Diesel Exhaust Treatment Using Catalysts/Zeolites

by

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UTCA

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UTCA Report 02201
September , 2004

Technical Report Documentation Page

1. Report No FHWA/	**2. Government Accession No.**	**3. Recipient Catalog No.**
4. Title and Subtitle Diesel Exhaust Treatment Using Catalysts/Zeolites	**5. Report Date** September 2004 **6. Performing Organization Code**	
7. Authors Robert W. Peters, Shirley Clark, and Mandeep Gill	**8. Performing Organization Report No.** UTCA Report 02201	
9. Performing Organization Name and Address Department of Civil and Environmental Engineering The University of Alabama at Birmingham 1075 13th Street South, Suite 120 Birmingham, Alabama 35294	**10. Work Unit No.** **11. Contract or Grant No.** UTCA 01-084	
12. Sponsoring Agency Name and Address University Transportation Center for Alabama P.O. Box 870205, 275 H.M. Comer Hall The University of Alabama Tuscaloosa, Alabama 35487	**13. Type of Report and Period Covered** Final Report, January 2001 – June 2003. **14. Sponsoring Agency Code**	
15. Supplementary Notes		

16. Abstract

The pollution emitted by diesel engines contributes greatly to America's continuing air quality problems. The objective of this project was to develop and test a catalyst/zeolite system for its ability to effectively treat synthetic diesel exhaust [primarily concentrating on the fate of hydrocarbons such as methane (CH_4)]. This project involved proof-of-concept testing in the laboratory. The research project involved the following two major experimental tasks:

- Task 1 – Identification of appropriate sorbents (e.g., zeolites) and catalysts to develop zeolites impregnated with catalyst(s) to treat diesel exhaust; and
- Task 2 – Perform laboratory studies testing the catalyst/zeolite materials using synthetic diesel exhaust at various temperature conditions and diesel exhaust flow rates.

Results were obtained on the system performance of the catalyst/zeolite system for its ability to degrade synthetic diesel exhaust. Despite the relatively low temperature involved in our study (compared to exhaust temperatures in the 600-800^{o}F range from exhaust stacks from diesel engines), efficiencies typically ranged from ~30 percent to ~90 percent, depending on the particular combination of catalyst and zeolite involved. Using thermodynamic principles, the removal efficiency was estimated at 750^{o}F. At this elevated temperature, removals of nearly 100 percent were estimated. System performance data was in close agreement with concentrations obtained using gas chromatography analyses (performed at The University of Alabama at Birmingham) and cermet microsensor technology (performed at Argonne National Laboratory). Based on the results obtained in this study, this concept involving treatment of diesel exhaust using catalysts/zeolites showed technical merit and is worth pursuing in the development phase.

17. Key Words diesel exhaust; catalyst; zeolite; canister; methane; cermet microsensor; gas chromatography		**18. Distribution Statement**	
19. Security Classif (of this report)	**20. Security Classif. (of this page)**	**21. No of Page**	**22. Price**

Form DOT F 1700.7 (8-72)

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Executive Summary

The pollution emitted by diesel engines contributes greatly to America's continuing air quality problems. To date, most diesel buses and trucks have not used pollution control devices similar to those used on passenger cars for the last 25 years. Even though more stringent heavy–duty highway engine standards were set to take effect in 2004, these engines continue to emit vast amounts of air pollutants like nitrogen oxides, particulate matter, ozone, sulfur oxides and volatile organic compounds (VOCs), including toxic compounds such as formaldehyde. All of these pollutants pose a serious threat to public health as well as the environment in the United States.

The objective of this project was to develop and test a catalyst/zeolite system for its ability to effectively treat synthetic diesel exhaust [primarily concentrating on the fate of hydrocarbons such as methane (CH_4)]. This project involved proof-of-concept testing in the laboratory. Once it was confirmed that the catalyst/zeolite samples effectively reduce the concentration of methane in exhaust gas, these samples will be further used to degrade more complex hydrocarbon and nitrogen oxide in the exhaust in the next phase of this project.

The research project involved the following two major experimental tasks:

- Task 1 – Identification of appropriate sorbents (e.g., zeolites) and catalysts to develop zeolites impregnated with catalyst(s) to treat diesel exhaust; and
- Task 2 – Perform laboratory studies testing the catalyst/zeolite materials using synthetic diesel exhaust at various temperature conditions and diesel exhaust flow rates.

Under Task 1, appropriate support media and catalysts were identified. Compatibility of the catalysts with the support media was assessed in consultation with the Chemical Technology Division's Heterogeneous Catalysis Group of the Argonne National Laboratory. The "shake-and-bake" approach was used to prepare the catalyst/zeolite system.

Under Task 2, canisters having a packed–bed containing the zeolite embedded with the catalyst were prepared for testing in the laboratory. The catalyst and zeolite system was placed in a canister system equipped with a manifold to measure the temperature, pressure, and diesel gas composition before and after contact with the catalyst and zeolites. In the laboratory experiments, the canister system was heated electrically using heating tape; temperatures were typically in the range of 200 – 300^{o}F. Space velocity through the canister was ~8,000 hr^{-1}. The temperature was monitored from thermocouple measurements, the pressure drop across the canister was determined using pressure gauges, and the diesel composition was determined using gas chromatograph analyses and sensor analyses (from samples collected in Tedlar bags). Various synthesized formulations were tested to compare the effectiveness of each catalyst/support media matrix. These samples were analyzed to determine the system performance as a function of gas throughput, operating temperatures, etc.

Results were obtained on the system performance of the catalyst/zeolite system for its ability to degrade synthetic diesel exhaust. Despite the relatively low temperature involved in our study (compared to exhaust temperatures in the 600-800^{o}F range from exhaust stacks from diesel

engines), efficiencies typically ranged from ~30 percent to ~90 percent, depending on the particular combination of catalyst and zeolite involved. Using thermodynamic principles, the removal efficiency was estimated at 750^{o}F. At this elevated temperature, removals of nearly 100 percent were estimated. System performance data was in close agreement with concentrations obtained using gas chromatography analyses (performed at The University of Alabama at Birmingham) and cermet microsensor technology (performed at Argonne National Laboratory). Based on the results obtained in this study, this concept involving treatment of diesel exhaust using catalysts/zeolites showed technical merit and is worth pursuing in the development phase.

Section 1.0
Introduction, Problem Statement, Overall Project Approach

1.1. Introduction

The emissions from diesel trucks represent both a nuisance and an environmental problem that can severely impact human health and ecology. Everyone is familiar with the emissions of black soot and smoke billowing from diesel trucks operating on the roadways. The pollution emitted by diesel engines contributes greatly to America's continuing air quality problems. "Anyone who has ever driven behind a large truck or bus is very well familiar with the smell of diesel fuel and suffocation caused by clouds of thick exhaust emissions." An older, dirtier diesel vehicle can generate nearly eight tons of air pollution each year [EPA Environmental News, 2000]. To date, most diesel trucks and buses have not used pollution control devices similar to those used on passenger cars for the last 25 years [EPA Environmental News, 2000]. Cost-effective treatment techniques are vitally needed to handle and treat diesel emissions from trucks at their source. Current standards established in 1998 regarding NO_x and particulates from diesel engines are 4.0 and 0.1 gms/(bhp-hr), respectively. Stricter emission standards will take effect in 2007 with regulations of 0.1 and 0.1 gms/(bhp-hr), respectively. Current techniques typically remove 35 percent to 60 percent and ~70 percent of NO_x and particulates, respectively. With tightening regulations being imposed for truck emissions in 2007, the need for improving diesel emissions involving diesel, particulates, and NO_x is becoming more imminent. Techniques such as selective catalytic reduction (SCR) using ammonia have been studied at Oak Ridge National Laboratory; NO_xTech has been working on an after-treatment device to handle diesel NO_x emissions. With increasing concerns and stricter environmental regulations involving vehicle emissions, this projects seeks to develop a cost-effective catalytic treatment technique that can effectively handle and treat diesel emissions from trucks at their source.

Even though more stringent heavy–duty highway engine standards are set to take effect in 2004, these engines will continue to emit vast amount of air pollutants like nitrogen oxides, particulate matter, ozone, sulfur oxides and volatile organic compounds (VOCs) including toxic compounds such as formaldehyde. All of them pose a serious threat to public heath as well as the environment in the United States. These problems comprise of aggravation of respiratory and cardiovascular disease, aggravation of existing asthma, premature mortality, decreased lung function, and acute respiratory symptoms [EPA Environmental News, 2000]. Numerous studies indicate that diesel exhaust might increase chances of lung cancer. Ozone causes crop and forestry losses, Particulate matter (PM) causes damage to materials and soiling of commonly used building materials. NO_x, SO_x and PM also contribute to visibility impairment in many parts of the US. NO_x emissions cause acidification, nitrification and eutrophication of water bodies like lakes, rivers etc. Moreover it has been approved by the Clean Air Scientific Advisory Committee, that diesel exhaust is likely to have carcinogenic effects on the human body [EPA

Environmental News, 2001]. All these ill effects of diesel exhaust forces the regulatory body to establish a comprehensive national control program that is capable of regulating the heavy-duty vehicle and its fuel as a single system. As a result, new emissions standards will begin to take effect in model year 2007. These regulations will be applicable to heavy-duty highway engines as well as trucks and buses [EPA Environmental News, 2001].

In December 2000, U.S. Environmental Protection Agency (EPA) announced new standards for heavy-duty engine and vehicle sulfur control requirements for highway diesel fuel sulfur. The Control of Air Pollution From New Motor Vehicles: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements; Final Rule (2007 HD Rule) was promulgated on Thursday, January 18, 2001, and its emissions standards will begin to take effect in model year 2007 [EPA Regulatory Assessment, 2000]. This rule emphasizes the use of high-efficiency catalytic exhaust emissions control devices, particulate filters, and other advanced technologies. Since these devices are damaged by sulfur, there is a need of reducing the level of sulfur in highway diesel fuel significantly. The standards also require reducing the amount of sulfur in highway diesel fuel by 97 percent (from 500 ppm to 15 ppm) by mid-2006. It is estimated that heavy-duty trucks and buses today account for about one-third of nitrogen oxides emissions and one-quarter of particulate matter emissions from mobile sources. Once the 2007 HD Rule comes into effect, it will reduce particulate matter and oxides of nitrogen emissions from heavy-duty engines by 90 percent and 95 percent below 2001 levels, respectively. PM emissions standards have been set at 0.01 g/bhp-h for model year 2007 for heavy-duty vehicles. NO_x and non-methane (NHMC) standards are set at 0.2 grams per brake-horsepower-hour (g/bhp-h) and 0.14 g/bhp-h, respectively. These NO_x and NHMC standards will be phased in together between 2007 and 2010 for diesel engines [EPA Regulatory Assessment, 2000].

Once this rule is fully implemented, 2.6 million tons of smog causing nitrogen oxide emissions will be reduced each year. Soot or particulate matter will be reduced by 110,000 tons of year [EPA Environmental News, 2000]. It has been estimated that 8,300 premature deaths, 5,500 cases of chronic bronchitis and 17,600 cases of acute bronchitis in children can be prevented annually. It will help to avoid more than 360,000 asthma attacks and 386,000 cases of respiratory symptoms in asthmatic children every year. EPA estimates the costs of this program will raise prices of new vehicles by $1,200 to $1,900 per vehicle. EPA also estimates that the cost of diesel fuel could increase by four to five cents per gallon. The benefits of the action outweigh costs by 16 to one [EPA Environmental News, 2000].

All these efforts, rules and regulations demand an innovative breakthrough in the field of catalytic exhaust emission control technology to comply with the 2007 HD Rule. Various efforts are been taken to reduce the greenhouse gas emissions and soot from the tail pipe. This problem can be resolved through the application of high-efficiency emissions control technologies, which can result into large emissions reductions especially through the use of catalytic emission control devices installed in vehicles' exhaust systems and integrated with engine controls. For the technology to be feasible and capable of meeting the standards, it will require diesel fuel with sulfur content at the 15 ppm level.

1.2. Study Objective (Problem Statement)

The objective of this study was to develop and test a catalyst/zeolite system for its ability to effectively treat synthetic diesel exhaust (mainly concentrating on the fate of the hydrocarbon).

1.3. Scope of Study (Overall Project Approach)

The project involved the following tasks:

- Task 1 – Identified appropriate sorbents (e.g., zeolites) and catalysts to develop zeolites impregnated with catalysts(s) to treat diesel exhaust.
- Task 2 – Performed laboratory tests of catalyst/zeolite materials using synthetic diesel exhaust at various temperature conditions and diesel exhaust flow rates.

Under Task 1, appropriate support media and catalysts were identified. Compatibility of the catalysts with the support media was conducted under the supervision of the principal investigators at UAB and Argonne National Laboratory. The media was prepared for subsequent testing in the experimental phase of the project.

Incorporating metals, oxides, or other compounds onto supports can be done by a number of methods. The most common is the method of incipient wetness. In this technique, the support is first analyzed by various means such as pore size distribution to determine the void volume on a weight basis. A solution of the incorporating species is then made such that, on a weight basis, a volume of this solution equivalent to the void volume of the support contains the desired amount of material to be impregnated. This solution is then added drop wise to the support material, such that all of the solution is drawn into the support pores by capillary action. The wetted sample is then typically dried above 100°C for several hours to remove the water, and calcined at high temperatures to stabilize the impregnated species and to remove any volatile species from the sample. Since no other species besides water and volatile components are removed from the sample at any time, this method is very useful to obtain precise loading conditions on a support; however, except at very low loading conditions, the amount of dispersion is typically hard to control and is a function of support, species, and calcining conditions [Bekkum *et al*., 2001]. Formulations of various types of catalyst/zeolite systems were prepared and their subsequent testing performed to check their ability to treat diesel exhaust at various temperatures, pressures, and flow rates and so on in the laboratory conditions. Then the canisters containing catalyst/zeolite system can be used to treat the exhausts of diesel trucks on Alabama roadways.

Media was prepared for subsequent testing in the experimental phase of the project. Samples of the catalysts embedded in the zeolites were prepared, and sub samples were sent to Argonne National Laboratory (ANL) for chemical characterization and microscopic analysis. Table 1-1 describes the catalyst and the zeolite used in our project.

Table 1-1. Catalyst and zeolites selected.

Sample No.	Catalyst	Name of zeolite	SiO_2/Al_2O_3
1	Copper (Cupric nitrate)	Zeolyst CBV – 21A; NH4 MOR; 0.08% Na	20
2		Zeolyst CBV – 10A; Na MOR; 6.6% Na	13
3		Zeolyst CBV – 3024E; NH4 MFI; 0.05% Na	30
4		Zeolyst CBV – 28014a; NH4 MFI; 0.05% Na	280
5		Zeolyst CP 811E – 75; HBEA – 75 (Zeolite H – Beta Powder); 0.05%Na	----
6		Zeolyst CP 811C – 300; HBEA (LOT 1822-20); 0.05% Na	300
7		Zeolyst CBV 100 Zeolite Na-Y; Na-Fau; 13% Na	5.1
8		Zeolyst CBV 720; H.Y. Zeolite; 0.03% Na	30.0

The catalyst/zeolite system was prepared using the "shake-and-bake" approach described in Appendix A. Argonne National Laboratory provided technical assistance regarding catalyst/zeolite system fabrication, appropriate sensors to monitor system performance, and provided advice and consultation on this project.

Under Task 2, canisters having a packed-bed containing the media embedded with the catalyst were prepared for testing in the laboratory. The canisters allowed input of the gaseous feed stream and exhaust gas following treatment through the packed bed. Various formulations synthesized at The University of Alabama at Birmingham (UAB) were tested in UAB's research facilities in the Department of Civil and Environmental Engineering to compare the effectiveness of each catalyst/support media matrix. The canisters had sampling ports both before and after the canisters to enable samples to be collected by gas tight syringes (10 mL) and in Tedlar bags and analyzed to determine the system performance as a function of gas throughput, operating temperature, etc. The diesel gas flow rate was regulated through gas regulators. The temperature is controlled using a temperature controller coupled with heating tapes. A thermocouple was inserted into the packed-bed canister to monitor the temperature of the gas at the inlet and outlet of the canister. Sensors were used to monitor the system performance in near real-time conditions. The samples collected were analyzed for the petroleum hydrocarbon composition (Methane). Additionally, during the course of an experiment, the pressure drop through the packed-bed canister was monitored with pressure gauges, to address the impact of potential fouling caused by particulates contained in diesel exhaust.

Section 2.0
Background

Over the past thirty years, the emphasis of regulations has shifted from one pollutant to another, but the overall trend has been towards stricter emissions control on all types of motor vehicles [White, 1982]. In particular, NO_x emissions from heavy-duty diesel-powered vehicles have been the target of aggressive regulation during the last decade [Schimek, 1998].

NO_x emissions from mobile sources occur as a result of physical conditions present in an internal combustion engine that enable the chemical processes that form nitric oxide (NO) to take place. Generally, ambient air consists of 3.76 moles of nitrogen (N_2) for every mole of oxygen (O_2) [Schafer and van Basshuyen, 1995]. The combustion process results in sufficient temperatures and pressures to allow the N_2 and O_2 in the air drawn into a vehicle's engine cylinder to combine to form two moles of NO. This phenomenon is represented by the "Zeldovich mechanism" and is shown below [Schafer and van Basshuyen, 1995].

$$N_2 + O \rightarrow NO + N$$
$$O_2 + N \rightarrow NO + O$$

For this reason, NO_x emissions are not particularly sensitive to changes in fuel types or chemical compositions and require exhaust treatment technologies for their reduction as previously discussed [Schafer and van Basshuyen, 1995; Sawyer *et al*., 2000].

Studies have shown that heavy-duty trucks contribute a significant portion of the overall mobile source emissions of NO_x [Sawyer *et al*., 2000; Nelson *et al*., 1991]. In many cases, diesel-powered heavy trucks constitute a significant percentage of total traffic volumes [Bureau of Transportation Statistics, 1998]. In addition, truck traffic continues to increase in total vehicle-miles traveled, implying that heavy-duty vehicles have an increasingly important role in the emission of ozone precursors.

Studies have shown that diesel-powered heavy-duty vehicles account for greater NO_x emissions per vehicle than gasoline-powered passenger cars due to the relatively high combustion temperatures and pressures associated with diesel engines [TRB, 1995; Sawyer *et al*., 2000; Guensler, 1991]. The mobile source emissions model developed by the EPA, *MOBILE5*, reports NO_x emission rates for trucks seven times greater than those of passenger cars [Schimek, 1998].

Several studies of ozone formation have indicated that mobile source emissions are capable of contributing to ozone levels around 120 ppbv [Winner and Cass, 2000; Proyou *et al*., 1998; Harley *et al*., 1997]. To date, there has been considerable effort devoted to the reduction of emissions from heavy-duty diesel engines. For example, techniques such as selective catalytic

reduction (SCR) using ammonia have been studied at Oak Ridge National Laboratory and NOxTech is working to develop an after-treatment device to further reduce NO_x emissions from diesel exhaust. In response to increasing concerns and stricter environmental regulations on vehicle emissions, this project searched for a cost-effective catalytic treatment technique that can effectively handle and treat diesel emissions from heavy-duty diesel-powered vehicles, both as a retrofit item on older engines as well as a supplemental device to achieve further NO_x reductions from post-2007 engines.

Section 3.0
Methodology/Experimental Procedure

3.1 Chemicals Used

- Copper (II) Nitrate Hemipentahydrate Crystalline (from Fisher Scientific International) ($Cu(NO_3)_2$•$2.5H_2O$), CAS Reg. 19004-19-4, Cat. No. C467-500.
- Silicon Carbide (SiC) – It was provided by Electro Abrasives, Inc. (Buffalo, NY). 4-lb. samples of various grit sizes of silicon carbide of the following mesh sizes were provided: 24, 150, and 240. The SiC serves as the inert packing material above and below the catalyst/zeolite material.
- Eight samples of the zeolites (~100 grams each from Zeolyst International, Valley Forge, PA) for use on the project were provided to UAB from Argonne National Laboratory (www.zeolyst.com/html/company.html, 2003). The samples are listed in Table 3-1.

Table 3-1. Zeolites samples with specifications.

Sample No.	Name of Zeolite	% Na	SiO_2/Al_2O_3 (wt/wt)
1	Zeolyst CBV – 21A; NH_4 MOR	0.08%	20
2	Zeolyst CBV – 10A; Na MOR	6.6%	13
3	Zeolyst CBV – 3024E; NH_4 MFI	0.05%	30
4	Zeolyst CBV – 28014a; NH_4 MFI	0.05%	280
5	Zeolyst CP 811E – 75; HBEA – 75 (Zeolite H – Beta Powder)	0.05%	----
6	Zeolyst CP 811C – 300; HBEA (LOT 1822-20)	0.05%	300
7	Zeolyst CBV 100 Zeolite Na-Y; Na-Fau	13%	5.1
8	Zeolyst CBV 720; H.Y. Zeolite	0.03%	30.0

- The specialty gas was obtained from BOC gases. It had a synthetic diesel gas composition and contained a mixture of gases as described in Table 3-2. The specialty gas made is representative of typical diesel exhaust composition, with the exception of the concentration of methane. Typical hydrocarbon composition in diesel exhaust ranges from 6.3–14.6 ppm; however, for detection in the gas chromatography system, the concentration was increased to ~1000 ppm to detect and quantify the diesel exhaust before and after contact in the catalyst/zeolite canister system.

Table 3-2. Composition of synthetic diesel exhaust and typical diesel exhaust

Parameter	Synthetic Diesel Exhaust	Typical Diesel Exhaust Composition
CO_2, (%)	4.4 – 5.1 %	5.1
O_2, (%)	14 – 15 %	14.8
CO, (ppm)	82 – 108 ppm	108
Hydrocarbons [HC], (ppm)	~1000 ppm	200
Nitrogen, (ppm)	Balance of mixture is nitrogen	784

3.2 Equipment Used

The following equipment was used in this investigation:

- Precision vacuum oven – needed for the preparation of the catalyst/zeolite matrices;
- Thermolyne furnace (400°C) – to calcine the catalyst/zeolite matrix;
- Heating tapes – to provide heat to the experimental equipment (copper tube and canister);
- Electrothermal controller – to control the heat input for the canisters and preheat the inlet line to the canisters;
- Thermocouples – to monitor the temperature before and after the canister containing the catalyst/zeolite matrix;
- Digital indicators – to display the temperature measured by the thermocouples;
- Pressure gauge and capillary tubes – to measure the pressure difference (ΔP) at the outlet and inlet of the canister;
- Solid state speed control (Masterflex) pump – to pass air at different air flow rates (0, 500-, and 900-mL/min) through the copper tube, to determine the cooling effect on the copper tube; and
- Chemware Tedlar gas sampling bags – to collect gas samples to send to Argonne National Laboratory for chemical analysis.

3.3 Accessories Used

Accessories used to perform this research included the following:

- Gas regulators for the compressed hydrogen, helium, and air lines were used to control the flow rates delivered to the GC unit; and
- Hamilton gas tight syringes (10-mL) were used to grab gaseous samples during an experiment and to inject the gaseous sample into the GC system. Hamilton Series 1000 Gastight Syringes (from Fisher Scientific International, Suwannee, GA) available in mL capacities were used.

3.4 Fabrication of Canister

The preliminary experimental equipment layout design was established. Additionally, the design and preliminary schematic of the canister to hold the catalyst/zeolite system was made. The canisters were fabricated at the University of Alabama at Birmingham's (UAB's) machine shop and were used for the laboratory demonstration phase of this project. The unassembled catalyst/zeolite canister system is shown in the Figure 3-1. The experimental set up of the catalyst/zeolite system is shown in Figure 3-2.

A manifold system was fabricated to attach to the top and bottom of the canister. The manifold system allows taps to measure the temperature and pressure of the system, both before and after the canister system. The manifold system was equipped with sample collection ports (involving septa) enabling samples to be collected using gas-tight syringes for direct injection into the gas chromatography (GC) system for analysis.

3.5 Experimental Layout

A canister having a packed bed containing the media embedded with the catalyst was prepared for testing in the laboratory. Synthetic diesel gas was passed through the packed bed at different gas flow rates and temperatures. Various formulations synthesized at UAB were tested at UAB's facilities to compare the effectiveness of each catalyst/support media matrix. The canister has sampling ports both before and after the canister to enable gaseous samples to be collected and analyzed to determine the system performance as a function of gas throughput and operating temperatures. Samples were collected using gas tight syringes (10-mL) for analysis by GC techniques. The diesel gas flow rate was regulated using gas regulators. The temperature was controlled using a temperature controller using heating tape. A thermocouple was inserted at the inlet and the outlet of the packed-bed canister to monitor the temperature within the bed. Sensors were used to monitor the system performance. Additionally, the pressure drop through the packed-bed canister was monitored during the course of an experiment.

Simultaneously samples were also collected in Tedlar bags that were sent to Argonne National Laboratory for analysis using chemical sensors. A description of Argonne's cermet microsensor as well as the results of analysis of the Tedlar bags is described in Section 5.5.

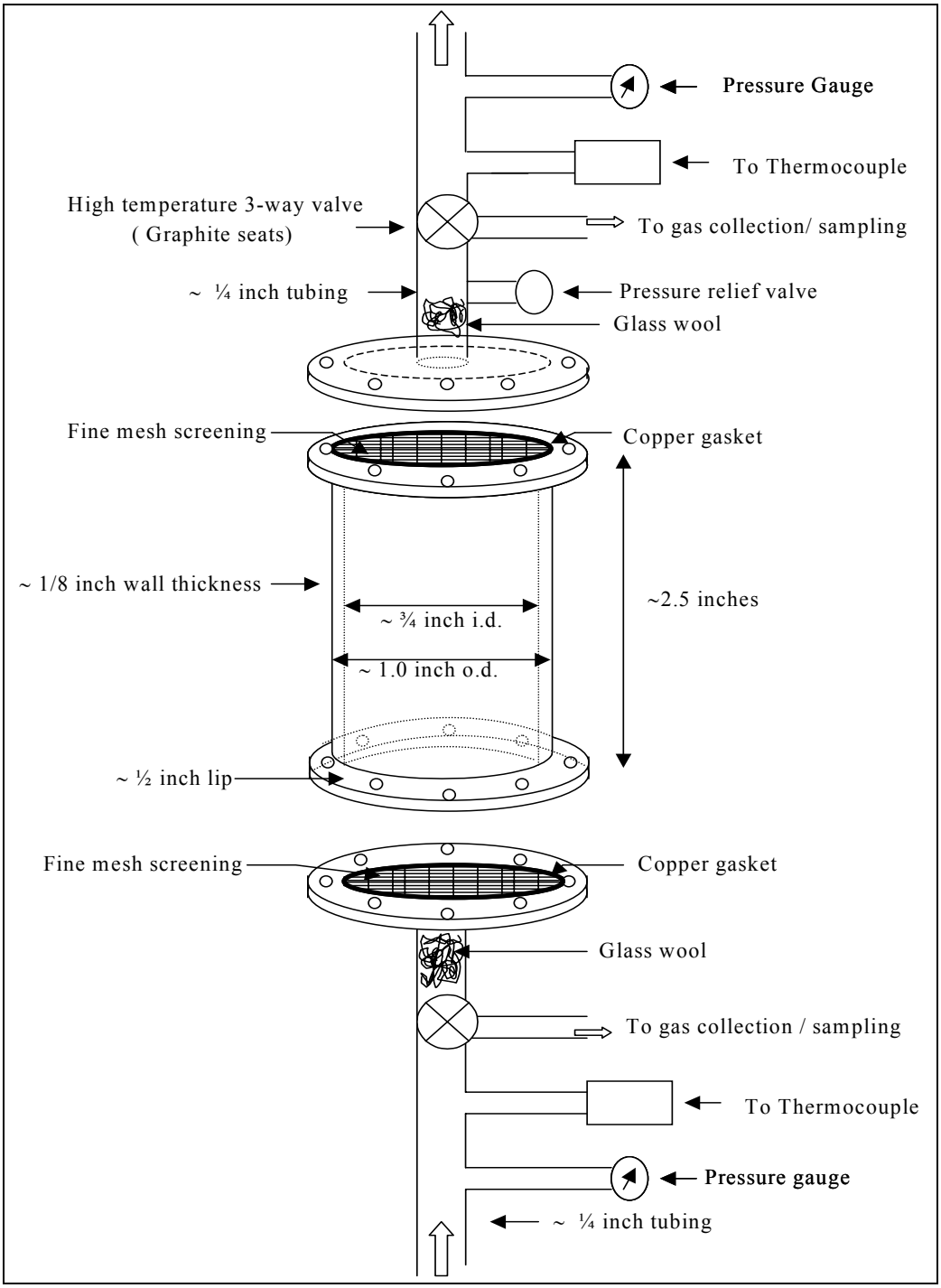

Figure 3-1. Schematic diagram of the catalyst/zeolite canister

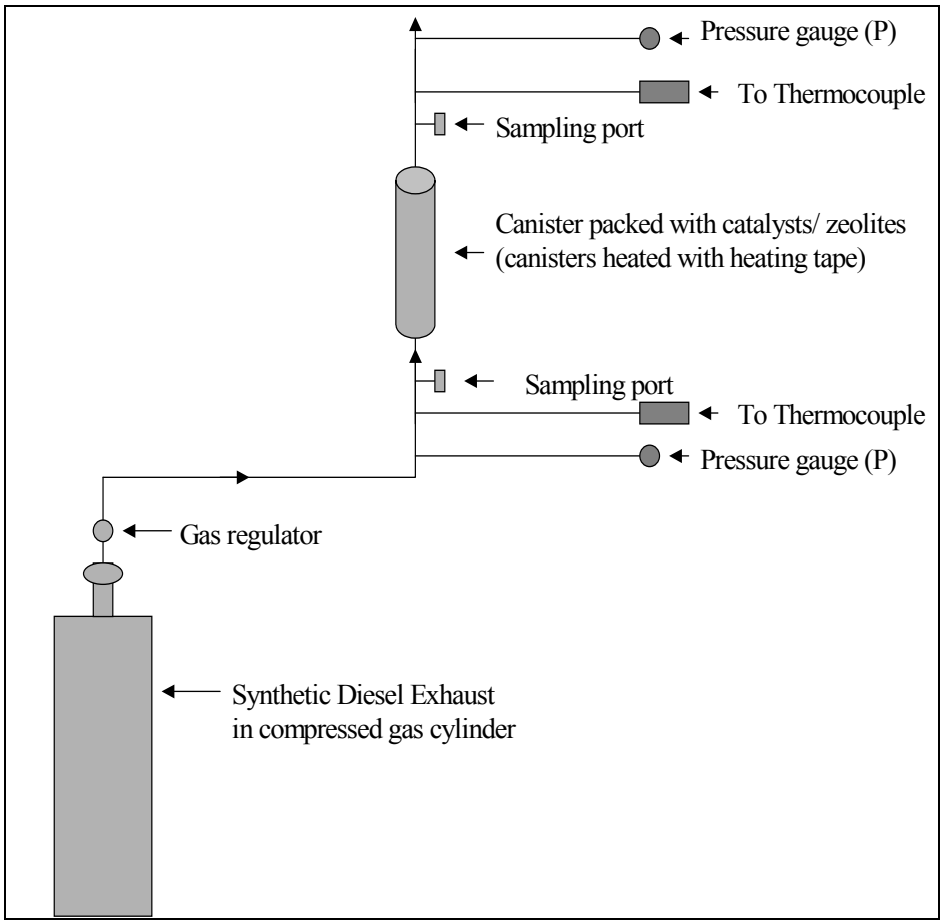

Figure 3-2. Schematic diagram of the experimental set-up of the catalyst/zeolite canister.

3.6. Cook Book Recipe for the Entire Experimental Procedures and Analysis

Beginning with the catalyst/zeolite synthesis to catalyst fabrication, the procedure for conducting the experimental runs and analysis of the gaseous samples is summarized in the following steps:

- Various formulations of catalyst/zeolite were synthesized at UAB, according to "Shake-and-bake" approach, as described in detail in Appendix A. Eight samples of zeolites were provided from Argonne National Laboratory, these samples were treated with copper (II) nitrate hemipentahydrate, to synthesize catalysts.
- Fabrication of Canister. The stainless steel canister and manifold system shown schematically in Figure 3-2 were fabricated at UAB's machine shop. The manifold system was equipped with sample collection ports, and ports for temperature and pressure measurement both at top and bottom of the canister.
- Packing of the canister. Before setting up the whole equipment, the canister was packed with the mixture of catalyst/zeolite and silicon carbide (grade – 150), 50/50 by weight. After packing the canister, the manifolds had to be attached to the canister tightly, to minimize air leakage.

- Final experimental setup. After the canister was packed, the entire assembly was erected with the help of clamp stands. The bottom manifold was connected to the BOC gases cylinder. Gas flow was regulated with the help of the gas regulators. The bottom manifold had three ports for pressure measurement, temperature measurement, and sample collection. The first port from the bottom was used to measure pressure using a capillary tube, approximately 10 inches long, connected to the port and to the pressure gauge. The second port from the bottom was used to measure temperature, with a J-type thermocouple (J28) inserted in the port. The thermocouple was in turn connected to the digital indicator (Doric trendicator 400 series), which displayed the temperature of the synthetic gas before entering the canister in °F. The third port from the bottom was used for sample collection. Hamilton gas tight syringes were used to collect gaseous samples during an experiment. This port was also used to collect samples in Tedlar bags.
- The bottom manifold was wound with low heating tape (Silicon rubber and grounded heating tape) to preheat the synthetic diesel exhaust before it entered the catalyst/zeolite and SiC mixture. Then, the high heating tape (Fibroxt and Grounded heating tape) was wound around the canister, to heat the catalyst/zeolite and SiC mixture. Both of these heating tapes were connected to a 2-way proportional electrothermal controller. The low heating tape was connected to the left hand knob of the electrothermal controller and the high heating tape was connected to the right hand knob of controller.
- The top manifold had three ports for sample collection, temperature measurement, and pressure measurement.
- Experimental Procedure. Once the entire assembled unit was placed in the ventilation hood, the heating tapes around the canister were switched on. Synthetic diesel exhaust was passed through the canister at two different pressures (6 psi and 12 psi); samples at the inlet and outlet of the canister were collected with the help of Hamilton gas tight syringes and were collected in Tedlar bags. The temperature at the canister inlet and outlet were measured with the help of thermocouples, with temperature displayed on the digital indicators in °F. The pressure at the canister inlet and outlet was measured with the help of pressure gauges. This parameter measures the pressure drop across the canister, indicating whether cake formation had occurred in the canister.
- Analysis with GC. Once the gaseous samples were collected with gas tight syringes, they were manually injected in the Agilent gas chromatography 6890N model (GC/FID).
- Analysis of Tedlar bag samples. Gaseous samples were collected at the canister inlet and outlet in Tedlar bags. They were shipped to Argonne National Laboratory for cermet microsensor testing. The results of the Argonne testing are described in Section 5.5.

Section 4.0
Equipment Calibration

Prior to performing the experiments on the catalyst/zeolite canister system, various calibrations were performed on the equipment. Figure 4-1 shows the flow chart of the calibration experiments.

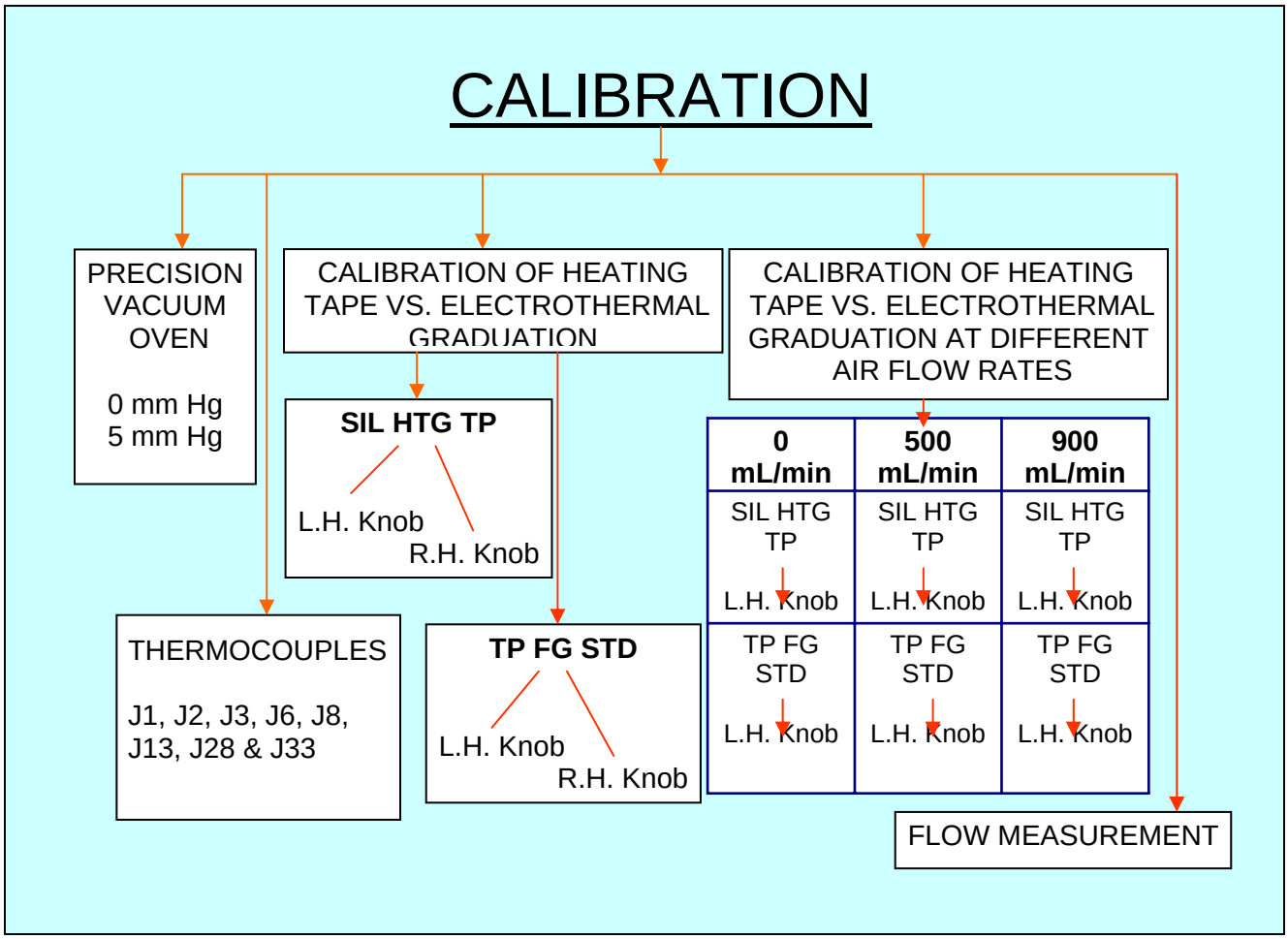

Figure 4-1. Flowchart for calibration experiments

4.1 Calibration of Precision Vacuum Oven

The vacuum oven was calibrated to prepare the catalyst/zeolite solid matrices. The temperature inside the oven was observed several times using an infrared (IR) thermometer. After equilibration was reached (generally after ~30 minutes), the temperature was read for various dial settings. The temperature calibration was performed for 0 mm Hg vacuum (i.e., atmospheric pressure) and for 5 mm Hg vacuum. The results from these calibrations were determined both increasing the dial setting (from 0 to ~ 9) and decreasing the dial setting (from ~9 to 0), to determine whether there was a significant hysteresis effect. Results for the calibration of the vacuum oven are presented in Figures 4-2 and 4-3 for the case of a vacuum oven of 0 mm Hg; similar results were obtained for the case of a vacuum of 5 mm Hg as shown in Figures 4-4 and 4-5.

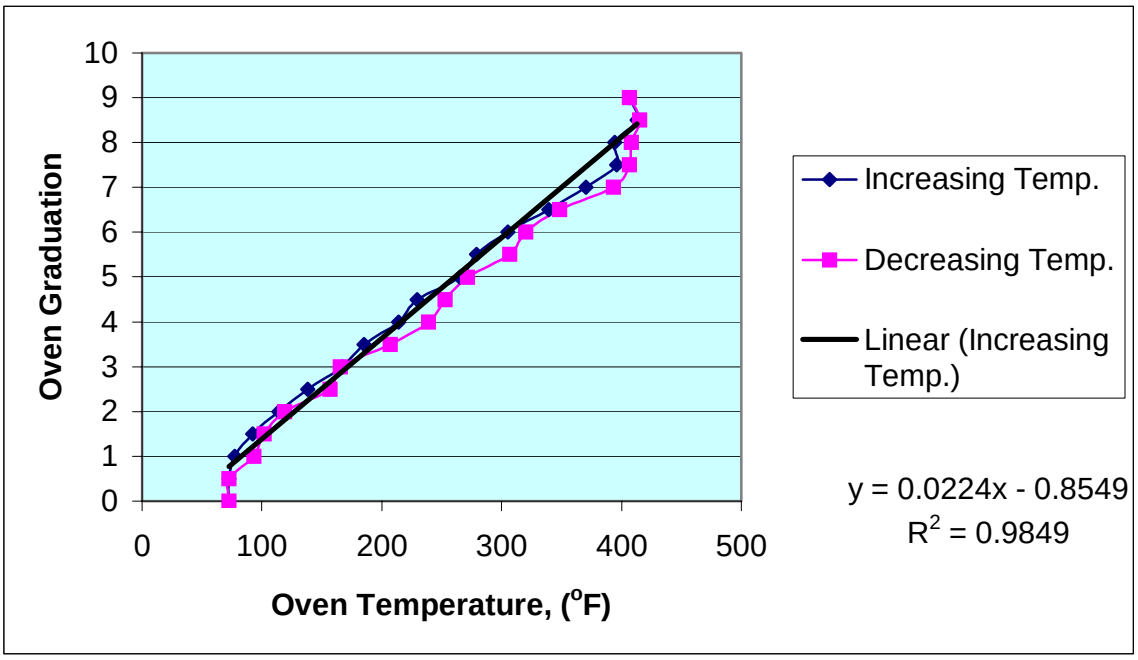

Figure 4-2. Oven graduation to measured oven temperature (pressure = 0 mm Hg)

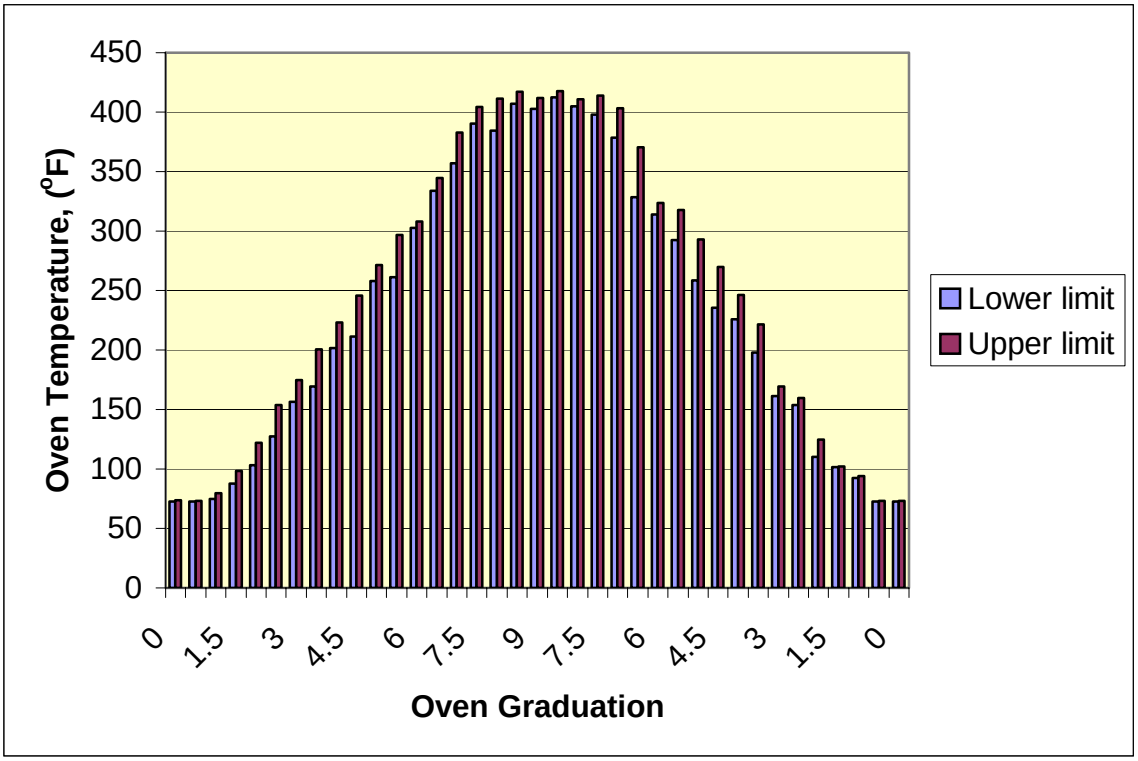

Figure 4-3. Measured oven temperature as a function of oven graduation (increasing and decreasing) at 0 mm Hg vacuum

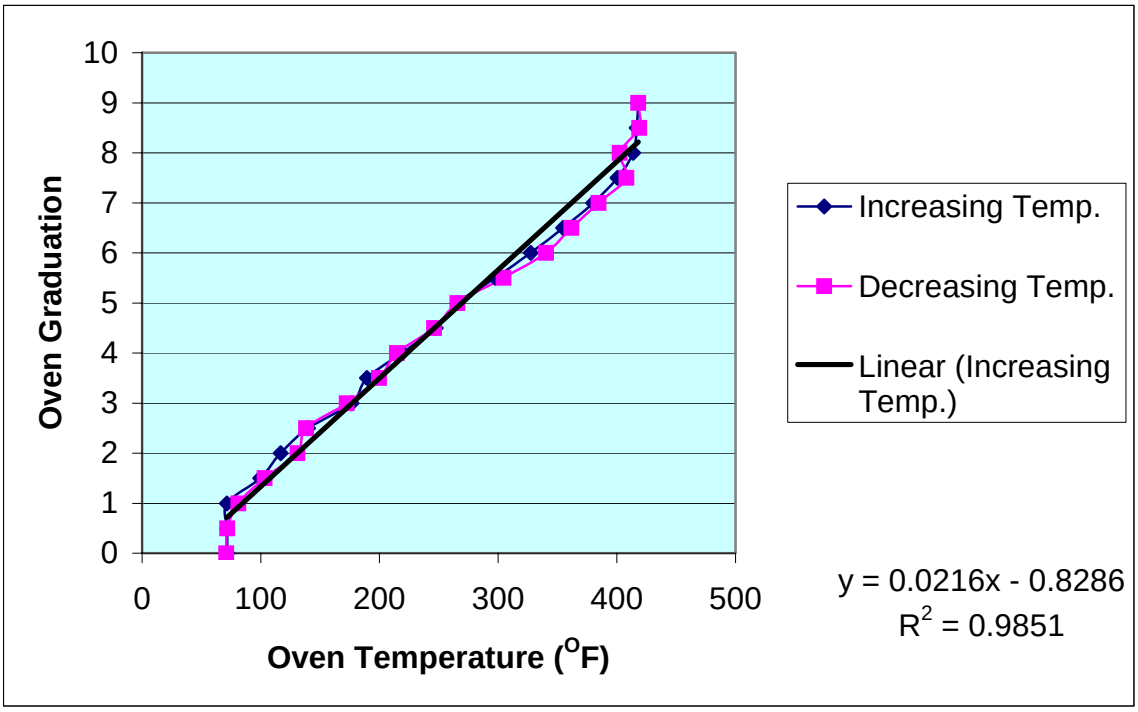

Figure 4-4. Oven graduation to measured oven temperature (5 mm Hg vacuum).

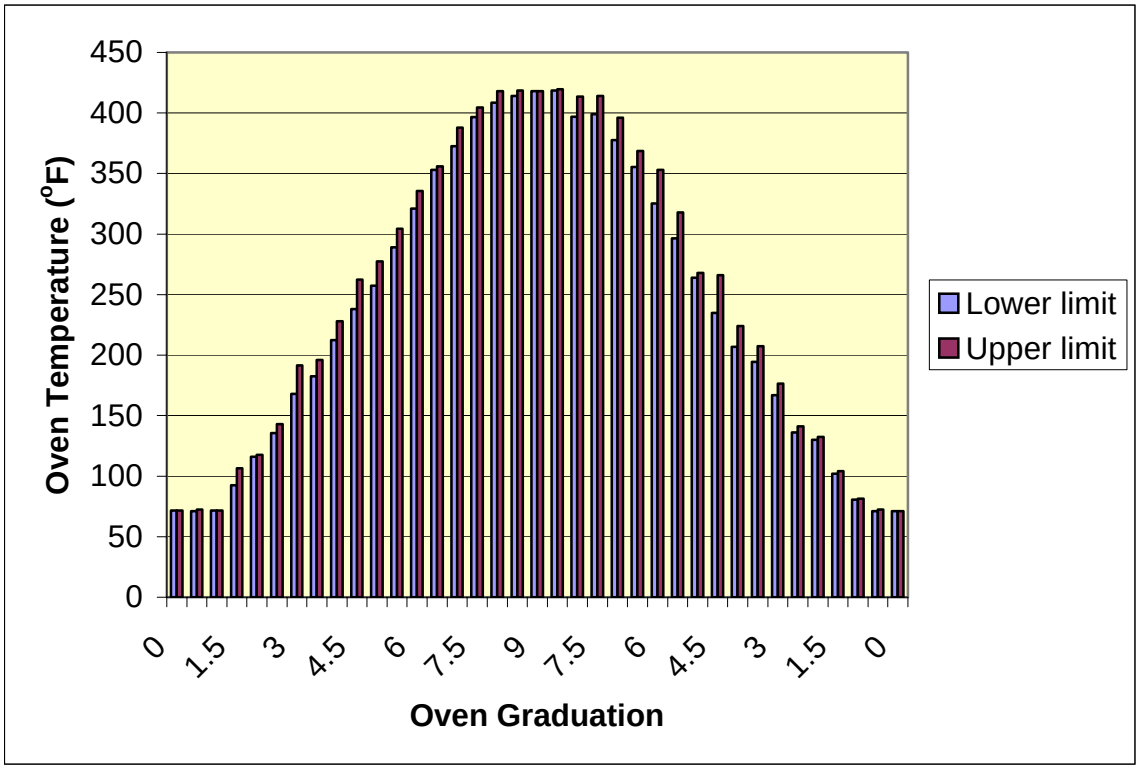

Figure 4-5. Measured oven temperature as a function of oven graduation (increasing and decreasing) – 5 mm Hg vacuum.

4.2 Calibration of Thermocouples

Prior to performing the experiments on the catalyst/zeolite canister system, the heating tape and its associated controller had to be calibrated. This system was calibrated using the J-type thermocouples and the power supply received from Argonne National Laboratory. As a precursor, the system was calibrated using ice water (0^{o}C) and boiling water (100^{o}C). The calibration procedures and results of the calibrations are provided by Gill [2003].

4.3 Analysis of Calibration Results

t-tests were performed to determine whether the calibration curves using the left-hand knob versus using the right-hand knob were statistically different, or could be considered to be identical. Results from the t-tests are summarized in a thesis by Mandeep Gill [2003]. We concluded that the difference was not significant and the temperature measured by the same thermocouple at different knobs (left-hand and right-hand) can be considered to be the same.

4.3.1 Calibration of J-Type Thermocouples versus Electrothermal Graduation, Using Different Air Flow Rates through the Copper Tubing

The effect of the air flow rate through the copper tubing was tested to determine whether it had a significant effect on the temperature of the copper tubing achieved using the heating tapes. Air movement within the copper tubing could have a cooling effect on the steady-state temperature obtained using the heating tape. Three different air flow rates were tested: 0, 500-, and 900-mL/min. Results of the t-tests are listed and described in the Gill's Master's thesis [2003]. Results on the calibration curves show that the various air flow rates in the range of 0- to 900-mL/min had a negligible effect on the temperature achieved using the heating tape.

4.4 Conclusion

By comparing the mean values of variable one and variable two, as described by Gill [2003], the conclusion is that the difference was not significant and the temperature measured by the same thermocouple at two different air flow rates (0, 500, and 900 mL/min) can be considered to be the same.

4.5 Measurement of Flow Rates

The gas flow rate was measured using gas, by passing it through a soap solution in a burette (6-cm in diameter). Compressed gas cylinders (95% Argon and 5% methane) were used. Two sets of data were collected at each pressure and then the mean flow rate was calculated. The results are presented in Figure 4-6.

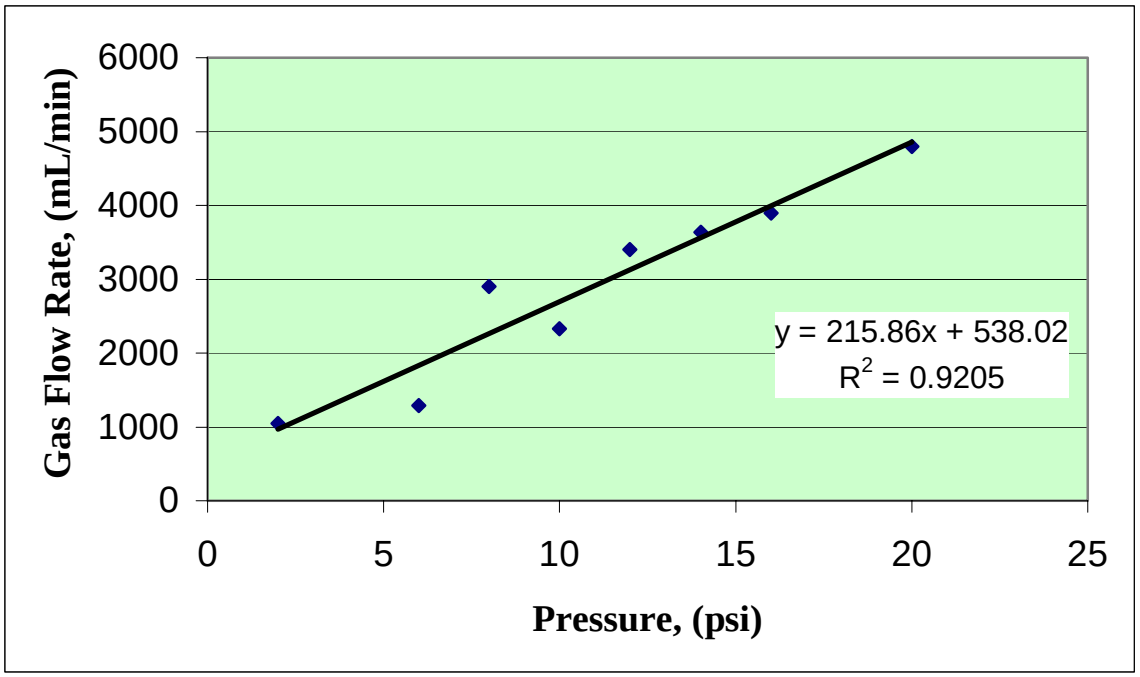

Figure 4-6. Graph showing gas flow rate as a function of the applied pressure.

Section 5.0
Project Findings/Results and Discussion

5.1 Zeolite Characterization

Analysis was performed on the synthetic diesel exhaust collected before and after it passed through the catalyst/zeolite canister system. Exhaust gas was passed at different pressures (and hence different flow rates) through different catalyst/zeolite matrices and through a the zeolite matrix. The experimental sets are listed in Table 5-1.

Table 5-1. Permutations and combinations of experiments performed

Number of sets of experiments	Catalyst/zeolites matrix or only zeolite matrix	Pressure (psi)
1	Catalyst/Zeolite of Set I	6
2	Catalyst/Zeolite of Set II	6
3	Zeolite	6
4	Catalyst/Zeolite of Set I	12
5	Catalyst/Zeolite of Set II	12

The experimental operating conditions, the removal efficiencies obtained, and the calculations to predict the performance at higher temperatures (750^{o}F) are listed in section 5 of Gill's thesis [2003]. The data were used to calculate the number of samples to be tested and to conduct statistical analyses (t-tests). More extensive information related to the data collected in each experiment, statistical testing results, and estimates of the removal efficiencies at the temperature of the experiment and at 750^{o}F are contained in a thesis authored by Mandeep Kaur Gill [2003]. In the project, eight types of zeolites (supplied by Argonne National Laboratory) were used to prepare copper catalysts:

- Zeolyst CBV – 21A; NH_4 MOR
- Zeolyst CBV – 10A; Na MOR
- Zeolyst CBV – 3024E; NH_4 MFI
- Zeolyst CBV – 28014a; NH_4 MFI
- Zeolyst CP 811E – 75; HBEA – 75 (Zeolite H – Beta Powder)
- Zeolyst CP 811C – 300; HBEA (LOT 1822-20)
- Zeolyst CBV 100 Zeolite Na-Y; Na-Fau
- Zeolyst CBV 720; H.Y. Zeolite

The catalyst/zeolite matrices were prepared using the "shake-and-bake" technique, described in Appendix A. A subsample of these samples was sent to Argonne National Laboratory for x-ray diffraction (XRD) analysis; results of those analyses are summarized in Table 5-2.

Table 5-2. Results of the catalyst/zeolite analysis using x-ray diffraction analysis

Sample Description	XRD Identification No.	Average Crystallite Thickness, (Å)
CP811C-300; H-BEA	MN02	235
CP811E-75; H-BEA-75	MN06	274
CBV-28104a, NH_4-MF1	MN01	362
CBV-3024E; NH_4-MF1	MN04	295
CBV-10A; Na-MOR	MN03	>2000
CBV-21A; NH_4-MOR	MN05	420

A surface area analysis was performed by Argonne National Laboratory using BET analysis to compare the surface area of virgin zeolite with the catalyst zeolite samples and to estimate the percentage crystallinity of each sample. The results are summarized in Table 5-3.

Table 5-3. Results of the catalyst/zeolite analysis using surface area analysis

Catalyst	Zeolite Type	Surface Area (native), (m^2/g)	Surface Area (new sample), (m^2/g)	% Crystallinity (estimate)
CP811C-300; H-BEA	Beta	620	496.6	80.10
CP811E-75; H-BEA-75	Beta	620	512.8	82.71
CBV-28104a, NH_4-MF1	ZSM-5	400	321.1	80.275
CBV-3024E; NH_4-MF1	ZSM-5	400	308.8	77.20
CBV-10A; Na-MOR	Mordenite	425	373.9	87.98
CBV-21A; NH_4-MOR	Mordenite	500	412.6	82.52

The average (mean) percent crystallinity of these samples was 81.80 percent. All of the individual results exceeded 77 percent. Dr. Christopher Marshall, Group Leader of Argonne's Heterogeneous Catalysis group, indicated that the percent crystallinity should exceed 75 percent for the catalyst to be effective for treatment of petroleum hydrocarbon contaminants. Thus, the preparation of the catalyst/zeolite samples was considered to be successful, with all the percent crystallinities exceeding 75 percent.

5.2 Removal Efficiency for Different Catalyst/Zeolites at Various Operating Conditions

Results from the individual experiments for removal of synthetic diesel exhaust using the catalyst/zeolite matrix are summarized by Gill [2003]. The results indicate a significant pressure drop across the canister. This pressure loss was due to plugging and losses around the canister openings. Similar patterns were observed in the other sets of experiments.

Table 5-4 summarizes the mean removal efficiencies obtained for the various catalyst/zeolite and zeolite systems used in the study. The data in this table was used to compare the removal efficiency of the catalyst/zeolite system versus the global (overall) catalyst/zeolite system, and to compare the removal efficiencies obtained using the catalyst/zeolite system with the corresponding zeolites used without a catalyst.

Table 5-4. Comparison of Removal Efficiencies Obtained for the Various Catalyst/ Zeolite and Zeolite Alone Systems over all Experimental Conditions

Sample Description		Removal Efficiency, (%)					
Catalyst/Zeolite	Cu/NH4 MOR	64.57	46.08	40.98			
Zeolite	Zeolyst CBV-21A	81.08	10.23				
Catalyst/Zeolite	Cu/Na MOR	36.09	30.07	65.02			
Zeolite	Zeolyst CBV-10A	94.70	38.52				
Catalyst/Zeolite	Cu/NH4 MFI	66.58	56.35	32.44	38.50	46.08	
Zeolite	Zeolyst CBV-28014a	31.78	23.15				
Catalyst/Zeolite	Cu/NH4 MFI	40.70	49.32	45.05	37.95	77.17	68.41
Zeolite	Zeolyst CBV-3024E	40.41	15.91				
Catalyst/Zeolite	Cu/HBEA-75	64.80	89.41	48.03	43.26		
Zeolite	Zeolyst CP811E-75	35.12	21.22				
Catalyst/Zeolite	Cu/HBEA	62.49	77.67	55.75	66.18		
Zeolite	Zeolyst CP 811C-300	48.53	35.09				
Catalyst/Zeolite	Cu/NA FAU	80.33	51.30	55.49	48.51		
Zeolite	Zeolyst CBV-100	81.89	19.02				
Catalyst/Zeolite	Cu/HFAU	65.54	64.04	55.88	49.06	46.05	
Zeolite	Zeolyst CBV-720	31.51	29.33				

Results from the various test sets are described in detail by Gill [2003]. Figure 5-1 summarizes the removal efficiencies obtained using the various catalyst/zeolite matrices at an operating pressure of 6 psi. The copper nitrate/Na-FAU system had the highest mean removal efficiency with 80.33 percent. For all the catalyst/zeolite matrices, the removal efficiencies ranged from 40.70 percent to 80.33 percent, despite operating at a relatively low temperature (ranging from 170^{o}F to 295^{o}F). It was encouraging to achieve a mean removal efficiency of 59.1 percent averaged over all the catalysts/zeolite matrices, despite the low temperatures involved. Use of higher temperatures is examined in UTCA Project No. 03203.

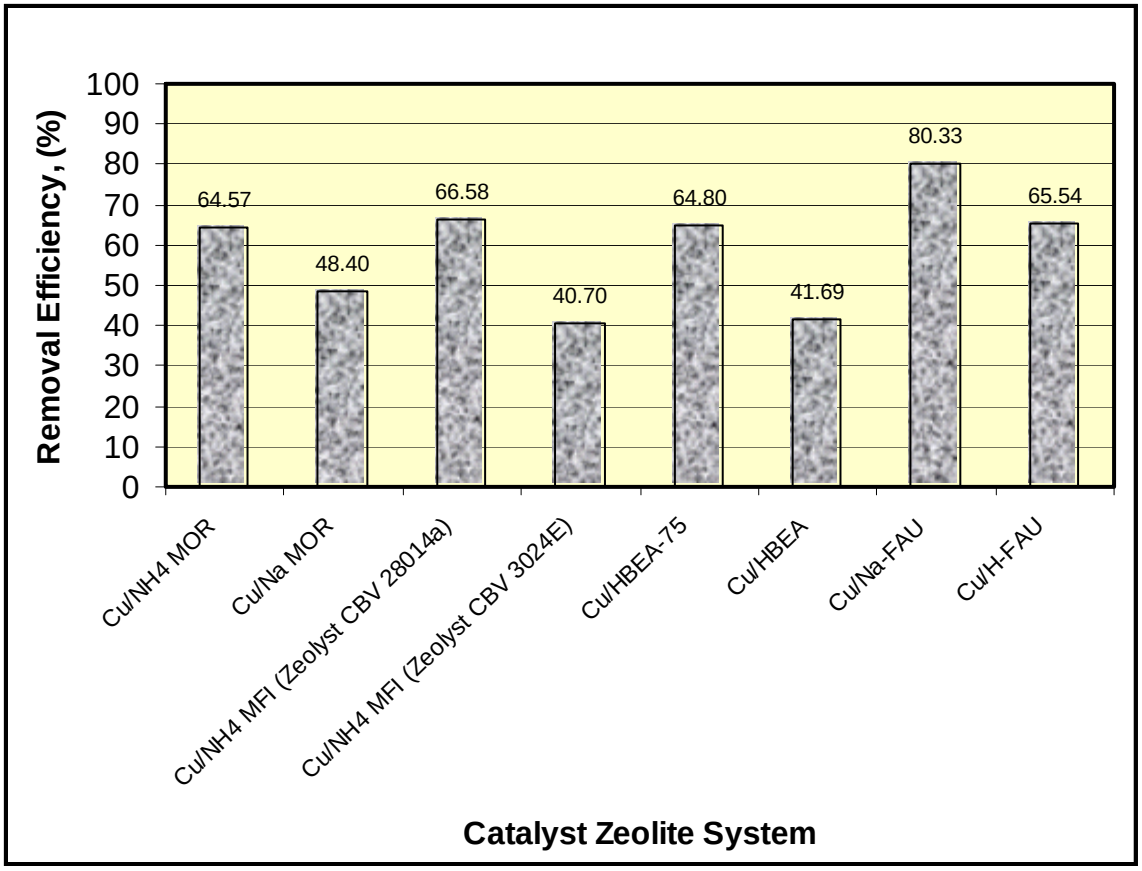

Figure 5-1. Removal efficiency of catalyst/zeolite (set I) at pressure 6 psi.

Figure 5-2 presents the mean removal efficiencies for the various catalyst/zeolite matrices in a separate set of experiments for an operating pressure of 6 psi. The operating temperature of the canister ranged from 190^{o}F to 310^{o}F during this set of experiments. The copper/HBEA catalyst/zeolite system had the highest mean removal efficiency with 77.67 percent. The removal efficiencies ranged from 19.9% to 77.7 percent, with a mean removal efficiency of 43.6 percent averaged over the eight catalyst/zeolite combinations.

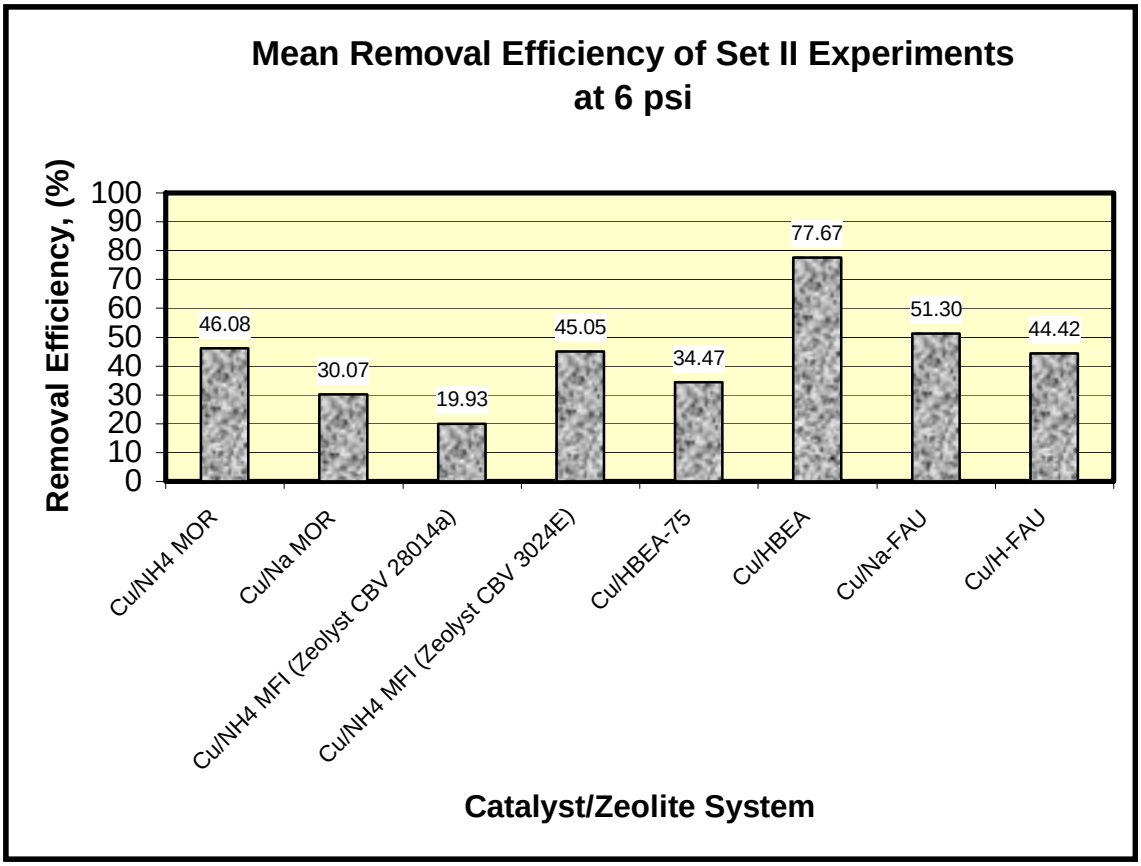

Figure 5-2. Removal efficiency of catalyst/zeolite (Set II) at pressure 6 psi

Figure 5-3 presents the results in terms of the mean removal efficiencies obtained from analogous experiments for removal of synthetic diesel exhaust using only the individual zeolite systems (conducted in the absence of catalyst), again operating at a pressure of 6 psi. The temperature of the canister ranged from 230^{o}F to 300^{o}F during this set of experiments. The mean removal efficiencies for removal of synthetic diesel exhaust ranged from 31.5 percent to 94.7 percent in this set of experiments. The mean removal efficiency averaged over the eight zeolites was 55.6 percent, which was comparable to the results obtained for the copper nitrate/zeolite systems. It is interesting to note that the highest removal efficiency was obtained for the Na-mordenite zeolite (removal efficiency ~94.7 percent), followed closely by Na-FAU zeolite (removal efficiency ~81.9 percent) and ammonium-mordenite zeolite (removal efficiency ~81.1 percent). These results indicate that of the eight zeolites tested in this investigation, the following all appear promising as a base solid monolith in which to support the catalyst: HBEA, NH_4-MOR, Na-MOR, and Na-FAU.

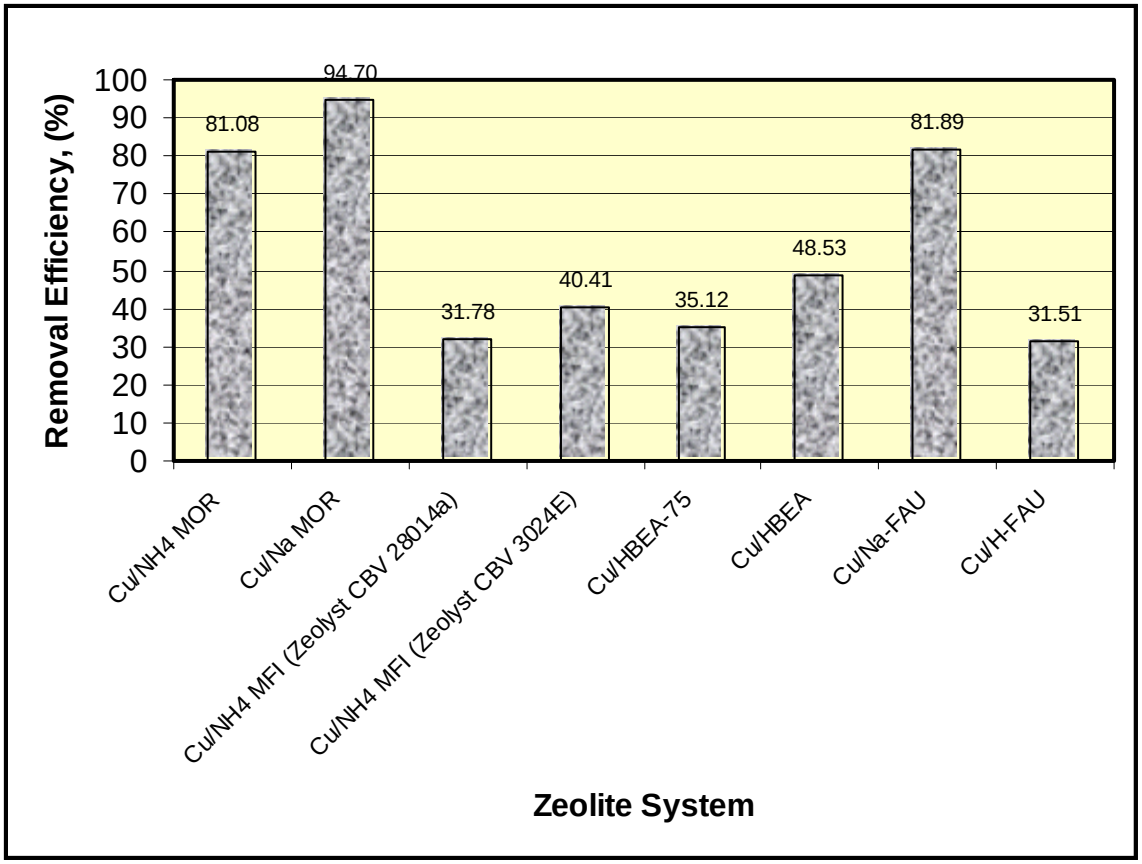

Figure 5-3. Removal efficiency of catalyst/zeolite (set I) at pressure 6 psi

Figure 5-4 shows the results of the eight combined copper nitrate/zeolite matrices tested in this investigation operating at a pressure of 12 psi. The temperature of the canister ranged from 175°F to 300°F during this set of experiments. The mean removal efficiencies for removal of synthetic diesel exhaust ranged from 31.5 percent to 94.7 percent in this set of experiments. The mean removal efficiency averaged over the eight catalyst/zeolite systems was 52.3 percent. The highest removal efficiency was obtained for the copper nitrate/HBEA zeolite (removal efficiency ~89.4 percent), followed closely by the copper nitrate/NH_4 MFI (Zeolyst CBV 28014a) zeolite (removal efficiency ~77.2 percent).

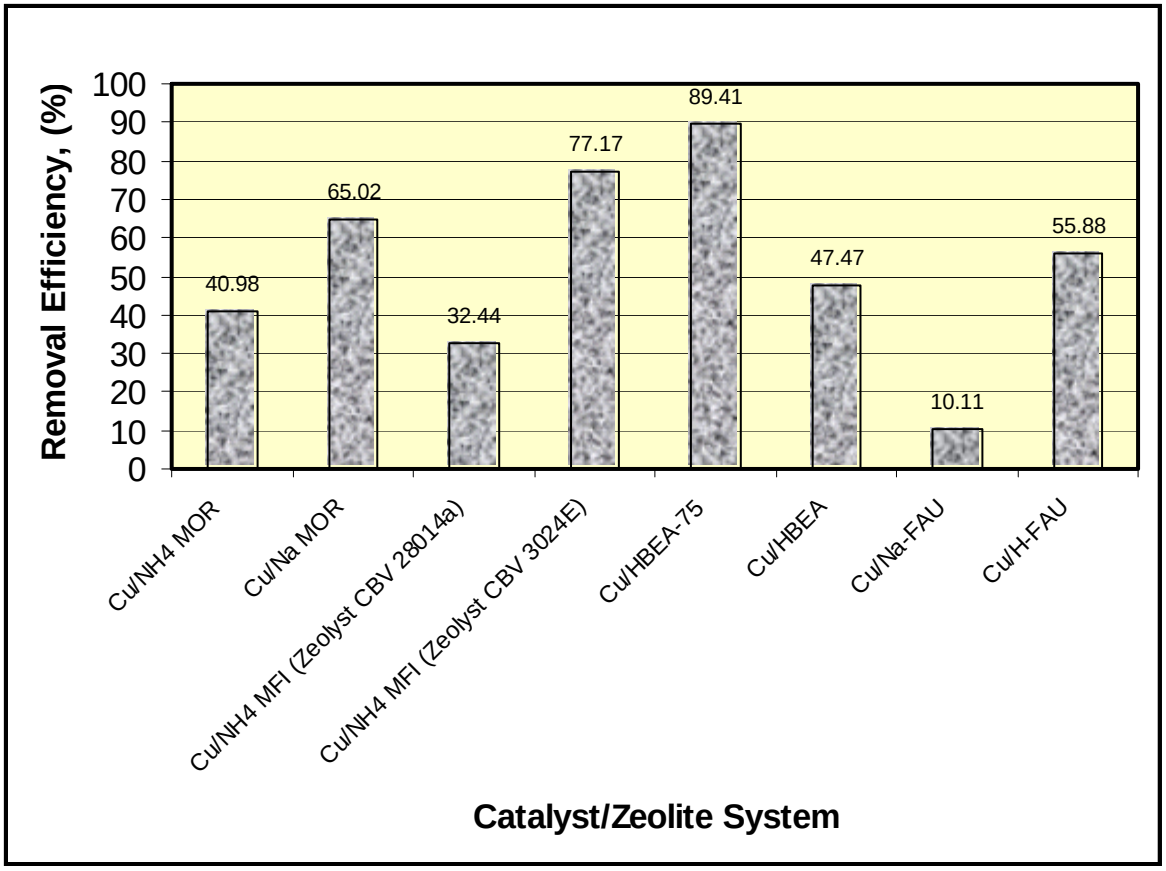

Figure 5-4. Removal efficiency of catalyst/zeolite (set I) at pressure 12 psi

These various laboratory performance tests were conducted for temperatures of the casing of the canister ranging from 170°F to 310°F and applied pressures of 6 to 12 psia, corresponding to gas flow rates through the canister from 1830 to 3130 mL/min. This corresponds to space velocities on the order of 8,000 hr^{-1}. This is about an order of magnitude lower that typical space velocities exiting from diesel engines. Higher space velocities are addressed in the continuation grant of this project. In this project, the stainless-steel canister was heated with electrical heating tape. Typical temperatures out of the exhaust stack from mobile diesel-powered vehicles are in the range of 600 to 800°F, with 750°F being a very representative temperature. Despite operating at much lower temperatures (170 to 310°F), reasonable removal efficiencies were still obtained. Removal efficiencies by the combined copper nitrate catalyst/zeolite matrices typically exceeded 50 percent, with removal efficiencies as high as 94.7 percent being achieved. Using reaction engineering principles involving the Arrhenius relationship to predict the removal efficiency at typical operating temperatures around 750°F, removal efficiencies were estimated to be nearly 100 percent.

Figure 5-5 shows the results of five combined copper nitrate/zeolite matrices tested in this investigation operating at a pressure of 12 psi. The temperature of the canister ranged from 190°F to 305°F during this set of experiments. The mean removal efficiencies for removal of synthetic diesel exhaust ranged from 43.3% to 68.5% in this set of experiments. The mean

removal efficiency averaged over the eight catalyst/zeolite systems was 55.55 percent. The highest removal efficiency was obtained for the copper nitrate/NH_4 MFI (Zeolyst CBV 28014a) zeolite (removal efficiency ~68.5 percent), followed closely by the copper nitrate/NH_4 MFI (Zeolyst CBV 3024E) zeolite (removal efficiency ~68.4 percent).

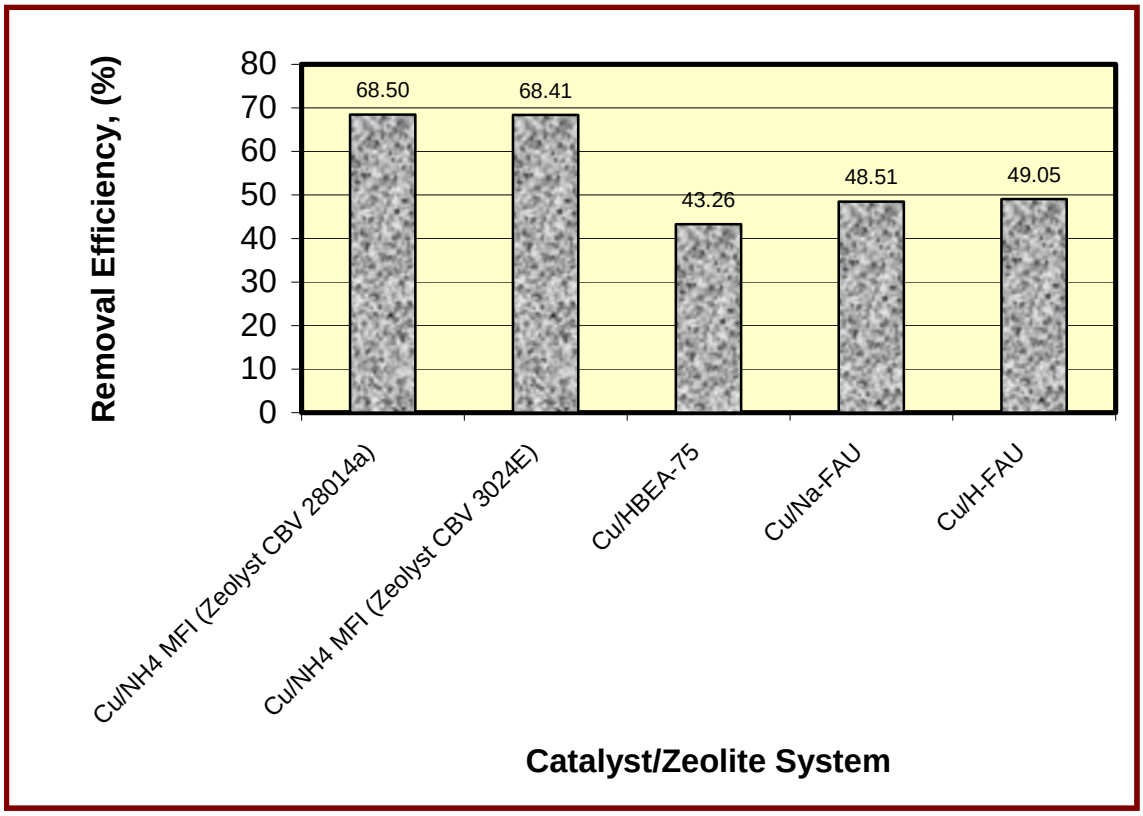

Figure 5-5. Removal efficiency of catalyst/zeolite (Set II) at pressure 12 psi

5.3 Comparison of the Effect of Different Operating Pressures on the Removal Efficiency of Synthetic Diesel Exhaust Using the Various Catalyst/Zeolite Systems

Figure 5-6 shows a comparison of the mean removal efficiencies obtained at the lower operating pressure employed (6 psi) and the higher operating pressure employed (12 psi), performed under Set I and Set II experiments. t-tests were performed to determine whether the removal efficiency was statistically different for the two operating pressures. From the t-tests, the value of α exceeded 0.4; thus, the removal efficiency at the two pressures can be considered to be statistically identical. The t-tests are summarized in more detail in a thesis by Gill [2003].

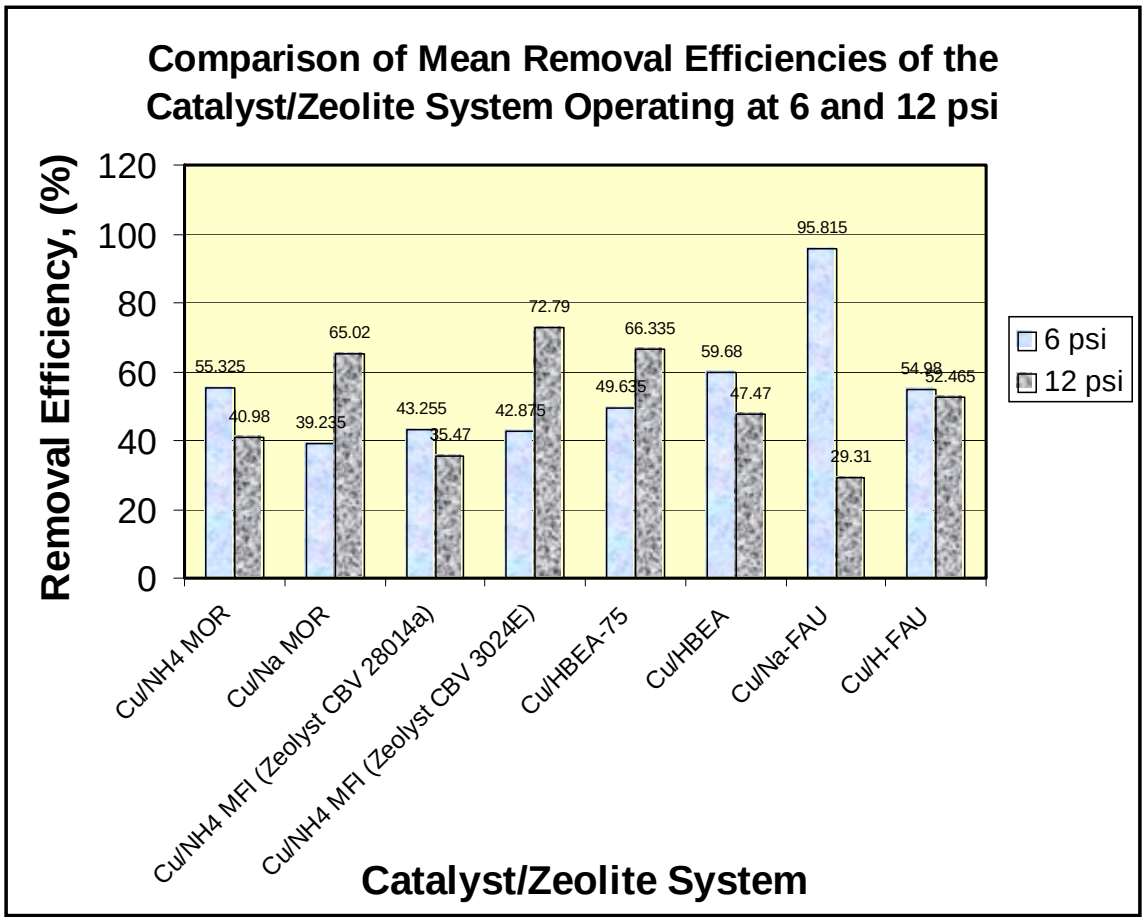

Figure 5-6. Comparison of removal efficiency of synthetic diesel exhaust using various catalyst/zeolite systems operating at 6 and 12 psi

5.4 Statistical Hypothesis Testing

The performance for the removal of synthetic diesel exhaust using the various catalyst/zeolite matrices was compared using t-tests for the differences in mean values. The estimation of the number of required samples for the difference are contained in the Master's thesis authored by Mandeep Gill [2003]. With the exception of the allowable difference being 20 ppm, all were typically less than 25 samples. For the lower allowable difference (20 ppm), the number of samples was estimated to range from 78 to ~1500. Additionally, t-tests were performed to determine whether the difference in means (of the experimental removal efficiencies) between various experiments was statistically significant. t-tests performed and their results are summarized for the following set of conditions [Gill, 2003]:

- Mean removal efficiency of catalyst/zeolite versus the overall catalyst/zeolite removal efficiency – the removal efficiency of both the samples was statistically the same;

- Mean removal efficiency of catalyst/zeolite versus mean removal efficiency from the zeolites alone – the removal efficiency of both the samples was statistically the same; and
- Comparison of the removal efficiency for the catalyst/zeolite system at two different operating pressures – For catalyst of Set 1 (pressure – 6 psi) versus catalyst of Set 1 (pressure – 12 psi), removal efficiency of a catalyst at two different pressures is not statistically same. For catalyst of set 1 (pressure – 6 psi) versus catalyst of set 2 (pressure – 6 psi), the removal efficiency of a catalyst of set 1 and corresponding catalyst of set 2 at pressure 6 psi were unequal. For the catalyst of set 2 (pressure – 6 psi) compared versus the catalyst of set 2 (pressure – 12 psi), the removal efficiency of both samples was the same.

5.5 Results from Argonne National Laboratory's Cermet Microsensor Testing of UAB Tedlar Bag Samples

5.5.1 Results and Observations

A number of gas samples were drawn from UAB emissions studies apparatus, bagged, and were delivered to Argonne National Laboratory for exposure to the experimental gas microsensors. Two different types of ceramic-metallic (cermet) gas microsensors were tested (yttria-stabilized zirconia [YSZ], and tungsten bismuth oxide [WBO]), both of the voltammetric operating principle but differing in the materials composition of the solid electrolyte film incorporated in the sensing element. The voltammetric gas microsensors are active devices and work as a detection system, coupling a cermet electrochemical cell, a voltammetric measurement technique, and advanced pattern recognition for response signature analysis. The system is described and pictures of the system are presented in Argonne websites [Argonne National Laboratory, 2004a,b,c]. This was the first series of tests of the laboratory devices against samples received from an outside source. The results were interesting; clearly showing that concentrations of gases were changing in the samples tested, and showed that both types of microsensors were appropriate for the application (see Figures 5-7 and 5-8), though the WBO devices exhibited a more obvious functional relationship to changing gas composition. Additional microsensor responses are presented and described by Gill [2003].

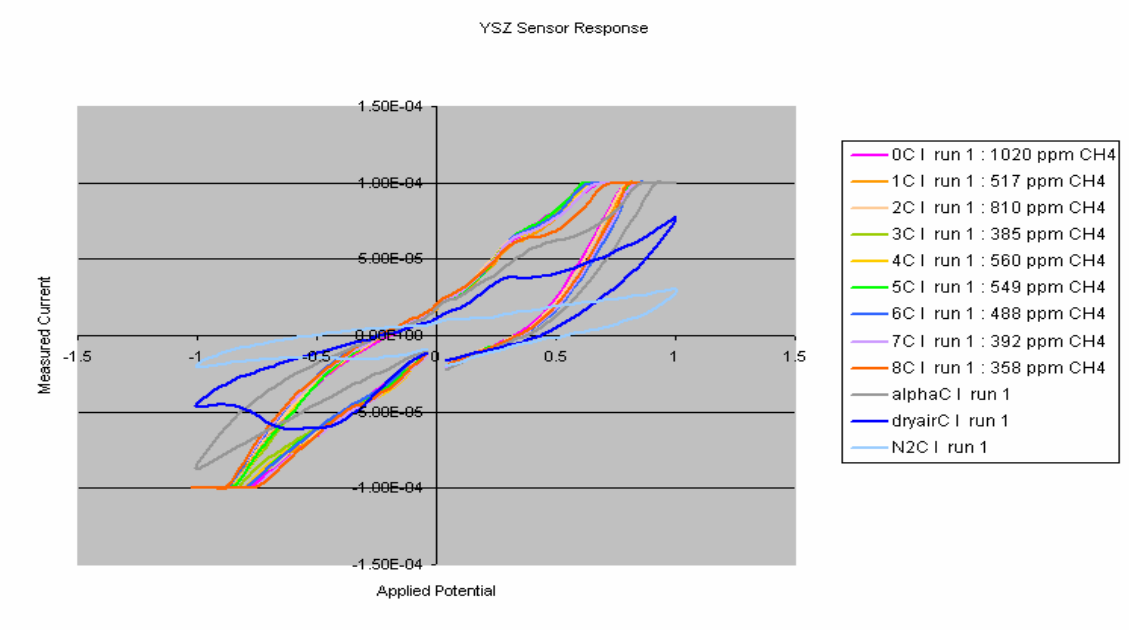

Figure 5-7. YSZ microsensor responses to subset of the test gases

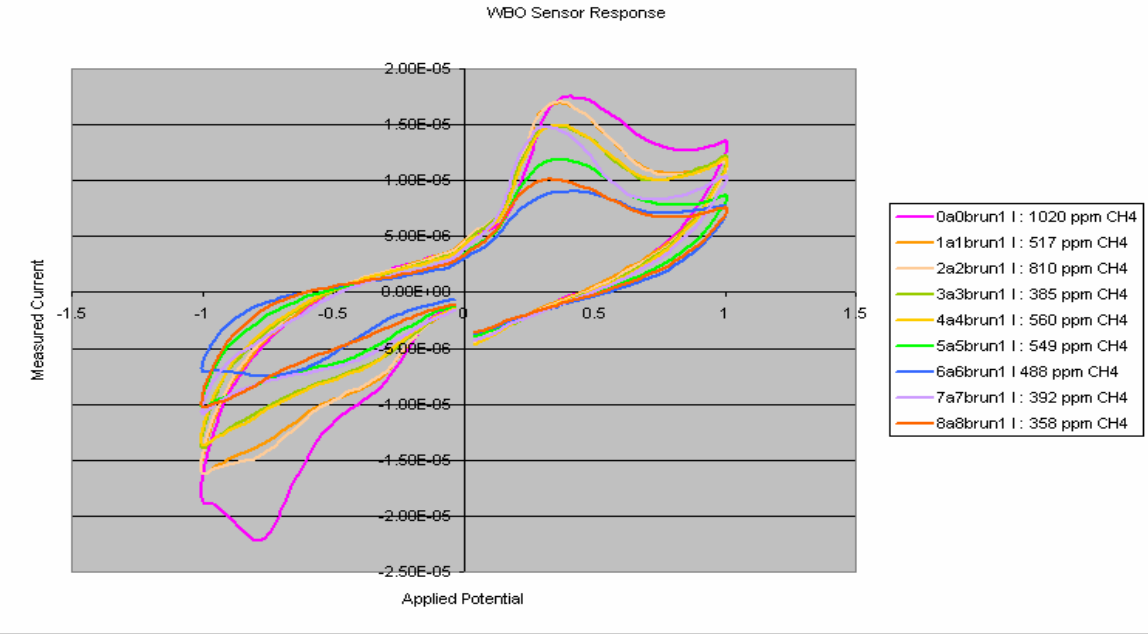

Figure 5-8. WBO microsensor responses to subset of the test gases

Several shortcomings in this first series of tests were observed and were used as feedback to alter future tests. The sample sizes were smaller than was ideal to produce multiple voltammetric results using the existing pumping/miniature test chamber apparatus at Argonne. This series of

tests clearly showed that the sample was diluted as it was introduced and the composition changed measurably as each successive voltammetric test was completed.

Argonne National Laboratory did not perform duplicate gas testing to calibrate the sensor prior to receiving the UAB samples. This limited the testing results to only a subset of gas signatures with no or limited concentration/composition information for which to train the [probabilistic neural network (PNN)] pattern recognition algorithm. It is the PNN that performs either composition analysis of the signatures or categorization depending upon the content and details of the concentration/composition information. Attempts were made to perform several different types of neural network training using the range values for specific components in the UAB samples. Performance was not reliable and only reinforced the need to prepare a second test matrix, correcting the dilution issues for the small samples size and insuring that the comprehensive composition information is gathered, with actual measured values vs. ranges for the sample compositions. The use of ranges compounded the error observed from the each successive sample being diluted.

The promising aspect of the effort was observed by comparing only the first 'run' of each test gas, with the YSZ sensor and with the WBO sensor. These first voltammograms should be comparable as each experiences the same level of dilution during sample pumping. These voltammetric signatures clearly show a sensitivity level useful for this application, with visually obvious changes in the voltammograms as a function of concentration changes of low 1's to 10's of ppms of CH_4. Past experience has shown that if the changes in voltammograms can be visually detected, then the numerical methods [PNNs] can readily convert this to a numerical measurement with an associated confidence factor.

A second series of test was executed a few days after the first set. These tests followed the same protocol as the first set, but passed the samples past various zeolites before sampling. The results reinforce the findings of the initial tests – *that a more rigorous calibration matrix must be developed and provided if accurate, quantifiable, results are to be produced from the Argonne microsensor array*. Only partial concentration information was gathered and provided along with the Tedlar-bagged samples. This information included a broad concentration range for only the CH_4 (methane) component in the mixtures. This CH_4 measurement was sampled over a significant time period during which each sample was gathered. The average CH_4 concentration was attached to the charts below to identify them, but, this average is not statistically useful as the range of concentrations over which it was acquired is dramatically different for each sample. This made it impossible to calibrate any pattern recognition algorithms for either analysis or broad classification. To compound the problem, the actual concentration of CH_4 in each sample was dynamic as the sample sizes were too small to be used effectively with the original Argonne sampling chamber – each sample was diluted and changed as it was introduced into the chamber. This is clearly indicated in the first of the following figures (see Figures 5-9 through 5-11). Referring to Figure 5-9, for each sample 9, 14, and 15 – Run 1 was executed as soon as the sample was introduced into the test chamber, and Run 2 was executed after the sample was moved from the Tedlar bag to the chamber. There was not enough of each sample to flush out past contents and the captured signatures changed for each case.

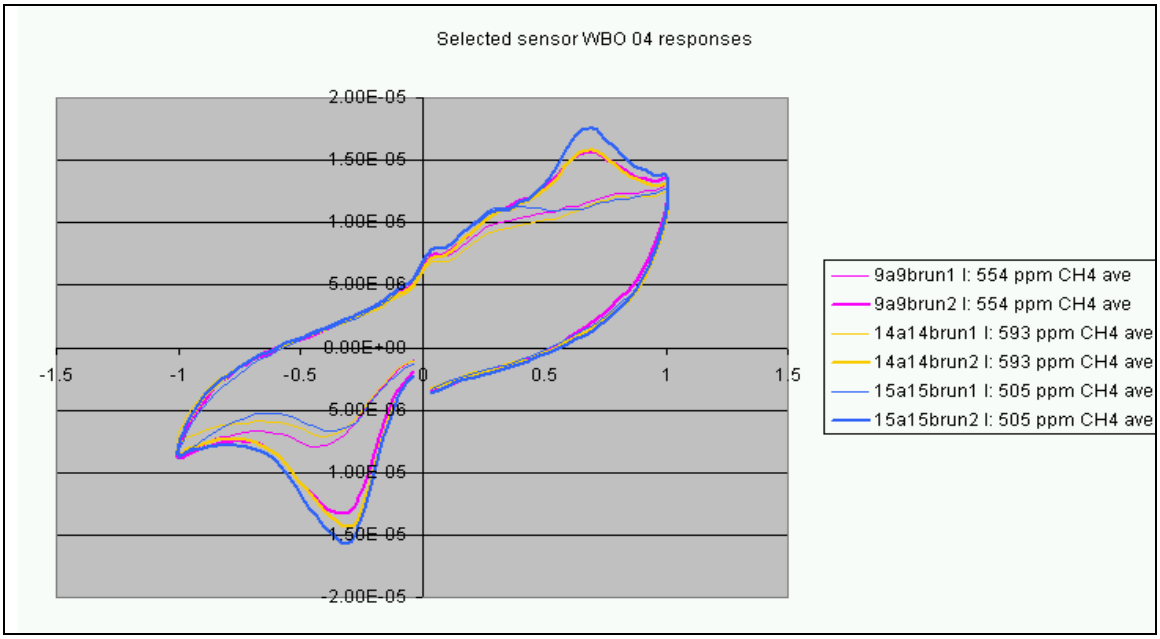

Figure 5-9. WBO microsensor responses, post-zeolites, to subset of the test gases. Significant change in signature due to small analyte sample size – dramatic concentration change during test. Run 1-Run 2 changes for sample 9, 14, and 15

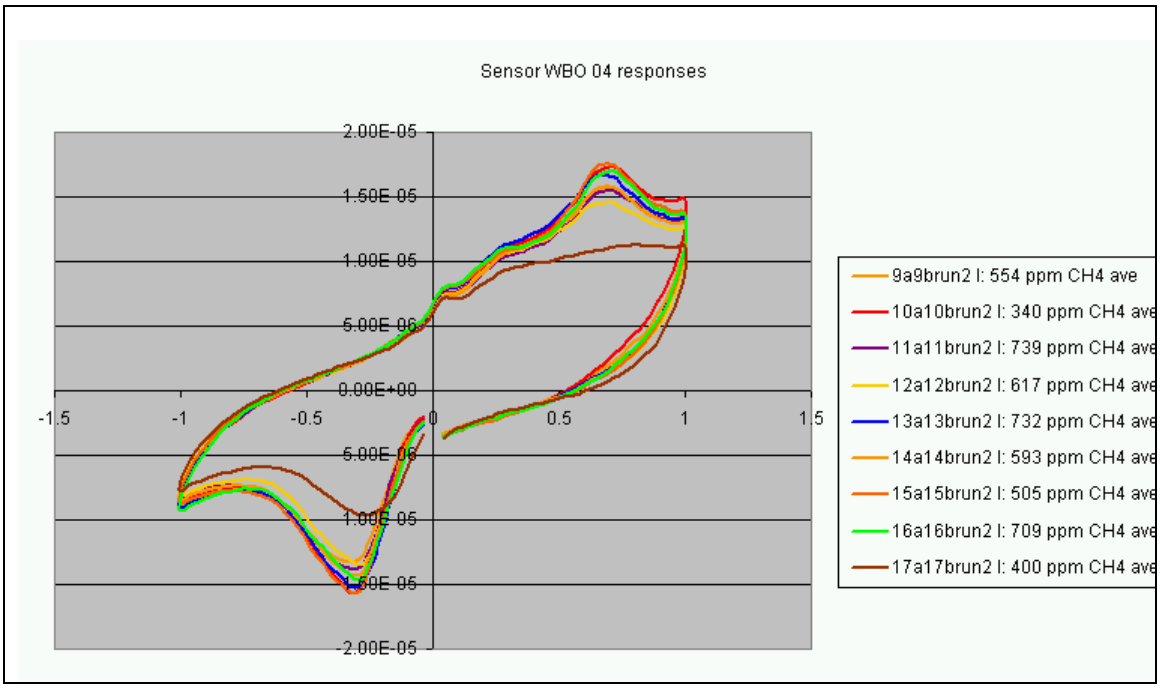

Figure 5-10. WBO microsensor responses, post-zeolites, to subset of the test gases. Good separation of reaction peaks at clearly gas-specific potentials, but, poor functional relationship between signatures

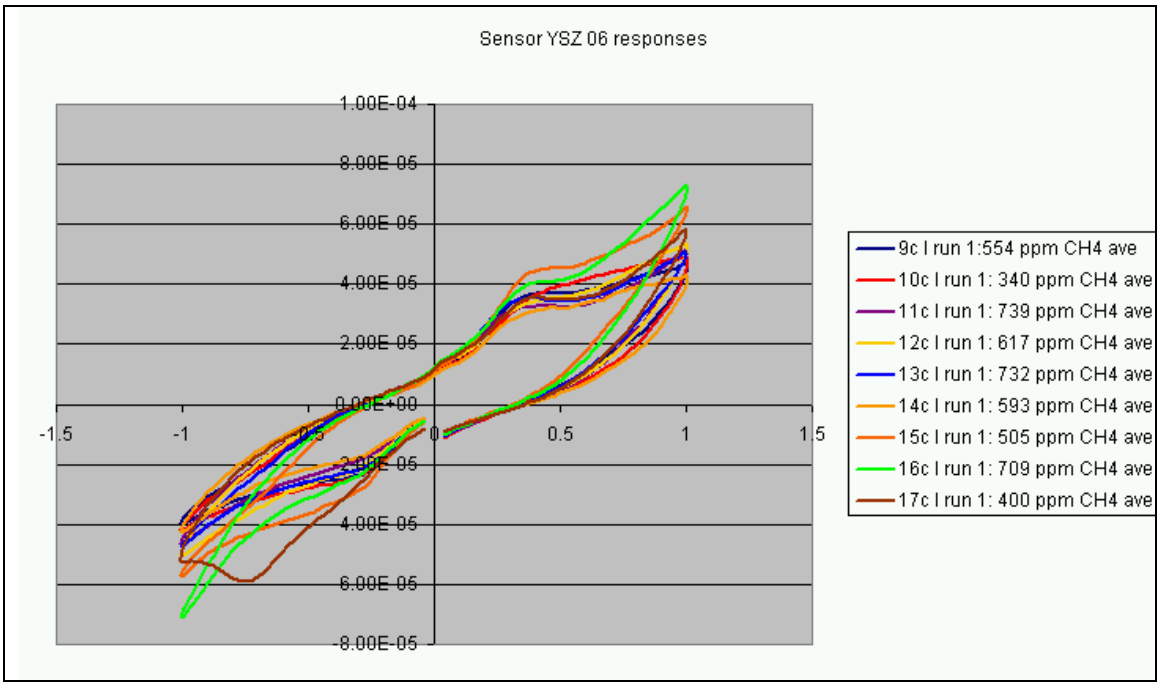

Figure 5-11. YSZ microsensor responses, post-zeolites, to subset of the test gases

5.5.2 Testing Protocol and Sample Contents

Samples were sent to Argonne National Laboratory by Federal Express immediately following the sampling. The samples were introduced to the Argonne cermet sensor array(s) within a few days, and the samples processed weeks later along with results from other testing.

The concentrations determined using gas chromatography techniques (performed at UAB) were compared with the concentrations determined using the cermet microsensors technique. The results from various samples analyzed at both UAB and Argonne National Laboratory are summarized in Tables 5-5 to 5-7. Tables 5-5 and 5-6 present the comparison of methane concentrations for the first and second set of samples determined using both GC and cermet microsensor analyses. Table 5-7 presents the overall comparison of the concentrations determined by GC and cermet microsensor analyses (from the two sets of samples).

Table 5-5. Comparison of methane concentrations determined by gas chromatography and cermet microsensor techniques (for first set of samples).

First Set of Samples	
Concentration of Methane, (ppm)	
GC Analysis	Cermet Microsensor
366.8	358
382.65	392
436.5	385
594.8	488
604.9	580
673.1	517
740.7	549
970.6	810
1020	1020

Table 5-6. Comparison of methane concentrations determined by gas chromatography and cermet microsensor techniques (for second set of samples)

Second Set of Samples	
Concentration of Methane, (ppm)	
GC Analysis	Cermet Microsensor
340.25	340
400.0	400
505.4	505
554.37	554
628.7	617
662.05	593
720.8	709
783.85	739
803.5	732

Table 5-7. Overall comparison of methane concentrations determined by gas chromatography and cermet microsensor techniques (for the two sets of samples)

Overall Comparison	
Concentration of Methane, (ppm)	
GC Analysis	Cermet Microsensor
340.25	340
366.8	358
382.65	392
400.0	400
436.5	385
505.4	505
554.37	554
594.8	488
604.9	580
628.7	617
662.05	593
673.1	517
720.8	709
740.7	549
783.85	739
803.5	732
970.6	810
1020	1020

The results of comparison for gas chromatography and cermet microsensors are shown in Figures 5-12, 5-13, and 5-14, for the first set, second set, and combined sets of samples, respectively.

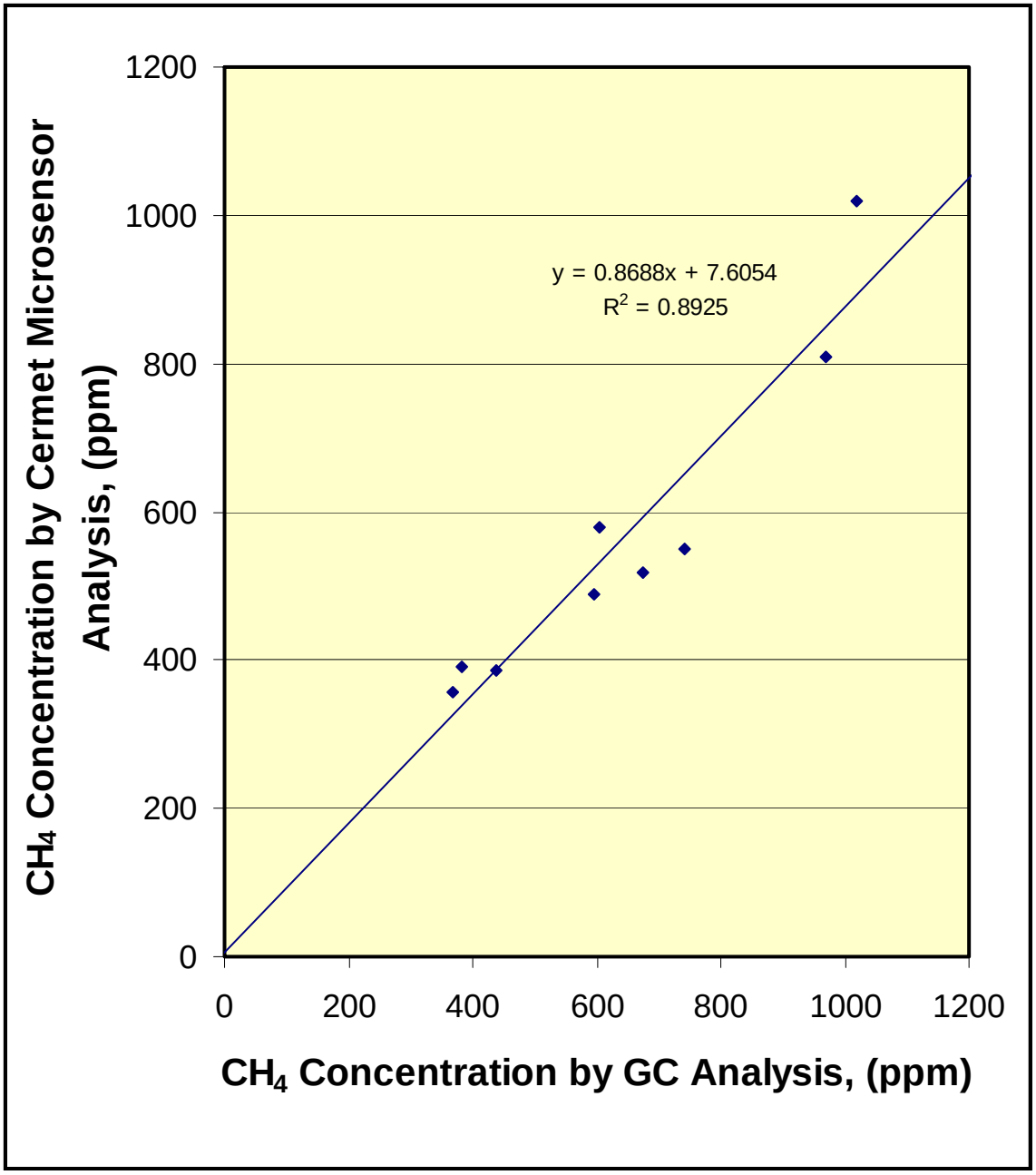

Figure 5-12. Comparison of methane concentration exiting from the packed bed canister containing catalyst/zeolite using gas chromatography and cermet microsensor techniques for the first set of samples

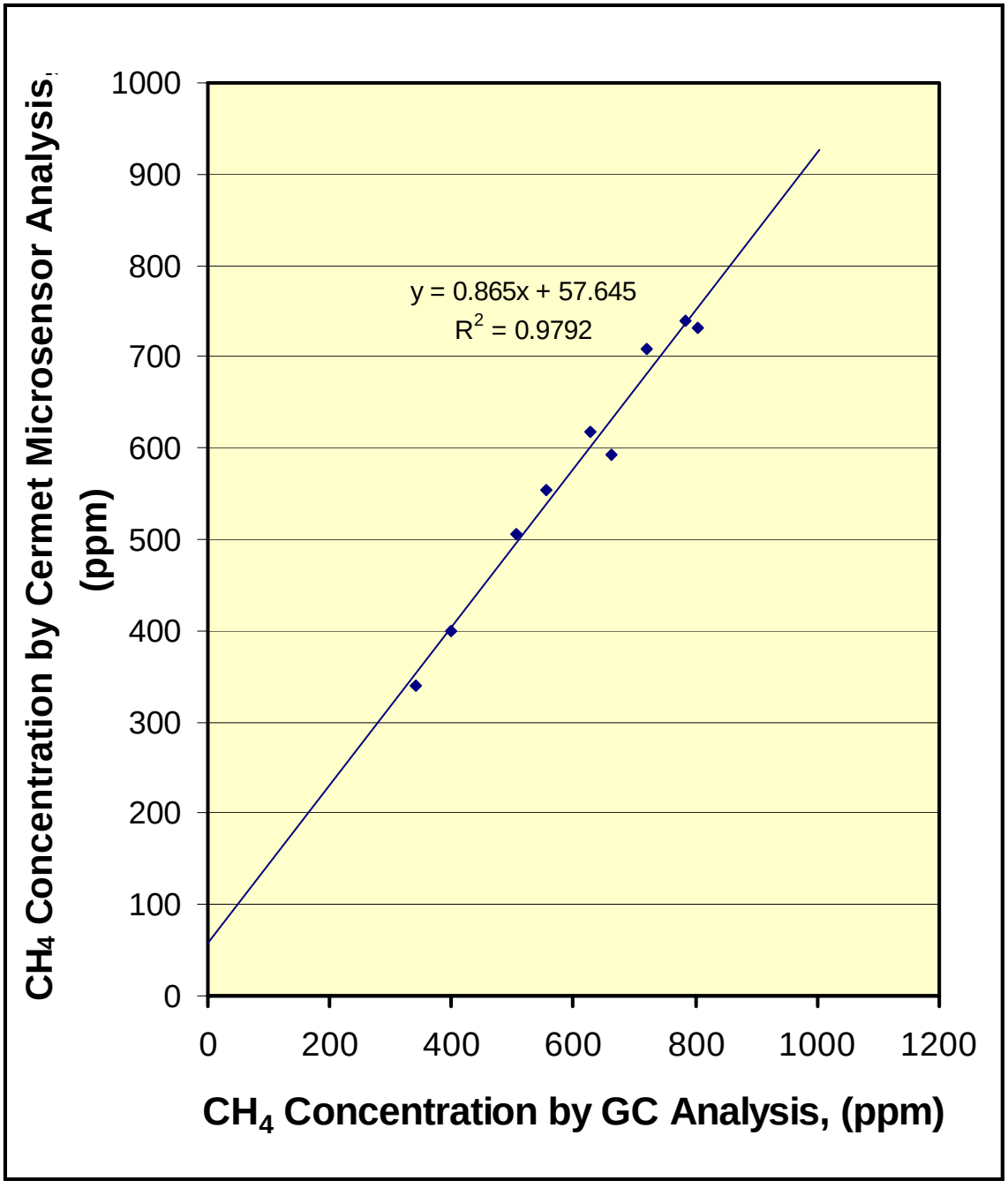

Figure 5-13. **Comparison of methane concentration exiting from the packed bed canister containing catalyst/zeolite using gas chromatography and cermet microsensor techniques for the second set of samples.**

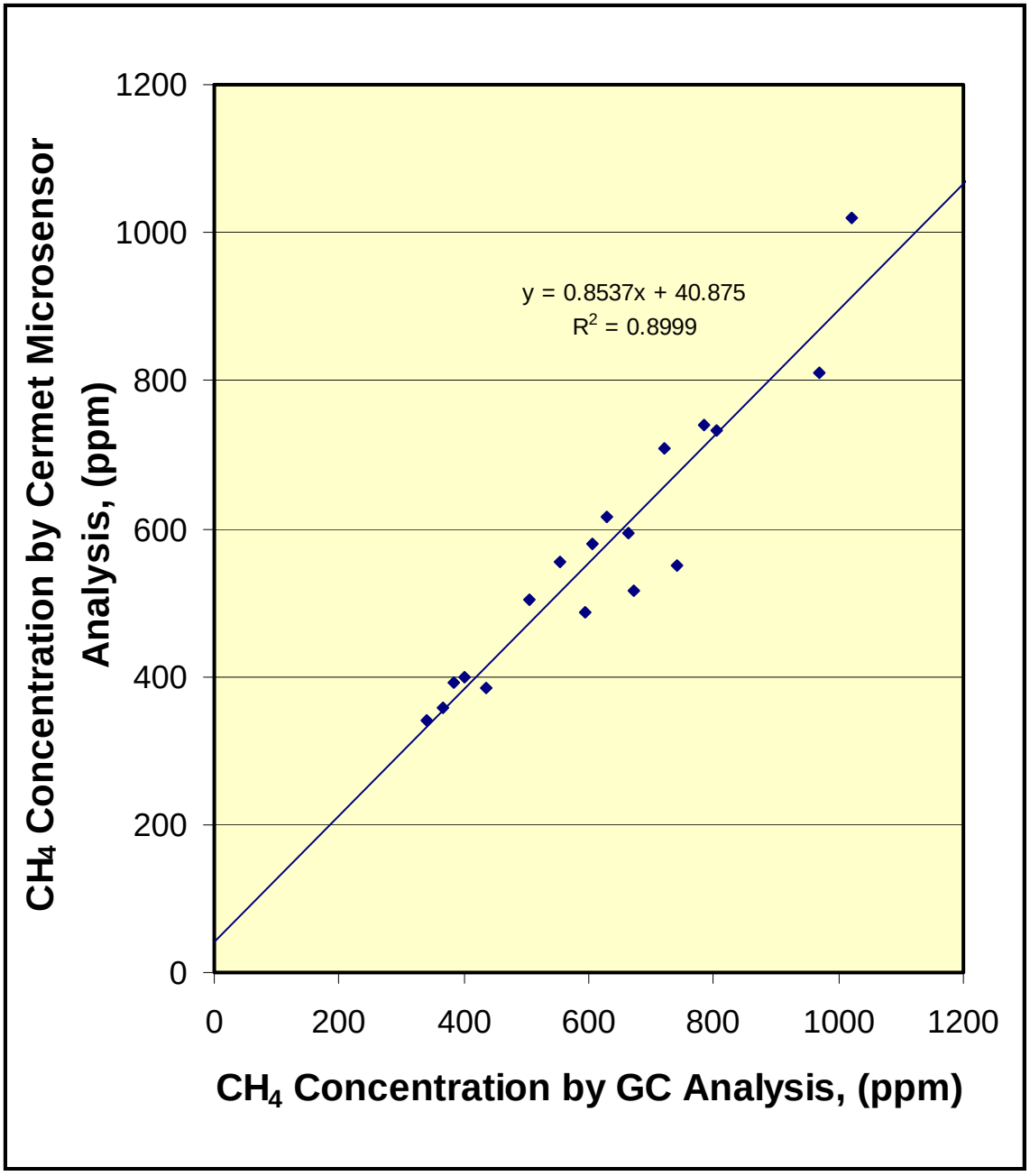

Figure 5-14. **Overall comparison of methane concentration exiting from the packed bed canister containing catalyst/zeolite using gas chromatography and cermet microsensor techniques for the two sets of samples**

These three figures show that there is a strong correlation between the concentrations determined by gas chromatography techniques and the cermet microsensor technique. The correlation coefficients for these three data sets were 0.8925, 0.9792, and 0.8999, respectively, indicating a strong correlation between results obtained by GC and cermet microsensors. Tables 5-6 through 5-8 and Figures 5-12 through 5-14 indicate the cermet microsensor provides slightly lower concentrations than obtained by gas chromatography techniques. This is noted from the slopes

of the least squares lines in Figures 5-12 through 5-14, being 0.8925, 0.9792, and 0.8999. All the slopes are less than 1.0. This indicates that the results obtained by the cermet microsensor techniques typically are slightly less than those obtained by GC analysis. This may be due to factors such as storage in the Tedlar bags (adsorption on the methane on the plastic), potential leakage in the Tedlar bags, small sample sizes involved, delay in time due to shipping and scheduling at Argonne National Laboratory, etc. However, the results are extremely encouraging as the two analytical techniques provide comparable results for the methane concentrations.

Section 6.0
Project Conclusions and Recommendations

This final report has outlined the phases involved during the development of catalyst/zeolite matrix to bench testing of the catalyst/zeolite systems on synthetic diesel exhaust. The theoretical and experimental bench tests have been successfully applied to achieve the research objective. The significant results achieved from the catalyst/zeolite matrix development and testing are summarized below.

6.1 Calibration of Precision Vacuum Oven

For preparation of catalyst/zeolite system, the Precision vacuum oven was calibrated using an infrared thermometer, as described in Section 4.1. Temperature was read for various dial settings in increasing as well as decreasing order, to determine if there was any hysteresis effect. The temperature calibration was performed for 0 mm Hg vacuum (i.e., atmospheric pressure) and for 5 mm Hg vacuum.

6.2 Calibration of Thermocouples

J-type thermocouples and a power supply were supplied by Argonne National Laboratory. From them, eight thermocouples (J3, J13, J28, J33, J2, J8, J1 and J6) were initially calibrated using ice water (0^oC) and boiling water (100^oC).

6.3 Calibration of J-type Thermocouples versus Electrothermal Controller Graduation

Prior to performing the experiments on the catalyst/zeolite canister system, heating tape and its associated controller were calibrated using thermocouples. Two heating tapes, Fibroxt and Grounded (TP FG STD) and Silicon Rubber and Grounded Heating (SIL HTG TP), were used to heat the equipment. A calibration curve was determined for various graduations on the knobs (i.e., left-hand and right-hand knob) of the two–way controller. Both the heating tape and the thermocouples (such as J2 and J8) were wound around the equipment. t-tests was performed on this data to determine whether the calibration curves, using the left-hand knob versus using the right-hand knob, were statistically different or could be considered to be the same. Results from the t-tests indicated that the difference was not significant by the same thermocouple at two different knobs and could be considered to be the same.

6.4 Calibration of J-type Thermocouples versus Electrothermal Graduation, Using Different Air Flow Rates through the Copper Tubing

The effect of air flow rate through the copper tubing was tested in calibration tests to determine whether it had a significant effect on the temperature of the copper tubing achieved using the heating tapes. Three different air flow rates were tested: 0, 500-, and 900-mL/min. The results and t-tests indicated that the difference in temperature for the various air flow rates was not significant and the temperature measured by the same thermocouple at two different air flow rates (0, 500, and 900 mL/min) could be considered to be statistically the same. The values of the level of significance, α, were all greater than 0.05 (the usual value for such tests). Therefore, for the null hypotheses considered, the two data sets could be considered to be statistically the same.

6.5 Measurement of Gas Flow Rates

The flow rate was measured using gas from the compressed gas cylinder, by passing it through a soap solution. The data indicated that the gas flow rate varied linearly (correlation coefficient ~ 0.9205) for applied pressure from 2 to 20 psi), resulting in gaseous flow rates ranging from 1050 to 4800 mL/min.

6.6 Statistical Hypothesis Testing

t-tests were performed to compare removal efficiency of the following:

a. *Removal efficiency of catalyst versus catalyst globally* – t-tests were performed involving two samples (i.e., catalyst versus catalyst) assuming equal variance. Due to the small number of samples taken, the statistical analyses generally indicated $\alpha > 0.4$, meaning that all the sets of catalyst were statistically the same.
b. *Removal efficiency of the catalyst and corresponding zeolites* – t-tests were performed involving two samples (i.e., catalyst and zeolite) assuming equal variance. Due to the small number of samples taken, the statistical analyses generally indicated $\alpha > 0.4$, meaning that all the sets of catalyst versus zeolite can be considered to be statistically the same.
c. *Catalyst of Set 1 (pressure – 6 psi) versus catalyst of Set 1 (pressure – 12 psi)* – t-tests were performed. Due to the small number of samples taken, the statistical analysis indicated that $\alpha > 0.4$, meaning that all the sets of catalyst could be considered to be statistically the same. The removal efficiency of a catalyst at two different pressures cannot be considered to be statistically the same [Gill, 2003]; the removal efficiency of a catalyst of set 1 at two different pressures (6 psi and 12 psi) is not the same.
d. *Catalyst of Set 1 (pressure – 6 psi) versus catalyst of Set 2 (pressure – 6 psi)* – t-test results were performed. Due to the small number of samples collected, the statistical analysis indicated $\alpha > 0.4$, meaning the removal efficiency of both the samples is statistically the same. Two sets of catalyst at the same pressure are not statistically the same [Gill, 2003].
e. *The catalyst of Set 2 (pressure – 6 psi) was compared versus the catalyst of Set 2 (pressure – 12 psi)* – t-tests were performed. Due to small number of samples taken, the statistical analysis indicated $\alpha > 0.4$, meaning that the removal efficiency of both samples is the same.

6.7 Comparison of Analyses by Gas Chromatography and MicroSensor Techniques

The removal efficiency of catalyst/zeolite system was analyzed using our GC system. It was also cross-checked by sensors available at Argonne National Laboratory (ANL). There was a strong correlation between the concentrations determined by gas chromatography techniques (performed at The University of Alabama at Birmingham) and the cermet microsensor technique (performed at Argonne National Laboratory). The cermet microsensor is observed to provide slightly lower concentrations than that obtained by gas chromatography techniques; this may be due to factors such as storage in the Tedlar bags (adsorption on the methane on the plastic), potential leakage in the Tedlar bags, small sample sizes, delay in time due to shipping and scheduling on the analytical instrumentation at Argonne National Laboratory, etc. However, the results are extremely encouraging as the two analytical techniques (gas chromatography and cermet microsensors) provide comparable results for the methane concentrations.

6.8 Assessment of Results Obtained

Results were obtained at lower temperatures (~200-300ºF); despite this low temperature range involved in this study, reasonable removal efficiencies were still obtained (typical removal efficiencies ranged from 30 percent to 90 percent), depending on the particular combination of catalyst and zeolite involved. Using thermodynamic principles, the removal efficiency was estimated at 750^{o}F. At this elevated temperature, removals of nearly 100% were estimated.

Due to higher removal efficiencies obtained, the following zeolites all appear promising as a base solid monolith in which to support the copper nitrate catalyst: HBEA, NH_4-MOR, Na-MOR, and Na-FAU.

Despite the statistics indicating that the performance was essentially the same for these various catalysts and zeolites used, the following systems gave the best results:

a. From statistical analysis, the catalyst (Cu/H FAU) and zeolite (Zeolyst CBV 720) are not statistically the same and the efficiencies can not be considered to be the same.
b. From statistical analysis, the removal efficiency of a catalyst (Cu/NH_4MFI, Zeolyst CBV 28014a) at two different pressures is not statistically the same. The removal efficiency of a catalyst (Cu/NH_4MFI, Zeolyst CBV 28014a) of set 1 at two different pressures (6 psi and 12 psi) is not the same.
c. From statistical analysis, it was concluded that two sets of catalyst at the same pressure are not statistically the same. The removal efficiency of a catalyst (Cu/NH_4MFI, Zeolyst CBV 28014a) of set 1 and corresponding catalyst (Cu/NH_4MFI, Zeolyst CBV 28014a) of set 2 at pressure 6 psi is not the same.
d. The performance of two sets of catalyst at the same pressure are not statistically the same. The removal efficiency of a catalyst (Cu/H-FAU) of Set 1 and corresponding catalyst (Cu/H-FAU) of Set 2 at pressure 6 psi is not the same.
e. Many of the statistical analyses showing essentially the same performance were direct results of the extremely small number of samples used. If the sample size was greater (say 10-20) samples, different conclusions could have been drawn to give a much clearer picture about the best systems to treat diesel exhaust. From results generated in the laboratory and

analyzed and presented in this final report, the concept of using catalysts/zeolites to treat diesel exhaust emissions has strong technical merit and is worth pursuing in the developmental phase.

6.9 Recommendations for Future Work

While performing the experiments, various observations were made. Based upon those observations, several suggestions are made to further improve the canister system and experimental procedures:

1. If the catalyst/zeolite powder is made into a pelletized form and inserted in the canister system, it will likely result in lower pressure drops and minimal cake formation on the outlet side of canister. This technique is being studied in the continuation project.
2. If the catalyst is spread on the honeycomb structure, there will be less pressure drop and more surface area for reaction and contact time.
3. To minimize pressure losses and loss of exhaust while passing through the canister, the design of the canister should be altered slightly, making it more air-tight. High temperature tolerable seals can be used to seal the openings around the nuts or adjoining surfaces.
4. If noble metals could be selected for study in the next phase of the project instead of copper nitrate, they may have better removal efficiencies.
5. While analyzing the gaseous samples in the GC system, a calibration curve should be prepared for the pollutants to be analyzed. Such a calibration curve should be prepared for the next phase of the study.
6. For analysis purpose, gas samples were stored in Tedlar bags (1.6-L) which were shipped to ANL for analysis using microsensors. Due to the time lapse between sample grabbing and analyzing, exposure to light or possible leakage, results obtained were less then the actual concentration observed by the GC. For this purpose, samples should be stored in larger Tedlar bags of volume ~10-L to 15-L, in opaque or dark boxes.

Section 7.0
Papers Presented at National Conferences

Gill, M.K., and R.W. Peters, 2003. "Treatment of Synthetic Diesel Exhaust Using Catalysts/Zeolites", Paper submitted for presentation at the 1st UTCA Research Results Symposium, Birmingham, AL, (November 17).

Gill, M., S. Jones, and R.W. Peters, 2002. "Overview of Treatment Technologies for Removal of Diesel Compounds and NO_x from Mobile Sources", Paper presented at the IEEE Vehicular Technology Conference, Birmingham, AL, (May 6-9).

Section 8.0
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APPENDIX A. METHOD FOR PREPARING THE CATALYST/ZEOLITE SYSTEM: "Shake–and-Bake" Approach

1. Create a suspension of pure water and zeolite. The suspension concentration should be approximately 5–10% zeolite (by weight), i.e., 10-g zeolite and 190-g distilled water.
2. Add cation at a concentration of 1-2 M.
   - Select the cation based on requirements. Copper nitrate hemipentahydrate [$Cu(NO_3)_2 \cdot 2.5H_2O$] was selected because its counter ion, i.e., nitrate decomposes upon heating.
   - Determine the amount of copper nitrate hemipentahydrate to be added:
     Mass of zeolite to be added = 10-g
     Volume of 190-g distilled water = 190.0 mL = 0.19-L
     Formula weight of copper nitrate hemipentahydrate = 232.59 g/mole
     Let mass of copper nitrate hemipentahydrate = 'x'g
     - Let molarity of solution be = 1 M
       $1\ M = \frac{[(x/232.59)]}{0.19}$
       x = 44.2 g
     - Let molarity of solution be = 2 M
       $2\ M = \frac{[(x/232.59)]}{0.19}$
       x = 88.38 g
     - In our experiment, we have added cation at a concentration of 1.0 M, i.e., 44.2-g of copper nitrate hemipentahydrate.
3. Stir the zeolite suspension with added salt for 1–2 hours. The suspension was continuously stirred for 2 hours on a magnetic stirrer.
4. Filter the suspension. Filter recommendation: fritted vacuum filters – medium sized (zeolite particle size 10 – 20 μm).
5. Side by side, prepare a solution of 190-g distilled water and 44.2-g copper nitrate hemipentahydrate. To this solution, add the zeolite impregnated with copper cations residue obtained on the filter paper, from filtration.
6. Repeat steps 3 - 5.
7. Stir the suspension again for 2 hours and filter it (as per Step No. 4). Finally the residue obtained on the filter paper must be scrapped off and put in the ceramic drying dish.
8. Dry the residue in a vacuum oven at 100–150ºC under a vacuum pressure of 5 mm Hg for 3 hrs.
9. Calcine the residue (air/400ºC) in a ceramic drying dish.
10. For the first few trials, running XRD is recommended to see if the structure of zeolite is still intact.