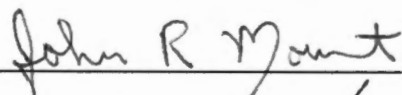
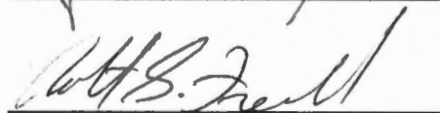


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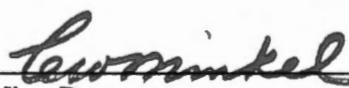
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Dr. Luther R. Wilhelm, Major Professor

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**COMPUTER-BASED ON-SITE CONTINUOUS
CUSTOM GAS MIXING SYSTEM FOR
THE MODIFIED ATMOSPHERE PACKAGING
OF FOOD PRODUCTS**

A Thesis

Presented for the

Master of Science Degree

The University of Tennessee

Kevin Andrew Alfont

August 1994

Ag-VetMed

Thesis
94
.A436

TO:

My mother, Mrs. Rita Tuttle, for her understanding and support throughout my long and challenging academic endeavors. In memory of my father, Dale Alfont, from whom I inherited much of what I am. To my sister, Michele Alfont, for being my big sister. To my wife Suzan, for her love, patience, understanding and encouragement. To my son Andrew, for showing me that God's greatest gift is your children. To my stepdaughter Jessica, for her understanding, patience and support.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation and thanks to the following individuals:

The Department of Agricultural Engineering and its head, Dr. Fred Tompkins, for accepting me into the Graduate Program and making departmental resources available.

Dr. Luther Wilhelm who served as my major professor, for his support, time and guidance which made the learning experience enjoyable.

Dr. John Mount, committee member, for his support, guidance, and assistance in the understanding of current food science practices.

Dr. Robert S. Freeland, committee member, for his patience, time, and technical assistance on this project.

In memory of Dr. R.N. Biswal, committee member, for his guidance and support on this project.

Dr. John Wilkerson, for his help in designing computer software for this project.

Mr. Paul Elliot in the Agricultural Engineering Research Shop for their advice and skill in fabricating essential components for this project.

Dr. Arnold Saxton, for his technical assistance with the statistical analysis of the data obtained during the course of this study.

Special thanks to Mr. Larry Click, undergraduate professor, for preparing me for the challenges of graduate school and beyond.

ABSTRACT

Controlled and modified atmosphere packaging of agricultural products has often been used to provide an environment that will extend the freshness and quality of a product through the distribution chain. Strong emphasis has been placed on developing gas mixtures which will provide optimum environments for specific food products. Development and research into ways of administering these mixtures has been minimal. The purpose of this study was to continue research into the development of an efficient system for on-site custom mixing of three gases.

Flows of three gases suitable for controlled and modified atmosphere packaging (carbon dioxide, oxygen, and nitrogen) were controlled by plug valves. Control of these valves was accomplished by pneumatic actuators, electro-pneumatic positioners, and a D/A PC-bus card. A computer software program was developed to allow the percentages of the various gases in the mixture to be changed "on-line".

Experiments were conducted to verify the percentages of the various gases in a specified mixture. Gas samples were withdrawn using a 10-ml syringe. Gas chromatography was used to measure the concentration of each gas in the mixture. The gas mixing system consistently achieved three target mixtures within an 8.5% accuracy for the vacuum purge procedure. It was able to quickly alternate between the target mixtures without loss of accuracy.

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CHAPTER I

INTRODUCTION

BACKGROUND AND STATEMENT OF PROBLEM

Using modified atmospheres as a method of preservation for perishable products has long been practiced. Most applications of this method have been reserved for bulk shipments of meat and fruits. The use of modified atmospheres in the packaging of retail perishables is a comparatively new development. Only within the last decade have retail product processors and marketers expressed great interest in this method of preservation. Processors and retailers realize that fresh product must endure long distribution chains and maintain a quality and shelf-life acceptable to consumers.

Controlled atmosphere packaging (CAP) and modified atmosphere packaging (MAP) are one answer to extending the shelf-life and quality of perishable food products as they make their way through the distribution chain. Processors or producers who can keep their product in the distribution system for a longer period of time and at a high state of quality (freshness) have a definite advantage over competitors. For this reason, processors have a new interest in using MAP as a method of increasing profits, decreasing product return, and increasing the shelf-life of agricultural perishables.

Presently, equipment systems used in the processing industry to proportion gases for MAP are limited and expensive. Most research concerning CAP/MAP has centered around devising optimum gas mixtures for specific commodities. The problem of developing a low-cost, accurate gas proportioning system for industry has eluded most research. Research literature available on the subject is very limited. Development of a simple, low-cost, accurate gas proportioning system would likely reduce capital and operating costs, reduce labor and supervisory requirements on processing lines, and increase profits.

OBJECTIVES OF THE RESEARCH

The purpose of this study is to extend previous research by designing an efficient apparatus for on-site mixing of three gases used in modified atmosphere packaging. Specifically, the objectives of this research study were:

1. To modify an existing apparatus by replacing solenoid valves with pneumatically actuated, electro-pneumatic positioned plug valves to proportion specific gas volumes at determined flow rates for mixing purposes;
2. To adjust and calibrate the modified system such that it can switch among specified gas mixtures with a 3% accuracy. Mixtures to be used can be seen in Table 1.

Table 1. Percentages of gases in target mixtures.

Mixture	CO ₂	O ₂	N ₂
A	20.19	10.16	69.66
B	15.29	15.00	69.70
C	10.03	5.09	84.88

3. To develop calibration curves for flow of component gas through the flow valves;
4. To design computer software that will control the components of the system allowing it to quickly change from one mixture to another.

CHAPTER II

REVIEW OF LITERATURE

The use of modified atmospheres to preserve food is not a new development but its use in the food industry as a means of preserving food products during distribution and storage is a comparatively recent event. This technique was used for the preservation of meats as early as the 1930's (Silliker, 1977). More recently, research about modified atmosphere packaging has been centered around safety, ideal gas quantities for specific commodities, and development of packaging (films, etc.). Only limited information is available concerning gas mixing systems and their principles of operation. This may partly be due to aggressive competitive actions among those in the private sector who are engaged in the use of modified atmosphere packaging. These aggressive actions warrant the use of secrecy when it comes to processing procedures. There is, however, extensive general information available on modified atmosphere packaging.

GASES USED IN PACKAGING

"Proper packaging" can be defined as a system which protects a perishable product from physical damage caused by handling or pests, atmospheric extremes of

temperature and moisture, or the atmosphere itself where it contains elements which may degrade the product during transport or storage (Myers, 1989). Gas packaging is often a term that is used to describe both modified atmosphere packaging and controlled atmosphere packaging. MAP is one technique that can be employed to answer the need for improved shelf-life of food products. MAP may be defined as the packaging of a perishable product in an atmosphere which has been modified so that its composition is other than that of air (Hinthian, 1986). This contrasts with controlled atmosphere packaging in which the perishable product is continually exposed to a precisely defined mixture of gases in a storage chamber (Farber, 1990). Deliberate attempts to modify the atmosphere to aid food preservation can occur at three levels of sophistication:

- (i) Controlled atmospheres: mainly used for bulk storage and requires precision in controlling the gas mixture;
- (ii) Modified Atmosphere packaging: used for bulk and retail packs in which the packs are flushed and filled with nitrogen or gas mixtures. The gas composition may subsequently change as a consequence of pack permeability, chemical and biological activities;
- (iii) Vacuum packaging: predominately used for retail packs. The original air atmosphere is evacuated and the atmosphere which develops is mainly the result of the biological activity (Gould, 1989).

The gases normally used for MAP include carbon dioxide (CO₂), oxygen (O₂), and nitrogen (N₂) (Farber, 1990). The most important gas from a microbiological standpoint is CO₂, which effectively inhibits the growth of many micro-organisms, including spoilage bacteria (Farber,1990). Carbon dioxide can affect bacterial and mold growth when present in concentrations approximately 20% or above (Paine, 1987). Nitrogen is inert, tasteless and is virtually insoluble in water. By excluding oxygen, nitrogen can inhibit the oxidation of fats (lipids) and reduce the possibility of mold growth (Paine, 1987). The presence of oxygen is generally avoided with many products because its presence causes oxidation and enhances the growth of aerobic bacteria. However, it is necessary to sustain the basic metabolism of respiring fruits and vegetables, is instrumental in maintaining the red color of meat, and prevents growth of anaerobic bacteria (Paine, 1987).

The use of other gases has been considered and in some cases has found limited applications. Ozone has been proposed for use on meats, butter, cheese, shellfish, and poultry chill water (Gould,1989). The use of [¹⁴C] carbon monoxide at a low level (1% or less) has been suggested as a means of preventing the discoloring noted when red meats are stored in an elevated level of carbon dioxide (Watts, 1978). This approach may have met resistance by packagers due to the fact that [¹⁴C] carbon monoxide is radioactive, even though it was shown that levels less than 0.09 ppm [¹⁴C] carbon monoxide remained in precipitate fraction of samples following cooking (Watts,1978). Table 2 shows some of the relative gas concentrations found in modified atmospheres used in the processing of several different foods.

Table 2. Relative gas concentrations in modified atmospheres for shipping/storage of selected agricultural products.

Food Product	Percent Gas	
	O ₂	CO ₂
Meats, fish, poultry	20	20
Tomatoes, lettuce	10	--
Cauliflower, mushroom	10-20	10-20
Cantaloupe	10	10-20
Citrus fruits	10	10-20
Strawberries	10-20	10-20

Baker, R.C. Hahn, P.W. Robbins, K.R. 1988. Fundamentals of New Product Development, Elsevier Science Publishing Co. Inc. New York, N.Y.

PACKAGING OF FRUITS AND VEGETABLES USING MAP

Primary factors that maintain the quality and extend the postharvest life of fresh fruits and vegetables are harvesting at maturity, minimizing mechanical injuries, using proper sanitation procedures, and providing optimum temperature and relative humidity during all marketing steps (Kader, 1989). Secondary factors include modification of O_2 , CO_2 , and or C_2H_4 concentrations in the atmosphere surrounding the commodity to levels from those different than air (Kader, 1989). There is rapidly growing interest in the application of MAP to maintain quality and extend shelf-life of fruits, vegetables, and salads during distribution and marketing (Geeson, 1989). Correct gaseous mixtures used in packaging depends greatly on the commodity, cultivar, maturity stage, initial quality, and the temperature of the fruit or vegetable (Kadar, 1989)(Kyzlink, 1990). The potential for extending the market-life of many fruits and vegetables requires a detailed understanding of behavior (particularly respiration rates), optimum and tolerance limits for O_2 , optimum and tolerance limits for CO_2 , and relative humidity of each particular commodity (Geeson, 1989).

When fruits or vegetables are enclosed in a sealed pack the internal atmosphere becomes modified-depleted in O_2 and enriched in CO_2 (Geeson, 1989). Successful MAP must obtain near optimum O_2 and CO_2 levels for each specific living product. Tables 3 and 4 show a classification of fruits and vegetables according to their tolerance to low O_2 concentrations and to maximum CO_2 concentrations.

Table 3. Classification of fruits and vegetables according to their tolerance to low O₂ concentrations.

Minimum O ₂ concentrations tolerated (Percent)	Product
0.5	Tree nut, dried fruits and vegetables, apples.
1.0	Golden Delicious Apples, broccoli, mushrooms, cut or sliced fruits or vegetables.
2.0	Most cultivars of apples, pears, apricots, cherries, nectarines, strawberries, green beans, lettuce, cabbage, cauliflower.
3.0	Avocado, tomatoes, peppers, cucumbers.
5.0	Citrus fruits, green peas, potatoes, asparagus.

Kader, A.A. Zagory, D. Kerbel, E.L. 1989. Modified Atmosphere Packaging of Fruits and Vegetables. Critical Reviews in Food Science and Nutrition, Vol. 28 (1):1-24.

Table 4. Classification of fresh fruits and vegetables according to their tolerance to elevated CO₂ concentrations.

Maximum CO ₂ concentrations tolerated (Percent)	Product
2	Apples(Golden Delicious), Asian pears, European Pears, grapes, apricots,tomatoes, lettuce, celery.
5	Apples (most cultivars), peaches, plums, bananas, papaya, peppers (chili), eggplant, cauliflower, cabbage.
10	Grapefruit, lemons, limes, pineapples, cucumbers, snap beans,okra,broccoli, green onions, dry onions, potatoes.
15	Strawberries, raspberries, blackberries, cherries, figs, cantaloupe, sweet, corn, mushrooms, spinach.

Kader, A.A. Zagory, D. Kerbel, E.L. 1989. Modified Atmosphere Packaging of Fruits and Vegetables. Critical Reviews in Food Science and Nutrition, Vol 28 (1):1-24.

Ballentyne agrees that successful MAP depends on selecting optimum gas levels by stating that broccoli yellowing was decreased by levels of CO₂ up to 10%. He noted that off-odors were observed at levels of CO₂ at 11-15% (Ballantyne, 1988). Storage potential of tomatoes using MAP showed levels of CO₂ at 3% and O₂ at 1% were optimum for avoiding injuries due to anoxia (Nakhasi, 1991).

In addition to the use of specific gas mixtures for each commodity, many researchers have found that barrier films provide added stability to products. It was found that packaging of apples in permeable plastic films was effective in retarding ripening when the apples were harvested at optimum times (Smith, 1988). Devising a MAP system of optimum gaseous conditions and relative humidity for a particular commodity requires selecting a film with correct permeability properties (Nakhasi, 1991).

PRESERVATION OF MEATS USING MAP

One of the most common modified atmosphere packaging techniques used today in the meat industry is vacuum packaging. Recently, there has been an increased interest in the use of gases for preserving meat products. MAP may be preferred over vacuum packaging and air packaging because it: 1) improves the shelf-life substantially, and simultaneously provides protection against the compression and crushing of products, and; 2) the gas may prevent the development of off-odor, off-taste, and poor appearance by retarding the growth of yeast and molds (Ahvenainen, 1989).

The use of nitrogen gas (100%) in the packaging of frankfurters has been shown to inhibit the growth of yeast and molds and to reduce greening and off-odors in the product (Bentley, 1989). It has been suggested that lamb may be well suited for packaging in atmospheres that have been modified (Semas, 1989). In the study of lamb chops, the population of psychrotrophic bacteria at 1° C decreased in atmospheres containing 20% CO₂ and 20% CO₂ with low (<1%) O₂ (Brody, 1989). In early studies, the shelf-life of chicken increased linearly with increased CO₂ concentrations up to 25% (Farber, 1990). There is sufficient laboratory evidence and practical experience to demonstrate that modified atmospheres containing 20% or more carbon dioxide can extend the shelf-life of fresh poultry beyond that of current practices. Poultry processors who are using elevated levels of CO₂ to ship and store fresh poultry have increased the shelf-life of their products 16-21 days. Laboratory experiments indicate that this could be increased to 35 or more days with increased control of gas concentration, storage temperature, bag integrity, and permeability (Brody, 1989). Ground beef patties were found to retain acceptable microbial quality and sensory characteristics up to seven days of storage when packed using carbon dioxide and storage temperatures of less than 2° C (Bentley, 1989). MAP of cured meats using N₂/CO₂ protected the red-colored nitrosomyoglobin (the bright red color that consumers find most attractive) from oxidative fading, it can reduce the chance of oxidative rancidity, and it extends the shelf-life by delaying the microbial spoilage that can be caused by oxidative organisms (Gould, 1989). Table 5 gives some details of the gaseous composition of the atmospheres used in packaging meat products.

Table 5. Gaseous composition of atmospheres used in packaging meat products.

Nitrogen	100	80	70	50	30	10	--	--
Carbon Dioxide	---	20	30	50	60	20	80	60
Oxygen	---	--	--	--	10	70	20	40
Thin sliced meats	X	X						
Luncheon meats	X							
Meat filled pasta			X					
Pizza				X				
Mackerel, herring, sprats					X			
Fresh red meat, beef, pork						X		
Fresh red meat, sausage							X	X
Fresh white fish Sole								X

Paine, F.A. 1987. Modern Processing, Packaging, and Distribution Systems for Foods.
 AVI Van Nostrand Reinhold Co. New York, N.Y.

GAS PACKAGING EQUIPMENT

Most processing equipment used in modified atmosphere packaging requires operators to order their mixtures in bulk quantities from gas suppliers. Having to order predetermined mixtures severely limits the ability of the processor to vary mixtures. The function of the proportioner is to blend individual constituent gases to achieve a specific gas mixture that will be of consistent quality and less expensive to the average size processing plant (Williams, 1991).

Thermco Instrument Corporation manufactures two specific models for proportioning gases into mixtures required for food packagers. The Model 8625 is specifically designed for mixing carbon dioxide, oxygen, and nitrogen for modified atmosphere packaging. The three gases are supplied from a bulk storage system and fed to the mixing system. The outlet pressure for all models is 170-444 kPa. The 8625 is able to mix three gases in any proportion (0 to 100%) within a claimed 2% accuracy (Thermco, 1993).

The three gases enter the mixing unit and flow through a metering valve. The outlet of each valve is connected to a mixing fitting, where the streams are combined. The mixture then flows through a solenoid valve and into a surge tank. Once the pressure in the surge tank reaches the upper setpoint on a pressure switch, the mixed gas flow is turned off with the solenoid valve.

A gas analyzer is part of the Model 8625 gas proportioner. The analyzer continuously monitors the mixture in the surge tank. The proper mixture is set by the operator by turning the mixture adjustment valve to the desired setting shown on

the scale. To precisely set the gas mixture the operator may then observe the analyzer and change the mixture adjustment valve accordingly. This model has a flow rate of 0-750 SCFM and a supply inlet pressure of 752-923 kPa absolute (110-135 psig). At present the cost for this unit is \$12,435.00 (Thermco, 1993).

Thermco also produces a Model 8525 food packaging gas mixer at a substantially lower cost than the Model 8625. The price of the Model 8525 at present is about \$4,000.00. The model is specifically designed for mixing carbon dioxide into nitrogen for modified atmosphere packaging purposes. The principles of operation and degree of accuracy are comparable to the Model 8625. One limiting factor of this model is that it is a two gas mixing system. If a processor requires that three gases be used simultaneously then the more expensive model is necessary.

Smith Equipment manufactures a three gas blending system for controlled and modified atmosphere packaging of food products. The Model 299-037 mixes oxygen and carbon dioxide into nitrogen. The Model 299-08F mixes the same three gases and has an electronic monitoring system. The 299-08F was available at a limited discount price of \$ 2,805.00 (Smith Equipment, 1993) at the time this paper was written.

The Model 299-037 is able to blend nitrogen in an adjustment percentage range of 0-100%. It blends oxygen and carbon dioxide in ranges of 100-0%. Regulators are available for all three gases for \$ 117.00 each. The outlet pressure is 341 kPa and the required inlet gas pressure is 718-786 kPa. A Smith representative said that all of their food product packaging blenders are accurate within 1%.

CHAPTER III

APPROACH AND PROCEDURE

APPARATUS DESIGN

The apparatus used in this study was a modification of a laboratory scale prototype mixing system used in a previous research project. According to the designer of the original prototype, the system was based upon an actual industrial gas mixing system used for controlled/modified atmosphere packaging machines.

Several modifications were made to the existing apparatus. An additional manifold was added in the expectation of improving flow and mixability. Operating pressure was set at 170.25 kPa. Unless otherwise indicated, all pressures given are absolute pressures. The upstream pressure (pressure of the valve supply) was set at 307 kPa. One collection tank, vented to the atmosphere, was used instead of the two-tank closed system previously used. A pressure relief valve was installed on the collection tank to maintain a constant pressure.

The major modification to the existing system was in the method used to control flow of the gases. Previously, solenoid valves were used in the system and gas proportions in the mixture were determined by duration of the valve activation. This previous approach only allowed for batch mixing of the gases. The present design incorporated the use of three plug valves with actuators and positioners. It relied on

magnitude of valve opening rather than valve opening time to control gas flow. The present approach allowed for continuous mixing of the gases.

The previous design used a programmable controller to open each valve for a specific time interval. The valve for the first gas remained open for a specified time and then closed. The second and third gases were administered in the same manner. The cycle was then repeated. Valve opening times were constant for N_2 at 4.5 seconds for each cycle. Times ranged from 1.9 to 2.4 seconds for O_2 , and 0.5 to 0.7 seconds for CO_2 over seven different cycles.

The present system used a personal computer equipped with a D/A board which allowed all three valves to be opened simultaneously. Flow of each gas was controlled by the degree of valve opening. Increasing valve openings permitted more gas to flow. This increased the percentage of a particular gas in the mixture, if the remaining valves were unchanged. Conversely, decreasing the opening of the valve decreased the percentage of a gas in the mixture, if the remaining valves were unchanged. The preliminary design was for the entire system to be closed. That is, it would not be vented to the atmosphere. The problem with a closed system was that any test run made with the system was limited to the amount of time it takes to increase the pressure in the collection tank to the pressure supplied by the regulators on the supply tanks. Flow calibration for the closed system was also more complex.

Thus, the final system design vented the gases to the atmosphere. This served two purposes. First, it eliminated the effects of a continually increasing downstream

pressure found in a closed system. Second, it would more closely mimic the operation of the proportioner in a continuous processing environment. The final design maintained a maximum downstream pressure of 170.25 kPa through the use of a relief valve vented to the atmosphere.

MATERIALS AND METHODS

The primary gases used during this project were oxygen, carbon dioxide, and nitrogen. These gases were chosen due to their widespread use in the food packaging industry. Appropriate combinations of these three gases are usually considered to improve effectiveness against microbial spoilage, oxidation, and mold spoilage.

The three gases were obtained from a local commercial gas supplier. The oxygen and nitrogen gases were contained in 76 500 liter (2 700 SCF) cylinders. The CO₂ cylinder had a capacity of 34 000 liters (1 200 SCF). All cylinders were fitted with precision regulators. The CO₂ regulator was designed to operate at low temperatures resulting from high CO₂ flow rates from the pressurized cylinder. The regulators were the double-acting type supposedly capable of maintaining a very accurate and constant delivery pressure. The regulators were specified to withstand upstream pressures of 8 300 kPa (1 200 psi) and produce regulated output from seven to 345 kPa, which included the selected design pressure of 307 kPa.

Gas flowed from the regulators through 1.27 cm (1/2 inch) copper tubing. The tubing was used in previous research and was chosen for its rigidity and ease of installation in the system. Air for the system was supplied by the building's

compressed air system regulated to 649 kPa and routed to the integral components by 0.635 cm (1/4 inch) flexible tubing.

Control Valves

Three Durco G432AK plug valves were used for this project. The prefix G4 identified a straight nonlubricated plug valve. The three indicated a pressure class of ANSI C.I. 300. The two indicated the end configuration which corresponded to a screw connection. The AK indicated that the valve had flange flats that were drilled and tapped for an actuator and that the valve was actuated (Durco, 1992).

A screw connection was selected due to ease of assembly and design. All available pressure classes would have been appropriate for our applications. It was important for the valves to be compatible with actuators since automatic control of the valves was inherent in the design. A plug valve design was selected due to its superior sealing qualities. In this particular valve design a sleeve totally surrounded the circumference of the plug, the primary seal to the atmosphere was the sleeve itself. A diaphragm with reverse lip design provided both static and self-adjusting dynamic stem sealing.

The tapered plug was a feature of the valves that increased its sealing ability. Adjuster bolts allowed the plug to be pushed deep into the sleeve. A rocker arm gave one plane contact and a resultant force down the centerline of the plug. Figure 1 shows the complete valve with its components visible in an exploded view.

Copper tubing was connected to each of the three valves. Pneumatic actuators, electro-pneumatic positioners, and a personal computer were used as hardware for

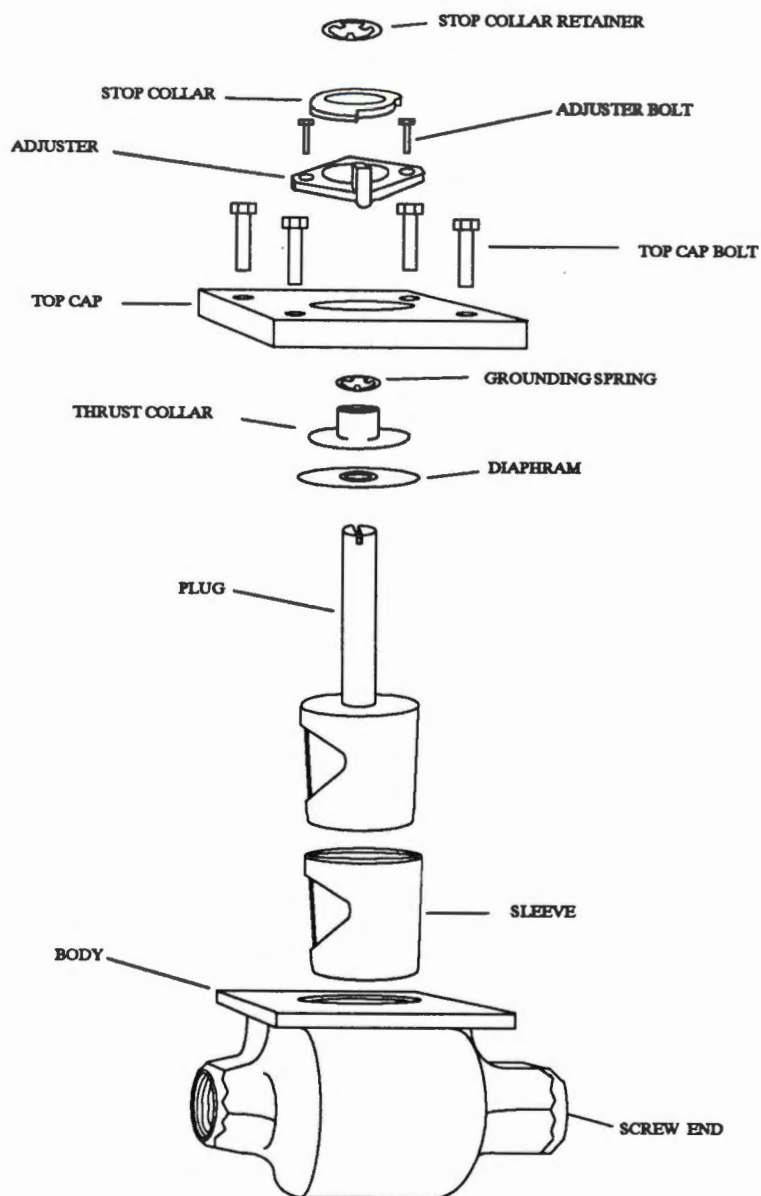


Figure 1. Durco 1.27 cm G432AK plug valve exploded view.

controlling the opening and positioning of the valves. By using pneumatically actuated valves, valve opening time could be made a constant for all three valves. The variable of concern thus became size of the valve opening. The valves were normally closed and opened in response to movement of the actuator. The valves were mounted on a plywood base using three steel mounting brackets fabricated and mounted to an aluminum base. The steel brackets were attached between the valves and actuators. The valves were mounted side by side with the oxygen valve located between the carbon dioxide and nitrogen valves. Figure 2 shows the schematic of the complete system with position of the valve assemblies.

Actuators

Automax S85DA pneumatic actuators were used to move and position the plug valves. The actuators were dual rack and pinion design featuring a hard anodized extruded aluminum housing and a one piece nickel plated pinion with gear teeth machined 360° around the pinion. The actuators were also designed for 100° travel (-5° to 95°) with clockwise and counterclockwise travel adjustments for both open and closed positions. The air supply ports were NAT and NAMUR standards which allowed direct mounting of various NAMUR standard control devices. The actuators were rated for maximum and minimum supply pressures of 1 127 kPa and 512 kPa respectively (Automax, 1992). A supply pressure of 649 kPa was used to operate the actuators during the course of this project.

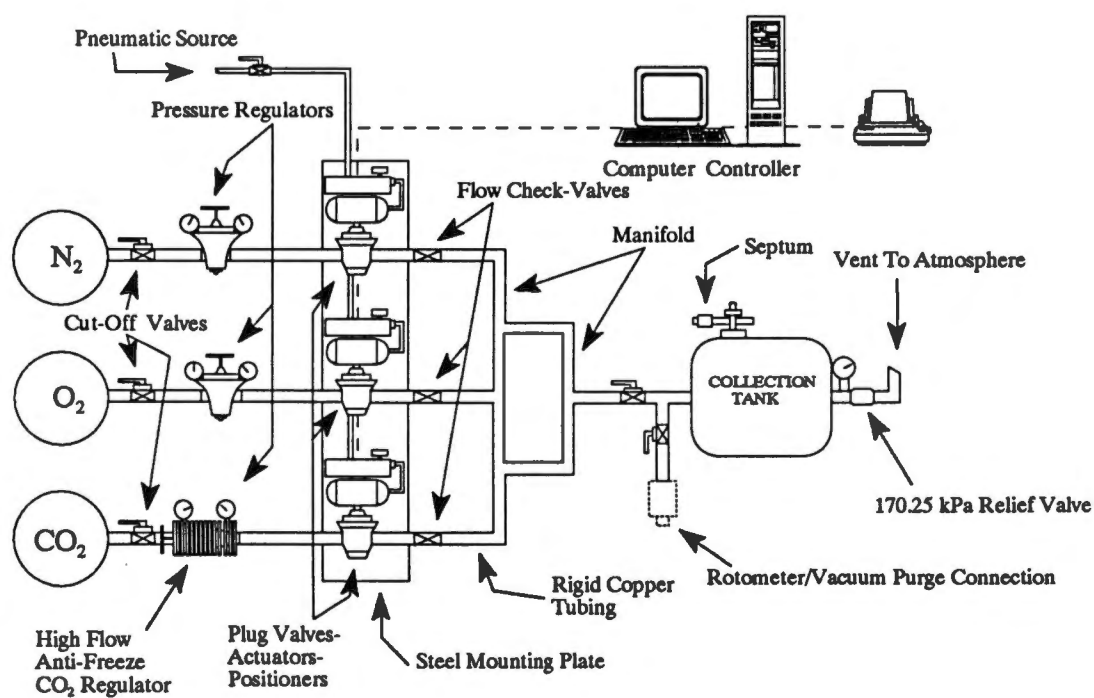


Figure 2. Schematic of prototype gas mixing system.

The operating mechanism of the actuators is shown in Figure 3. Application of pressure to port two drove the actuator pistons outward turning the pinion (and the valve) counterclockwise as the air volume on the outside of the pistons exited through port one. Applying air pressure to port one drove the pistons inward which turned the pinion (and the valve) clockwise as the air volume on the inside of the pistons exhausted through port two. A supply pressure of 649 kPa was used with all three actuators. This pressure was chosen so that one supply source was sufficient to operate both the actuators and positioners.

According to Automax literature, a 1.27 cm valve required 4 N•m (3.0 Ft.-lbs.) of average turning torque. The S85DA actuator at 648.83 kPa provided 67.52 N•m (49.8 Ft.-lbs.) of output torque (Automax, 1992) This was sufficient torque for both turning and breakaway requirements.

Positioners

The positioner was the heart of the mixing unit control system. It was the component that received the electrical signal and converted that signal to a pressure. The pressure was then used to position an actuator that in turn positioned the valve. For this apparatus, an electro-pneumatic positioner was selected. The positioner was equipped with a standard 4-20 mA signal input interfaced to a digital to analog computer control card (described later).

Calibration of the positioner was a simple procedure. The current to pneumatic conversion section (I/P) was factory precalibrated and required no field calibration. Automatic compensation was provided for changes in supply air pressure,

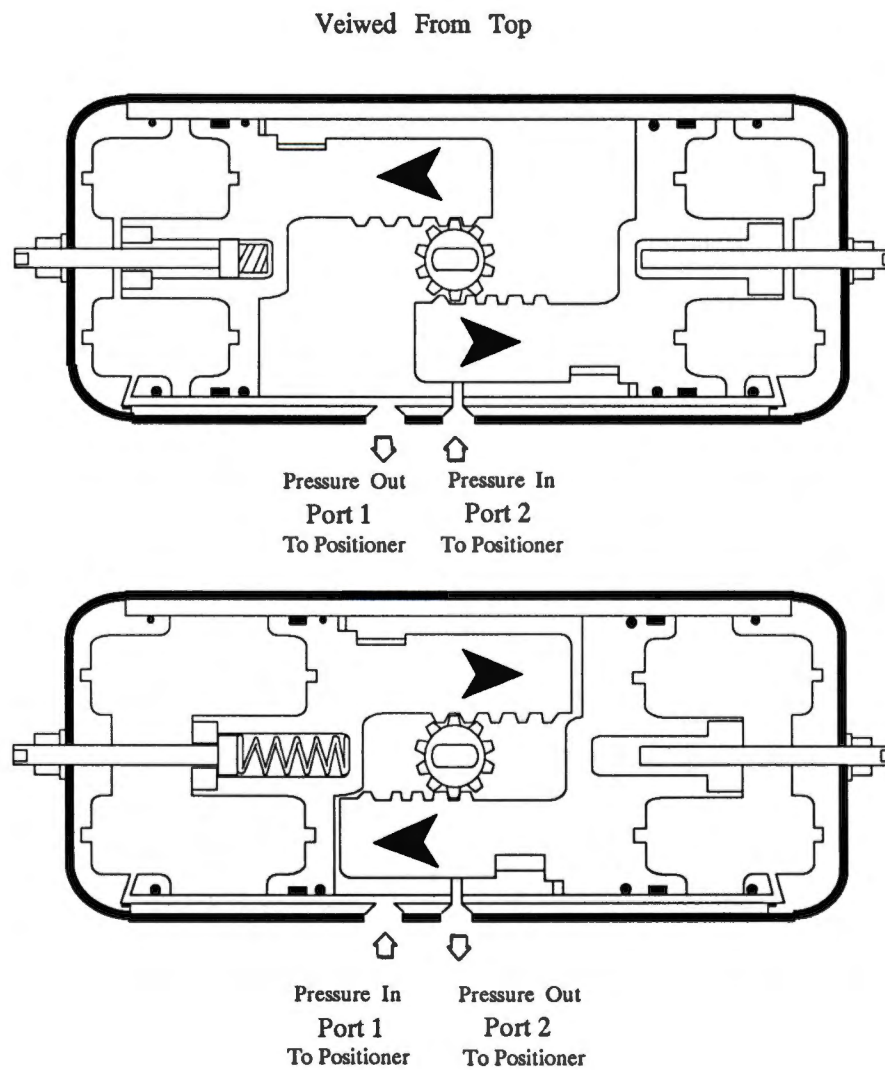


Figure 3. Automax double-acting pneumatic actuator operation.
(Automax, Inc. 1992. Pamphlet 10M-GU-9/92 SNS)

atmospheric pressure and ambient temperature. The only field calibrations required for the positioners were the mechanical ZERO and SPAN adjustments which controlled the range of travel for the final control element. A flat position indicator gauge was standard on the positioners that were selected. It was initially assumed that this indicator gauge provided an indication of valve position. It was later discovered that the indicator actually gave the degrees of rotation for the positioning cam. This may or may not have been the same position as the valve, depending upon the cam type. Figure 4 shows the control schematic of the Automax H40137 electro-pneumatic positioner unit.

Actual calibration was more difficult than described by the manufacturer. According to the manual, calibration was achieved by sending a 4 mA signal to the positioner and adjusting the zero potentiometer until a reading of 20.5 kPa was obtained on the current to pneumatic output gauge. A 20 mA signal was then sent and the span potentiometer was adjusted until a reading of 102.5 kPa was obtained on the current to pneumatic output gauge. The two steps were interactive and had to be repeated until complete calibration was achieved. Correct adjustment of the zero and span potentiometers should have insured correct values for all points. For example, based upon positioners equipped with standard cams, a 12 mA control signal should have corresponded to a 45° of rotation and an 8 mA signal should have corresponded to a 22.5° of rotation. The position indicators showed significant differences from the theoretical values. The theoretical and actual degrees of cam rotation observed for the standard cam at a particular control signal can be seen

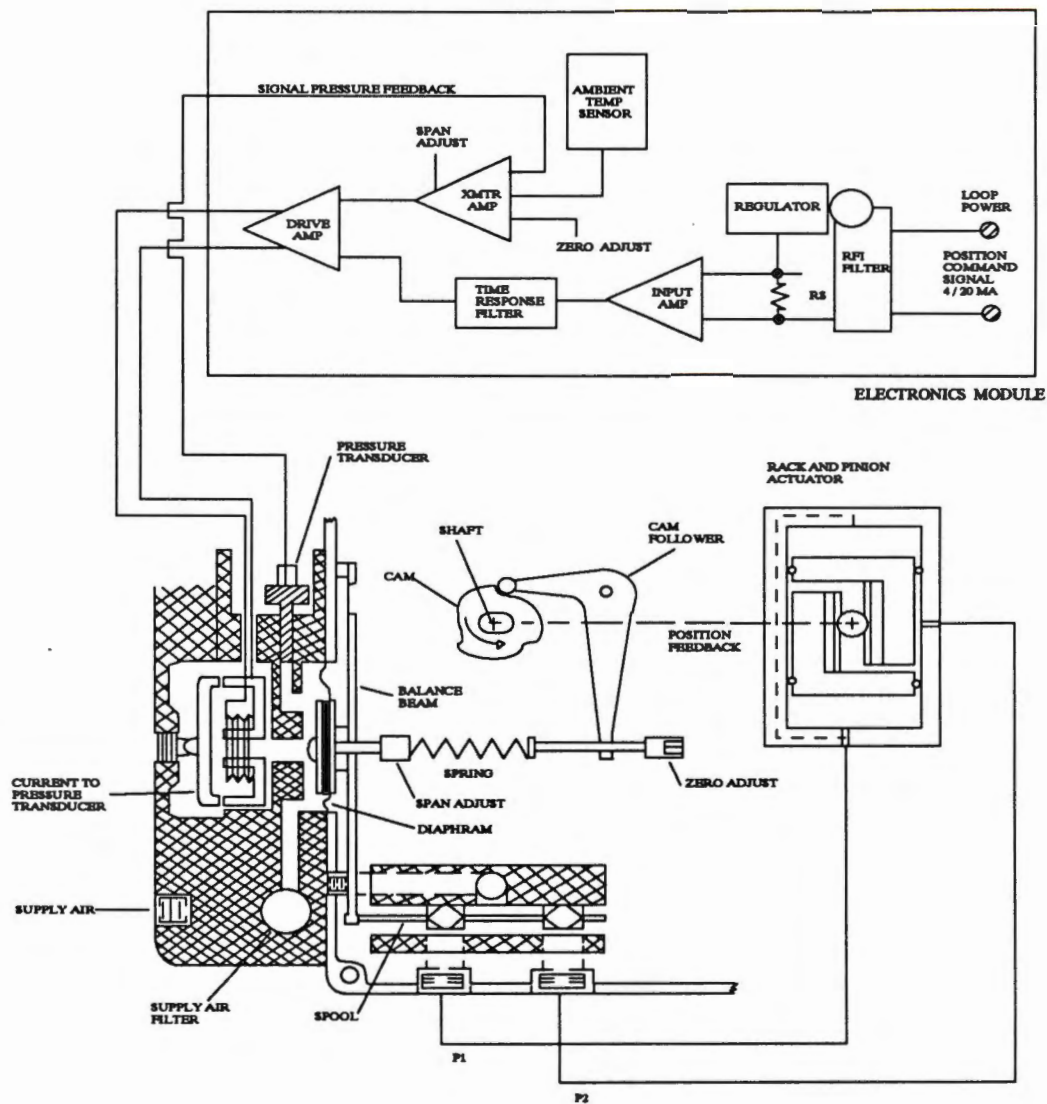


Figure 4. Automax H40137 electro-pneumatic positioner flow schematic.
(Automax, Inc. 1991. Pamphlet 10M-GU-9/91 XP)

in Table 6. The decimal equivalents of binary numbers, used in the computer software to produce each milliamp control signal, are also represented in Table 6. After the installation of different cams to correct a flow sensitivity problem (described in detail later), recalibration of the positioner was attempted. The recalibration was based on a range of travel from 0 to 30° and netted results that were much more acceptable than those seen with the standard cams. Table 7 shows the theoretical and actual degrees of cam rotation as a function of the control signal input after the installation of the limiting cams.

During the assembly and testing of the positioners it was found that the response of the positioners did not correspond to the specifications provided by the manufacturer. More specifically, the positioners were designed to respond (move the valve open by increasing the air pressure to the actuator units) to very small increases in a control signal provided by the digital to analog output card installed in the computer. During the initial testing of the system, a simple BASIC program was written to increase the control signal output from the computer D/A card in small milliamp increments. This process is often referred to as "ramping the signal". The specifications for the positioners stated that the units would respond to increments as small as 0.5°. In initial tests, the unit responded in 5.0° incremental jumps. The incremental jumps were observed over the entire range of valve rotation.

Table 6. Theoretical and actual degrees of cam rotation at various milliamp signals for the initial system configuration.

Signal Sent (mA)	Decimal #	Theoretical Degree of Rotation	Actual Rotation Valve #1	Actual Rotation Valve #2	Actual Rotation Valve #3
4.0	0	0	0	0	0
6.0	512	11.25	10	2	0
8.0	1024	22.50	23	16	17.5
10.0	1536	33.75	35	27.5	29
12.0	2048	45	47	39	42
14.0	2560	56.26	60	50	54
16.0	3072	67.52	72	62	67.5
18.0	3584	78.80	85	76	80
20.0	4095	90	90	90	90

Table 7. Theoretical and actual degrees of cam rotation at various millamp signals after installation of limiting cams.

Signal Sent (mA)	Decimal #	Theoretical Degree of Rotation	Actual Rotation Valve #1	Actual Rotation Valve #2	Actual Rotation Valve #3
4.0	0	0	0	0	0
6.0	512	3.75	5	3	3
8.0	1024	7.5	7	5	6
10.0	1536	11.25	11	11	11
12.0	2048	15	15	15	15
14.0	2560	18.75	18	18	18
16.0	3072	22.5	22	22	23
18.0	3584	26.25	26	26	26
20.0	4095	30	30	30	30

A second BASIC program was then written to determine the positioners ability to move quickly from one position to another (e.g. from 10° to 45°). Again, the positioners did not respond as expected. When a 12 mA control signal was sent the valve should have opened to 45° from 0°. Instead, the positioner responded by overshooting to 50° and slowly moved back toward 45°. This was typical for all input signals.

The source of the problem was found to be the type of spool valves originally installed in the positioners. The spool valves control the amount of air released to the actuator. High flow spool valves were originally installed in the units. Since the supply pressure was limited to 649 kPa, these spools were not effective. The high flow spools were replaced with low flow spools and the problem was corrected.

Early test runs (fully described later) revealed that the 0-90° range of travel was counterproductive. For openings beyond 50° there was a minimal increase in gas flow for all three valves. Thus the final 40° of rotation provided little or no control over the system. The gas flow curves obtained during the test runs showed a curvilinear response. Standard cams were replaced with a limited range cam that produced openings from 0 to 30°. This resulted in increased control sensitivity for the system.

Computer Controls

An IBM personal computer was used as the primary system control unit. The computer was equipped with a six channel D/A output card (Model PCL-726) obtained from Omega Engineering, Inc (Stanford, CT).

The Model PCL-726 D/A output card provided six separate 12-bit D/A output channels on a single PC-BUS add-on card. Each channel was able to be individually user configured to any of the following ranges: 0-5 V, 0-10V, -5-5V, -10 to 10V, and 4-20 mA, the signal required by the positioner. The card also provided 16 channels of digital input and 16 channels of digital output. The output card was designed to be compatible with a wide range of PC configurations (Omega, 1991). Figure 5 shows a block diagram of the card. Three of the six D/A outputs were used to control the three positioning units.

Once the card was installed and all connections were made to the electro-pneumatic positioners, a computer software program was written in BASIC which allowed the desired mixture to be formulated and quickly changed. The program was written for ease of use. A sample of the computer menu is presented in Figure 6. The complete program is listed in Appendix A. The operator would start the program and be requested to enter decimal numbers corresponding to control signals determined for a specific mixture from the simulation model. The program required the decimal numbers for all three valves prior to opening any of the valves.

When the decimal numbers were properly entered into the computer program, the computer sent a control signal to the positioners. The valves opened simultaneously for all three gases, remained open for 30 seconds, and then closed. A time interval of 30 seconds was chosen as the testing period due to the quick venting of gases to the atmosphere. Venting to the atmosphere began five seconds after the control valves were opened. A 30 second test run gave 25 seconds of uniform operating

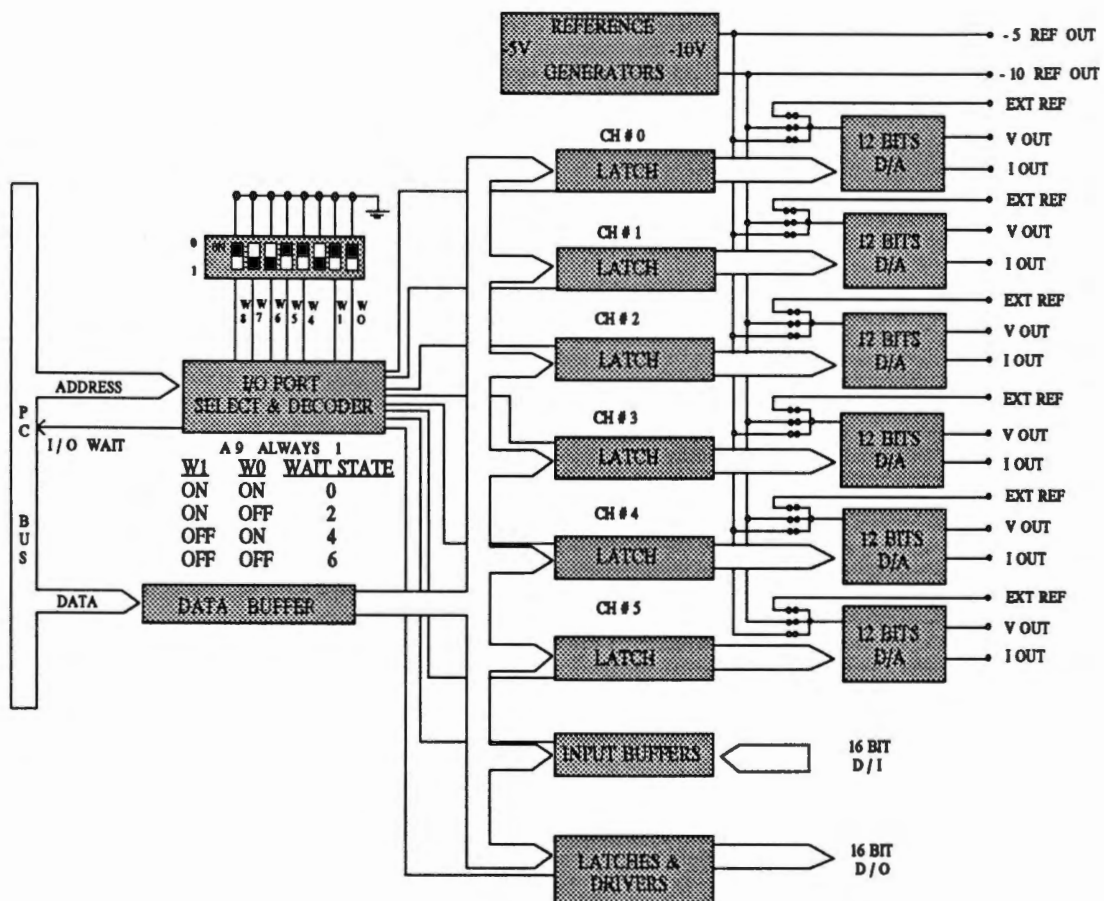
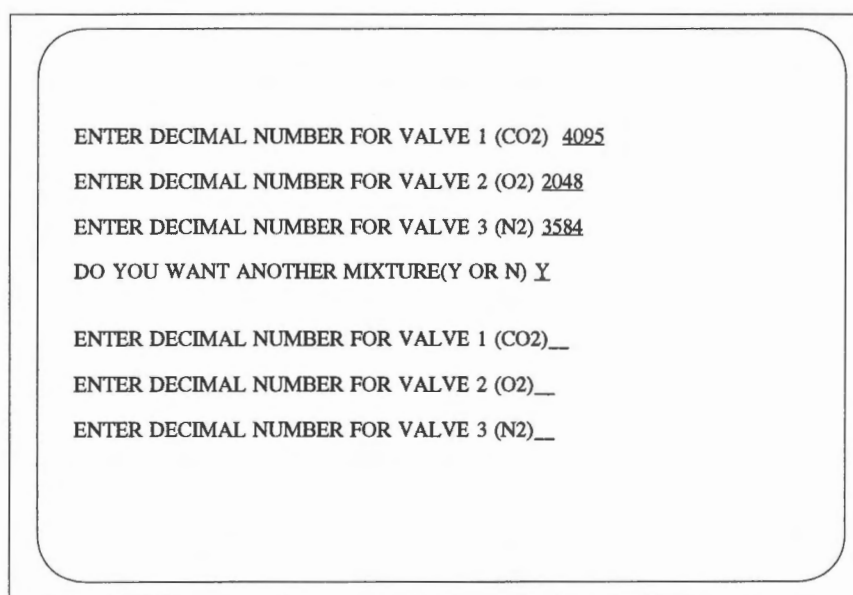


Figure 5. Block diagram of model PCL-726 six-channel D/A output card.
(Omega Engineering, Inc. 1991. Data Acquisition Systems
Handbook Supplement)



ENTER DECIMAL NUMBER FOR VALVE 1 (CO2) 4095

ENTER DECIMAL NUMBER FOR VALVE 2 (O2) 2048

ENTER DECIMAL NUMBER FOR VALVE 3 (N2) 3584

DO YOU WANT ANOTHER MIXTURE(Y OR N) Y

ENTER DECIMAL NUMBER FOR VALVE 1 (CO2)___

ENTER DECIMAL NUMBER FOR VALVE 2 (O2)___

ENTER DECIMAL NUMBER FOR VALVE 3 (N2)___

Figure 6. Example of computer menu used to send signal to positioners.

conditions during venting. The program was designed to run in a loop so that the control signal for the next mixture could be entered quickly.

Mixing Manifold

Three 20 cm lengths of rigid copper tubing were connected to the inlets of the plug valves. Hoses were connected to the regulators on the supply tanks and to these rigid pipes. The rigid copper tubing was used in the construction of the entire manifold. One-way flow check valves were installed in each line to insure flow of gases in only one direction. Standard copper elbows and T connections were utilized. Nominal 1.27 cm copper tubing and fittings were used. Connections were provided in the piping system for the connection of a rotameter and vacuum purge line. The piping was secured to a 2.4 meter X 1.1 meter plywood base by using 5 cm X 10.16 cm wooden strips. Approximate dimensions of the piping are shown in Figure 7.

A second mixing manifold downstream was added to improve mixing of the gases. In the previous design, a single pipe exited the manifold to the surge tank. This pipe was located directly opposite the pipe exiting the middle valve. This meant that the gas exiting the middle valve had a direct path to the surge tank while the gases exiting the outside valves had to flow against 90° elbows. By adding the extra manifold, all gases had to flow against the same number of obstructive turns, thus flow characteristics were more equal.

The previous research relied on two 37.8 liter (10 gallon) surge and collection tanks. This project used only one 34.1 liter (9 gallon) tank. The change in tank size was due entirely to availability of the tanks. No significant changes should

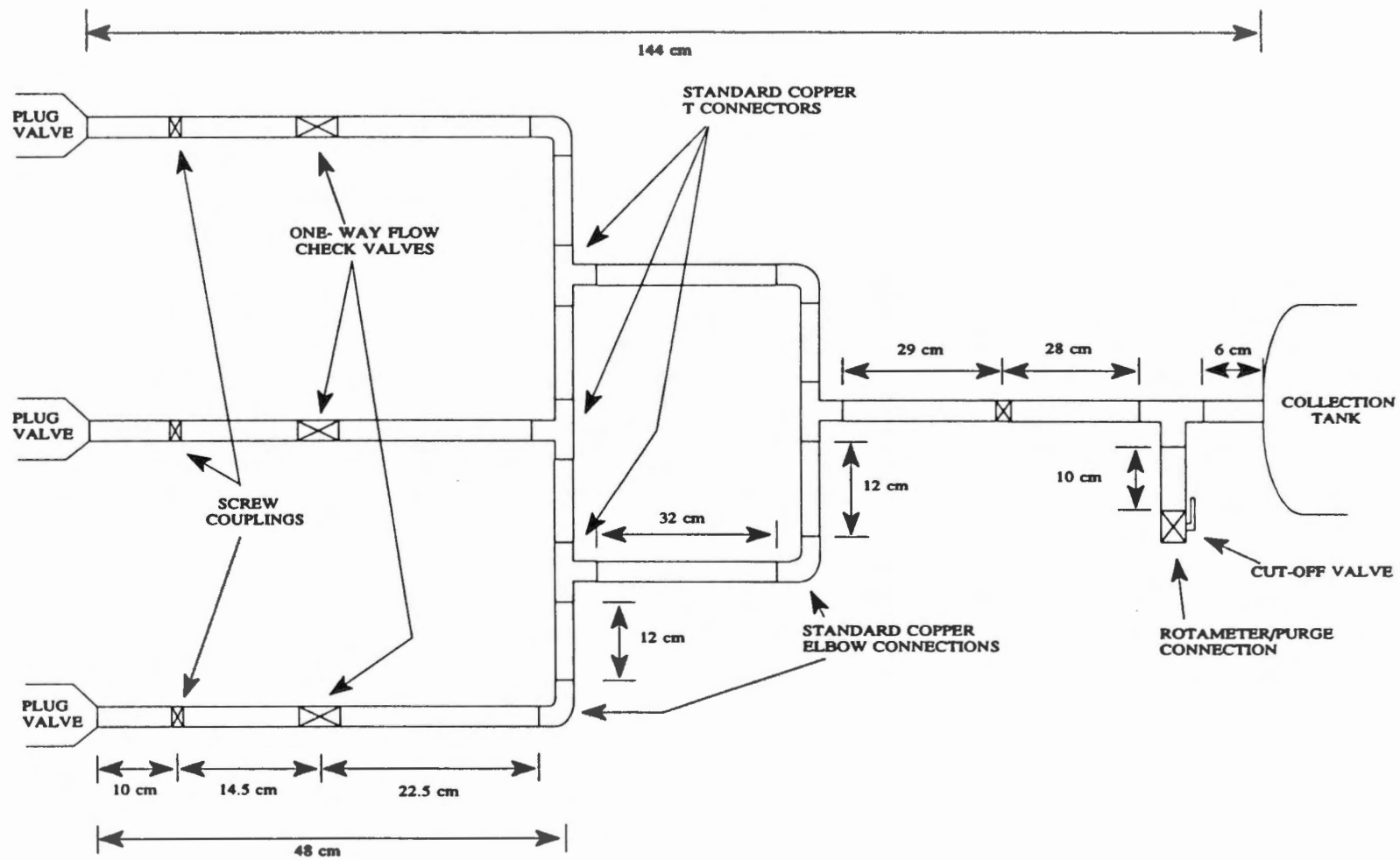


Figure 7. Approximate dimensions of mixing manifold.

have resulted from this change. The tank (manufactured by Midwest Products, Inc. Strafford, MO.) was purchased from a local hardware company. Constant pressure was maintained in the 34.1 liter (9 gallon) collection tank used in this project by installing a 170.25 kPa relief valve in the rigid pipe exiting the tank. When the pressure in the collection tank exceeded 170.25 kPa, the gas was released into the atmosphere through the relief valve.

The only purpose of the collection tank was to trap gases after each test for later chromatographical analysis. In a processing environment, the collection tank would not be necessary. However, it could be included to allow for sample collection during processing without affecting the performance of the system. Venting gases to the atmosphere allowed the prototype to more closely resemble an industrial process continuous mixing system. Gases remained in the collection tank after a run until they were purged. As noted earlier, the complete system is shown in Figure 2.

DETERMINING FLOW THROUGH VALVES FOR EACH GAS

Determination of the flow rates of gases through each of the three valves was necessary to develop an equation for calculating percentages of each gas in a final mixture. Automax Corporation provided flow coefficient charts for liquids but charts for gases were not available.

Flow Measuring Device

One characteristic of the valves that made flow rate determination more difficult was that the orifices in the valves were not round. Instead, the orifices were a square shape with rounded corners. Literature on the calibration of this type of orifice was not available.

It was decided to use a rotameter to calibrate the valves. By doing this, a calibration curve could be constructed for the flow of each gas as a function of valve opening.

One acrylic, variable area, rotameter (Model FL4604) was purchased from Omega Engineering, Inc. Stamford, CT. The rotameter was 38.1 cm long, had a 2% accuracy, and was calibrated for air flow ranges of 0-40 SCFM. As noted later, an adjustment for density differences was necessary for other gases. The collection tank was removed from the copper pipe mixing manifold and a plug was installed. The rotameter was then attached to the manifold. The outlet of the rotameter was vented to the atmosphere.

Nine control signal inputs (equal 2 mA increments from 4 to 20 mA) were used for flow calibration of each valve. The resulting flow for each milliamp input was recorded. A calibration curve was then constructed for each valve and its corresponding gas. The curve shows flow as a function of the milliamp signal input.

Positioner Cam Determination

The three gases (uncorrected for density effects) provided curvilinear flow curves for the standard cam that came with the positioners. That is, flows for all three gases

were low when the cam degree of rotation was low. As cam degree of rotation increased, gas flow rapidly increased. As the degree of rotation neared 60 degrees the flow increased at a decreasing rate. From the data obtained, the critical range (fastest increase) for flow seemed to occur between 8 and 14 mA input signals for all three gases. Figures 8, 9, and 10 present information obtained with carbon dioxide, oxygen, and nitrogen respectively.

It was discovered during these tests that the pressure regulators did not keep a constant 307 kPa delivery pressure throughout the range of travel for any of the three valves. As the valve opening increased, the regulated pressure decreased. The previously mentioned gas flow curves do not include compensation for the decrease in supply pressure. It was concluded that adjusting the regulator pressure throughout the range of travel would simply shift the graph and not alter its basic shape. Thus, the tests were not repeated with a compensation for this drop. All subsequent tests included manually adjusting the pressure regulator to maintain a constant 307 kPa pressure throughout the range of valve opening.

The valve manufacturer indicated that the gas flow should be a linear function of valve opening angle (Hagerty, 1993). No explanation was given for the above results. The manufacturer provided two new special cams for evaluation as replacements for standard cams in the positioners. A square root cam and a limiting cam were provided. The limiting cam (limiting the range of travel of the valve) provided more linear gas flow curves and increased the overall controllability of the system.

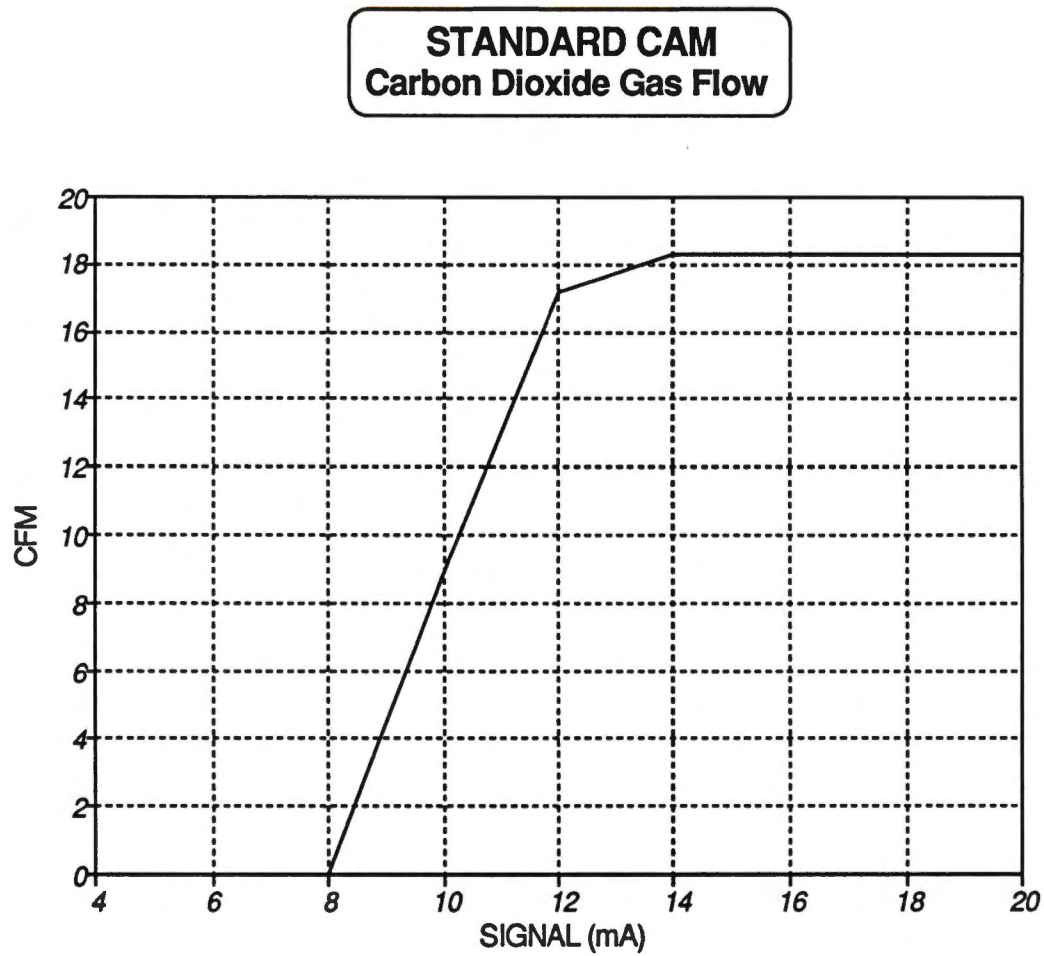


Figure 8. Carbon dioxide gas flow through valve #1 with standard cam.

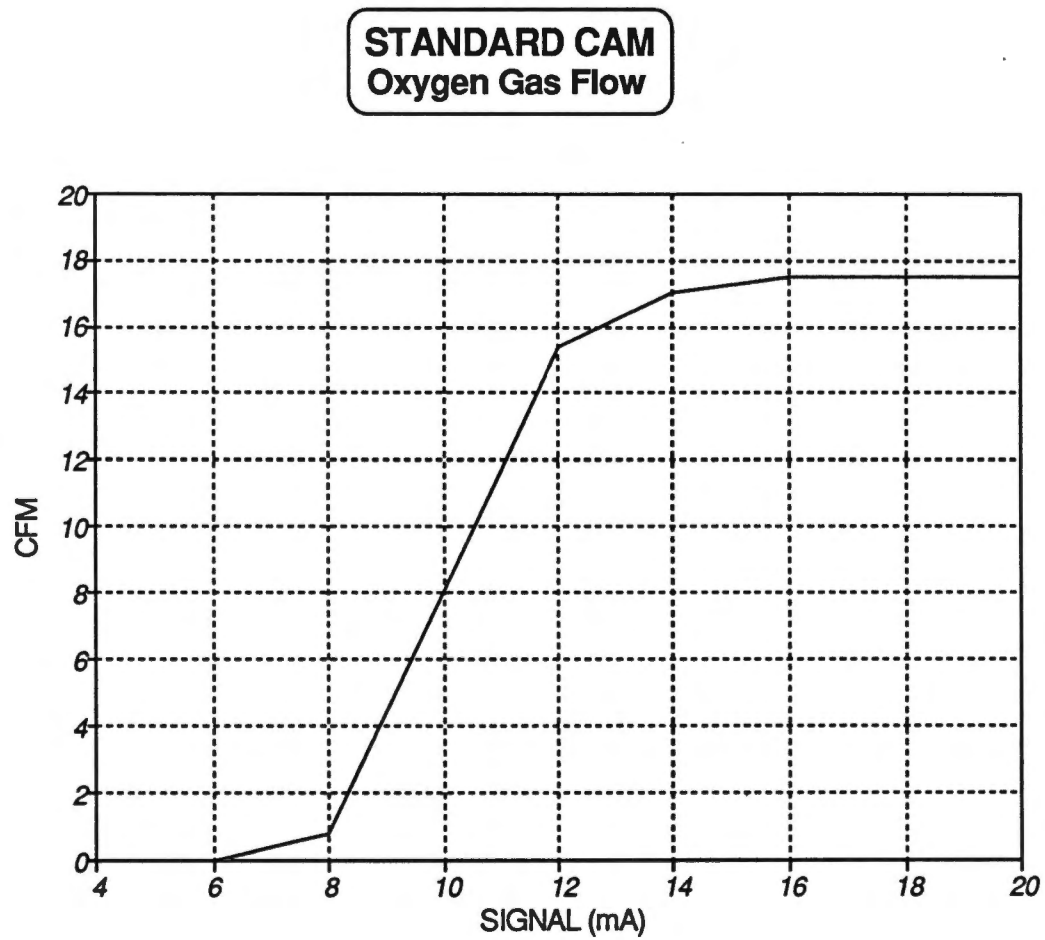


Figure 9. Oxygen gas flow through valve #2 with standard cam.

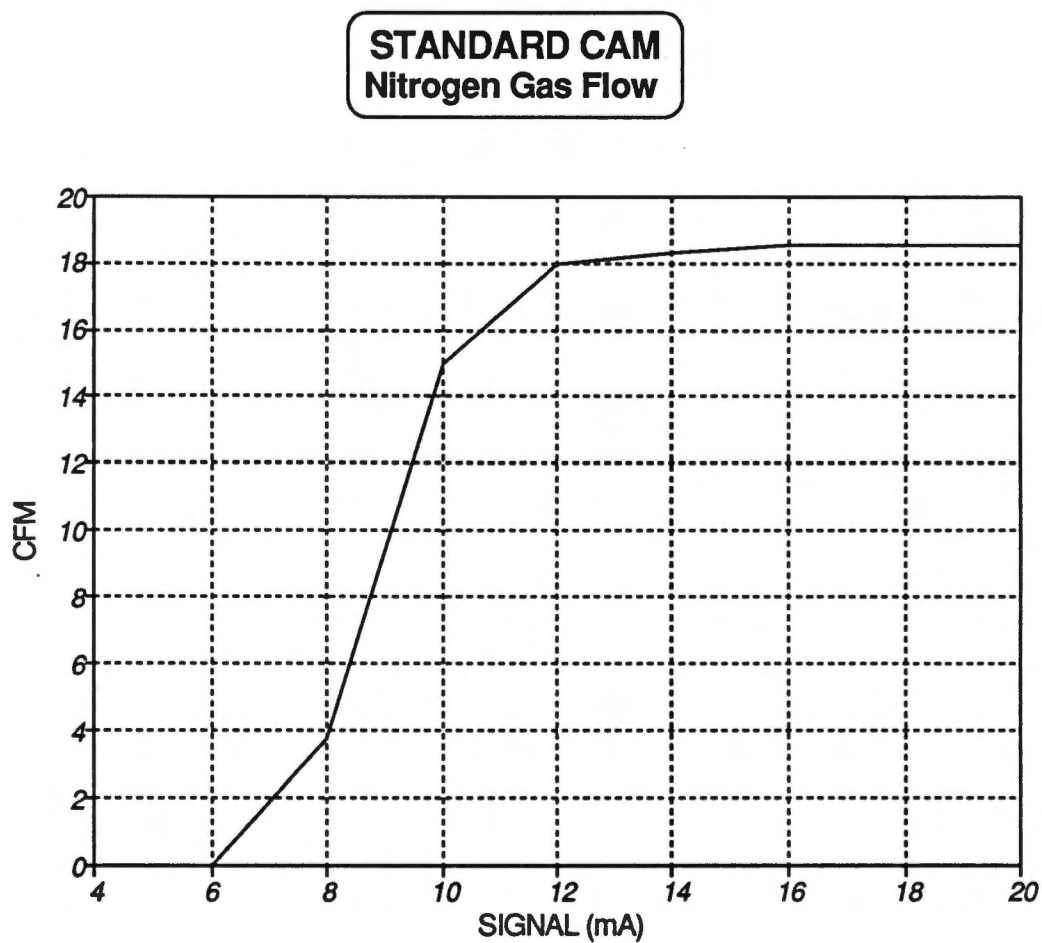


Figure 10. Nitrogen gas flow through valve #3 with standard cam.

Figure 11 shows a comparison of gas flows for the cams tested. The limiting cam could be set to 0-90°, 0-60°, 0-45°, or 0-30°. The square root cam could be set to 122-163, 122-204, or 163-204 kPa. As seen in Figure 11, the limiting cam set at 0-45° and 0-30° provided the most linear flow condition over the gas flow range. The 0-30° setting of the limiting cam was selected for use due to its greater sensitivity in flow control. The square root cams were eliminated from consideration primarily due to limited milliamp range and steep gas flow curves observed. The standard cam showed a low maximum flow in this comparison due to the previously mentioned problems with maintaining a constant delivery pressure from the regulators.

Reduction of the maximum valve opening from 90° to 30° was of little concern since the previous tests showed little ability to gain added control of gas flow above 50° of valve opening. It was not as important for this apparatus to provide high flow rates as it was to provide accurate control of the flow. Figures 12, 13, and 14 show the gas flow information obtained with CO₂, O₂, and N₂ after the installation of the limiting cams in the positioning units. In each case no gas flow occurred until a control current of at least 10 mA was provided to the positioner by the computer controller.

Corrections To Flow Rates

With the limiting cams installed and calibrated with the rotameter, it was necessary to adjust the rotameter readings for the gases used. The rotameter was calibrated for SCFM of air. Since the gas density affected the float position in the

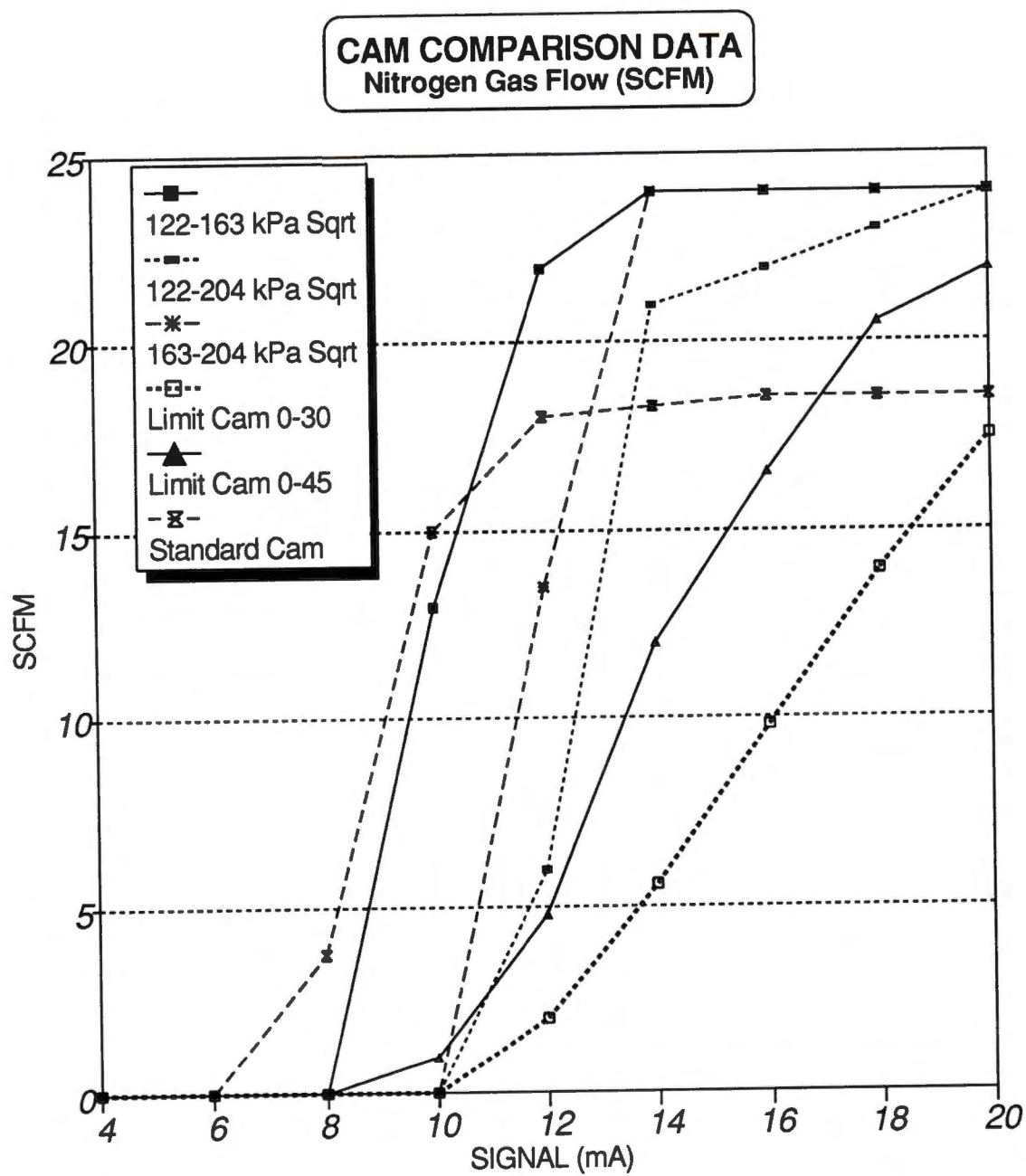


Figure 11. Comparison of nitrogen gas flow for valves with standard, square root, and limiting cams.

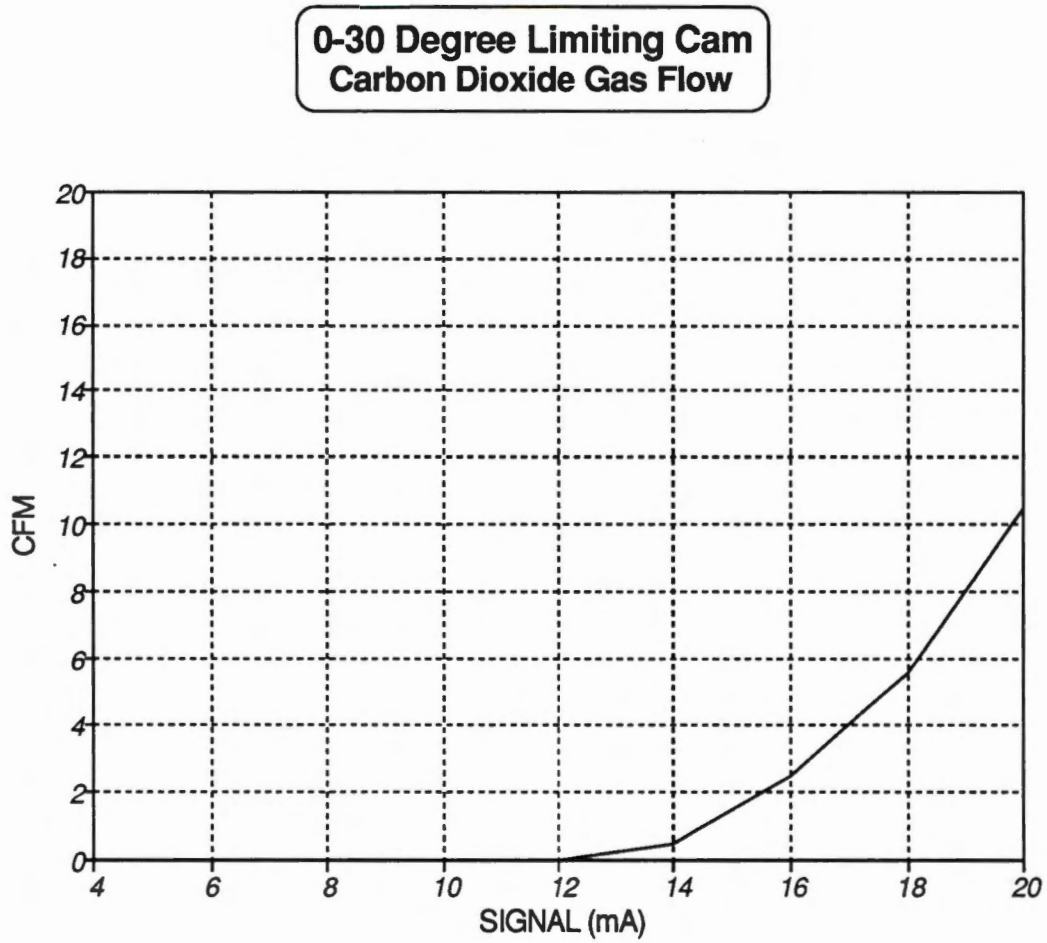


Figure 12. Carbon dioxide gas flow through valve #1 with 0-30° limiting cam.

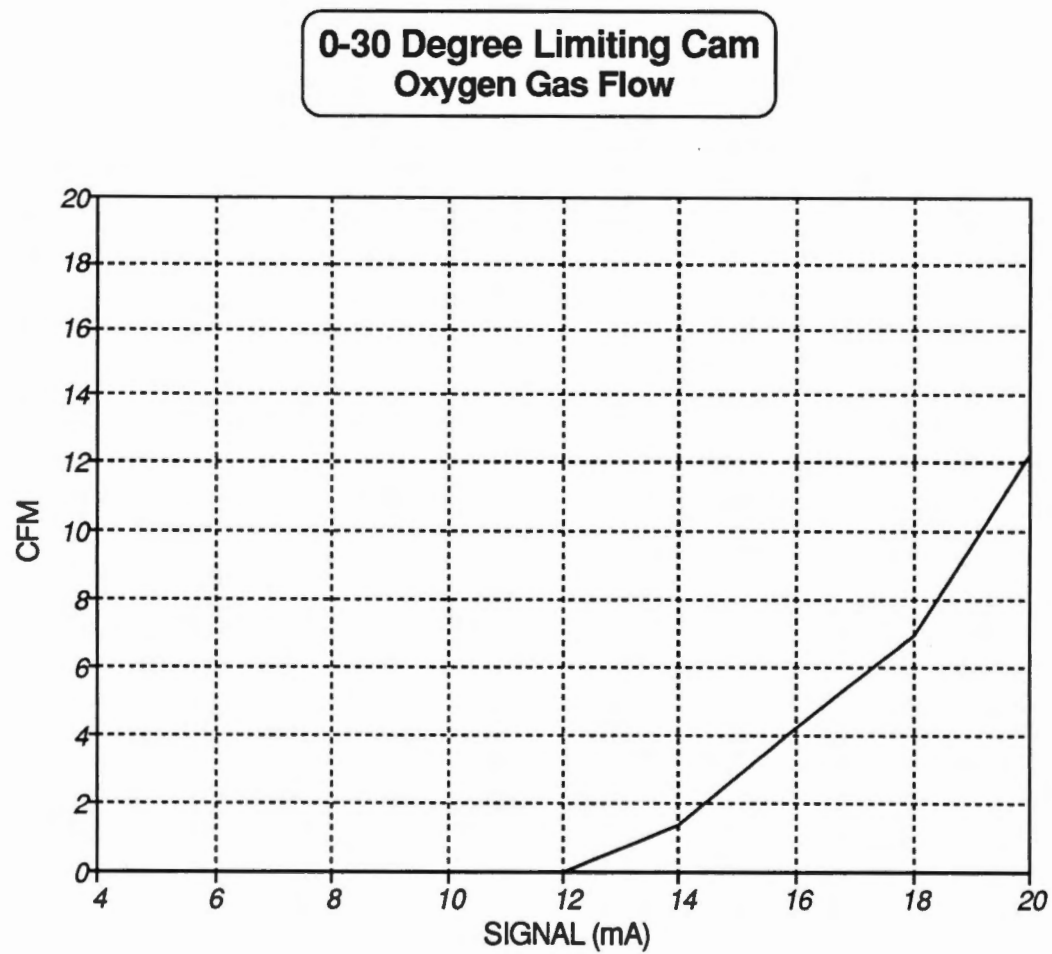


Figure 13. Oxygen gas flow through valve #2 with 0-30° limiting cam.

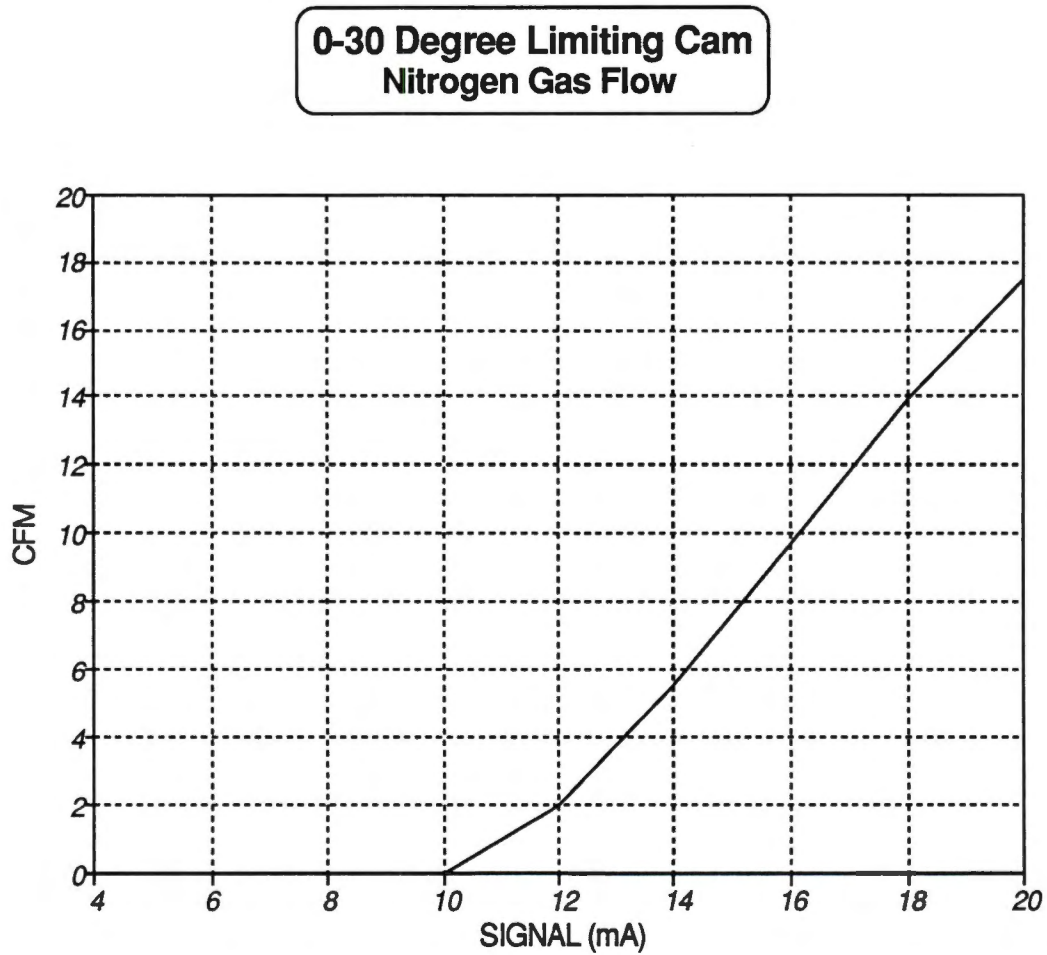


Figure 14. Nitrogen gas flow through valve #3 with 0-30° limiting cam.

rotameter, it was necessary to correct the gas flow rates read from the rotameter for the differences in density of each gas.

During testing, a problem was encountered with the operation of the CO₂ regulator which hindered flow of the gas. During early test runs the CO₂ regulator froze. That is, as flow of the gas was sustained, the regulator developed frost on the casing. If flow continued, complete control over the regulator was lost and the ability of the regulator to maintain a constant pressure was severely affected.

It was first thought that the CO₂ tank was equipped with a dip tube and liquid CO₂ was being delivered to the valve. The tank was checked by a representative of the supply company and found to be compressed CO₂ (no dip tube). It was suggested that some liquid CO₂ was being forced through the regulator with the gas due to the relatively high flow rates. To correct the problem, a regulator modified for high flow was installed. This regulator had a heat sink casing between the regulator mechanism and the tank. This permitted additional heat gain from the atmosphere prior to flow entering the regulator mechanism. Although frost still appeared on the casing, constant regulation of the pressure and the ability to adjust the pressure of the gas was maintained. Recalibration of the CO₂ gas flow was made. All calibration results are included in Appendix B.

The adjustments to correct for density variation were based upon the ideal gas equation and a rotameter equation. Equation 1 is the ideal gas relationship used to calculate the density of each gas.

$$\rho = \frac{P}{R T} \quad \text{Equation (1)}$$

Where T is the temperature (K), P is the absolute pressure (kPa), and R is the gas constant for the specific gas (kJ/kgK). Values of R were determined by dividing the universal gas constant $R_u=8.314$ (kJ/KmolK) by the molecular weight of that gas. The values of R were 0.2967, 0.2598, 0.1889, 0.2870 for N_2 , O_2 , CO_2 , and air respectively.

The general equation for flow of gas through a given rotameter is:

$$Q = C_R * (A_T - A_F) * \sqrt{\frac{2 * g * V_f}{\rho * A_F} * (\rho_F - \rho)} \quad \text{Equation (2)}$$

Where Q is the flow, C_R is a valve of 0.6, A_T is the flow meter tube cross-section, A_F is the float cross-section, V_f is the float volume, and ρ_F is the float density.

This general equation can be used to relate the flow of two different gases. Cancelling common terms, and noting that $\rho_F \gg \rho$, results in the following simple relationship (equation 3).

$$\frac{Q_i}{Q_{air}} = \sqrt{\frac{\rho_{air}}{\rho_i}} \quad \text{Equation (3)}$$

A pressure of 170.25 kPa was used in the calculations. This was the pressure during tests runs. Temperatures of the gases were obtained by recording the coldest temperature of each gas at the regulator during test runs. It was decided, after the test runs had been made, that the regulator temperature readings were not

representative of the temperatures of the gases throughout the system. Temperature readings were taken downstream of the valves and the results were averaged with the regulator temperatures. These averaged temperatures were used in the calculations.

Using equation (1), we can determine the density for any gas at 170.25 kPa and the respective temperature (K). Example (1) shows the corrected density for CO₂ using equation (1).

$$\rho_{CO_2} = \frac{170.25 \text{ kPa}}{(0.1889 \text{ kJ/KgK}) (264.99 \text{ K})} = 3.40 \text{ Kg/m}^3 \quad \text{Example (1)}$$

The same procedure was used to determine the corrected densities for each gas. The corrected flow rate for each gas was then determined using equation 3. Air density was calculated based on the temperature measured for the gas involved in the flow adjustment. Example (2) shows the corrected flow rate for carbon dioxide at 0.5 SCFM. The corrected density of air for this adjustment was 2.238 Kg/m³ (at 265°K).

$$\frac{Q_{CO_2}}{0.5 \text{ SCFM}} = \sqrt{\frac{2.238 \text{ Kg/m}^3}{3.40 \text{ Kg/m}^3}} \quad \text{Example (2)}$$

$$Q_{CO_2} = 0.406 \text{ SCFM}$$

Similar calculations were made for all gases and all flow rates using respective air densities. Corrected densities, flow rates, and temperatures are in Appendix B.

Conversion To Mole Fraction

It was decided to calculate all mixture concentrations in molar units. A mole is a specialized unit used in chemistry for counting at the molecular level. A mole

has a numerical value of 6.02×10^{23} . The number 6.02×10^{23} was chosen as the basic counting unit in chemistry because it represents the experimentally determined number of atoms or molecules contained in a sample of a pure substance with weight in grams numerically equal to the atomic or molecular weight of the substance (Stoker, 1982). Therefore, 1 mole of CO_2 equals 44 grams of CO_2 $[12+(16*2)]=44$.

Continuing with the flow rate derived for example (2), the number of moles in 0.406 SCFM could be determined. First, the units were converted from standard to metric. 0.406 SCFM CO_2 was converted to yield 39.11 g/min CO_2 as follows:

$$\begin{aligned} 0.406 \text{ SCFM} / 35.31467 \text{ m}^3/\text{ft}^3 * 1000 \text{ L/m}^3 &= 11.50 \text{ L/min} \\ 11.50 \text{ L/min} &\text{ was then multiplied by the corrected density of } \text{CO}_2 \\ 11.50 \text{ L/min} * 3.401 \text{ g/L} &= 39.11 \text{ g/min } \text{CO}_2 \end{aligned}$$

Next, the number of moles were calculated from the grams per minute.
 $39.11 \text{ g/min} / 44 \text{ g/mole} = 0.888 \text{ moles/min } \text{CO}_2$

A complete table of volumetric flow rates and corresponding molar flow rates as a function of control signal input can be found in Appendix B. Using these data, a model could be developed, evaluated, and used to predict the necessary control signals for each gas to produce the objective target mixtures.

SIMULATION AND MODEL DESIGN

Both simulation and modelling are forms of representation. Simulation is a physical representation while modelling is a symbolic representation of equipment or events. The development of a simulator is not or should not simply be a matter of

requiring engineers to reproduce an operational system. The proper development of simulators begins with an analysis of what one wishes the simulator to do (Wilson, 1990). The objective in the case of this study was to determine what amounts of three constituent gases were present in a mixture. Amounts were a function of valve openings at a specific pressure and temperature. Several steps were involved in going from the development of the model to its use as a predictor of control signal for the target mixtures. Figure 15 shows the flow chart used to develop the model, test the model output by evaluation and validation, produce a predicted control signal for each gas in the specific target mixture, and use gas analysis methods to validate the percentages of each gas in the produced mixture.

A model is not a theory. The purpose of a theory is to describe functional relationships. A model incorporates such functional relationships, but the goal of the model is to predict and control the effects resulting in the manipulation of model variables. Models become necessary when the actual system or physical simulation is not available. This is usually the case when a new system is being developed and there is need to explore new parameters whose values are unknown (Wilson, 1990).

An effective model is developed for a specific purpose and has certain goals that it is intended to achieve. The model developed for this study was designed to predict the opening necessary for each valve to produce a certain gas mixture. In this study, the model will determine the percentages of three constituent gases in a final mixture when variable control signals have been sent.

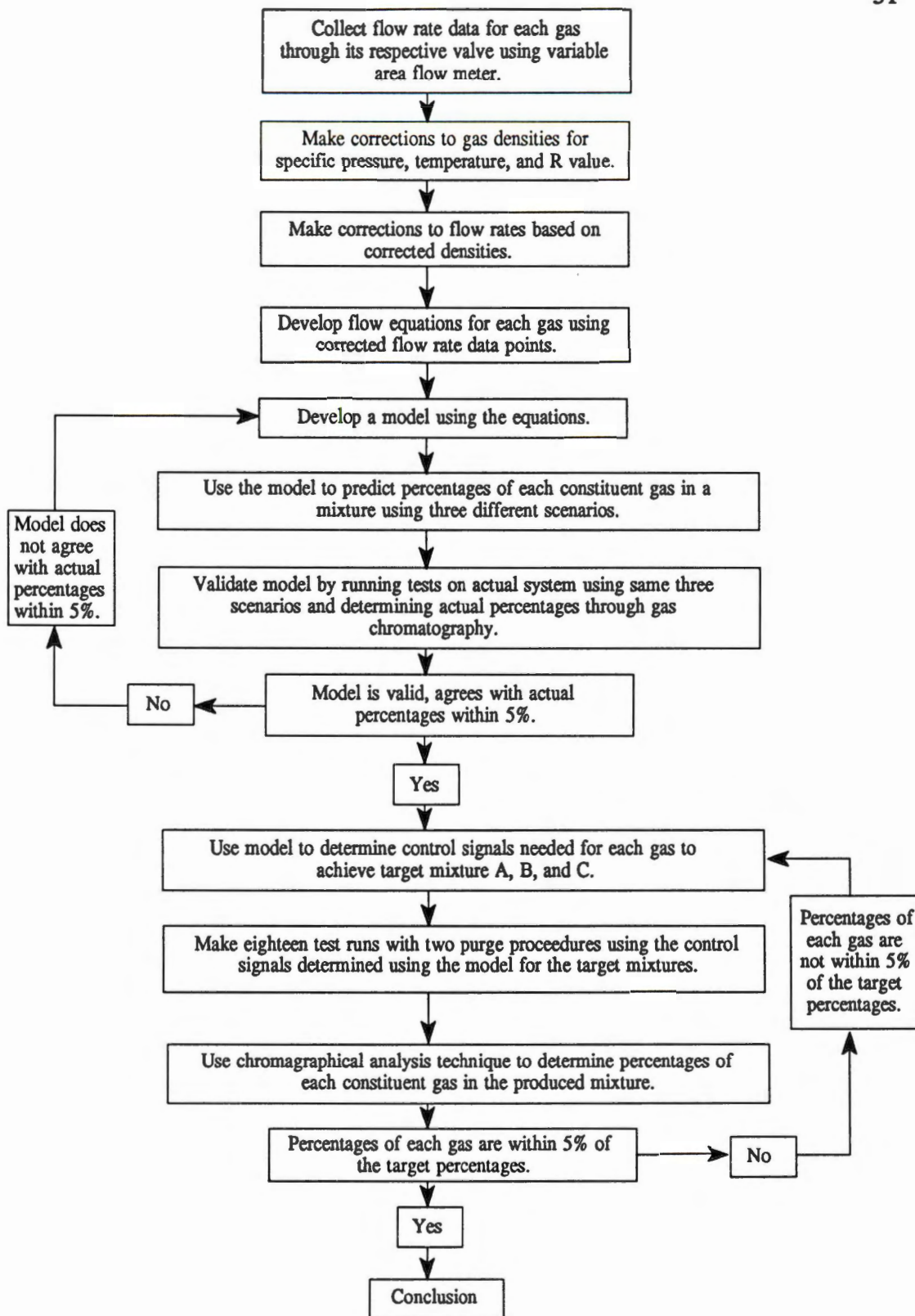


Figure 15. Flow of model development and implementation.

The curves produced from the corrected flow rates (Figure 16) were plotted and the data points collected were entered into a spreadsheet. Equations were developed, using a computer software program, giving a mathematical model for each gas flow at any milliamp control signal. Figures 17, 18, and 19 show the developed equations, plotted data points, and relevant statistical information for each gas.

A computer spreadsheet was developed that incorporated the equations from the curves produced from the corrected molar flow rates. The complete spreadsheet can be found in Appendix A. The spreadsheet (model) allowed any combination of three control signals (one for each valve) to be entered. Concentrations (percentages) of each gas in the final mixture were calculated and displayed within the spreadsheet model.

To fully evaluate the model and its effectiveness it would be necessary to obtain several percentages of each gas at various control signals and in various combinations with the other gases. Three scenarios were run using the model to simulate three percentages of each gas at various control signals. The validity of the modeled results would be confirmed by running the actual system at the same control signal outputs and obtaining actual percentages from gas analysis (described later).

The three scenarios were run prior to running the actual test procedure. This was necessary to first see if the model was effective at predicting the actual percentages of gases in a desired mixture. The three scenarios were designed so that the percentages of any one gas would vary greatly from scenario to scenario. This would show if the gas mixing system could efficiently change from one gas mixture to

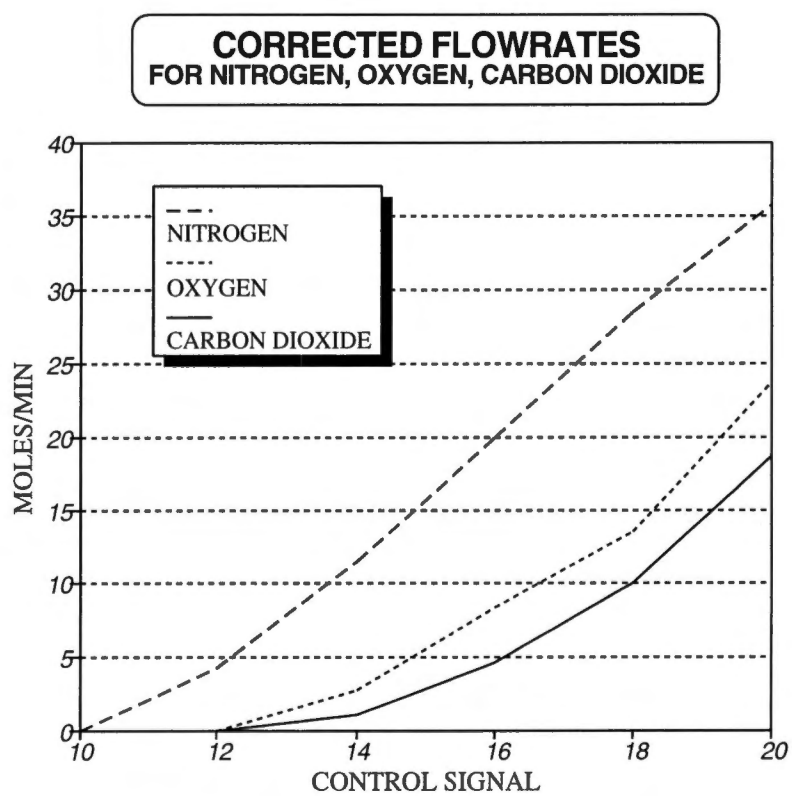


Figure 16. Corrected gas flow rates.

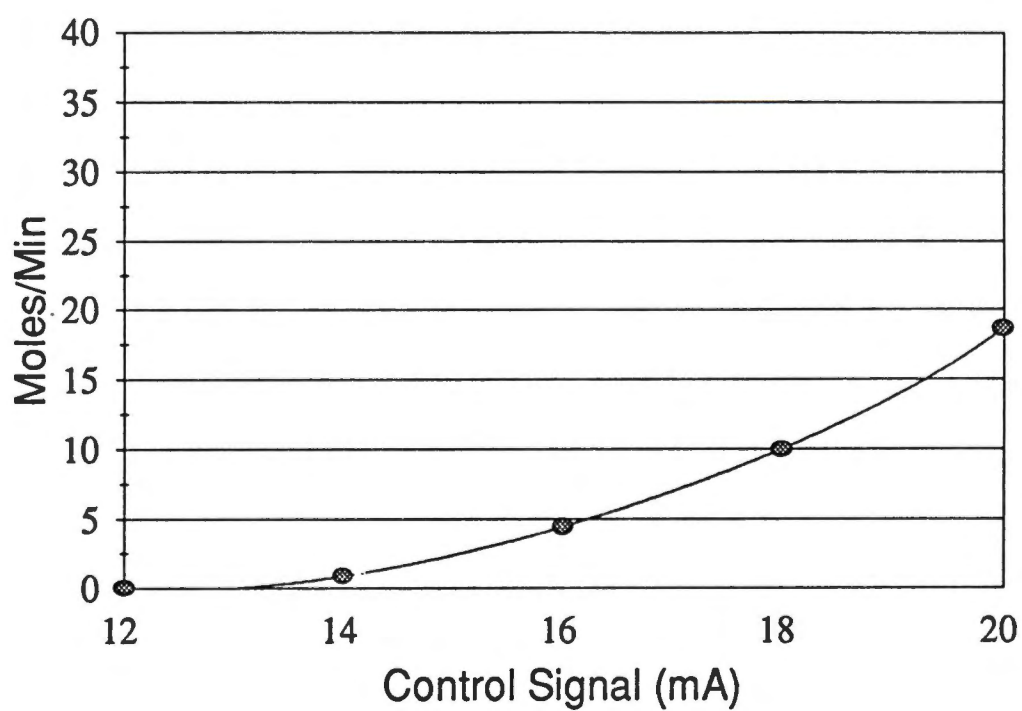
Equation For CO₂ at 170 kPa $r^2 = 0.999999999$ FitStdErr = 0.000412635221 Fstat = 464651665Rank 2 Eqn 2108 $y=a+bx+c\exp x+d/x$ $a=-142.08211$ $b=5.7022228$ $c=5.1363241e-9$ $d=883.85596$ 

Figure 17. Equation, graph, and statistics for carbon dioxide gas.

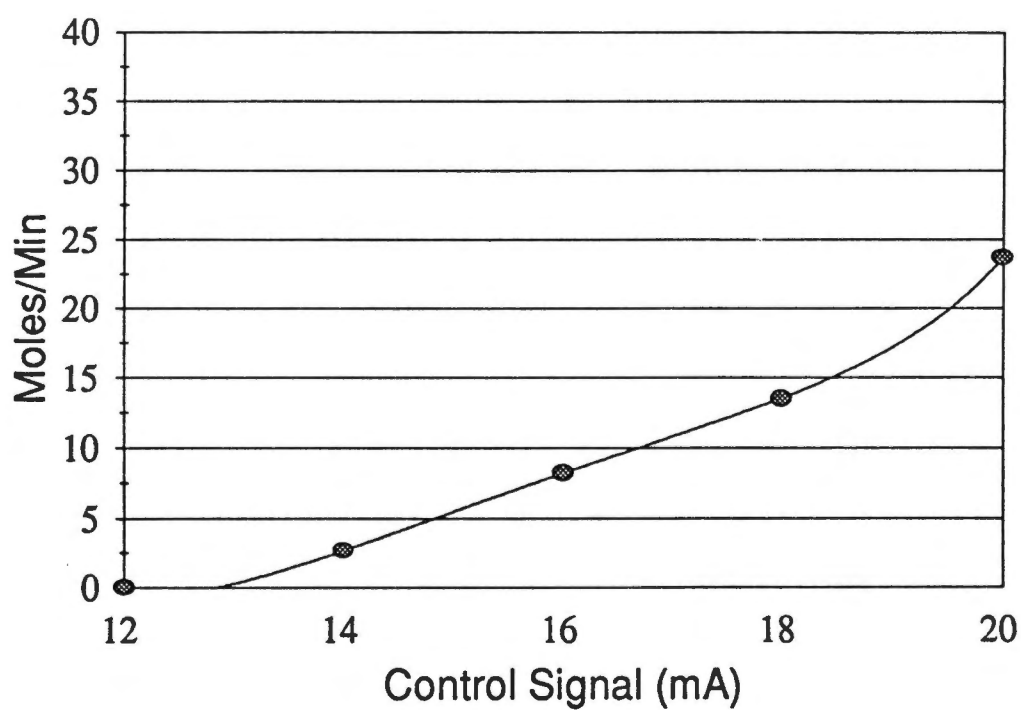
Equation For O₂ at 170 kPa $r^2 = 0.99999913$ FitStdErr = 0.0176059377 Fstat + 383119.319Rank 1 Eqn 3043 $y=a+b\exp x+\ln x/x^2+d\exp-x$ $a=33.701022$ $b=1.16100739e-8$ $c=-2379.6039$ $d=1197684.4$ 

Figure 18. Equation, graph, and statistics for oxygen gas.

Equation For N₂ at 170 kPa $r^2 = 0.999999993$ FitStdErr = 0.0026028047 Fstat = 35918420.8Rank 9 Eqn 4359 $y=a+bx+cx^2+dx^3+ex/\ln x$

a=-3100.4079 b=-532.02308 c=4.9408053

d=-0.059548355 e=1838.869

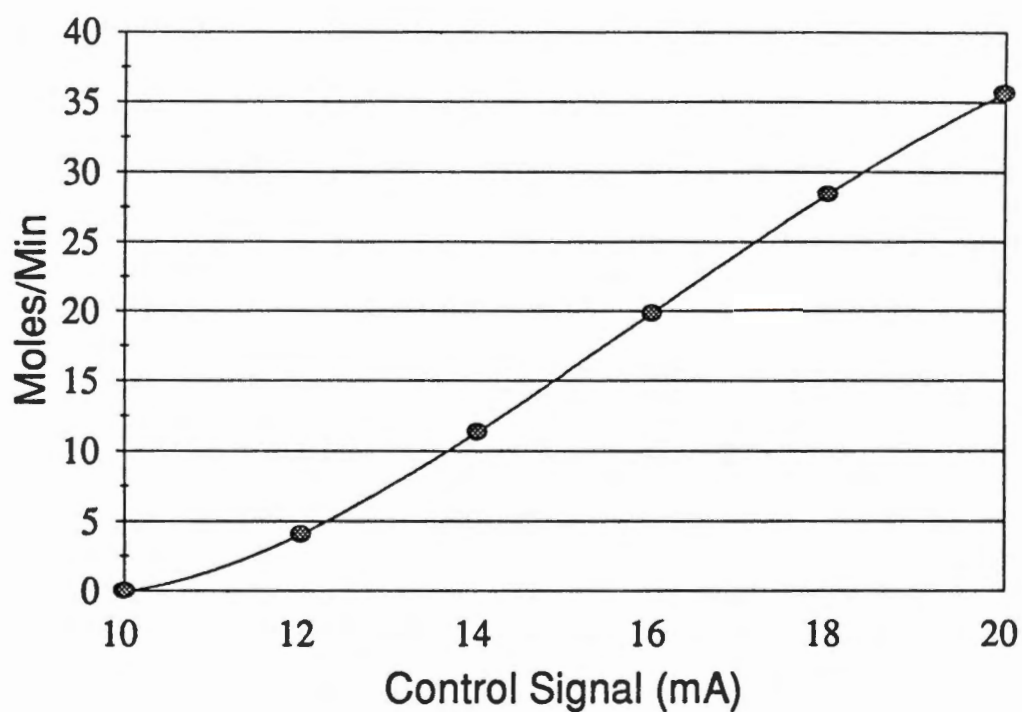


Figure 19. Equation, graph, and statistics for nitrogen gas.

another. The arrangement of control signals and simulated percentages for each gas in each scenario can be seen in Table 8. The control signals used in the simulation were next entered into the actual system and tests were made to validate the model results.

Validation of Model Results

Validity was one criterion of the effectiveness of a model. Validity is the agreement of model outputs with actual system performance. Since the model is only a representation of reality (not reality itself), effectiveness of that representation must be demonstrated (Wilson, 1991). In our case, validity was arrived at by looking for experimentally quantitative validation or tests of model accuracy.

The prototype gas system was programmed to run the same scenarios as the simulation by entering the same control signals. After each test, samples were drawn and concentrations of each gas in the mixture was determined using gas analysis methods. The results of the actual test runs can be seen in Table 8. Figures 20 and 21 graphically compare the actual results to the results of the model.

Comparisons between volume, mass, and molar percentages were made for one of the above simulated mixtures. This was done to compare gram percentages to volume and molar percentages (volume and molar percentages are theoretically equal). Table 9 shows the comparison of percentages for scenario one. The results showed that molar and volumetric percentages were the same. While actual mass percentages differed from molar percentages, the percent of differences between simulated and actual measurements were very close to the values for molar

Table 8. Results of model evaluation predicting percent (molar basis).

Scenario	Control Signal Sent (mA)			% Gas Observed In Tank			% Gas Simulated In Tank		
	CO ₂	O ₂	N ₂	CO ₂	O ₂	N ₂	CO ₂	O ₂	N ₂
1	16	14	20	10.32	6.69	82.97	10.38	6.26	83.36
2	18	16	20	19.90	16.16	63.40	18.56	15.24	66.20
3	20	16	18	32.53	16.08	51.73	33.75	14.85	51.40

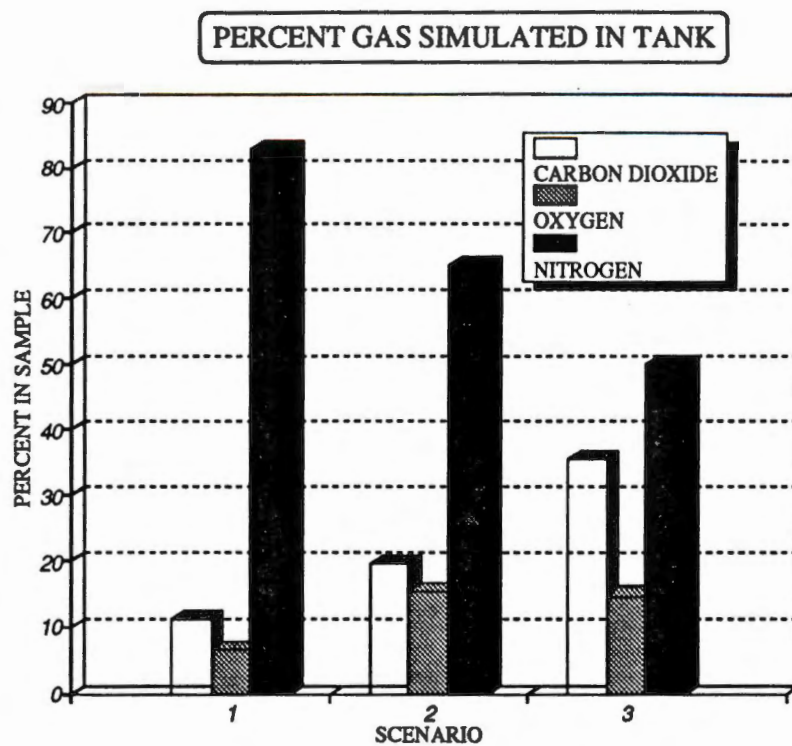


Figure 20. Percent gas simulated in collection tank.

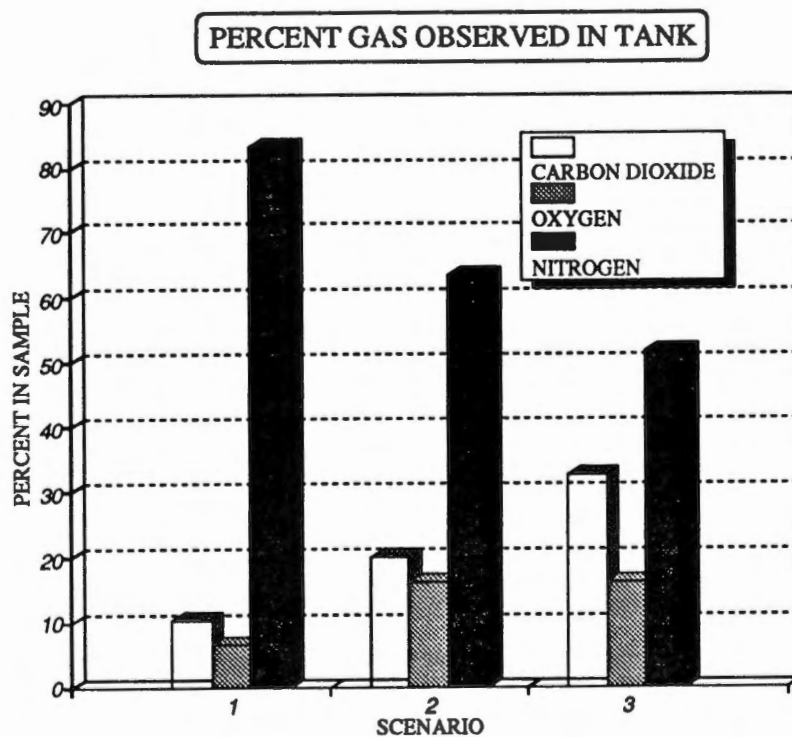


Figure 21. Percent gas observed in collection tank.

Table 9. Comparison of mole, mass, and volume percentages used in simulation scenario 1.

GAS	SIMULATED % (MOLE %)	ACTUAL % (MOLE %)	DELTA % (MOLE %)	SIMULATED % (MASS %)	ACTUAL % (MASS %)	DELTA % (MASS %)	SIMULATED % (VOLUME %)	ACTUAL % (VOLUME %)	DELTA % (VOLUME %)
CO ₂	10.38	10.32	0.06	15.27	15.18	0.09	10.38	10.32	0.06
O ₂	6.26	6.69	-0.43	6.70	7.15	-0.45	6.26	6.69	-0.43
N ₂	83.36	82.97	0.39	78.03	77.66	0.37	83.36	82.97	0.39

measurements. Use of molar percentages appeared preferable since actual gas analysis were made on a volume (molar) basis.

TEST PROCEDURE

After validating the effectiveness of the model, it could be used to determine the combinations of control signals required to yield the three objective target mixtures. Tests could then be made to determine the accuracy and repeatability of the actual gas mixing system at producing the target mixtures. The model was used to determine the three specific control signals needed for each of the target mixtures. For simplicity, the flow for N_2 was held constant at maximum flow. Flows for the two remaining gases were then determined and the corresponding mA signal was determined from the model. Table 10 shows the milliamp control signals used for each valve during the testing procedure.

The first step in the testing procedure was to open the valves on the gas cylinders allowing the flow of gas through the regulators (set at a static absolute pressure of 307 kPa) to the control valves. The computer was booted and the software program initialized. The desired decimal numbers were entered into the computer software program and each control valve was opened to the specified angle. The regulated pressure was observed during flow to ensure a constant 307 kPa. Observations were made to ensure the venting of gases to the atmosphere at 170 kPa. The valves remained open 30 seconds. Since venting of the gases began five seconds after the test began, 30 seconds was adequate time for producing the desired mixture. Two

Table 10. Control signals used to achieve target mixtures.

TARGET MIXTURE	CONTROL SIGNAL (mA)		
	CO ₂	O ₂	N ₂
A	18.1	14.9	20
B	17.3	15.8	20
C	15.9	13.8	20

purging procedures (described later) were used to purge the collection tank between the tests. Two samples were taken for each replication. There were two replications for each test.

Two procedures (A and B) were used during this study. Both of the testing procedures were similar in design except for the method used to purge the collection tank between test runs. The first test procedure (A) used a vacuum to purge the collection tank. The vacuum was supplied by the building's vacuum supply lines that were at a negative 204 kPa. The vacuum purge was made for three minutes between each test run. The second procedure (B) used an extra flow of the next test mixture to purge the collection tank. The time for this extra flow used in the second procedure was based upon flow rate and collection tank volume. Procedure B used one minute of flow for each test (instead of 30 seconds as used in procedure A). This was believed to be a sufficient amount of time to purge the collection tank of the previously run mixture, since the flow replaced the gas volume in the collection tank up to 25 times over the purge period. Figure 22 outlines the entire testing process with indications for the type of purge that was utilized.

Sample Extraction

A brass manifold installed in the top of the collection tank allowed for the mounting of a septum. A valve was part of the septum manifold. Before a sample was extracted the valve was opened to allow a flow of collected gas to purge the manifold. A 10-ml syringe was used to withdraw a sample. Half of the 10-ml sample was analyzed.

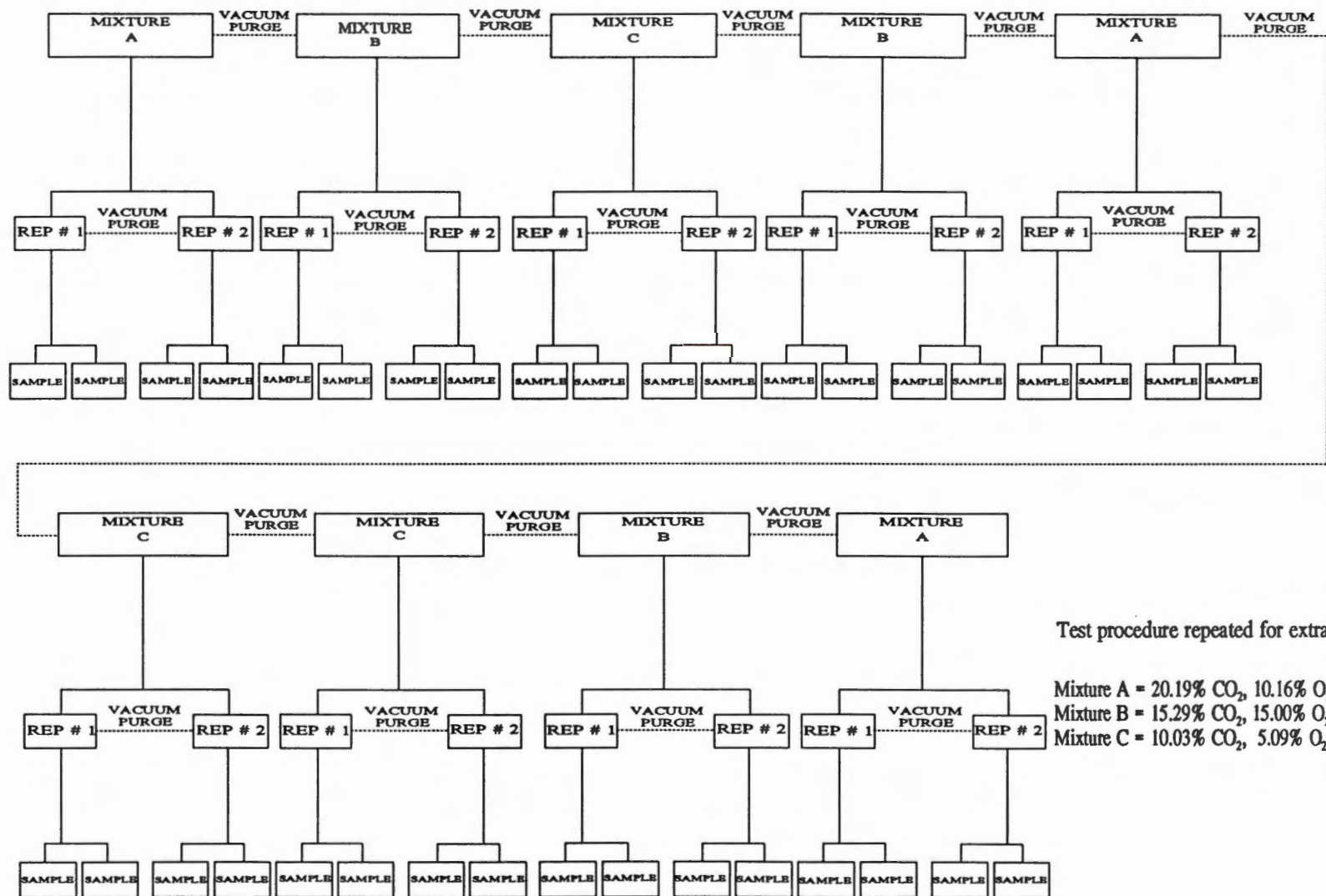


Figure 22. Schematic for test procedures A and B.

When gas flow stopped and pressure in the collection tank had reached 107.25 kPa, the cylinder of the syringe was evacuated and the needle was inserted into the rubber septum. A 10-ml sample was extracted. The procedure was repeated to obtain a second sample of the same mixture. The collection tank was purged and the mixture run again. Two more samples were taken using the same method described above. With a total of nine test runs for the three target mixtures, two replications of the of the target mixtures, and two samples collected per replication; the complete test series required that 36 syringes be filled. When both purging procedures A and B were complete there were 72 syringes filled. The filled syringes were taken to the Food Science and Technology laboratory where gas chromatographical analysis was made.

Gas Chromatography

In chemistry and biology it is frequently necessary to separate, isolate, and identify the components of mixtures. In this research project it was also necessary to isolate and separate each constituent gas in the mixture so that percentages of each gas could be calculated. The technique of gas chromatography is commonly used to accomplish this separation, isolation and identification.

The term chromatography, which literally means "color writing", was coined to describe the phenomenon (Abbott, 1965). Although the word chromatography implies color, there is no direct connection except that the first compounds separated by the specialized technique were the pigments of plants that were green (Gritter, 1985).

Almost every chemical mixture from low to high molecular weight can be separated into its components by some chromatographical method. Gas chromatography is used routinely in industrial and academic laboratories. The method uses the gas phase to carry substances over the surface of an adsorbent (Keenan, 1980).

The basic technique of gas chromatography is simple but lengthy. A small sample of the material being examined is injected into a stream of an inert gas such as nitrogen, carbon dioxide, argon or helium, which carries it into a column. The gas used to carry the sample is usually referred to as the carrier gas. The column contains a suitable medium capable of retarding the flow, by varying degrees, of the individual components of the sample as they flow through the column. The separated components then emerge from the column at discrete intervals (characteristic of each component) and pass through some form of detector. Differences in absorption or partition in the material in the column is the factor which makes separation possible (Abbott, 1965).

The most popular carrier gases are nitrogen, helium, and hydrogen. Their only purpose is to carry the analyte vapors through the column. Helium was used during this project. Sample introduction is most often accomplished with a microsyringe through a self-sealing rubber septum. Columns are usually made of metal (stainless steel, copper or aluminum) or glass. Since columns are usually coiled, metal is the material of choice due to its ability to be easily bent (Miller, 1988). Useful adsorption agents for gas analysis include alumina, activated carbon, silica gel, and

molecular sieves. Having decided which medium to use, the column is packed (Abbott, 1965). The column is positioned in an oven which provided elevated temperatures and thermostatic control. Gas chromatographic separations are usually carried out at elevated temperatures (Abbott, 1965). The detector is a device placed at the end of a column that analyzes the emerging gas stream and provided data to a data recorder. The data recorder shows, graphically, the results of the chromatograph (Gritter, 1985). Commonly, a heat conductivity detector is put at the end of the column. Because the heat conductivities of various gases differ greatly, the presence of a second, third, etc. gas mixed with the carrier gas is easily detected. Figure 23 is a drawing of the gas chromatograph and the relevant components.

The specific gas chromatograph used in this study was the Hewlett-Packard 5890A. This chromatograph was equipped with two thermal conductivity detectors (TCD) designated A and B. Each detector was a single filament, single column, fluidic switching detector. Both detectors had switch-selectable optimization for carrier gas type. The oven had a temperature range of 7° C to 400° C. For the samples analyzed during this project, a temperature of 25° C was used. The oven was temperature programmable to three ranges. The 5890A was also equipped with a 3.18 mm column. Two channels of flow sensing were present on the chromatograph. The electronic flow sensing permitted monitoring flow rates during analysis.

Septum bleed to the atmosphere could cause the chromatograph to indicate inaccurate concentrations in a mixture. The 5890A chromatograph was equipped with

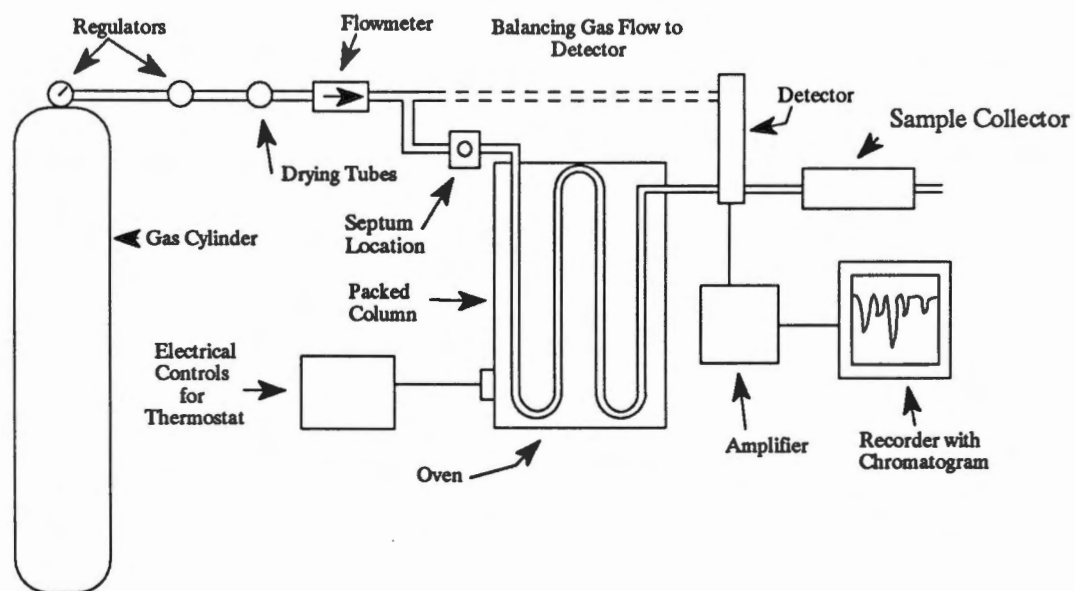


Figure 23. Apparatus and components for gas chromatography.

a septum-purged packed column inlet. The ability to purge the septum eliminated ghost peaks due to septum bleed or septum-retained sample (Hewlett-Packard, 1988).

Chromatograph Interpretation

The 5890A permitted interfacing to an integrator which allowed the integrator to receive and transmit chromatographical setpoints. The integrator was used to process the signal from the chromatograph into a readable record. The integrator used in this study (Hewlett-Packard Model 3393A) was a separate unit from the chromatograph itself but designed to work specifically with the chromatography unit. The integrator produced a gas chromatogram, a series of peaks, representing gas percentages. Figure 24 shows the chromatogram obtained from the analysis of test six, mix C, repetition one, sample one, procedure A. Indications of the gas corresponding to each peak have been added to the chromatogram for descriptive purposes. The position of the peaks in relation to the start of the analysis identified the compound while the area under the peak related the compounds concentration in the mixture. The integrator recorded the peak and calculated the area under the peak.

Standards (precise known gas percentages) were used to develop standard curves for desired gases in different percentages. The standard curve was then used to determine the concentration of a gas in a mixture. The mean peak area of the gas standard was found by running several tests of the standard gas through the chromatograph, then taking the mean peak area for a gas at a particular percentage.

Six standards were used during this study. The six gas standards and the percentages of each gas in the standard mixture can be seen in Table 11.

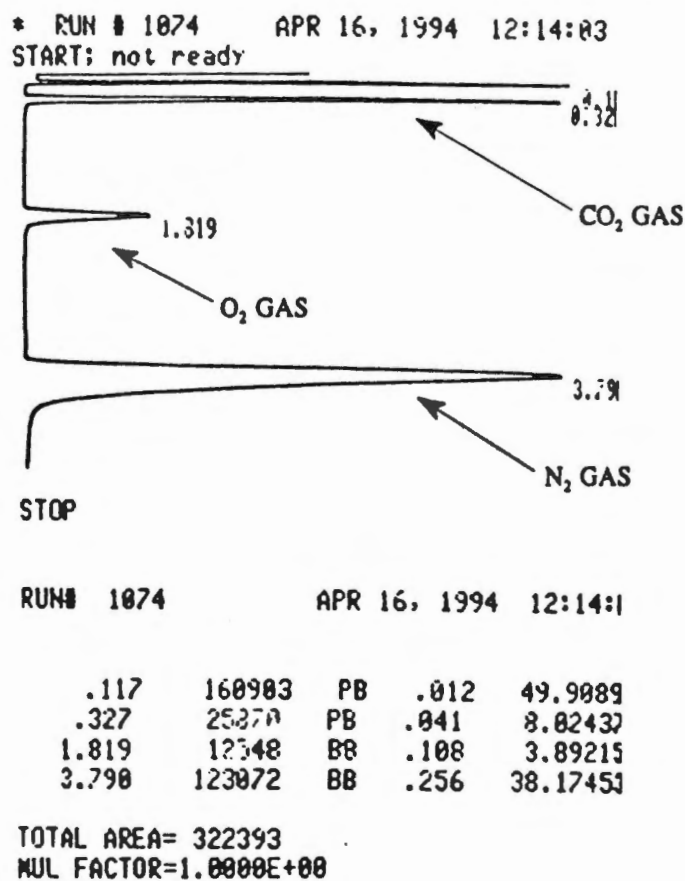


Figure 24. A sample chromatogram (procedure A, test 6, mixture C, rep 1, sample 1).

Table 11. Percentages of gases in standards.

Standard	Percent		
	CO ₂	O ₂	N ₂
1	0.99	1.01	98
2	5.10	4.92	89.98
3	10.10	15.20	74.40
4	14.70	20.10	65.20
5	25.00	25.30	49.70
6	30.00	30.20	39.80

The standards gave six data points for peak areas at a particular percentage of each gas in a mixture. These points were plotted and an equation for a line through the points was developed. These equations allowed percentages to be calculated from any given peak area obtained from the chromatogram. Figure 25, 26, and 27 shows the plotted data points, equation, and statistics developed for CO₂, O₂, and N₂ respectively.

The percentages obtained from the standard curves were based on a volume percentage. The percentages of each gas in the standards themselves were based upon volume percentages. Percentages obtained from the standard curve were converted to a volume fraction which made comparisons to simulated percentages (molar percentages) possible. After the corrections were made to the percentages derived from the flow rates, direct comparisons were made between the simulated percentages of each gas and the actual volume fractions found from the standard curves.

A spreadsheet was developed that utilized the equations developed from the simulation and from the standard curves. Figure 28 shows the spreadsheet with the peak areas from the example chromatogram seen in Figure 24. A prediction was first made using the model. The control signals used to produce mixture C (10.03% CO₂, 5.09% O₂, and 84.88% N₂) were 15.9 mA for the CO₂ valve, 13.8 mA for the O₂ valve, and 20 mA for the N₂ valve. The spreadsheet cell formulas can be seen in Appendix A.

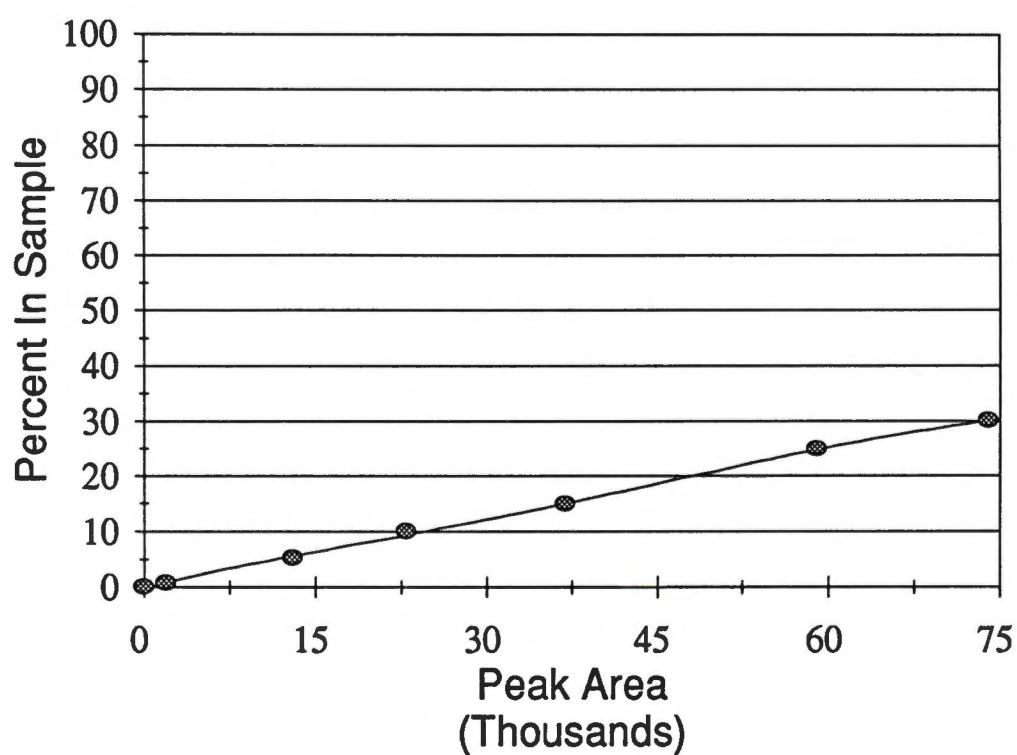
Equation For CO₂ Gas Standard $r^2 = 0.998395434$ FitStdErr = 0.80922148 Fstat = 311.110677Rank 1 Eqn 4341 $y=a+bx+cx^2+dx^2\sqrt{x}+ex^3$ $a=-0.18734791$ $b=0.00058842462$ $c=-2.747866e-8$ $d=1.8110065e-10$ $e=-3.2741397e-13$ 

Figure 25. Plotted data points, equation, and statistics for CO₂ gas standard.

Equation For O₂ Gas Standard $r^2 = 0.997252344$ FitStdErr = 1.09686414 Fstat = 181.473262Rank 1 Eqn 4341 $y=a+bx+cx^2+dx^2\sqrt{x}+ex^3$

a=0.040511092 b=0.00040084593 c=8.0855335e-8

d=-7.36844981e-10 e=1.8563362e-12

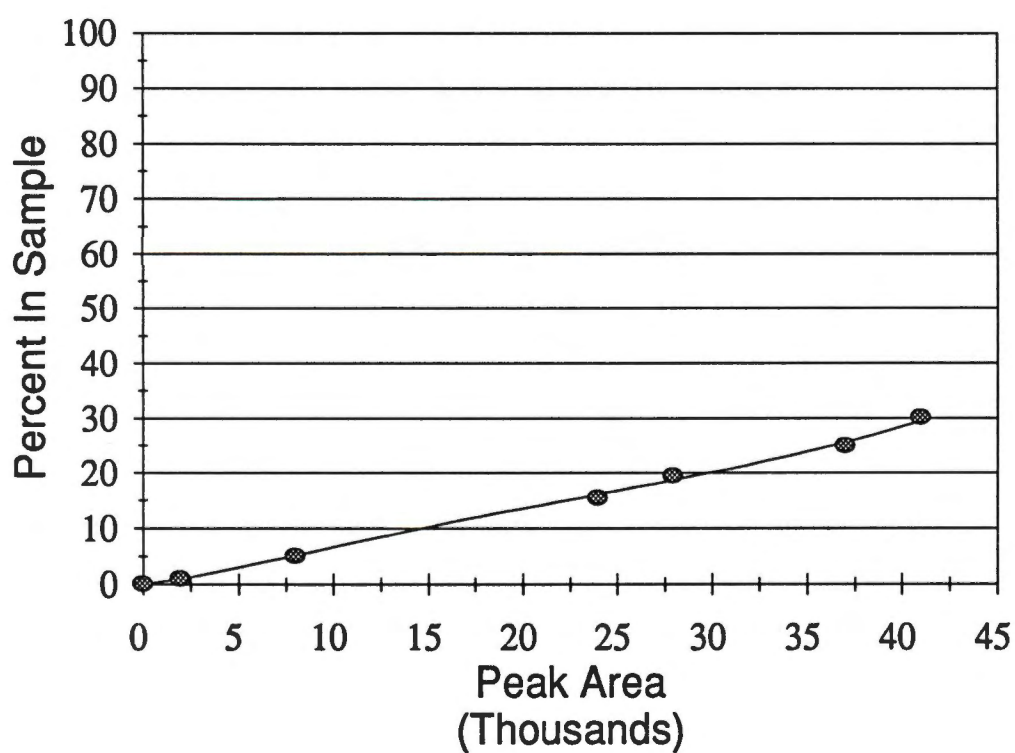


Figure 26. Plotted data points, equation, and statistics for O₂ gas standard.

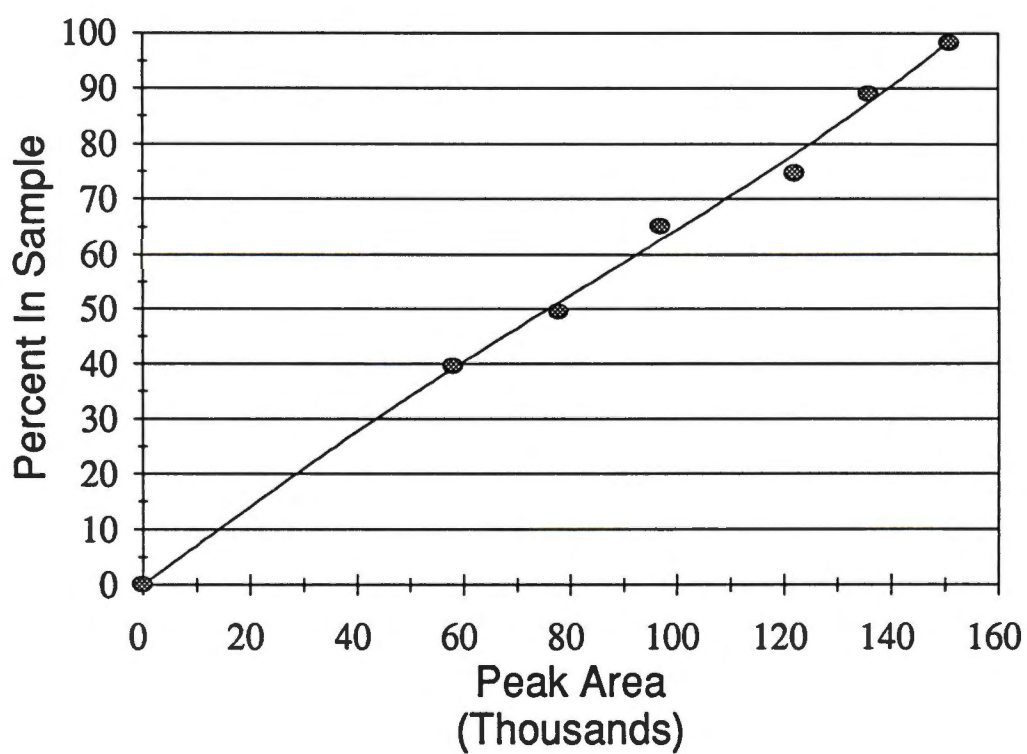
Equation For N₂ Gas Standard $r^2 = 0.995904595$ FitStdErr = 3.70374451 Fstat = 121.588038Rank 1 Eqn 4341 $y=a+bx+cx^2+dx^2\sqrt{x}+ex^3$ $a=0.0028545595$ $b=0.00068327492$ $c=3.6725036e-9$ $d=-2.5467965e-11$ $e=3.9885493e-14$ 

Figure 27. Plotted data points, equation, and statistics for N₂ gas standard.

Predicted Percent Gas In Mixture At Corrected Temperatures And 107 kPa

GAS	ENTER MILLIAMP SIGNAL	MOLES PER MINUTE	PREDICTED PERCENT IN MIXTURE
CO2 GAS	15.9	4.212956	10.03
O2 GAS	13.8	2.137274	5.09
N2 GAS	20	35.65682	84.88
			100

Actual Percentages Calculated From Peak Areas And Based On Volume Fraction

GAS	Enter Peak From Sample	Percent In Mixture From Standard Curve	Volume Fraction	Difference Between Predicted and Actual Percentages
CO2 GAS	27885	11.64	12.28	-2.25
O2 GAS	12463	8.412	8.87	-3.78
N2 GAS	116853	74.76	78.85	6.03
		94.81	100	

Figure 28. Spreadsheet used reflecting data from sample chromatogram.

After the test run was completed and the peak areas from the sample had been recorded, the recorded areas were entered into the spreadsheet. The equations from the standard curves were used to obtain percentages based on the peak areas obtained for the sample. For the example shown, the volume percentages obtained from the gas analysis were 11.64%, 8.41%, and 74.76% for CO₂, O₂, and N₂ respectively. The spreadsheet then converted volume percentages from the peak areas into volume fractions. The volume fractions for the sample were 12.28%, 8.87%, and 78.85% for CO₂, O₂, and N₂ respectively. Since volume and molar percentages were directly comparable no further conversions were made to the percentages. The difference between the simulated and actual percentages were -2.25%, -3.78%, and 6.03% for CO₂, O₂, and N₂ respectively.

Appendix C shows the peak areas, percent in sample, and mean percentages of each gas for each test from results obtained using the spreadsheet.

CHAPTER IV

RESULTS AND DISCUSSION

This study was undertaken to determine if a modified gas mixing apparatus was capable of creating three target mixtures and repeat the creation of those mixtures within a 3% accuracy. Modifications to the apparatus included the replacement of solenoid valves with plug valves, the addition of actuators and positioners, the use of a computer digital to analog control card, and minor modifications to the mixing manifold and gas collection system. Two purge procedures were used during the study. Gas mixture analysis was accomplished through the use of gas chromatography.

Statistical analysis of the data was performed on a personal computer equipped with PCSAS (SAS Institute, 1985). ANOVA and Least Square Means Procedures were used to determine significant differences between mean percentages of each gas. The ANOVA procedure gave general indications of how significant several parameters were on the formation of the gas percentages. LSMEANS procedure used the same parameters and interactions to clarify any significant findings found during the ANOVA procedure. The complete statistical program and relevant output can be seen in Appendix D.

MIXTURE ANALYSIS

Three target mixtures were analyzed. The statistical analysis attempted to explain variation in the mean percentages by showing the effects of procedure, mixture, time, interactions between procedure*mix, procedure*time, and procedure*mix*time on each individual gas. The affect of the previous gas mixture upon the new gas mixture was also analyzed. The time variable was added to the analysis in an attempt to observe the effect positioning in the test sequence had upon the creation of each test mixture and whether this positioning affected the mean percentages.

Analysis of variance procedure showed that different combinations of parameters affected the mean percentages of the three gases analyzed. Tables 12, 13, and 14 show the output from the ANOVA procedure for each gas.

Table 12. ANOVA on oxygen gas.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Proceede	1	1.7468027	1.7468027	4.99	0.0384
Mix	2	6.2376222	3.1188111	8.91	0.0020
Proceede*Mix	2	2.1983722	1.0991861	3.14	0.0677
Time	2	16.091126	8.0455631	22.98	0.0001
Proceede*Time	2	2.1041430	1.0520715	3.00	0.0748
Mix*Time	4	5.6042569	1.4010642	4.00	0.0171
Proceede*Mix*Time	4	2.0774819	0.5193704	1.48	0.2487
Error	18	6.3021000	0.3501166		

Table 13. Anova on carbon dioxide gas.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Procede	1	6.61280625	6.16280625	16.57	0.0007
Mix	2	2.99951250	1.49975625	4.03	0.0357
Procede*Mix	2	3.64726250	1.82363125	4.90	0.0200
Time	2	27.3468166	13.6734083	36.76	0.0001
Procede*Time	2	1.18531667	0.59265833	1.59	0.2306
Mix*Time	4	3.25063333	0.81265833	2.18	0.1119
Procede*Mix*Time	4	0.52658333	0.13164583	0.35	0.8379
Error	18	6.69518750	0.37195486		

Table 14. ANOVA on nitrogen gas.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Procede	1	15.1385840	15.13858	34.70	0.0001
Mix	2	14.3126291	7.156314	16.41	0.0001
Procede*Mix	2	1.10648472	0.553242	1.27	0.3053
Time	2	5.43827917	2.719139	6.23	0.0088
Procede*Time	2	5.98315139	2.991575	6.86	0.0061
Mix*Time	4	3.01230417	0.753076	1.73	0.1881
Procede*Mix*Time	4	1.60312361	0.400780	0.92	0.4745
Error	18	7.85181250	0.436211		

ANOVA for oxygen gas indicated that procedure, mix, time, and the interaction between mix and time were significant in affecting percentages for this gas in the mixtures. ANOVA for carbon dioxide indicated that procedure, mix, the interaction between procedure and mix, and time were significant in affecting percentages of this gas. ANOVA for nitrogen gas indicated that procedure, mix, time and interaction between procedure and time were significant in affecting percentages for this gas.

The LSMEANS procedure was used in an attempt to more fully understand how the above parameters affected the percentages of each gas in a mixture. The

LSMEANS procedure further explained the effects of significant parameters identified in the ANOVA. The complete LSMEANS output can be seen in Appendix D.

The LSMEANS procedure for oxygen showed that all parameters except the procedure*time interaction were significant in affecting this gas percentages in a mixture. Oxygen percentages were significantly different in procedure A (vacuum purge) than in procedure B (extra-flow purge). Gas percentages of oxygen in mixture A, B, and C were significantly different than each other. This indicates that the test was successful in producing three mixtures with significantly different oxygen percentages. The general trend for mix A and B indicates that the percentages of oxygen gas may have been affected more at the beginning of the test runs than as the testing procedure progressed. Oxygen percentages for mix C seemed to remain constant independent of the time at which the mixture was made.

The LSMEANS procedure for carbon dioxide showed that percentages in procedure A and B were significantly different than each other. Analysis showed that procedure B was slightly more effective in producing significantly different percentages of carbon dioxide. Time parameter indicated the same trend that was seen in the effect of time on oxygen. That is, mixtures at time one were significantly different than at time two or three. The interaction between mix and time on the percentages of carbon dioxide did not show any general trends other than mixtures produced at time one were indeed different than those produced at time two or three. Again, this corresponds to what was found in the time parameter and the procedure/mixture interaction.

The LSMEANS procedure for nitrogen gas showed that gas percentages in procedure A were significantly different than for procedure B. Analysis showed that percentages of nitrogen in mixture A and B were not significantly different. This was expected since the percentages of nitrogen in target mixtures A and B were 69.66 and 69.7 respectively. Analysis also showed that nitrogen percentages were significantly different between mixture C and mixtures A and B. This too was expected since target mixture C contained 84.88 nitrogen.

Generally, although all mixtures showed procedure A was significantly different from procedure B, it was difficult to statistically show that one purging procedure significantly produced more accurate target mixtures. The extra-flow purge method was slightly more accurate in producing carbon dioxide percentages. The time or placement in which a mixture was made in the testing procedure did affect the percentages of each gas. The percentages of each gas produced at time one seemed to follow the trend of being different than the percentages produced at time two or three. The percentages of each gas produced at times two and three tended not to be significantly different from one another. Generally, the target mixtures were significantly different from each other regardless of procedure.

The analysis of the effect a previous mixture had on the creation of a new mixture showed that previous mixtures significantly affected the formation of new mixtures. The statistical data set for this interaction was difficult to utilize in finding general trends. Based upon what was discovered through the ANOVA and LSMEANS procedure, it can be said that mixtures produced at the beginning of a test

run were significantly different than those produce at any other time during the testing procedure.

CHAPTER V

SUMMARY AND CONCLUSION

SUMMARY

The primary objectives of this study were: To modify an existing apparatus by replacing solenoid valves with pneumatically actuated, electro-pneumatically positioned plug valves; to design the system such that it could switch among three specified gas mixtures with a 3% accuracy; to develop calibration curves for flow of component gas through the flow valves; and to design computer software that would control the components of the system allowing it to quickly change from one mixture to another. A computer equipped with a six-channel digital to analog output card providing a 4-20 mA control signal to the positioners was also utilized as the primary control unit.

In the new system, three plug valve assemblies were constructed consisting of a plug valve, actuator, and positioner. Rigid copper tubing connected the valve assemblies to a mixing manifold that was directed to a single collection tank. The collection tank was fitted with a 170 kPa relief valve and a septum. Opening and closing of the valves was controlled by a six-channel D/A output card sending a 4-20 mA control signal to the positioners. Decimal values were entered into a computer software program corresponding to control signal needed to produce a specific

mixture. The target mixture was produced by opening the valves simultaneously, allowing flow to continue for 30 seconds, then closing the valves simultaneously. Flow rate was the controlled variable.

A rotameter connected to the manifold system was used to calibrate the plug valves prior to the testing procedure. The connection originally used for the rotameter also served as a point of connection for a vacuum line that was used to purge the collection tank between repetitions and target mixture tests. For comparison, extra-flow purge procedure was also employed.

Ten milli-liter samples of each target mixture were withdrawn using a 10-ml syringe and 5-ml samples were injected into a gas chromatograph for analysis. Two repetitions were included in each test. Two samples were drawn for each repetition.

CONCLUSIONS

The prototype mixing system performed as expected except that control accuracy did not always achieve the objective accuracy of three percent. The results indicate the following:

1. The mixing system achieved a consistent target mixture of 20.19 percent carbon dioxide, 10.16 percent oxygen, and 69.66 percent nitrogen within a 7.5 percent accuracy using the vacuum purge procedure.

2. The system was accurate within 8.5 percent in producing the second target mixture of 15.29 percent carbon dioxide, 15.00 percent oxygen, and 69.70 percent nitrogen using the vacuum purge procedure.
3. The mixing system was accurate within seven percent in producing a third target mixture of 10.03 percent carbon dioxide, 5.09 percent oxygen, and 84.88 percent nitrogen using the vacuum purge procedure.
4. Although the percentages obtained for all three gases were closer to the target mixtures using the vacuum purge method, no significant difference between the vacuum purge and extra-flow method could be statistically proven.
5. The mixing unit was capable of returning to a previous mixture and producing percentages with the same precision after running a different target mixture.
6. The design of the system could be improved by the addition of a feedback control to the computer. This control could take several forms. A gas analysis unit could be placed in the collection tank and provide information to the computer which could adjust the valves accordingly. Use of such equipment would increase cost. Insertion of an electronic flow measuring device might provide similar control at less expense. This may improve the accuracy of the system.

7. It is highly recommended that some type of device be installed to maintain a constant temperature around the CO₂ regulator. Even with the installation of the high-flow modified regulator some fluctuations in pressure regulation were evident during testing. This fluctuation can adversely effect the precise flow of CO₂.

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APPENDICES

APPENDIX A

COMPUTER SOFTWARE PROGRAMS

Computer Software Program Using Decimal Numbers to Control Valve
Size Openings.

```
10  INPUT "ENTER DECIMAL VALUE FOR VALVE #1";V1%
20  INPUT "ENTER DECIMAL VALUE FOR VALVE #2";V2%
30  INPUT "ENTER DECIMAL VALUE FOR VALVE #3";V3%
40  H1% = V1%\256
50  H2% = V2%\256
60  H3% = V3%\256
70  L1% = V1% MOD 256
80  L2% = V2% MOD 256
90  L3% = V3% MOD 256
100 OUT &H2CO,H1%
110 OUT &H2C1,L1%
120 OUT &H2C2,H2%
130 OUT &H2C3,L2%
140 OUT &H2C4,H3%
150 OUT &H2C5,L3%
151 PRINT H1%,L1%
152 PRINT H2%,L2%
153 PRINT H3%,L3%
160 GOTO 10
OK
```

Predicted Percent Gas In Mixture At Corrected Temperatures And 107 kPa

GAS	ENTER MILLIAMPS SIGNAL	MOLES PER MINUTE	PREDICTED PERCENT IN MIXTURE
CO2 GAS	15.9	4.212956	10.03
O2 GAS	13.8	2.137274	5.09
N2 GAS	20	35.65682	84.88
			100

Actual Percentages Calculated From Peak Areas And Based On Volume Fraction

GAS	Enter Peak From Sample	Percent In Mixture From Standard Curve	Volume Fraction	Difference Between Predicted and Actual Percentages
CO2 GAS	27885	11.64	12.28	-2.25
O2 GAS	12463	8.412	8.87	-3.78
N2 GAS	116853	74.76	78.85	6.03
		94.81	100	

Cell Formulas For Spreadsheet.

B1: 'Predicted Percent Gas In Mixture At Corrected Temperatures And 107 kPa

D3: [W11]^-

E3: [W1]^-

F3: [W6]^-

G3: ^-

H3: [W1]^-

I3: ^-

J3: [W1]^-

K3: [W18]^-

E4: [W1] ^'

F4: [W6] 'ENTER

H4: [W1] ^'

I4: 'MOLES

J4: [W1] ^'

K4: [W18] 'PERCENT

D5: [W11] 'GAS

E5: [W1] ^'

F5: [W6] 'MILLIAMP

H5: [W1] ^'

I5: 'PER

J5: [W1] ^'

K5: [W18] 'IN

E6: [W1] ^'

F6: [W6] 'SIGNAL

H6: [W1] ^'

I6: 'MINUTE

J6: [W1] ^'

K6: [W18] 'MIXTURE

C7: [W1] ^'

D7: [W11]^-

E7: [W1]^-

F7: [W6]^-

G7: ^-

H7: [W1]^-

I7: ^-

J7: [W1]^-

K7: [W18]^-

L7: [W1] ^'

C8: [W1] ^'

D8: [W11] 'CO2 GAS
 E8: [W1] 'I
 F8: [W6] 15.9
 H8: [W1] 'I
 I8: $-142.08211 + 5.7022228 * F8 + 5.1363241E-09 * \text{EXP}(F8) + 883.85596 / (F8)$
 J8: [W1] 'I
 K8: $(F2) [W18] (+I8 / (I9 + I8 + I10)) * 100$
 L8: [W1] 'I
 C9: [W1] 'I
 D9: [W11] 'O2 GAS
 E9: [W1] 'I
 F9: [W6] 13.8
 H9: [W1] 'I
 I9: $33.701022 + 1.6100739E-08 * \text{EXP}(F9) + 2379.6039 * \text{LN}(F9) / (F9^2) + 1197684.4 * \text{EXP}(-F9)$
 J9: [W1] 'I
 K9: $(F2) [W18] (+I9 / (I9 + I8 + I10)) * 100$
 L9: [W1] 'I
 C10: [W1] 'I
 D10: [W11] 'N2 GAS
 E10: [W1] 'I
 F10: [W6] 20
 H10: [W1] 'I
 I10: $-3100.4079 + 532.02308 * F10 + 4.9408053 * (F10^2) + 0.059548355 * (F10^3) + 1838.869 * F10 / \text{LN}(F10)$
 J10: [W1] 'I
 K10: $(F2) [W18] (I10 / (I9 + I8 + I10)) * 100$
 L10: [W1] 'I
 C11: [W1] 'I
 D11: [W11] '✓
 E11: [W1] '✓
 F11: [W6] '✓
 G11: '✓
 H11: [W1] '✓
 I11: '✓
 J11: [W1] '✓
 K11: [W18] '✓
 L11: [W1] 'I
 K12: [W18] +K9+K8+K10
 B14: 'Actual Percentages Calculated From Peak Areas And Based On Volume Fraction
 B15: '✓

C15: [W1] ✓
 D15: [W11] ✓
 E15: [W1] ✓
 F15: [W6] ✓
 G15: ✓
 H15: [W1] ✓
 I15: ✓
 J15: [W1] ✓
 K15: [W18] ✓
 L15: [W1] ✓
 C16: [W1] 'I'
 D16: [W11] 'Enter
 E16: [W1] 'I'
 F16: [W6] 'Percent In
 H16: [W1] 'I'
 I16: 'Volume
 J16: [W1] 'I'
 K16: [W18] 'Difference Between
 B17: 'GAS
 C17: [W1] 'I'
 D17: [W11] 'Peak From
 E17: [W1] 'I'
 F17: [W6] 'Mixture From
 H17: [W1] 'I'
 I17: 'Fraction
 J17: [W1] 'I'
 K17: [W18] 'Simulated and
 C18: [W1] 'I'
 D18: [W11] 'Sample
 E18: [W1] 'I'
 F18: [W6] 'Standard Curve
 H18: [W1] 'I'
 J18: [W1] 'I'
 K18: [W18] 'Actual Percentages
 B19: ✓
 C19: [W1] ✓
 D19: [W11] ✓
 E19: [W1] ✓
 F19: [W6] ✓

G19: \-
 H19: [W1] \-
 I19: \-
 J19: [W1] \-
 K19: [W18] \-
 L19: [W1] \-
 B20: 'CO2 GAS
 C20: [W1] 'I
 D20: [W11] 27885
 E20: [W1] 'I

$$F20: [W6] 0.18740727 + 0.00058850157 * (D20) + 2.7487517E-08 * (D20^2) + 1.8115178E-10 * (D20^2) * @SQRT(D20) + 3.2749615E-13 * (D20^3)$$

 H20: [W1] 'I

$$I20: (F2) + F20 / F24 * 100$$

 J20: [W1] 'I

$$K20: (F2) [W18] + K8 - I20$$

 B21: 'O2 GAS
 C21: [W1] 'I
 D21: [W11] 12463
 E21: [W1] 'I

$$F21: [W6] 0.040511092 + 0.00040084593 * (D21) + 8.0855335E-08 * (D21^2) + 7.3684981E-10 * (D21^2) * @SQRT(D21) + 1.8563362E-12 * (D21^3)$$

 H21: [W1] 'I

$$I21: (F2) + F21 / F24 * 100$$

 J21: [W1] 'I

$$K21: (F2) [W18] + K9 - I21$$

 B22: 'N2 GAS
 C22: [W1] 'I
 D22: [W11] 116853
 E22: [W1] 'I

$$F22: [W6] 0.0028545595 + 0.00068327492 * (D22) + 3.6725036E-09 * (D22^2) + 2.5467965E-11 * (D22^2) * @SQRT(D22) + 3.9885493E-14 * (D22^3)$$

 H22: [W1] 'I

$$I22: (F2) + F22 / F24 * 100$$

 J22: [W1] 'I

$$K22: (F2) [W18] + K10 - I22$$

 B23: \-
 C23: [W1] \-
 D23: [W11] \-
 E23: [W1] \-
 F23: [W6] \-
 G23: \-

H23: [W1] \-

I23: \-

J23: [W1] \-

K23: [W18] \-

L23: [W1] \-

F24: [W6] +F20+F21+F22

I24: +I20+I21+I22

APPENDIX B

GAS FLOW DATA SETS

Gas Flow Data Set For Standard Cams (Uncorrected for density effect)

Signal mA	Decimal Number	Oxygen				Average SCFM
		Test 1 SCFM	Test 2 SCFM	Test 3 SCFM	Test 4 SCFM	
4	0	0	0	0	0	0.00
6	512	0	0	0	0	0.00
8	1024	0.75	0.75	1	0.75	0.81
10	1536	8.25	7.75	8.25	8.25	8.13
12	2048	15.5	15.5	15.25	15.25	15.38
14	2560	17	17	17	17	17.00
16	3072	17.5	17.5	17.5	17.5	17.50
18	3584	17.5	17.5	17.5	17.5	17.50
20	4095	17.5	17.5	17.5	17.5	17.50

Signal mA	Decimal Number	Carbon Dioxide				Average SCFM
		Test 1 SCFM	Test 2 SCFM	Test 3 SCFM	Test 4 SCFM	
4	0	0	0	0	0	0.00
6	512	0	0	0	0	0.00
8	1024	0	0	0	0	0.00
10	1536	9	8.5	9.5	9	9.00
12	2048	17	17.25	17.25	17.25	17.19
14	2560	18.25	18.25	18.25	18.25	18.25
16	3072	18.25	18.25	18.25	18.25	18.25
18	3584	18.25	18.25	18.25	18.25	18.25
20	4095	18.25	18.25	18.25	18.25	18.25

Signal mA	Decimal Number	Nitrogen				Average SCFM
		Test 1 SCFM	Test 2 SCFM	Test 3 SCFM	Test 4 SCFM	
4	0	0	0	0	0	0.00
6	512	0	0	0	0	0.00
8	1024	3.5	4	3.75	3.75	3.75
10	1536	15	14.75	15	15	14.94
12	2048	18	18	18	18	18.00
14	2560	18.25	18.25	18.25	18.25	18.25
16	3072	18.5	18.5	18.5	18.5	18.50
18	3584	18.5	18.5	18.5	18.5	18.50
20	4095	18.5	18.5	18.5	18.5	18.50

Standard, Square Root and Limiting Cam Nitrogen Gas Flow
Comparison Data Set. (SCFM is not adjusted for density effect)

Signal mA	Decimal Number	SQUARE ROOT CAMS		
		3-9 PSI (SCFM)	3-15 PSI (SCFM)	9-15 PSI (SCFM)
4	0	0	0	0
6	512	0	0	0
8	1024	0	0	0
10	1536	13	0	0
12	2048	22	6	13.5
14	2560	24	21	24
16	3072	24	22	24
18	3584	24	23	24
20	4095	24	24	24

Signal mA	Decimal Number	LIMITING CAMS	
		0-30 DEGREE (SCFM)	0-45 DEGREE (SCFM)
4	0	0	0
6	512	0	0
8	1024	0	0
10	1536	0	1
12	2048	2	4.75
14	2560	5.56	12
16	3072	9.75	16.5
18	3584	13.94	20.5
20	4095	17.5	22

Signal mA	Decimal Number	STANDARD CAM	
		0-90 DEGREES (SCFM)	
4	0	0	
6	512	0	
8	1024	3.75	
10	1536	14.94	
12	2048	18	
14	2560	18.25	
16	3072	18.5	
18	3584	18.5	
20	4095	18.5	

Gas Flow Data Set For 0-30 Degree Limiting Cams

Adjusted SCFM For Density Effect Is Shown In The Last Column

Signal mA	Decimal Number	Test 1 SCFM	Oxygen		Test 3 SCFM	Test 4 SCFM	Average SCFM	Corrected SCFM
			Test 2 SCFM					
4	0	0	0		0	0	0.00	0.0000
6	512	0	0		0	0	0.00	0.0000
8	1024	0	0		0	0	0.00	0.0000
10	1536	0	0		0	0	0.00	0.0000
12	2048	0	0		0	0	0.00	0.0000
14	2560	1.5	1.5		1.25	1.25	1.38	1.3132
16	3072	4.25	4.25		4.25	4.25	4.25	4.0443
18	3584	7	6.5		7	7.5	7.00	6.6611
20	4095	12.5	12		12.5	12	12.25	11.6570

Signal mA	Decimal Number	Test 1 SCFM	Carbon Dioxide		Test 3 SCFM	Test 4 SCFM	Average SCFM	Corrected SCFM
			Test 2 SCFM					
4	0	0	0		0	0	0.00	0.0000
6	512	0	0		0	0	0.00	0.0000
8	1024	0	0		0	0	0.00	0.0000
10	1536	0	0		0	0	0.00	0.0000
12	2048	0	0		0	0	0.00	0.0000
14	2560	0.5	0.5		0.5	0.5	0.50	0.4057
16	3072	2.5	2.5		2.5	2.5	2.50	2.0284
18	3584	5.5	5.5		6	5.5	5.63	4.5681
20	4095	10.5	10.5		10.5	10.5	10.50	8.5195

Signal mA	Decimal Number	Test 1 SCFM	Nitrogen		Test 3 SCFM	Test 4 SCFM	Average SCFM	Corrected SCFM
			Test 2 SCFM					
4	0	0	0		0	0	0.00	0.0000
6	512	0	0		0	0	0.00	0.0000
8	1024	0	0		0	0	0.00	0.0000
10	1536	0	0		0	0	0.00	0.0000
12	2048	2	2		2	2	2.00	2.0340
14	2560	5.5	5.5		5.5	5.75	5.56	5.6546
16	3072	9.75	9.75		9.75	9.75	9.75	9.9159
18	3584	14	13.75		14	14	13.94	14.1772
20	4095	17.5	17.5		17.5	17.5	17.50	17.7978

Corrected Densities for Gases at Corrected Temperatures
and 170 kPa. Conversion From Flow Rate In SCFM to Molar
Flow Rate (Moles/Min) For 0-30 degree Limiting Cams.

Corrections to Density

Gas	R (KJ/KgK)	Temp (K)	P (kPa)	rho (Kg/m3)
Air	0.2870	264.99	170.25	2.239
CO2	0.1889	264.99	170.25	3.401
Air	0.2870	289.54	170.25	2.049
N2	0.2968	289.54	170.25	1.981
Air	0.2870	285.24	170.25	2.080
O2	0.2598	285.24	170.25	2.297

Conversion of SCFM to Moles per Minute

mA Signal	O2 SCFM	Corrected Flow-SCFM	Moles Per Min
10		0	0.0000
12		0	0.0000
14	1.38	1.3132	2.6692
16	4.25	4.0443	8.2205
18	7	6.6611	13.5396
20	12.25	11.6570	23.6943

mA Signal	CO2 SCFM	Corrected Flow-SCFM	Moles Per Min
10		0	0.0000
12		0	0.0000
14	0.5	0.4057	0.8880
16	2.5	2.0284	4.4398
18	5.63	4.5681	9.9984
20	10.5	8.5195	18.6471

mA Signal	N2 SCFM	Corrected Flow-SCFM	Moles Per Min
10		0	0.0000
12	2	2.0340	4.0750
14	5.56	5.6546	11.3286
16	9.75	9.9159	19.8657
18	13.94	14.1772	28.4029
20	17.5	17.7978	35.6564

APPENDIX C
DATA FROM MIXTURE TEST

Results From Vacuum Purge Procedure

		PEAK AREAS		% N SAMPLE				MEAN %	
PROCEDURE A		TEST 1 MIXTURE A		CO2=20.19%, O2=10.16%, N2=69.66%					
REP 1	SAMPLE	1	CO2	53610	O2	17564	N2	23.85	12.7
		2	CO2	52602	O2	18136	N2	22.96	12.88
REP 2	SAMPLE	1	CO2	56263	O2	17114	N2	25.01	12.35
		2	CO2	50778	O2	19727	N2	20.7	13.08
		Total		105626				23.125	12.755
		Total		64.115				64.115	64.115
PROCEDURE A		TEST 2 MIXTURE B		CO2=15.29%, O2=15.00%, N2=69.70%					
REP 1	SAMPLE	1	CO2	43607	O2	23736	N2	19.13	16.91
		2	CO2	42669	O2	24236	N2	18.54	17.06
REP 2	SAMPLE	1	CO2	41288	O2	27736	N2	18.01	19.72
		2	CO2	41316	O2	27554	N2	18.08	19.66
		Total		89946				18.44	18.34
		Total		63.22				63.22	63.22
PROCEDURE A		TEST 3 MIXTURE C		CO2=10.03%, O2=5.09%, N2=84.89%					
REP 1	SAMPLE	1	CO2	30912	O2	11879	N2	13.33	8.52
		2	CO2	28531	O2	13056	N2	11.52	8.83
REP 2	SAMPLE	1	CO2	30058	O2	11707	N2	12.87	8.33
		2	CO2	28037	O2	12952	N2	11.16	8.63
		Total		127191				12.02	8.48
		Total		79.21				79.21	79.21
PROCEDURE A		TEST 4 MIXTURE B		CO2=15.29%, O2=15.00%, N2=69.70%					
REP 1	SAMPLE	1	CO2	37834	O2	23622	N2	15.98	20.53
		2	CO2	37349	O2	30310	N2	15.58	20.78
REP 2	SAMPLE	1	CO2	39960	O2	28450	N2	17.23	20.11
		2	CO2	39201	O2	29013	N2	17	20.59
		Total		90592				16.45	20.50
		Total		63.05				63.05	63.05
PROCEDURE A		TEST 5 MIXTURE A		CO2=20.19%, O2=10.16%, N2=69.66%					
REP 1	SAMPLE	1	CO2	48749	O2	22659	N2	20.69	15.59
		2	CO2	50687	O2	21214	N2	22.28	15.13
REP 2	SAMPLE	1	CO2	49659	O2	22417	N2	21.25	15.56
		2	CO2	47698	O2	23073	N2	20.14	15.8
		Total		97706				20.7	15.68
		Total		63.62				63.62	63.62
PROCEDURE A		TEST 6 MIXTURE C		CO2=10.03%, O2=5.09%, N2=84.89%					
REP 1	SAMPLE	1	CO2	25870	O2	12548	N2	10.72	8.67
		2	CO2	26744	O2	11806	N2	11.6	8.51
REP 2	SAMPLE	1	CO2	25817	O2	11964	N2	10.74	8.24
		2	CO2	26221	O2	11777	N2	11.01	8.22
		Total		121622				11.02	8.41
		Total		80.58				80.58	80.58

		PEAK AREAS			% IN SAMPLE			MEAN %			
PROCEDURE A											
TEST 7	MIXTURE C	CO2=10.03%, O2=5.09%, N2=84.88%									
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2	
	1	26714	12017	112991	11.84	8.87	79.29	12	8.94	79.05	
	2	27276	12141	111554	12.16	9.02	78.81				
REP 2	SAMPLE	CO2	O2	N2							
	1	27885	12463	116853	11.93	8.91	79.16	12.24	8.84	78.92	
	2	28511	11975	112785	12.55	8.78	78.67				
								Total	12.12	8.89	78.99
PROCEDURE A											
TEST 8	MIXTURE B	CO2=15.29%, O2=15.00%, N2=69.70%									
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2	
	1	38527	31023	92960	16.27	21.51	62.22	16.64	21.42	61.94	
	2	39080	29896	89084	17.01	21.33	61.66				
REP 2	SAMPLE	CO2	O2	N2							
	1	38572	30558	92110	16.42	21.35	62.22	16.6	21.27	62.13	
	2	39084	30134	91113	16.77	21.19	62.04				
								Total	16.62	21.345	62.035
PROCEDURE A											
TEST 9	MIXTURE A	CO2=20.19%, O2=10.16%, N2=69.65%									
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2	
	1	51054	22611	93006	22.02	15.76	62.22	21.75	15.78	62.42	
	2	50384	22934	94973	21.48	15.8	62.63				
REP 2	SAMPLE	CO2	O2	N2							
	1	47735	23468	99219	19.92	15.87	64.21	20.72	15.9	63.39	
	2	49920	22842	93543	21.51	15.92	62.57				
								Total	21.235	15.84	62.905

Results From Extra-Flow Purge Procedure

		PEAK AREAS			% IN SAMPLE			MEAN %			
PROCEDURE B											
TEST 1	MIXTURE A	CO2=20.19%, O2=10.16%, N2=69.66%									
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2	
	1	58055	18346	85078	26.38	13.51	60.11	26.47	13.5	60.02	
	2	58431	18312	84790	26.56	13.49	59.94				
REP 2	SAMPLE	CO2	O2	N2							
	1	52743	20566	87305	23.77	15.01	61.22	23.66	14.98	61.36	
	2	51652	20213	86524	23.55	14.95	61.5				
								Total	25.06	14.24	60.69
PROCEDURE B											
TEST 2	MIXTURE B	CO2=15.29%, O2=15.00%, N2=69.70%									
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2	
	1	44441	27979	86732	19.62	20.01	60.37	19.88	19.94	60.18	
	2	45798	26937	83440	20.14	19.88	59.98				
REP 2	SAMPLE	CO2	O2	N2							
	1	44277	25157	86646	19.96	18.43	61.61	19.2	18.56	62.23	
	2	42672	26563	92343	18.45	18.69	62.85				
								Total	19.54	19.25	61.2
PROCEDURE B											
TEST 3	MIXTURE C	CO2=10.03%, O2=5.09%, N2=84.88%									
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2	
	1	29494	12177	108932	13.25	9.12	77.63	12.83	9.12	78.06	
	2	28609	12564	114187	12.41	9.11	78.48				
REP 2	SAMPLE	CO2	O2	N2							
	1	29642	13567	110828	12.99	9.97	77.04	13.27	9.96	76.76	
	2	30339	13296	107921	13.55	9.96	76.49				
								Total	13.05	9.54	77.41

PEAK AREAS					% IN SAMPLE			MEAN 5		
PROCEDURE B										
TEST 4	MIXTURE B	CO2=15.29%, O2=15.00%, N2=69.70%								
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2
	1	36268	27542	86179	17.71	20.34	61.95	17.76	20.37	61.88
	2	36851	27931	86957	17.81	20.4	61.8			
REP 2	SAMPLE	CO2	O2	N2						
	1	40342	28058	88105	17.85	20.27	61.88	17.51	20.4	62.1
	2	39461	28840	90290	17.17	20.52	62.31			
								Total	17.64	20.38 61.99
PROCEDURE B										
TEST 5	MIXTURE A	CO2=20.19%, O2=10.16%, N2=69.65%								
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2
	1	50547	20385	89009	22.89	14.99	62.12	22.36	14.96	62.68
	2	49807	20948	92835	21.84	14.92	63.24			
REP 2	SAMPLE	CO2	O2	N2						
	1	50564	20043	86862	23.12	14.9	61.98	22.71	15.08	62.22
	2	49729	20636	89347	22.3	15.25	62.46			
								Total	22.54	15.02 62.45
PROCEDURE B										
TEST 6	MIXTURE C	CO2=10.03%, O2=5.09%, N2=84.88%								
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2
	1	26983	12984	114083	11.77	9.48	78.76	11.16	9.53	79.32
	2	25628	13884	122794	10.55	9.58	79.87			
REP 2	SAMPLE	CO2	O2	N2						
	1	26250	13649	133581	10.05	8.76	81.19	10.67	9.46	79.88
	2	25880	13868	113834	11.29	10.15	78.56			
								Total	10.92	9.49 79.6
PROCEDURE B										
TEST 7	MIXTURE C	CO2=10.03%, O2=5.09%, N2=84.88%								
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2
	1	26678	14387	115234	11.44	10.37	78.19	11.7	10.32	77.98
	2	27200	13906	111619	11.96	10.27	77.77			
REP 2	SAMPLE	CO2	O2	N2						
	1	27947	13194	107689	12.65	10.01	77.34	11.7	10.21	78.1
	2	25684	14820	119402	10.74	10.41	78.86			
								Total	11.7	10.27 78.04
PROCEDURE B										
TEST 8	MIXTURE B	CO2=15.29%, O2=15.00%, N2=69.70%								
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2
	1	36877	29111	89758	16.18	21	62.82	16.88	20.89	62.57
	2	37693	28180	86785	16.94	20.78	62.28			
REP 2	SAMPLE	CO2	O2	N2						
	1	37447	28434	86804	16.81	20.95	62.24	16.74	20.97	62.29
	2	37227	28553	87160	16.67	20.99	62.34			
								Total	16.81	20.93 62.43
PROCEDURE B										
TEST 9	MIXTURE A	CO2=20.19%, O2=10.16%, N2=69.65%								
REP 1	SAMPLE	CO2	O2	N2	CO2	O2	N2	CO2	O2	N2
	1	51202	20520	87958	23.12	15.03	61.85	23.24	15	61.76
	2	51374	20278	86990	23.36	14.97	61.67			
REP 2	SAMPLE	CO2	O2	N2						
	1	49621	20370	88163	22.52	15.04	62.44	22.69	15.05	62.26
	2	49980	20245	86875	22.86	15.06	62.09			
								Total	22.96	15.02 62.01

APPENDIX D

STATISTICAL PROGRAM, TEST DATA, AND PARTIAL

LISTING OF ANALYSIS

```
OPTIONS PS=79 LS=92;
DATA THESIS;
INPUT TEST PROCEEDE $ MIX $ REP SAMPLE GAS $ PERCENT;
IF MIX='A' THEN DO;
  IF GAS ='CO2' THEN ERROR=PERCENT-20.19;
  ELSE IF GAS= 'O2' THEN ERROR=PERCENT-10.16;
  ELSE ERROR = PERCENT - 69.66;
END;
ELSE IF MIX ='B' THEN DO;
  IF GAS = 'CO2' THEN ERROR=PERCENT -15.29;
  ELSE IF GAS = 'O2' THEN ERROR=PERCENT-15.00;
  ELSE ERROR=PERCENT-69.70;
END;
ELSE IF MIX ='C' THEN DO;
  IF GAS ='CO2' THEN ERROR=PERCENT-10.03;
  ELSE IF GAS = 'O2' THEN ERROR= PERCENT-5.09;
  ELSE ERROR=PERCENT-84.88;
end;
ERROR=ABS(ERROR);
TRANS=ARSIN(SQRT(ERROR/100));
if test in(1,2,3) then time=1;
if test in(4,5,6) then time=2;
if test in(7,8,9) then time=3;
if time=1 then do;
  if mix='A' then do;
    if proceede='A' then prevmix='X';
    else prevmix='A';
  end;
  if mix='B' then prevmix='A';
  if mix='C' then prevmix='B';
end;
if time=2 then do;
  if mix='A' then prevmix='B';
  if mix='B' then prevmix='C';
  if mix='C' then prevmix='A';
end;
if time=3 then do;
  if mix='A' then prevmix='B';
  if mix='B' then prevmix='C';
  if mix='C' then prevmix='C';
end;
CARDS;
```

```

PROC SORT;
BY GAS proceede mix time rep ;
proc means noprint; by gas proceede mix time rep;
  var error ; id prevmix;
  output out=mmm mean= merror ;
run;
/*
data temp; set mmm;
file 'd.d';
  put proceede mix prevmix time rep merror gas;
run;
*/

```

```

PROC glm DATA=mmm;
  BY GAS ;
  CLASS proceede MIX time ;
  MODEL merror = proceede mix time ;
  lsMEANS proceede mix time /s p;
  * output out=rrr r=merror ;
RUN;

```

```

PROC glm DATA=mmm;
  BY GAS ;
  CLASS proceede MIX time prevmix;
  MODEL merror = proceede*mix*prevmix*time;
  LSMEANS proceede*mix*time*prevmix/s p;
  * output out=rrr r=merror ;
RUN;
/*
proc univariate plot normal; by gas;
  var merror;
run;

```

```

data uuu; set rrr;
  if abs(merror) > .8;
run;
proc print;
run;
*/
run;

```

PROCEDURE MIXTURE REP SAMPLE GAS PERCENT

A	A	1	1	CO2	23.85
A	A	1	2	CO2	22.96
A	A	1	1	O2	12.70
A	A	1	2	O2	12.88
A	A	1	1	N2	63.45
A	A	1	2	N2	64.16
A	A	2	1	CO2	25.01
A	A	2	2	CO2	20.70
A	A	2	1	O2	12.35
A	A	2	2	O2	13.08
A	A	2	1	N2	62.64
A	A	2	2	N2	66.22
A	B	1	1	CO2	19.13
A	B	1	2	CO2	18.54
A	B	1	1	O2	16.91
A	B	1	2	O2	17.06
A	B	1	1	N2	63.96
A	B	1	2	N2	64.40
A	B	2	1	CO2	18.01
A	B	2	2	CO2	18.08
A	B	2	1	O2	19.72
A	B	2	2	O2	19.66
A	B	2	1	N2	62.27
A	B	2	2	N2	62.26
A	C	1	1	CO2	13.33
A	C	1	2	CO2	11.52
A	C	1	1	O2	8.52
A	C	1	2	O2	8.83
A	C	1	1	N2	78.15
A	C	1	2	N2	79.64
A	C	2	1	CO2	12.87
A	C	2	2	CO2	11.16
A	C	2	1	O2	8.33
A	C	2	2	O2	8.63
A	C	2	1	N2	78.80
A	C	2	2	N2	80.21
A	B	1	1	CO2	15.98
A	B	1	2	CO2	15.58
A	B	1	1	O2	20.53
A	B	1	2	O2	20.78
A	B	1	1	N2	63.49
A	B	1	2	N2	63.65
A	B	2	1	CO2	17.23

PROCEDURE	MIXTURE	REP	SAMPLE	GAS	PERCENT
A	B	2	2	CO2	17.00
A	B	2	1	O2	20.11
A	B	2	2	O2	20.59
A	B	2	1	N2	62.66
A	B	2	2	N2	62.41
A	A	1	1	CO2	20.69
A	A	1	2	CO2	22.28
A	A	1	1	O2	15.59
A	A	1	2	O2	15.13
A	A	1	1	N2	63.72
A	A	1	2	N2	62.59
A	A	2	1	CO2	21.25
A	A	2	2	CO2	20.14
A	A	2	1	O2	15.56
A	A	2	2	O2	15.80
A	A	2	1	N2	63.19
A	A	2	2	N2	64.06
A	C	1	1	CO2	10.72
A	C	1	2	CO2	11.60
A	C	1	1	O2	8.67
A	C	1	2	O2	8.51
A	C	1	1	N2	80.61
A	C	1	2	N2	79.89
A	C	2	1	CO2	10.74
A	C	2	2	CO2	11.01
A	C	2	1	O2	8.24
A	C	2	2	O2	8.22
A	C	2	1	N2	81.02
A	C	2	2	N2	80.77
A	C	1	1	CO2	11.84
A	C	1	2	CO2	12.16
A	C	1	1	O2	8.87
A	C	1	2	O2	9.02
A	C	1	1	N2	79.29
A	C	1	2	N2	78.81
A	C	2	1	CO2	11.93
A	C	2	2	CO2	12.55
A	C	2	1	O2	8.91
A	C	2	2	O2	8.78
A	C	2	1	N2	79.16
A	C	2	2	N2	78.67
A	B	1	1	CO2	16.27
A	B	1	2	CO2	17.01
A	B	1	1	O2	21.51

PROCEDURE	MIXTURE	REP	SAMPLE	GAS	PERCENT
A	B	1	2	O2	21.33
A	B	1	1	N2	62.22
A	B	1	2	N2	61.66
A	B	2	1	CO2	16.42
A	B	2	2	CO2	16.77
A	B	2	1	O2	21.35
A	B	2	2	O2	21.19
A	B	2	1	N2	62.22
A	B	2	2	N2	62.04
A	A	1	1	CO2	22.02
A	A	1	2	CO2	21.48
A	A	1	1	O2	15.76
A	A	1	2	O2	15.80
A	A	1	1	N2	62.22
A	A	1	2	N2	62.63
A	A	2	1	CO2	19.92
A	A	2	2	CO2	21.51
A	A	2	1	O2	15.87
A	A	2	2	O2	15.92
A	A	2	1	N2	64.21
A	A	2	2	N2	62.57
B	A	1	1	CO2	26.38
B	A	1	2	CO2	26.56
B	A	1	1	O2	13.51
B	A	1	2	O2	13.49
B	A	1	1	N2	60.11
B	A	1	2	N2	59.94
B	A	2	1	CO2	23.77
B	A	2	2	CO2	23.55
B	A	2	1	O2	15.01
B	A	2	2	O2	14.95
B	A	2	1	N2	61.22
B	A	2	2	N2	61.50
B	B	1	1	CO2	19.62
B	B	1	2	CO2	20.14
B	B	1	1	O2	20.01
B	B	1	2	O2	19.88
B	B	1	1	N2	60.37
B	B	1	2	N2	59.98
B	B	2	1	CO2	19.96
B	B	2	2	CO2	18.45
B	B	2	1	O2	18.43
B	B	2	2	O2	18.69
B	B	2	1	N2	61.61

PROCEDURE	MIXTURE	REP	SAMPLE	GAS	PERCENT
B	B	2	2	N2	62.85
B	C	1	1	CO2	13.25
B	C	1	2	CO2	12.41
B	C	1	1	O2	9.12
B	C	1	2	O2	9.11
B	C	1	1	N2	77.63
B	C	1	2	N2	78.48
B	C	2	1	CO2	12.99
B	C	2	2	CO2	13.55
B	C	2	1	O2	9.97
B	C	2	2	O2	9.96
B	C	2	1	N2	77.04
B	C	2	2	N2	76.49
B	B	1	1	CO2	17.17
B	B	1	2	CO2	17.81
B	B	1	1	O2	20.34
B	B	1	2	O2	20.40
B	B	1	1	N2	61.95
B	B	1	2	N2	61.8
B	B	2	1	CO2	17.85
B	B	2	2	CO2	17.17
B	B	2	1	O2	20.27
B	B	2	2	O2	20.52
B	B	2	1	N2	61.88
B	B	2	2	N2	62.31
B	A	1	1	CO2	22.89
B	A	1	2	CO2	21.84
B	A	1	1	O2	14.99
B	A	1	2	O2	14.92
B	A	1	1	N2	62.12
B	A	1	2	N2	63.24
B	A	2	1	CO2	23.12
B	A	2	2	CO2	22.30
B	A	2	1	O2	14.90
B	A	2	2	O2	15.25
B	A	2	1	N2	61.98
B	A	2	2	N2	62.46
B	C	1	1	CO2	11.77
B	C	1	2	CO2	10.55
B	C	1	1	O2	9.48
B	C	1	2	O2	9.58
B	C	1	1	N2	78.76
B	C	1	2	N2	79.87
B	C	2	1	CO2	10.05

PROCEDURE	MIXTURE	REP	SAMPLE	GAS	PERCENT
B	C	2	2	CO2	11.29
B	C	2	1	O2	8.76
B	C	2	2	O2	10.15
B	C	2	1	N2	81.19
B	C	2	2	N2	78.56
B	C	1	1	CO2	11.44
B	C	1	2	CO2	11.96
B	C	1	1	O2	10.37
B	C	1	2	O2	10.27
B	C	1	1	N2	78.19
B	C	1	2	N2	77.77
B	C	2	1	CO2	12.65
B	C	2	2	CO2	10.74
B	C	2	1	O2	10.01
B	C	2	2	O2	10.41
B	C	2	1	N2	77.34
B	C	2	2	N2	78.86
B	B	1	1	CO2	16.18
B	B	1	2	CO2	16.94
B	B	1	1	O2	21.00
B	B	1	2	O2	20.78
B	B	1	1	N2	62.82
B	B	2	2	N2	62.28
B	B	2	1	CO2	16.81
B	B	2	2	CO2	16.67
B	B	2	1	O2	20.95
B	B	2	2	O2	20.99
B	B	2	1	N2	62.24
B	B	2	2	N2	62.34
B	A	1	1	CO2	23.12
B	A	1	2	CO2	23.36
B	A	1	1	O2	15.03
B	A	1	2	O2	14.97
B	A	1	1	N2	61.85
B	A	1	2	N2	61.67
B	A	2	1	CO2	22.52
B	A	2	2	CO2	22.86
B	A	2	1	O2	15.04
B	A	2	2	O2	15.06
B	A	2	1	N2	62.44
B	A	2	2	N2	62.09

----- GAS=CO2 -----

General Linear Models Procedure
Class Level Information

Class	Levels	Values
PROCEEDE	2	A B
MIX	3	A B C
TIME	3	1 2 3

Number of observations in by group = 36

----- GAS=CO2 -----

General Linear Models Procedure

Dependent Variable: MERROR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	45.11893125	2.65405478	7.14	0.0001
Error	18	6.69518750	0.37195486		
Corrected Total	35	51.81411875			

R-Square	C.V.	Root MSE	MERROR Mean
0.870784	27.90685	0.60988102	2.18541667

Source	DF	Type I SS	Mean Square	F Value	Pr > F
PROCEEDE	1	6.16280625	6.16280625	16.57	0.0007
MIX	2	2.99951250	1.49975625	4.03	0.0357
PROCEEDE*MIX	2	3.64726250	1.82363125	4.90	0.0200
TIME	2	27.34681667	13.67340833	36.76	0.0001
PROCEEDE*TIME	2	1.18531667	0.59265833	1.59	0.2306
MIX*TIME	4	3.25063333	0.81265833	2.18	0.1119
PROCEEDE*MIX*TIME	4	0.52658333	0.13164583	0.35	0.8379

Source	DF	Type III SS	Mean Square	F Value	Pr > F
PROCEEDE	1	6.16280625	6.16280625	16.57	0.0007
MIX	2	2.99951250	1.49975625	4.03	0.0357
PROCEEDE*MIX	2	3.64726250	1.82363125	4.90	0.0200
TIME	2	27.34681667	13.67340833	36.76	0.0001
PROCEEDE*TIME	2	1.18531667	0.59265833	1.59	0.2306
MIX*TIME	4	3.25063333	0.81265833	2.18	0.1119
PROCEEDE*MIX*TIME	4	0.52658333	0.13164583	0.35	0.8379

----- GAS=CO2 -----

General Linear Models Procedure
Least Squares Means

PROCEDE	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	Pr > T H0: LSMEAN1=LSMEAN2
A	1.77166667	0.14375034	0.0001	0.0007
B	2.59916667	0.14375034	0.0001	

MIX	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	Pr > T 1/j	H0: LSMEAN(i)=LSMEAN(j) 1 2 3
A	2.50666667	0.17605749	0.0001	1 .	0.3035 0.0115
B	2.24291667	0.17605749	0.0001	2 0.3035	. 0.0968
C	1.80666667	0.17605749	0.0001	3 0.0115	0.0968 .

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

PROCEDE	MIX	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	LSMEAN Number
A	A	1.68083333	0.24898288	0.0001	1
A	B	1.87833333	0.24898288	0.0001	2
A	C	1.75583333	0.24898288	0.0001	3
B	A	3.33250000	0.24898288	0.0001	4
B	B	2.60750000	0.24898288	0.0001	5
B	C	1.85750000	0.24898288	0.0001	6

Pr > |T| H0: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.5818	0.8337	0.0002	0.0169	0.6219
2	0.5818	.	0.7320	0.0006	0.0530	0.9535
3	0.8337	0.7320	.	0.0003	0.0264	0.7761
4	0.0002	0.0006	0.0003	.	0.0543	0.0006
5	0.0169	0.0530	0.0264	0.0543	.	0.0472
6	0.6219	0.9535	0.7761	0.0006	0.0472	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

TIME	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	Pr > T 1/j	H0: LSMEAN(i)=LSMEAN(j) 1 2 3
1	3.40458333	0.17605749	0.0001	1 .	0.0001 0.0001
2	1.41875000	0.17605749	0.0001	2 0.0001	. 0.2231
3	1.73291667	0.17605749	0.0001	3 0.0001	0.2231 .

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

----- GAS=CO2 -----

General Linear Models Procedure
Least Squares Means

MIX	TIME	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	LSMEAN Number
A	1	3.90750000	0.30494051	0.0001	1
A	2	1.63625000	0.30494051	0.0001	2
A	3	1.97625000	0.30494051	0.0001	3
B	1	3.70125000	0.30494051	0.0001	4
B	2	1.68375000	0.30494051	0.0001	5
B	3	1.34375000	0.30494051	0.0003	6
C	1	2.60500000	0.30494051	0.0001	7
C	2	0.93625000	0.30494051	0.0066	8
C	3	1.87875000	0.30494051	0.0001	9

Pr > |T| H0: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6	7	8	9
1	.	0.0001	0.0003	0.6382	0.0001	0.0001	0.0074	0.0001	0.0002
2	0.0001	.	0.4407	0.0001	0.9135	0.5062	0.0375	0.1219	0.5808
3	0.0003	0.4407	.	0.0008	0.5062	0.1597	0.1621	0.0268	0.8237
4	0.6382	0.0001	0.0008	.	0.0002	0.0001	0.0204	0.0001	0.0005
5	0.0001	0.9135	0.5062	0.0002	.	0.4407	0.0466	0.1001	0.6565
6	0.0001	0.5062	0.1597	0.0001	0.4407	.	0.0091	0.3572	0.2307
7	0.0074	0.0375	0.1621	0.0204	0.0466	0.0091	.	0.0011	0.1094
8	0.0001	0.1219	0.0268	0.0001	0.1001	0.3572	0.0011	.	0.0423
9	0.0002	0.5808	0.8237	0.0005	0.6565	0.2307	0.1094	0.0423	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

----- GAS=N2 -----

General Linear Models Procedure
Class Level Information

Class	Levels	Values
PROCEEDE	2	A B
MIX	3	A B C
TIME	3	1 2 3

Number of observations in by group = 36

----- GAS=N2 -----

General Linear Models Procedure

Dependent Variable: MERROR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	46.59455625	2.74085625	6.28	0.0002
Error	18	7.85181250	0.43621181		
Corrected Total	35	54.44636875			
	R-Square	C.V.	Root MSE	MERROR Mean	
	0.855788	9.732375	0.66046333	6.78625000	

Source	DF	Type I SS	Mean Square	F Value	Pr > F
PROCEEDE	1	15.13858403	15.13858403	34.70	0.0001
MIX	2	14.31262917	7.15631458	16.41	0.0001
PROCEEDE*MIX	2	1.10648472	0.55324236	1.27	0.3053
TIME	2	5.43827917	2.71913958	6.23	0.0088
PROCEEDE*TIME	2	5.98315139	2.99157569	6.86	0.0061
MIX*TIME	4	3.01230417	0.75307604	1.73	0.1881
PROCEEDE*MIX*TIME	4	1.60312361	0.40078090	0.92	0.4745

Source	DF	Type III SS	Mean Square	F Value	Pr > F
PROCEEDE	1	15.13858403	15.13858403	34.70	0.0001
MIX	2	14.31262917	7.15631458	16.41	0.0001
PROCEEDE*MIX	2	1.10648472	0.55324236	1.27	0.3053
TIME	2	5.43827917	2.71913958	6.23	0.0088
PROCEEDE*TIME	2	5.98315139	2.99157569	6.86	0.0061
MIX*TIME	4	3.01230417	0.75307604	1.73	0.1881
PROCEEDE*MIX*TIME	4	1.60312361	0.40078090	0.92	0.4745

----- GAS=N2 -----

General Linear Models Procedure
Least Squares Means

PROCEEDE	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	Pr > T H0: LSMEAN1=LSMEAN2
A	6.13777778	0.15567270	0.0001	0.0001
B	7.43472222	0.15567270	0.0001	

MIX	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	Pr > T i/j	H0: LSMEAN(i)=LSMEAN(j)	1	2	3
A	7.06500000	0.19065934	0.0001	1 .	0.2573	0.0005		
B	7.38041667	0.19065934	0.0001	2 0.2573	.	0.0001		
C	5.91333333	0.19065934	0.0001	3 0.0005	0.0001	.		

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

TIME	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	Pr > T i/j	H0: LSMEAN(i)=LSMEAN(j)	1	2	3
1	7.10583333	0.19065934	0.0001	1 .	0.0048	0.7367		
2	6.23916667	0.19065934	0.0001	2 0.0048	.	0.0101		
3	7.01375000	0.19065934	0.0001	3 0.7367	0.0101	.		

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

PROCEEDE	TIME	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	LSMEAN Number
A	1	5.90000000	0.26963302	0.0001	1
A	2	5.74166667	0.26963302	0.0001	2
A	3	6.77166667	0.26963302	0.0001	3
B	1	8.31166667	0.26963302	0.0001	4
B	2	6.73666667	0.26963302	0.0001	5
B	3	7.25583333	0.26963302	0.0001	6

Pr > |T| H0: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.6829	0.0346	0.0001	0.0416	0.0023
2	0.6829	.	0.0146	0.0001	0.0177	0.0009
3	0.0346	0.0146	.	0.0008	0.9279	0.2204
4	0.0001	0.0001	0.0008	.	0.0006	0.0127
5	0.0416	0.0177	0.9279	0.0006	.	0.1902
6	0.0023	0.0009	0.2204	0.0127	0.1902	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

----- GAS=02 -----

General Linear Models Procedure
Class Level Information

Class	Levels	Values
PROCEEDE	2	A B
MIX	3	A B C
TIME	3	1 2 3

Number of observations in by group = 36

----- GAS=O2 -----

General Linear Models Procedure

Dependent Variable: MERROR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	36.05980556	2.12116503	6.06	0.0002
Error	18	6.30210000	0.35011667		
Corrected Total	35	42.36190556			

R-Square	C.V.	Root MSE	MERROR Mean
0.851232	12.86008	0.59170657	4.60111111

Source	DF	Type I SS	Mean Square	F Value	Pr > F
PROCEEDE	1	1.74680278	1.74680278	4.99	0.0384
MIX	2	6.23762222	3.11881111	8.91	0.0020
PROCEEDE*MIX	2	2.19837222	1.09918611	3.14	0.0677
TIME	2	16.09112639	8.04556319	22.98	0.0001
PROCEEDE*TIME	2	2.10414306	1.05207153	3.00	0.0748
MIX*TIME	4	5.60425694	1.40106424	4.00	0.0171
PROCEEDE*MIX*TIME	4	2.07748194	0.51937049	1.48	0.2487

Source	DF	Type III SS	Mean Square	F Value	Pr > F
PROCEEDE	1	1.74680278	1.74680278	4.99	0.0384
MIX	2	6.23762222	3.11881111	8.91	0.0020
PROCEEDE*MIX	2	2.19837222	1.09918611	3.14	0.0677
TIME	2	16.09112639	8.04556319	22.98	0.0001
PROCEEDE*TIME	2	2.10414306	1.05207153	3.00	0.0748
MIX*TIME	4	5.60425694	1.40106424	4.00	0.0171
PROCEEDE*MIX*TIME	4	2.07748194	0.51937049	1.48	0.2487

----- GAS=02 -----

General Linear Models Procedure
Least Squares Means

PROCEEDE	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	Pr > T H0: LSMEAN1=LSMEAN2
A	4.38083333	0.13946658	0.0001	0.0384
B	4.82138889	0.13946658	0.0001	

MIX	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	Pr > T i/j	H0: LSMEAN(i)=LSMEAN(j) 1 2 3
A	4.57166667	0.17081097	0.0001	1 .	0.0343 0.0702
B	5.12500000	0.17081097	0.0001	2 0.0343 .	0.0005
C	4.10666667	0.17081097	0.0001	3 0.0702 0.0005	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

TIME	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	Pr > T i/j	H0: LSMEAN(i)=LSMEAN(j) 1 2 3
1	3.70000000	0.17081097	0.0001	1 .	0.0002 0.0001
2	4.80375000	0.17081097	0.0001	2 0.0002 .	0.0549
3	5.29958333	0.17081097	0.0001	3 0.0001 0.0549	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

MIX	TIME	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	LSMEAN Number
A	1	3.33625000	0.29585329	0.0001	1
A	2	5.10750000	0.29585329	0.0001	2
A	3	5.27125000	0.29585329	0.0001	3
B	1	3.79500000	0.29585329	0.0001	4
B	2	5.44250000	0.29585329	0.0001	5
B	3	6.13750000	0.29585329	0.0001	6
C	1	3.96875000	0.29585329	0.0001	7
C	2	3.86125000	0.29585329	0.0001	8
C	3	4.49000000	0.29585329	0.0001	9

Pr > |T| H0: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6	7	8	9
1	.	0.0005	0.0002	0.2873	0.0001	0.0001	0.1480	0.2256	0.0130
2	0.0005	.	0.7001	0.0057	0.4338	0.0241	0.0140	0.0081	0.1573
3	0.0002	0.7001	.	0.0024	0.6872	0.0531	0.0060	0.0034	0.0782
4	0.2873	0.0057	0.0024	.	0.0010	0.0001	0.6829	0.8760	0.1140
5	0.0001	0.4338	0.6872	0.0010	.	0.1140	0.0024	0.0014	0.0353
6	0.0001	0.0241	0.0531	0.0001	0.1140	.	0.0001	0.0001	0.0010
7	0.1480	0.0140	0.0060	0.6829	0.0024	0.0001	.	0.8001	0.2288
8	0.2256	0.0081	0.0034	0.8760	0.0014	0.0001	0.8001	.	0.1502
9	0.0130	0.1573	0.0782	0.1140	0.0353	0.0010	0.2288	0.1502	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

----- GAS=CO2 -----

General Linear Models Procedure
Class Level Information

Class	Levels	Values
PROCEEDE	2	A B
MIX	3	A B C
TIME	3	1 2 3
PREVMIX	4	A B C X

Number of observations in by group = 36

----- GAS=CO2 -----

General Linear Models Procedure

Dependent Variable: MERROR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	45.11893125	2.65405478	7.14	0.0001
Error	18	6.69518750	0.37195486		
Corrected Total	35	51.81411875			

R-Square	C.V.	Root MSE	MERROR Mean
0.870784	27.90685	0.60988102	2.18541667

Source	DF	Type I SS	Mean Square	F Value	Pr > F
PROCE*MIX*TIME*PREVM	17	45.11893125	2.65405478	7.14	0.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
PROCE*MIX*TIME*PREVM	17	45.11893125	2.65405478	7.14	0.0001

----- GAS=CO2 -----

General Linear Models Procedure
Least Squares Means

PROCEDE	MIX	TIME	PREVMIX	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	LSMEAN Number
A	A	1	X	2.94000000	0.43125101	0.0001	1
A	A	2	B	0.92500000	0.43125101	0.0459	2
A	A	3	B	1.17750000	0.43125101	0.0137	3
A	B	1	A	3.15000000	0.43125101	0.0001	4
A	B	2	C	1.15750000	0.43125101	0.0152	5
A	B	3	C	1.32750000	0.43125101	0.0065	6
A	C	1	B	2.19000000	0.43125101	0.0001	7
A	C	2	A	0.98750000	0.43125101	0.0343	8
A	C	3	C	2.09000000	0.43125101	0.0001	9
B	A	1	A	4.87500000	0.43125101	0.0001	10
B	A	2	B	2.34750000	0.43125101	0.0001	11
B	A	3	B	2.77500000	0.43125101	0.0001	12
B	B	1	A	4.25250000	0.43125101	0.0001	13
B	B	2	C	2.21000000	0.43125101	0.0001	14
B	B	3	C	1.36000000	0.43125101	0.0055	15
B	C	1	B	3.02000000	0.43125101	0.0001	16
B	C	2	A	0.88500000	0.43125101	0.0550	17
B	C	3	C	1.66750000	0.43125101	0.0011	18

Pr > |T| H0: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6	7	8	9	10	11
1	.	0.0039	0.0098	0.7346	0.0091	0.0165	0.2346	0.0049	0.1804	0.0053	0.3442
2	0.0039	.	0.6838	0.0018	0.7075	0.5176	0.0527	0.9195	0.0722	0.0001	0.0315
3	0.0098	0.6838	.	0.0046	0.9742	0.8085	0.1142	0.7590	0.1519	0.0001	0.0711
4	0.7346	0.0018	0.0046	.	0.0043	0.0079	0.1329	0.0023	0.0993	0.0111	0.2047
5	0.0091	0.7075	0.9742	0.0043	.	0.7836	0.1077	0.7836	0.1437	0.0001	0.0668
6	0.0165	0.5176	0.8085	0.0079	0.7836	.	0.1744	0.5841	0.2272	0.0001	0.1117
7	0.2346	0.0527	0.1142	0.1329	0.1077	0.1744	.	0.0642	0.8716	0.0003	0.7991
8	0.0049	0.9195	0.7590	0.0023	0.7836	0.5841	0.0642	.	0.0874	0.0001	0.0387
9	0.1804	0.0722	0.1519	0.0993	0.1437	0.2272	0.8716	0.0874	.	0.0002	0.6779
10	0.0053	0.0001	0.0001	0.0111	0.0001	0.0001	0.0003	0.0001	0.0002	.	0.0006
11	0.3442	0.0315	0.0711	0.2047	0.0668	0.1117	0.7991	0.0387	0.6779	0.0006	.
12	0.7898	0.0071	0.0174	0.5463	0.0162	0.0290	0.3502	0.0089	0.2761	0.0029	0.4923
13	0.0452	0.0001	0.0001	0.0874	0.0001	0.0001	0.0033	0.0001	0.0023	0.3209	0.0059
14	0.2469	0.0494	0.1077	0.1406	0.1015	0.1651	0.9742	0.0603	0.8462	0.0004	0.8242
15	0.0185	0.4848	0.7682	0.0088	0.7437	0.9581	0.1903	0.5490	0.2469	0.0001	0.1228
16	0.8971	0.0030	0.0073	0.8336	0.0068	0.0125	0.1903	0.0037	0.1447	0.0070	0.2847
17	0.0034	0.9484	0.6373	0.0016	0.6603	0.4774	0.0463	0.8684	0.0637	0.0001	0.0275
18	0.0514	0.2392	0.4322	0.0257	0.4140	0.5841	0.4029	0.2795	0.4973	0.0001	0.2795

Pr > |T| H0: LSMEAN(i)=LSMEAN(j)

i/j	12	13	14	15	16	17	18
1	0.7898	0.0452	0.2469	0.0185	0.8971	0.0034	0.0514
2	0.0071	0.0001	0.0494	0.4848	0.0030	0.9484	0.2392
3	0.0174	0.0001	0.1077	0.7682	0.0073	0.6373	0.4322
4	0.5463	0.0874	0.1406	0.0088	0.8336	0.0016	0.0257
5	0.0162	0.0001	0.1015	0.7437	0.0068	0.6603	0.4140
6	0.0290	0.0001	0.1651	0.9581	0.0125	0.4774	0.5841
7	0.3502	0.0033	0.9742	0.1903	0.1903	0.0463	0.4029
8	0.0089	0.0001	0.0603	0.5490	0.0037	0.8684	0.2795
9	0.2761	0.0023	0.8462	0.2469	0.1447	0.0637	0.4973
10	0.0029	0.3209	0.0004	0.0001	0.0070	0.0001	0.0001
11	0.4923	0.0059	0.8242	0.1228	0.2847	0.0275	0.2795
12	.	0.0262	0.3665	0.0323	0.6926	0.0062	0.0861
13	0.0262	.	0.0036	0.0002	0.0584	0.0001	0.0005
14	0.3665	0.0036	.	0.1804	0.2007	0.0434	0.3855
15	0.0323	0.0002	0.1804	.	0.0140	0.4462	0.6202
16	0.6926	0.0584	0.2007	0.0140	.	0.0026	0.0397
17	0.0062	0.0001	0.0434	0.4462	0.0026	.	0.2158
18	0.0861	0.0005	0.3855	0.6202	0.0397	0.2158	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

----- GAS=N2 -----

General Linear Models Procedure
Class Level Information

Class	Levels	Values
PROCEEDE	2	A B
MIX	3	A B C
TIME	3	1 2 3
PREVMIX	4	A B C X

Number of observations in by group = 36

----- GAS=N2 -----

General Linear Models Procedure

Dependent Variable: MERROR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	46.59455625	2.74085625	6.28	0.0002
Error	18	7.85181250	0.43621181		
Corrected Total	35	54.44636875			

R-Square	C.V.	Root MSE	MERROR Mean
0.855788	9.732375	0.66046333	6.78625000

Source	DF	Type I SS	Mean Square	F Value	Pr > F
PROCE*MIX*TIME*PREVM	17	46.59455625	2.74085625	6.28	0.0002
Source	DF	Type III SS	Mean Square	F Value	Pr > F
PROCE*MIX*TIME*PREVM	17	46.59455625	2.74085625	6.28	0.0002

----- GAS=N2 -----

General Linear Models Procedure
Least Squares Means

PROCEEDE	MIX	TIME	PREVMIX	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	LSMEAN Number
A	A	1	X	5.54250000	0.46701810	0.0001	1
A	A	2	B	6.27000000	0.46701810	0.0001	2
A	A	3	B	6.75250000	0.46701810	0.0001	3
A	B	1	A	6.47750000	0.46701810	0.0001	4
A	B	2	C	6.64750000	0.46701810	0.0001	5
A	B	3	C	7.66500000	0.46701810	0.0001	6
A	C	1	B	5.68000000	0.46701810	0.0001	7
A	C	2	A	4.30750000	0.46701810	0.0001	8
A	C	3	C	5.89750000	0.46701810	0.0001	9
B	A	1	A	8.96750000	0.46701810	0.0001	10
B	A	2	B	7.21000000	0.46701810	0.0001	11
B	A	3	B	7.64750000	0.46701810	0.0001	12
B	B	1	A	8.49750000	0.46701810	0.0001	13
B	B	2	C	7.71500000	0.46701810	0.0001	14
B	B	3	C	7.28000000	0.46701810	0.0001	15
B	C	1	B	7.47000000	0.46701810	0.0001	16
B	C	2	A	5.28500000	0.46701810	0.0001	17
B	C	3	C	6.84000000	0.46701810	0.0001	18

Pr > |T| H0: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6	7	8	9	10	11
1	.	0.2852	0.0835	0.1739	0.1116	0.0048	0.8374	0.0779	0.5975	0.0001	0.0212
2	0.2852	.	0.4745	0.7570	0.5747	0.0489	0.3835	0.0082	0.5797	0.0007	0.1718
3	0.0835	0.4745	.	0.6821	0.8755	0.1840	0.1218	0.0016	0.2118	0.0035	0.4973
4	0.1739	0.7570	0.6821	.	0.7998	0.0890	0.2429	0.0041	0.3914	0.0014	0.2820
5	0.1116	0.5747	0.8755	0.7998	.	0.1408	0.1602	0.0023	0.2710	0.0025	0.4056
6	0.0048	0.0489	0.1840	0.0890	0.1408	.	0.0076	0.0001	0.0154	0.0642	0.4997
7	0.8374	0.3835	0.1218	0.2429	0.1602	0.0076	.	0.0523	0.7457	0.0001	0.0325
8	0.0779	0.0082	0.0016	0.0041	0.0023	0.0001	0.0523	.	0.0270	0.0001	0.0003
9	0.5975	0.5797	0.2118	0.3914	0.2710	0.0154	0.7457	0.0270	.	0.0002	0.0623
10	0.0001	0.0007	0.0035	0.0014	0.0025	0.0642	0.0001	0.0001	0.0002	.	0.0159
11	0.0212	0.1718	0.4973	0.2820	0.4056	0.4997	0.0325	0.0003	0.0623	0.0159	.
12	0.0051	0.0515	0.1921	0.0934	0.1474	0.9792	0.0080	0.0001	0.0163	0.0610	0.5161
13	0.0003	0.0034	0.0166	0.0068	0.0118	0.2236	0.0005	0.0001	0.0010	0.4858	0.0670
14	0.0041	0.0421	0.1623	0.0773	0.1234	0.9405	0.0064	0.0001	0.0131	0.0741	0.4544
15	0.0170	0.1436	0.4349	0.2400	0.3509	0.5672	0.0262	0.0003	0.0508	0.0199	0.9168
16	0.0092	0.0859	0.2917	0.1502	0.2290	0.7712	0.0143	0.0001	0.0285	0.0359	0.6985
17	0.7012	0.1532	0.0393	0.0877	0.0538	0.0020	0.5572	0.1562	0.3660	0.0001	0.0092
18	0.0651	0.3995	0.8961	0.5898	0.7740	0.2276	0.0960	0.0012	0.1707	0.0047	0.5822

Pr > |T| H0: LSMEAN(i)=LSMEAN(j)

i/j	12	13	14	15	16	17	18
1	0.0051	0.0003	0.0041	0.0170	0.0092	0.7012	0.0651
2	0.0515	0.0034	0.0421	0.1436	0.0859	0.1532	0.3995
3	0.1921	0.0166	0.1623	0.4349	0.2917	0.0393	0.8961
4	0.0934	0.0068	0.0773	0.2400	0.1502	0.0877	0.5898
5	0.1474	0.0118	0.1234	0.3509	0.2290	0.0538	0.7740
6	0.9792	0.2236	0.9405	0.5672	0.7712	0.0020	0.2276
7	0.0080	0.0005	0.0064	0.0262	0.0143	0.5572	0.0960
8	0.0001	0.0001	0.0001	0.0003	0.0001	0.1562	0.0012
9	0.0163	0.0010	0.0131	0.0508	0.0285	0.3660	0.1707
10	0.0610	0.4858	0.0741	0.0199	0.0359	0.0001	0.0047
11	0.5161	0.0670	0.4544	0.9168	0.6985	0.0092	0.5822
12	.	0.2144	0.9197	0.5848	0.7912	0.0022	0.2372
13	0.2144	.	0.2515	0.0818	0.1372	0.0001	0.0219
14	0.9197	0.2515	.	0.5185	0.7150	0.0017	0.2018
15	0.5848	0.0818	0.5185	.	0.7769	0.0073	0.5137
16	0.7912	0.1372	0.7150	0.7769	.	0.0039	0.3528
17	0.0022	0.0001	0.0017	0.0073	0.0039	.	0.0301
18	0.2372	0.0219	0.2018	0.5137	0.3528	0.0301	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

----- GAS=02 -----

General Linear Models Procedure
Class Level Information

Class	Levels	Values
PROCEEDE	2	A B
MIX	3	A B C
TIME	3	1 2 3
PREVMIX	4	A B C X

Number of observations in by group = 36

----- GAS=O2 -----

General Linear Models Procedure

Dependent Variable: MERROR

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	36.05980556	2.12116503	6.06	0.0002
Error	18	6.30210000	0.35011667		
Corrected Total	35	42.36190556			

R-Square	C.V.	Root MSE	MERROR Mean
0.851232	12.86008	0.59170657	4.60111111

Source	DF	Type I SS	Mean Square	F Value	Pr > F
PROCE*MIX*TIME*PREVM	17	36.05980556	2.12116503	6.06	0.0002

Source	DF	Type III SS	Mean Square	F Value	Pr > F
PROCE*MIX*TIME*PREVM	17	36.05980556	2.12116503	6.06	0.0002

----- GAS=02 -----

General Linear Models Procedure
Least Squares Means

PROCEEDE	MIX	TIME	PREVMIX	MERROR LSMEAN	Std Err LSMEAN	Pr > T H0:LSMEAN=0	LSMEAN Number
A	A	1	X	2.59250000	0.41839973	0.0001	1
A	A	2	B	5.36000000	0.41839973	0.0001	2
A	A	3	B	5.67750000	0.41839973	0.0001	3
A	B	1	A	3.33750000	0.41839973	0.0001	4
A	B	2	C	5.50250000	0.41839973	0.0001	5
A	B	3	C	6.34500000	0.41839973	0.0001	6
A	C	1	B	3.48750000	0.41839973	0.0001	7
A	C	2	A	3.32000000	0.41839973	0.0001	8
A	C	3	C	3.80500000	0.41839973	0.0001	9
B	A	1	A	4.08000000	0.41839973	0.0001	10
B	A	2	B	4.85500000	0.41839973	0.0001	11
B	A	3	B	4.86500000	0.41839973	0.0001	12
B	B	1	A	4.25250000	0.41839973	0.0001	13
B	B	2	C	5.38250000	0.41839973	0.0001	14
B	B	3	C	5.93000000	0.41839973	0.0001	15
B	C	1	B	4.45000000	0.41839973	0.0001	16
B	C	2	A	4.40250000	0.41839973	0.0001	17
B	C	3	C	5.17500000	0.41839973	0.0001	18

Pr > |T| H0: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6	7	8	9	10	11
1	.	0.0002	0.0001	0.2241	0.0001	0.0001	0.1477	0.2347	0.0553	0.0217	0.0012
2	0.0002	.	0.5981	0.0031	0.8124	0.1133	0.0054	0.0029	0.0171	0.0442	0.4046
3	0.0001	0.5981	.	0.0009	0.7708	0.2741	0.0016	0.0009	0.0054	0.0147	0.1815
4	0.2241	0.0031	0.0009	.	0.0018	0.0001	0.8028	0.9767	0.4398	0.2256	0.0195
5	0.0001	0.8124	0.7708	0.0018	.	0.1716	0.0032	0.0017	0.0102	0.0272	0.2883
6	0.0001	0.1133	0.2741	0.0001	0.1716	.	0.0001	0.0001	0.0004	0.0012	0.0215
7	0.1477	0.0054	0.0016	0.8028	0.0032	0.0001	.	0.7803	0.5981	0.3299	0.0329
8	0.2347	0.0029	0.0009	0.9767	0.0017	0.0001	0.7803	.	0.4231	0.2153	0.0183
9	0.0553	0.0171	0.0054	0.4398	0.0102	0.0004	0.5981	0.4231	.	0.6477	0.0929
10	0.0217	0.0442	0.0147	0.2256	0.0272	0.0012	0.3299	0.2153	0.6477	.	0.2067
11	0.0012	0.4046	0.1815	0.0195	0.2883	0.0215	0.0329	0.0183	0.0929	0.2067	.
12	0.0012	0.4138	0.1866	0.0188	0.2955	0.0223	0.0318	0.0177	0.0901	0.2012	0.9867
13	0.0117	0.0776	0.0270	0.1394	0.0489	0.0024	0.2124	0.1324	0.4593	0.7740	0.3221
14	0.0002	0.9701	0.6241	0.0028	0.8416	0.1212	0.0049	0.0026	0.0157	0.0410	0.3844
15	0.0001	0.3482	0.6746	0.0004	0.4793	0.4920	0.0006	0.0003	0.0021	0.0058	0.0859
16	0.0057	0.1415	0.0526	0.0764	0.0922	0.0049	0.1212	0.0722	0.2901	0.5396	0.5024
17	0.0068	0.1230	0.0450	0.0887	0.0795	0.0041	0.1394	0.0839	0.3260	0.5924	0.4543
18	0.0004	0.7581	0.4069	0.0061	0.5867	0.0635	0.0106	0.0057	0.0326	0.0807	0.5953

Pr > |T| H0: LSMEAN(i)=LSMEAN(j)

i/j	12	13	14	15	16	17	18
1	0.0012	0.0117	0.0002	0.0001	0.0057	0.0068	0.0004
2	0.4138	0.0776	0.9701	0.3482	0.1415	0.1230	0.7581
3	0.1866	0.0270	0.6241	0.6746	0.0526	0.0450	0.4069
4	0.0188	0.1394	0.0028	0.0004	0.0764	0.0887	0.0061
5	0.2955	0.0489	0.8416	0.4793	0.0922	0.0795	0.5867
6	0.0223	0.0024	0.1212	0.4920	0.0049	0.0041	0.0635
7	0.0318	0.2124	0.0049	0.0006	0.1212	0.1394	0.0106
8	0.0177	0.1324	0.0026	0.0003	0.0722	0.0839	0.0057
9	0.0901	0.4593	0.0157	0.0021	0.2901	0.3260	0.0326
10	0.2012	0.7740	0.0410	0.0058	0.5396	0.5924	0.0807
11	0.9867	0.3221	0.3844	0.0859	0.5024	0.4543	0.5953
12	.	0.3143	0.3933	0.0887	0.4920	0.4446	0.6067
13	0.3143	.	0.0722	0.0110	0.7424	0.8028	0.1364
14	0.3933	0.0722	.	0.3671	0.1324	0.1150	0.7299
15	0.0887	0.0110	0.3671	.	0.0223	0.0188	0.2182
16	0.4920	0.7424	0.1324	0.0223	.	0.9369	0.2363
17	0.4446	0.8028	0.1150	0.0188	0.9369	.	0.2081
18	0.6067	0.1364	0.7299	0.2182	0.2363	0.2081	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

VITA

Kevin Andrew Alfont was born in Greencastle, Indiana on December 12, 1963. He attended elementary school in Marion, Indiana and was graduated from Bennett High School in May 1982.

In 1982 he entered Saint Meinrad College in Saint Meinrad, Indiana to pursue a Liberal Arts degree in History. In 1985 he moved to the western United States where he worked until the summer of 1988. In 1988 he moved to Tennessee to continue his education. He entered Tennessee Technological University in Cookeville, Tennessee. He received his Bachelor of Science degree from that university in August of 1992. During his undergraduate career he was awarded the Outstanding Agricultural Engineering Technology Senior Award, he was a member of the Agricultural Engineering Technology Club, Block and Bridle Club, Alpha Gamma Sigma Agricultural Fraternity, and University Agricultural Council.

In August 1992 he accepted a research assistantship and entered the Graduate School of The University of Tennessee at Knoxville. While at the University of Tennessee he was a member of the American Society of Agricultural Engineers, the Institute of Food Technologists, the Institute of Industrial Engineers and Gamma Sigma Delta National Honor Society. He completed his Master of Science degree with a major in Agricultural Engineering Technology in August of 1994. He is currently employed as an Environmental Specialist for the Division of Water Pollution Control in the Knoxville office of the Tennessee Department of Environment and Conservation.