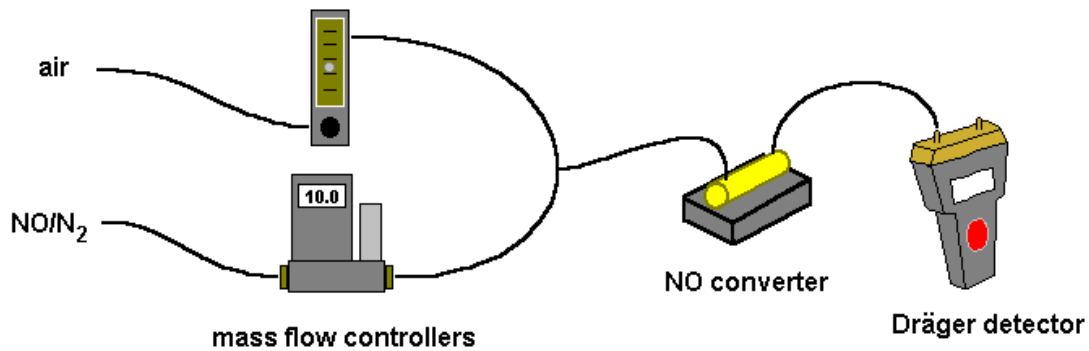


Figure 21 – NO Converter Experimental Setup

An interesting note is that even with the converter off the Dräger detector registered between 0 and 1.4 ppm NO₂, which indicates either oxidation of the NO within the tubing after mixing or improper calibration. The former seems unlikely because without the UV lamp there is not a sufficient energy source to drive the reactions. The instrument is supposed to come calibrated by the manufacturer, but it seems there could be an error with that.

The results from the experiment are shown in Table 9. Flow rates are reported in cubic centimeters per minute (ccpm), and the ppm of the mixed stream is calculated by multiplying the concentration of NO in the tank (100 ppm) by the NO/N₂ flowrate divided by the total flowrate. A graph of NO₂ concentration increase vs. total flowrate is included in Figure 22.

Table 9 – NO Converter Results

Air flowrate (ccpm)	NO/N ₂ flowrate (ccpm)	Total flowrate (ccpm)	Converter off		Converter on		NO ₂ conc. increase (ppm)
			NO conc. (ppm)	NO ₂ conc. (ppm)	NO conc. (ppm)	NO ₂ conc. (ppm)	
20	10.0	30	29.0	1.4	28.5	1.9	0.5
12	5.0	17	15.5	1.1	15.5	2.9	1.8

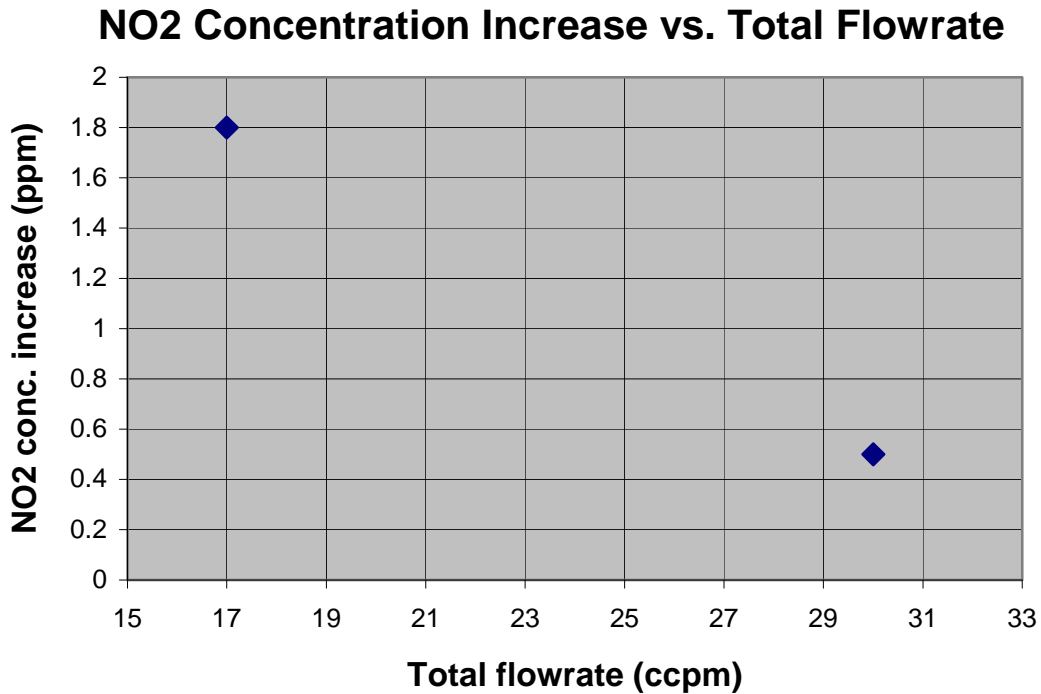


Figure 22

As can be seen, decreasing the total flowrate increases conversion. However, the flowrate could not be decreased any further because the accuracy of the MFCs is poor at such low flowrates.

Clearly the amount of time the gas spends in the converter is crucial. A fundamental chemical engineering principle is that of residence time, or simply the time the reagents spend in the reactor volume. The higher the time spent in the reactor, the higher the conversion. The residence time is calculated by dividing the reactor volume by the total flowrate of reagents. The reactor volume of the converter is 0.156 cubic centimeters. At total flowrate of 17 ccpm, the lowest used in the experiment, the residence time is only 0.55 seconds. This is clearly not enough time.

Another experiment, borne out of the residence time calculations, employed a unique equipment setup to increase the residence time. A balloon was filled with the aforementioned mixture and was squeezed to feed the gas through the converter to another balloon. The other balloon was squeezed to send the gas back. This setup is shown in Figure 23 and 24.

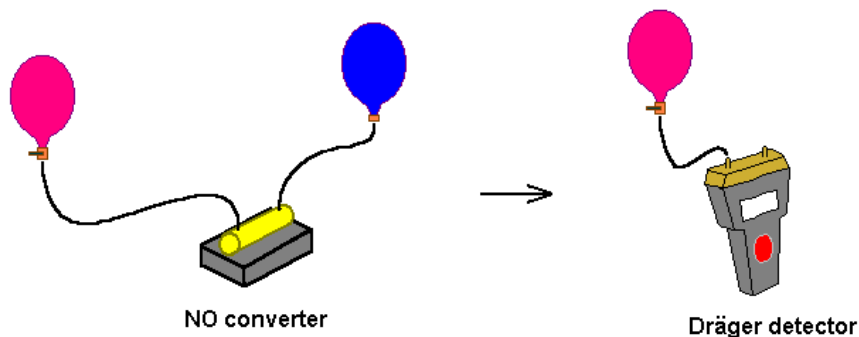


Figure – 23 Alternate NO Converter Setup

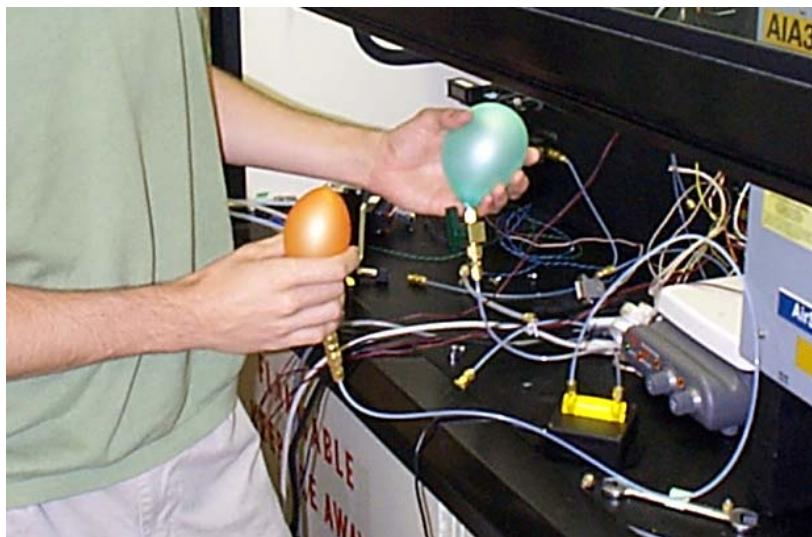


Figure 24– Photo of Alternate Setup

In this manner the residence time was increased dramatically, although it is uncertain exactly how much because not all of the gas traveled through the reactor. The squeezing was done for approximately 3 minutes. After this time the gas mixture was fed slowly to the Dräger detector, where ppm NO₂ reached a maximum of 4.0 ppm. Although quite crude, the experiment demonstrated that the principle of increasing residence time has validity.

Stage III Work

During stage three we began testing on an actual diesel engine (Figure 25, 26, 27). The purpose of these tests was to examine IMS performance under “real” diesel engine operating conditions. We conducted these tests in two separate sessions where information gathered in the first session was used to develop more in-depth experiments for the second session.



Figure 25 - Philadelphia Test Engine

Test Site

We signed a Cooperative Research And Development Agreement (CRADA) with the Naval Surface Warfare Center Carderock Division, Ship Systems Engineering Section (NSWCCD-SSES) in Philadelphia, to use their 1500 horsepower Fairbanks-Morse diesel engine. The engine was fully enclosed in a test facility with a manually operated control system where engine load could be controlled by a dynamometer.



Figure 26 - Engine Control System



Figure 27 - Dynamometer

NSWCCD-SSES also provided a chemiluminescence analyzer for comparison with the IMS. The chemiluminescence analyzer could determine overall NO_x and NO concentrations. The analyzer is pictured in Figure 28 and the Dilution probe in Figure 29. Our Dilution system designed to work with the analyzer is illustrated in Figure 30. Our data acquisition system is pictured in Figure 31.



Figure 28 - Chemiluminescence Analyzer



Figure 29 – Sample Probe

It drew samples from the engine exhaust through a sample probe, which was installed approximately six feet away from the exhaust manifold on the engine’s exhaust stack. This sample was then continuously pumped to the analyzer’s sample conditioning system, which consisted of filters, dryers, and coolers.

Experimental Setup

Since our goal was to compare results from the IMS with the chemiluminescence analyzer, a sampling system similar to the chemiluminescence analyzer’s needed to be developed to reduce sampling variability. After taking a closer look at the chemiluminescence analyzer’s setup, we found that the IMS could easily sample from a manifold after the chemiluminescence analyzer’s sample conditioning system. This way, both instruments would be looking at the same sample.

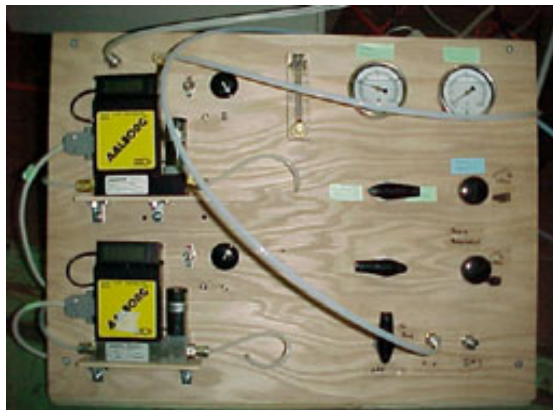


Figure 30 – Dilution System

NO₂ was expected to be in the range of 0-2000ppm. Since the IMS only has a range of 0-100ppm, we developed a dilution system. The primary components of the system were two mass flow controllers that controlled the mixing of air and exhaust sample to the IMS. The system also featured pressure gauges for the air and sample pressures and also a bypass valve for the sample to bypass the mass flow controller and feed pure sample directly to the IMS without dilution.



Figure 31 – IMS and Data Acquisition Computer

We acquired data from the IMS using a program that was developed during Stage 2. The program records the oscilloscope output signal of the IMS for later analysis. The chemiluminescence analyzer's output was recorded using a separate data acquisition system on a personal computer.

IMS Calibration

The IMS can be calibrated in two different ways. Span calibration is performed by feeding the IMS with the highest measurable concentration of NO₂, in this case 100ppm. Zero calibration is performed by feeding the instrument with instrument air. These calibrations were performed before Stage 3 testing.

Chemiluminescence Calibration

Similar to the IMS, there are two types of calibration for the chemiluminescence analyzer. Zero calibration is done by switching a valve near the sample probe and allowing instrument air into the analyzer. "Zero Calibration" is then selected on the instrument's input. Span calibration is accomplished by using standard 4200ppm concentrations of NO and NO_x. These concentrations have been previously programmed into the instrument and during span calibration, the instrument sets the range of each gas to 0-5000. The Navy personnel calibrated the instrument within three days before each test session and assured us that the calibration would be adequate for our testing purposes.

First Test Session

We designed experiments in this session to take an overall look at IMS response to diesel exhaust. Particularly, we were interested in seeing if the NO₂ signal, which was observed in the laboratory, remained in the signal when looking at actual exhaust. This session would also help us become more familiar with the engine running under testing conditions.

Tests in this session were conducted by varying NO₂ concentrations in two different ways. First, NO₂ concentrations were modified by changing the load on the engine. It had been observed, by the staff in Philadelphia, that NO₂ changed predictably by changing engine load and we wanted to recreate this behavior. Second, NO₂ concentrations were modified by keeping the engine at a constant load and diluting the sample stream.

The IMS performance was measured in two different ways. First, the reading on the front panel of the IMS was observed. This reading relied on an algorithm pre-programmed by Molecular Analytics using pure concentrations of NO₂. Second, readings were taken from the raw oscilloscope signal from the IMS. This signal was fed into a data acquisition system where it was converted into Excel files. Figure 32 shows an example of a set of signals produced by the IMS. First the maximum value of each curve is found then these values are averaged for each test; e.g. each load setting. Outliers were also excluded from analysis.

In this session, readings from the chemiluminescence analyzer were taken by hand since the data recorder was not working. Although a representative value was sought, it is not considered precise since the NO_x levels changed so rapidly. Because the maximum values from the IMS and readings from chemiluminescence analyzer are in two different scales, they have to be compared by observing the changes of each graph with respect to their own full scales.

IMS Data

It was evident in the first test that the IMS was not overwhelmed by other impurities in the exhaust stream. Although the curves did not exactly match those observed in the lab, they did change according to NO_x concentration.

During the first test (Figure 32), the engine was set to 25% load and a sample with 5% exhaust was fed to the IMS. After looking at the data, it is evident that there is quite a range (.1197mV) at the maximum values.

Looking at only the maximum values vs. time (Figure 33) shows that the NOx concentration seemed to be changing over time. This could be an indication that the engine temperature had not yet stabilized.

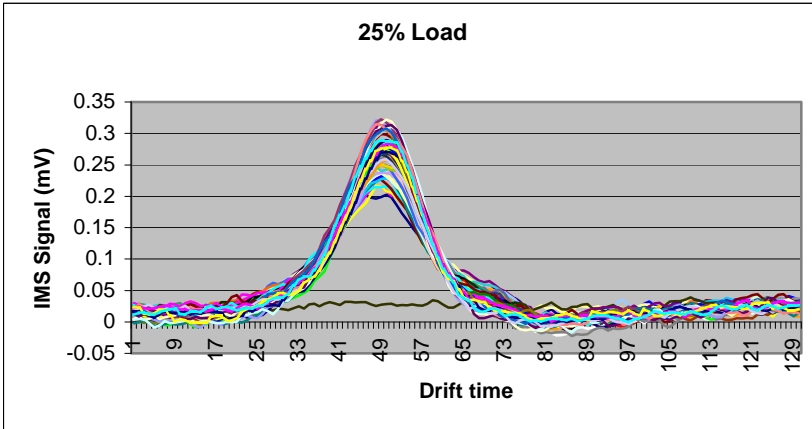
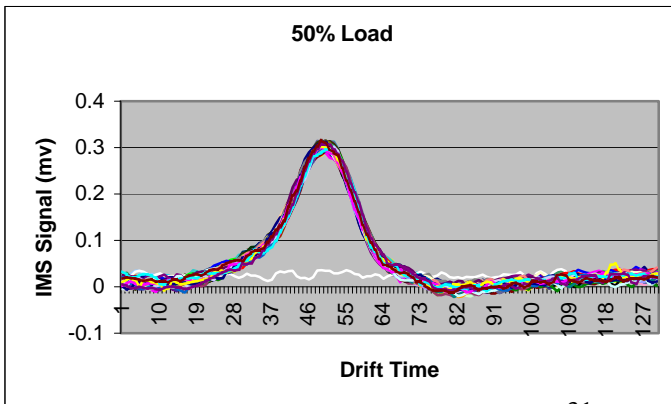
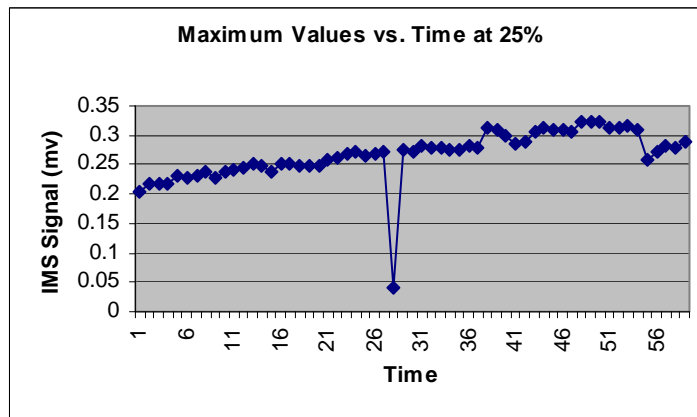


Figure 32

Figure 33



We then proceeded to a test at 50% (Figure 34) engine load and again with 5% sample. The NOx concentration seemed to be more consistent during this test with a mean maximum value at 0.301mv and a range of 0.026.

Figure 34

At 75% load and 5% sample (Figure 35), a noticeable increase was seen in the IMS out put. There was a consistent signal and a mean of maximum values of 0.465 mV and a range of .045 mV.

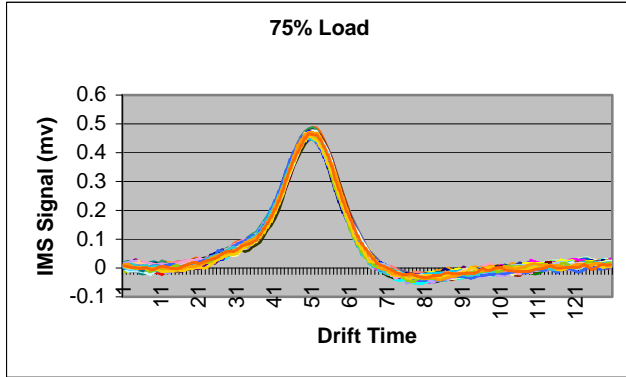
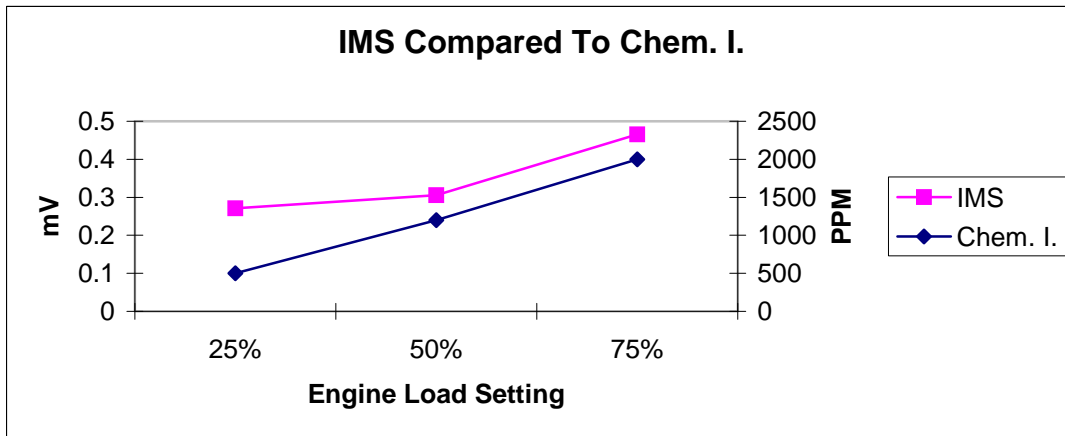


Figure 35

Comparison to Chemiluminescence Analyzer

The chemiluminescence analyzer readings were also taken at each engine setting. The readings showed a regular increase in NOx concentration. The graph (Figure 36) also shows a comparison of the maximum IMS values with the chemiluminescence analyzer data.

Figure 36



Dilution Test

To perform the dilution test, the engine was kept at 75% load. The chem. I analyzer held relatively constant at 2000ppm NOx. One continuous reading was taken from the raw IMS signal and readings (Table 10) were also recorded from the IMS front panel when the value stabilized. The data is as follows:

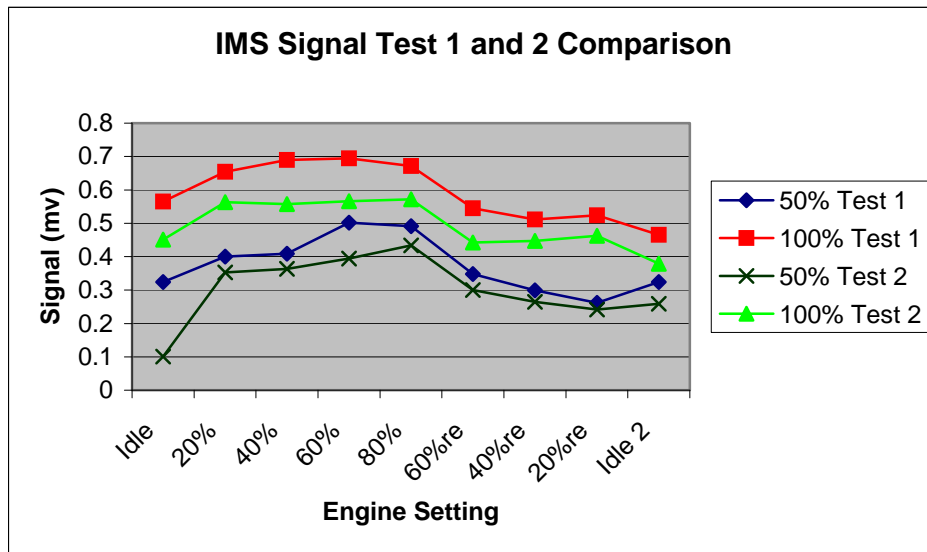
	Undiluted	25%	9%	6%	4%
Signal Average	0.64754	0.59156	0.44919	0.38130	0.33866
Panel Reading	64ppm	38ppm	19ppm	15ppm	14ppm

Second Test Session

For the second set of tests, we made a few changes based on our experiences from the first test session. First and foremost, the dilution scheme was changed. Since we found that a more concentrated sample of gas would produce a better response in the IMS, two sample dilutions were tested, 100% and 50%. The engine was also set to 9 different load settings to observe the response in the IMS and the chemiluminescence analyzer as the load on the engine was increased from idle (0%) to 80% and brought back down to idle in gradual increments.

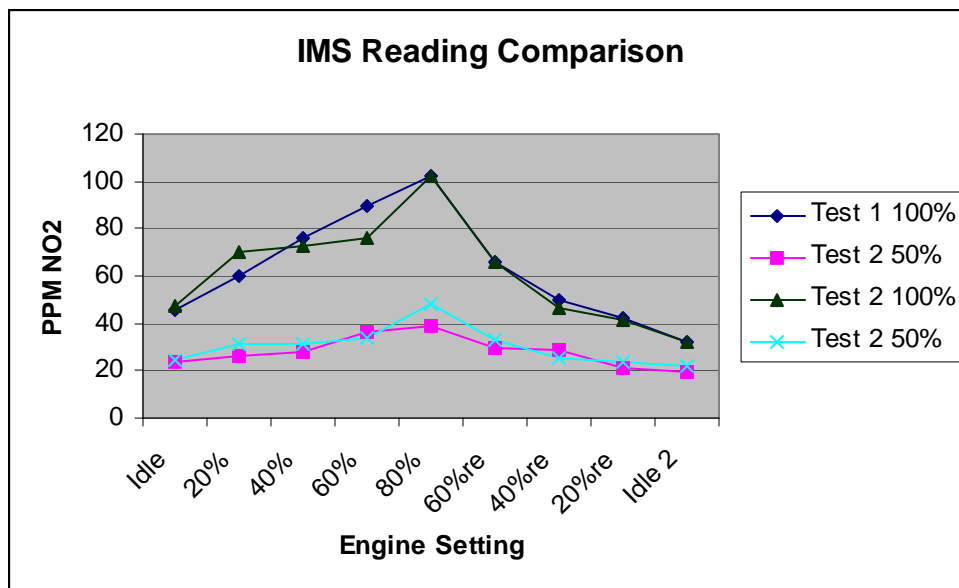
Before any data was taken, the engine was allowed to warm for an hour. The data was then taken at each setting for approximately fifteen minutes starting at idle (0% load). Before testing at a new load setting, the engine was allowed to stabilize for five minutes. Once at 80% load, the load was brought back down in the same increments and data was taken the same way as before until the engine was returned to idle. Two separate but identical tests were run at two dilutions to verify consistency (Figure 37).

Figure 37



The IMS readings show good consistency between the two tests (Figure 38).

Figure 38



Discussion and Conclusions

The results of both the laboratory and Diesel engine tests were inconclusive. The laboratory comparisons of the wet chemical method and IMS method with known concentrations of NO₂ indicated serious errors and nonlinearities with both methods. These problems were assumed to be associated with the laboratory procedures used. The investigators anticipated that they could be resolved with proper calibration procedures for the Diesel engine tests. In retrospect, the Diesel engine tests should not have been conducted until these problems with the laboratory tests had all been resolved. The result was using a prototype IMS system for the Diesel engine tests whose accuracy and performance had not been demonstrated in the laboratory.

The results of the Diesel engine tests were also inconclusive. Problems with the data recording equipment and with the calibration procedures resulted in data of questionable value that could not be properly analyzed using standard statistical analysis techniques. The chemiluminescence analyzer data had to be taken by hand in the first test, and its accuracy is questionable. Comparisons of IMS and chemiluminescence data such as shown in Figure 36 are inconclusive. The IMS data are non-linear, and the accuracy of the reference chemiluminescence data are suspect. For the second Diesel engine test, no chemiluminescence data were available, and the comparisons of two tests, each using two different sample dilutions (Figure 37) shows nonlinear responses, hysteresis, and poor repeatability.

Based on the potential of IMS sensor technology for such applications, further testing and evaluation of this concept deserves consideration. Such testing should use the latest developments in IMS sensors, and a rigorous test protocol should be designed and followed. Such protocol should include comprehensive laboratory and Diesel engine test procedures that specify data to be collected, sample size, data collection and analysis procedures, and instrumentation calibration procedures.