GAS CHROMATOGRAPHY FOR COMBUSTION GAS ANALYSIS

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A basic discussion of the principles of gas chromatography and a description of a combustion gas analyzer using this chemical analysis technique are presented. During the past several years the combustion gas analyzer has been used extensively in airbreathing propulsion research projects at the APL Propulsion Research Laboratory to analyze samples from supersonic combustion and fuel-air mixing tests. The techniques used to obtain and analyze samples from the complex flow fields along with examples to illustrate the importance of these measurements to the testing program are discussed.

THE DEVELOPMENT OF GAS CHROMATOGRAPHY into a rapid and accurate method of analysis of gaseous combustion products has become increasingly important to propulsion research. A combustion gas sampling and analysis system based on gas-solid chromatography is a valuable tool in the analysis of flow-field data from fuel-air mixing tests, supersonic combustion tests, and supersonic combustion ramjet (SCRAM) engine tests at the Applied Physics Laboratory Propulsion Research Laboratory (PRL). The system is basically set up to analyze the gaseous combustion products of hydrocarbon or metallized-hydrocarbon fuels that are essentially mixtures of N_2, O_2, Ar, CO_2, CO, and H_2O. However, as will be discussed below, the system can rapidly be modified to analyze other mixtures as well.

Before describing the PRL combustion gas analysis system, a brief discussion of the history and techniques of chromatographic chemical analysis is in order.

A Basic Discussion of Gas Chromatography

The term "chromatography," from the Greek words for color-writing, was first used in 1906 by Michael Twsett, a Russian botanist, to describe the separation of green and yellow bands of plant extract by dissolving the extract in petroleum ether and passing it through a glass column (tube) filled with calcium carbonate adsorbent.[1,2] However, it was not until the 1930's that "adsorption chromatography" started to become widely used. A notable example of this use was the preparative separation of plant carotene, a red crystalline hydrocarbon, $C_{40}H_{56}$, used as pigment, into its components by R. Kuhn, A. Winterstein, and E. Lederer.[3] Work of this type led to the following definition of *chromatography:* A separation of closely related compounds by allowing a solution (*mobile phase*) of them to seep through an adsorbent (*stationary phase*) so that the different compounds become adsorbed in separate colored layers comprising a *chromatogram.*

The process of *adsorption* is: The adhesion, in an extremely thin layer, of the molecules of gases, dissolved substances, or liquids to the surfaces of solid bodies with which they are in contact.

In 1941 a second type of chromatography was developed by A. J. P. Martin and R. L. M. Synge[4] who used one liquid adsorbed on a solid as the stationary phase and another liquid as the mobile phase. This separation process is referred to as

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[1] D. R. Browning, *Chromatography,* McGraw-Hill, London, 1969.
[2] A. F. M. Keulemans, *Gas Chromatography,* 2nd Ed., Reinhold Pub. Corp., New York, 1959.
[3] R. Kuhn, A. Winterstein, and E. Lederer, "The Xanthophylls," *Z. Physiol. Chem.* **197,** 1931, 141–160.
[4] A. J. P. Martin and R. L. M. Synge, "The Separation of Higher Monamino Acids by Counter Current Liquid-Liquid Extraction; The Amino Acid Composition of Wool," *Biochem. J.* (London), **35,** 1941, 91–121.

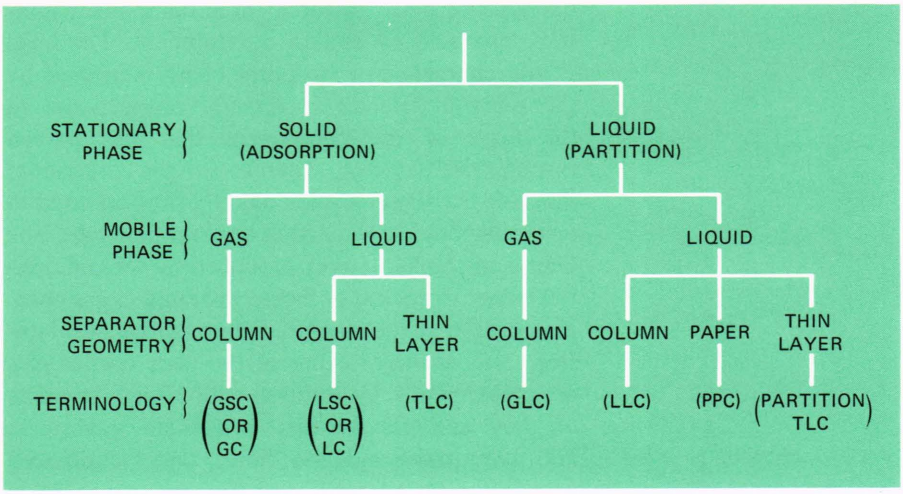

Fig. 1—Classification of chromatographic methods.

partition which is: the separation of solute between two liquid solvents, one stationary and one mobile. This technique became so useful in the fields of biological and medical research that, in 1952, a Nobel Prize was awarded for this work.

In their paper Martin and Synge[4] also envisioned the use of a gas as the mobile phase. However, it was not until the 1950's and later that gas-liquid partition chromatography and gas-solid adsorption chromatography became widely developed. The rapid technological advances in the past twenty-year period, especially in electronics, have led to numerous advances in chromatographic techniques. Mixtures of colorless compounds are readily separated and quantitatively analyzed with the chromatograms being the recorded output charts from electronic detectors instead of the colored layers in the stationary phase. Nevertheless, the original term of "chromatography" for the analysis technique has become fixed. The use of thin layers of adsorbents and sheets of paper instead of packing the stationary phase in a tube (column) has broadened the field and added to the terminology.

An overall classification of the present chromatographic methods is shown in Fig. 1. The first branch in the diagram recognizes the historical division according to stationary phase; solid (adsorption chromatography) or liquid (partition chromatography). Further sub-branching in the classification diagram is according to the state of the mobile phase, gas or liquid and the geometry of the separator. The order of the initials in the terminology of each individual method refers to the mobile phase and stationary phase in that order; or it may refer to geometry in the cases of thin layer chromatography (TLC), paper partition chromatography (PPC), and partition thin layer chromatography (Partition TLC).

There are three different techniques used for chromatographic separation: elution development, frontal analysis, and displacement development (Fig. 2). Of the three, elution development is the most widely used technique, especially for chromatographic chemical analysis, for reasons that will be explained shortly. In elution development, a small amount of sample mixture is introduced into a steady flow of the mobile phase (carrier gas for GSC and GLC, solvent for LSC, etc.). As the mixture is swept through the stationary phase, which has little or no attraction for the mobile phase, the components of the mixture, X and Y, are retained for different times by the stationary phase, depending upon relative adsorptivity or solubility. The difference in attractions, which can be enhanced through proper control of mobile phase flow rate, sample size, column length and temperature, causes the two components to emerge from the column as discrete, but highly diluted, bands of component and solvent. Thus, with a suitable characteristic of difference between component and solvent, say color, thermal conductivity, index of refraction, etc., each component can be detected and quantitatively measured.

The method of frontal analysis is useful when a relatively small concentration of a highly retained component is to be separated from a two-component mixture. The mixture is continuously fed into the column. The purified, more weakly

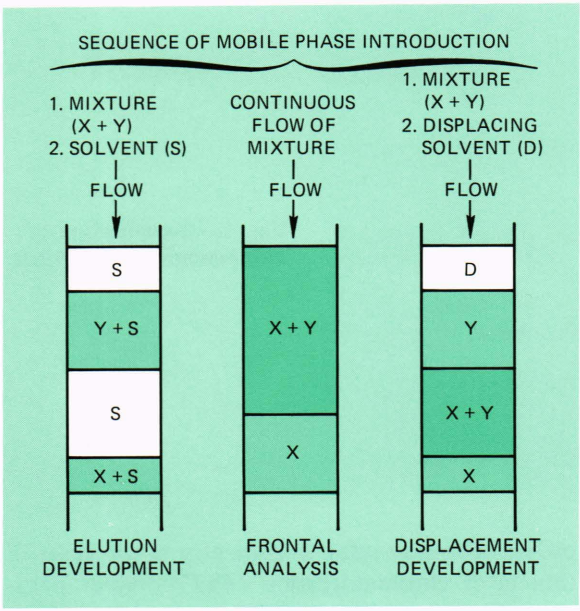

Fig. 2—Chromatographic separation techniques.

attracted compound (X) elutes from the other end of the column until the stationary phase is saturated with the more highly retained compound (Y). From this point on the mixture elutes in the original concentration. Since only the first compound appears as a separate band and large amounts of sample are required for continuous flow, this method is not very useful for analysis.

Displacement development is similar to elution development in that a small amount of sample is injected into the stationary phase. However, the sample is followed by a fluid that is more strongly attracted to the stationary phase than any of the mixture components. As the mixture is displaced by the displacing solvent, the difference in retention of the various components causes them to separate, but not completely. Thus, relatively pure bands of X and Y, which would be useful for chemical preparations, are eluted. However, analysis of the sample is complicated by the existence of the intermediate zone of mixed components between each constituent band.

Since elution development is the most useful separation technique for chromatographic analysis, it is the technique used with the PRL combustion gas analyzer and the following discussions of detection and measurement apply to that technique.

Figure 3 compares the signal output from an integral type of detector with that of a differential type of detector for a three component mixture separated by elution development. The level of the characteristic property being measured by the integral detector is directly proportional to the mass of the component that has passed through the detector, whereas for the differential detector the signal level is direetly proportioned to instantaneous concentration or mass flow rate. The Gaussian-shaped curves produced by the differential detector, typical of those generated in gas chromatography as the measured characteristic deviates from and returns to that of the pure carrier gas, are called peaks. Calibration with known amounts of pure samples permits immediate qualitative and quantitative analysis. Since, under controlled carrier gas temperature and flow rate, each component has a fixed elution time, the time from sample insertion to maximum signal (peak height) identifies the sample. The sample size is determined by comparison of the values of peak height and/or the measured peak area (an integration) with the calibration values.

The first chromatographs used crude but effective forms of integral detection. Color identified the component and the band width indicated quantity. Another classic example of integral-type detection is to record the pH of a solution in which titrated acids and/or bases are collected. Other examples are the measurement of conduc-

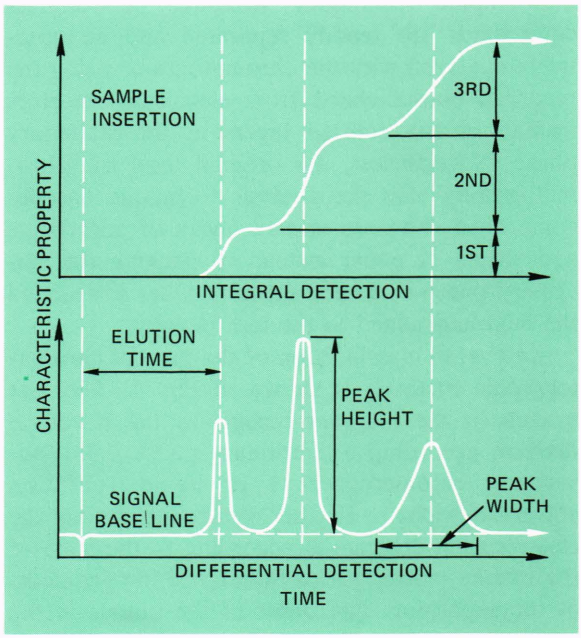

Fig. 3—Methods of detection and measurement.

tivity of collected solutions, measurement of volume or pressure increments in a collection vessel and, of course, the electronic or mechanical integration of the electronic signal from a differential type of detector. The recent rapid advances in analog-to-digital converter, counter, and solid-state amplifier technology have made electronic integration of the signals from differential detectors very accurate and the most widely used method of sample measurement for gas chromatography. The original development of this detection and measurement technique for the PRL combustion gas analysis system has been described.[5] However, the availability of sophisticated commercial integration units, which can be programmed to selectively integrate peaks of interest and ignore baseline drift and instantaneous upsets, now makes it possible to obtain the stability of integrated measurements with the sensitivity of differential detection.

Over the years the most common type of differential detector has been the thermal conductivity cell, schematically shown in Fig. 4. Because it responds to the light, inorganic gases as well as organic gases, it is used in the PRL combustion gas analyzer. With pure carrier gas flowing in both legs, the Wheatstone bridge circuit is balanced. Bridge current and temperature are important parameters and must be carefully controlled. The cell is designed so that heat generated in the resistances is mostly removed by conduction through the carrier gas. As a sample with different thermal conductivity passes through one side of the cell, the resistance of the sample leg circuit changes, causing an out-of-balance potential across the recorder terminals. The output signal is generally nonlinear with respect to large changes in thermal conductivity and is also sensitive to variations in flow rate. However, proper cell design and the dilute mixtures involved in gas chromatography minimize the nonlinearities involved with thermal conductivity measurement. Careful calibration with constant values of current, temperature, and carrier gas flow yields an accurate quantitative analysis.

Another type of differential detector is the flame ionization detector. Because of its high sensitivity and a large range of linearity ($\sim 10^7$),

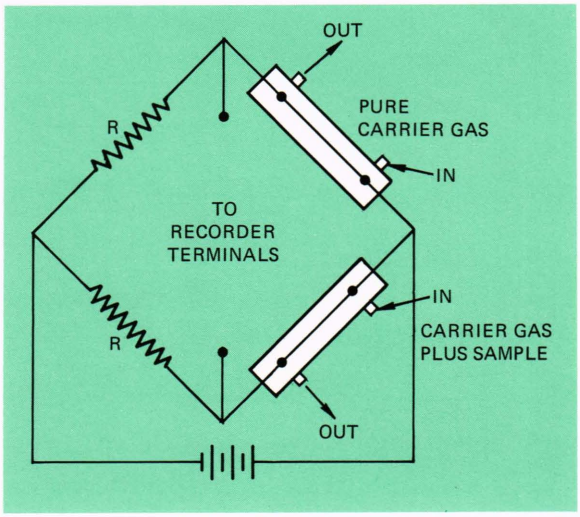

Fig. 4—Schematic of thermal conductivity cell differential detector.

it has recently become the most popular detector for detecting and measuring combustible compounds, i.e., those that will ionize in a hydrogen-air flame. Small amounts of sample are injected into the H_2 burner which is connected as the positive electrode of a DC potential. The negative electrode, which is part of a high impedance amplifier circuit, is placed above the flame. Extreme care to avoid contamination in the flame and the complexity of handling two extra gases in addition to the carrier gas are the price paid for high sensitivity. Since the detector does not respond to CO_2 and H_2O, it is not suitable as a primary detector for the combustion gas analyzer.

Many other differential detectors, such as electron capture detectors, cross-section detectors, argon ionization, and nondispersive infrared detectors, are available for biochemical and other specific analysis situations. The ultrasonic detector, which operates on phase shifts due to differences in sound speed in the samples, is a new device that appears to have potential for wide application.

A schematic illustration of a simple gas chromatograph is shown in Fig. 5. For detector stability and repeatable analyses, a steady flow of carrier gas at typical flow rates of 20 to 100 cc/min is controlled and monitored with the precision gas regulating valve, pressure transducer, and rotameter. For a thermal conductivity cell detector, He, Ar, H_2, or N_2 are generally used as carrier gases depending upon the samples ex-

[5] R. C. Orth and H. B. Land, "A Production Type G. C. Analysis System for Light Gases," *J. Chromatographic Sci.* **9,** June 1971, 359–363.

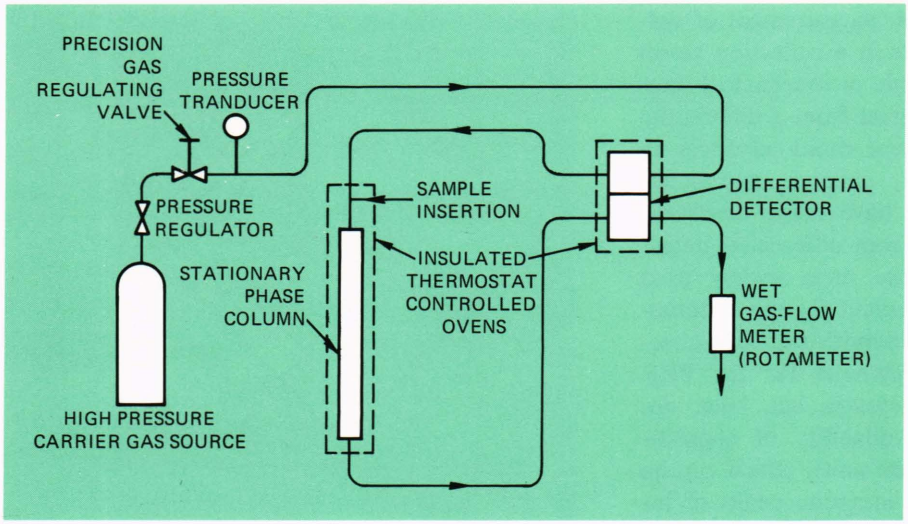

Fig. 5—Schematic of gas-solid chromatograph.

pected to be analyzed. Sample elution and separation are inversely proportional to flow rate. Peak width generally varies inversely with flow rate, the peaks becoming wider with reduced flow. However, column parameters such as length, stationary phase particle size, etc. strongly alter the effect of flow-rate variation on peak width.

The separation column (stationary phase) and the detector are contained in thermostatically-controlled ovens. A thermal conductivity cell is very sensitive to temperature changes, and temperature should be maintained to within $\pm$ 0.05°C for maximum sensitivity. Sample elution time and peak separation vary inversely with column temperature, generally doubling for a 50°C reduction. If components of the sample are in the liquid phase, they must be vaporized for analysis and the entire system downstream of the sample injection point must be heated above the boiling point of the liquid in question.

Gas sample injection into the carrier gas at the head of the column is usually accomplished with a commercially available gas sample valve which physically inserts a small volume (0.2 to 10 cc) into the carrier gas line. Liquid samples may be inserted by using a syringe which pierces a rubber septum on the column inlet.

It is beyond the scope of this paper to give a detailed discussion of separation columns. Basically, since the separation processes of adsorption and partition are surface area phenomena (for partition the stationary phase liquid is held on packed solid particles), columns with small particles nearly all the same size are the most efficient separators. Generally, particles of 60 to 80 or 80 to 100 BS Mesh are used. The list of substances used for chromatographic separation fills a rather large catalog. For separation of combustion gases, columns packed with silica gel, molecular sieves (finely powdered zeolites), and poropak P or Q (commercially synthesized porous-polymer beads [6]) have proven useful.

Commercial columns are commonly available as ⅛-inch O.D. or ¼-inch O.D. tubes in lengths of from 3 ft to 12 ft. If used with small volume detectors, the ⅛-in. O.D. columns have higher separation efficiencies and require less packing material. However, their performance is more susceptible to small amounts of impurities. Separation increases with column length. However, this is accompanied by peak broadening or spreading which reduces detectability somewhat.

PRL Combustion Gas Analysis System

The current configuration of the PRL combustion gas analyzer system is shown in Figs. 6 and 7. For flexibility in analyzing samples from simulated fuel mixing studies with Freons as well as combustion gas samples, the essential parts of the analyzer, (i.e., sample loop, sample pressure transducer, sample valve, separation columns, and a known-sample bottle for calibration checks) are enclosed in a single large temperature-controlled oven to maintain a constant temperature

[6] W. F. Wilhite and O. L. Hollis, "The Use of Porous-Polymer Beads for Analysis of the Martian Atmosphere," *J. Chromatography* **6,** Feb. 1968, 84–88.

A – TEMPERATURE CONTROLLER
B – VACUUM GAUGE
C – VALVE TIMER
D – CHROMATOGRAPH IN OVEN
E – SAMPLE CONDITIONING MANIFOLD
F – CALIBRATION MANIFOLD
G – LOW FLOW ROTAMETERS
H – CRYOGENIC DRYER
J – LOW VAPOR PRESSURE SAMPLE INLET
K – SAMPLE VALVE OPERATOR
L – FLOW CONTROL
M – DETECTOR POWER SUPPLY

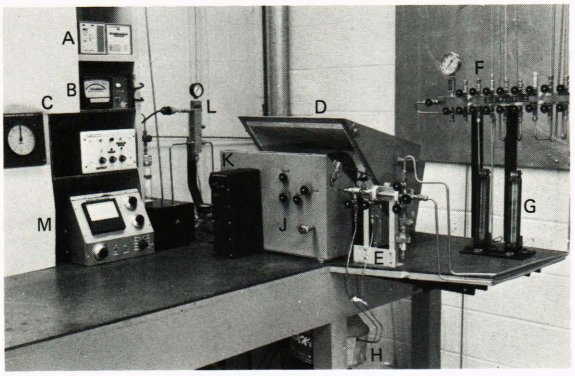

Fig. 6—Combustion gas analyzer.

environment (up to 250°C) during the entire analysis.

Two alternative sample entry points are shown. The one at the lower left of Fig. 7 was used for products of H_2-air combustion. The dryer, filter, and cryogenic dryer (included in the sample conditioning manifold in Fig. 6) are used to remove such combustion products as H_2O, HNO_3 (formed from NO_2 in arc-heated-air tests), and solid combustion products that would contaminate the molecular sieve and silica gel columns. The sample entry point at the right (Fig. 7) illustrates the heated-sample-bottle technique used for low vapor pressure samples.

The sample loop is a calibrated ¼ cc volume. Sample pressure and pressure in the vacuum system are measured by a 0 to 760 Torr pressure transducer and a thermocouple-type vacuum gauge, respectively. Sample pressure can be measured to ± 0.25 Torr and vacuum pressure to ± 10^{-2} Torr. Calibration and analysis are done with respect to sample pressure, at fixed oven temperatures. Thus, direct volumetric sample concentrations can be readily obtained. Furthermore, comparison of a summation of the sample pressures with the measured sample pressure gives an immediate check on analysis accuracy. Typical analysis accuracy is such that the sum of the sample partial pressures agrees with the measured sample pressure to within ± 0.5%.

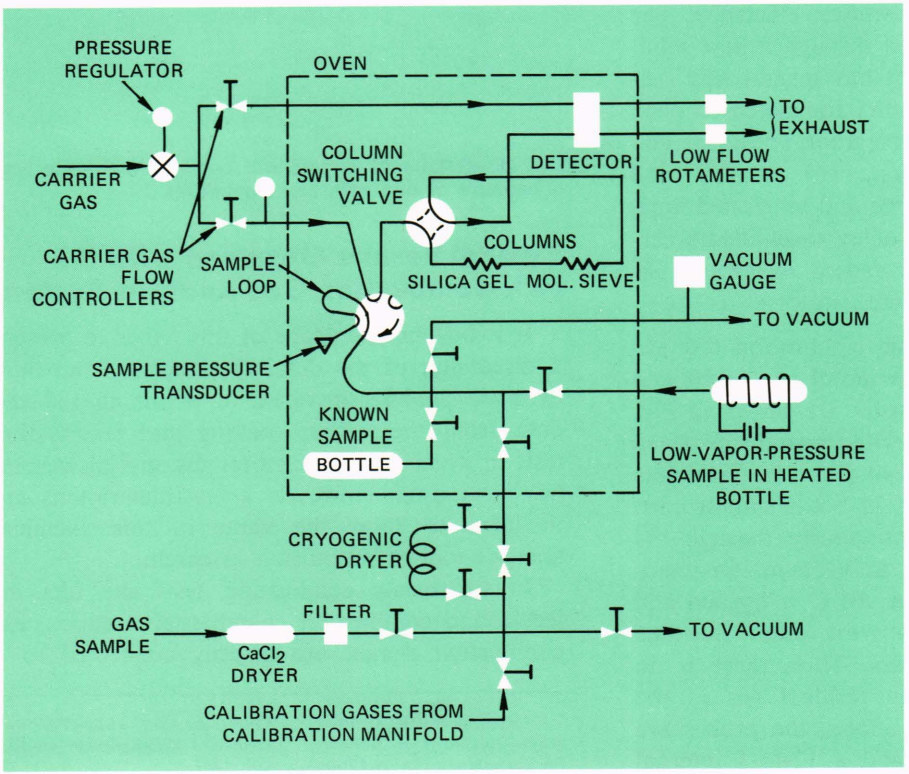

Fig. 7—Schematic of combustion gas analyzer.

Column arrangement can be readily changed to meet various analysis requirements. In the series back-flush arrangement shown in Fig. 7, samples containing H_2, O_2, N_2, CO, CH_4, and CO_2 are analyzed as follows: The sample is introduced into the silica gel column, and all of the foregoing constituents except CO_2 are separated by either the silica gel or molecular sieve (O_2 and N_2 cannot be separated with a silica gel column) and pass through the detector prior to entry of the more slowly eluting CO_2 into the molecular sieve. The position of the column switching valve is then reversed, causing CO_2 to be back-flushed from the silica gel column as a separate peak. This technique permits complete separation of the sample and prevents contamination of the molecular sieve by CO_2. An electronically controlled command function is used for accurate timing of pneumatically operated column-switching and back-flush operations.

Sample component detection is accomplished with a new low-volume thermal conductivity cell detector. The reduction in cell volume has increased sensitivity and reduced detector response time to less than 1 second, as opposed to 4 to 5 seconds with the original detector. Reduction of the tubing size from ¼-inch O.D. to ⅛-inch O.D. has increased column separation efficiency. The detector signal is processed through a new solid-state digital integrator that has several new features: (a) adjustable circuitry for increased peak selectivity that eliminates integration of noise, (b) baseline-drift compensation, (c) display and printout of peak elution time and integrated area, and (d) integration time delay to eliminate certain gross baseline upsets caused by sample insertion, column switching, etc.

Details of the supersonic combustion test gas sample probes and a schematic of one probe and three sample collection bottles are shown in Fig. 8. The gas samples are withdrawn from seven probes in the combustor exit plane into stainless steel bottles mounted on a 21-bottle sample cart. Sample gas is drawn continuously through the sample line and exhausts to vacuum. On command, one of the valves A, B, C is opened and D is closed, thereby diverting the sample into one of the pre-evacuated bottles. Thus, there is no dilution of the sample by residual gas in the lines. To minimize probe effects, the probes are designed with sharp lips and a 12-to-1 internal area expansion. In this way, there is no stand-off shock,[7] and the flow is expanded areodynamically prior to the wall cooling to help effect a rapid quench. The Republic Aviation Corp.[7] built and tested a probe patterned after the APL design. Schlieren photographs showed that the flow was attached, with no stand-off shock.

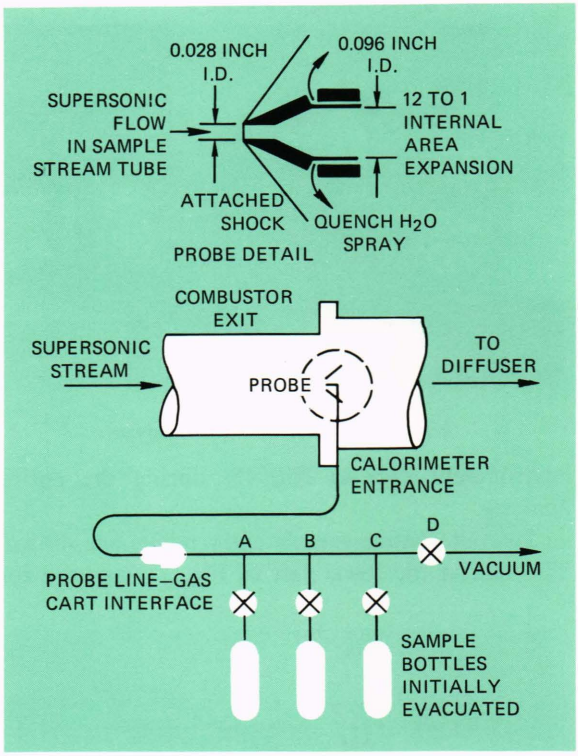

Fig. 8—Details of supersonic combustion probe and schematic of one with sample bottles.

Typical Results Obtained with the PRL Combustion Gas Analysis System

It is beyond the scope of this paper to present a discussion of the detailed chemistry and fluid dynamic analysis involved in obtaining reduced data from the various mixing and combustion tests in which the combustion gas analysis system has been used. However, a few illustrations are included to show the value of this chemical analysis tool in propulsion research.

In supersonic combustion tests the fuel injector and combustion chamber of a supersonic combustion ramjet are directly connected to a

[7] A Casaccio and R. L. Rupp, *A Supersonic Combustion Test Program Utilizing Gas Sampling, Optical and Photographic Measuring Techniques*, NASA CR-66393, Aug. 1967.

supersonic nozzle which, in turn, is connected to an air heater.[8] A commonly used type of heater is a 10 MW DC electric arc heater in which cold air is heated to a nominal nozzle plenum temperature (T_{t_o}) of 4500°R at a pressure of 450 psia. Figure 9 shows the radial variation of O_2 deficiency (ambient air O_2 concentration minus the measured O_2 concentration) deduced from gas sample measurements in the exit plane of the combustor. The data is for various values of T_{t_o} without combustion, i.e., no fuel was injected into the combustor.

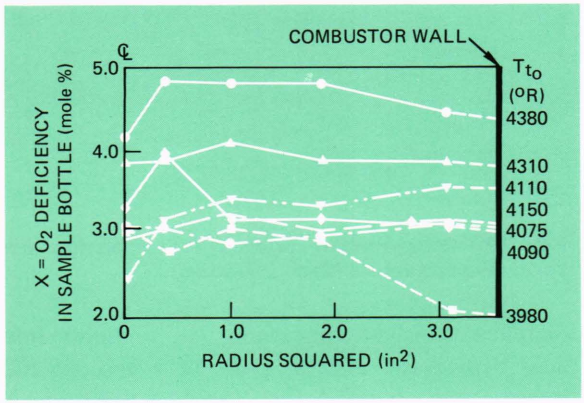

Fig. 9—Oxygen deficiency deduced from gas sample measurements.

Although the data presented give the O_2 deficiency that exists in the sample bottles at some time after the samples have been cooled to ambient temperature from the conditions existing at the combustor exit, it can be shown that the averaged oxygen deficiency in the bottles is approximately equivalent to the amount of NO existing in the plenum of the supersonic wind tunnel nozzle ahead of the combustor section.[8] Comparison of these deduced values of NO with the concentration of NO present in air in thermodynamic equilibrium (Fig. 10) shows that the existing NO concentration in the arc heater wind tunnel is more than three times the equilibrium value at typical testing conditions. A correct definition of the air chemistry at the test section plenum conditions is important for determining correct values for the energy balance on the tunnel and an overall or bulk combustion efficiency for combustion tests.

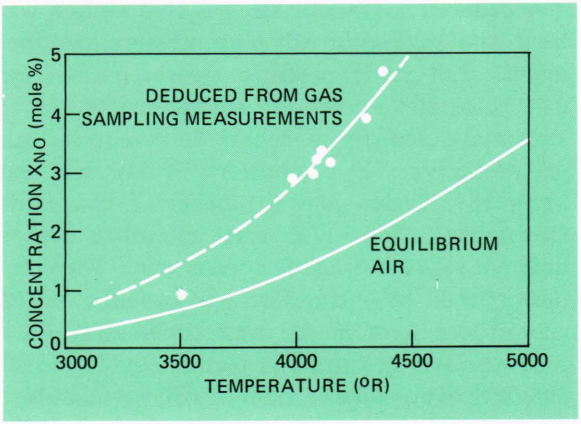

Fig. 10—Nitric oxide concentration in PRL arc heater wind tunnel deduced from gas sample analysis.

In hydrogen combustion tests,[8] gas sample data from the combustor exit plane were used to deduce combustor-exit gas composition, expressed as equivalence ratio (ER), the local fuel-air ratio divided by the stoichiometric fuel-air ratio, and local combustion efficiency η_c (Fig. 11).

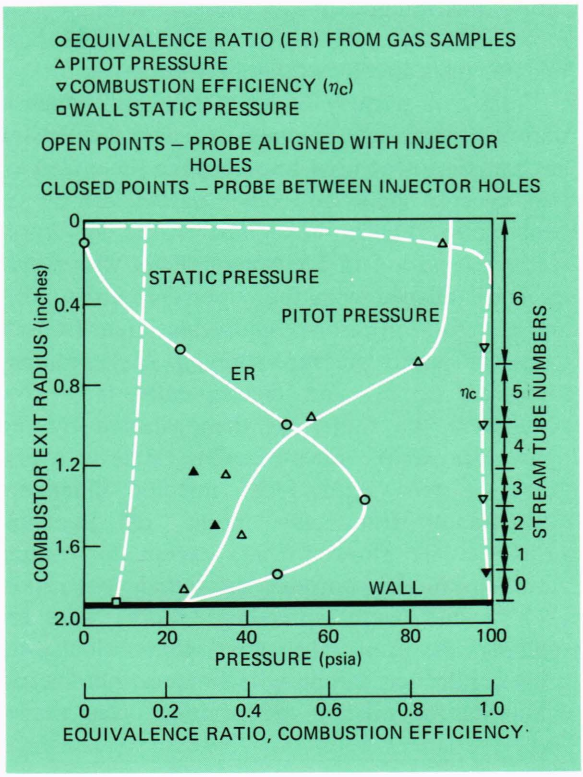

Fig. 11—Hydrogen supersonic combustor exit gas properties.

[8] R. C. Orth, F. S. Billig, and S. E. Grenleski, "Measurement Techniques for Supersonic Combustor Testing," presented at the Symposium on Instrumentation for Airbreathing Propulsion, Sept. 19–21, 1972, Monterey, Cal., to be published in AIAA *Progress in Astronautics and Aeronautics*.

The deduced combustor-exit gas composition was used with combustor exit pitot pressure measurements, wall static pressure measurements, and exit cone-static-pressure measurements in a streamtube analysis to define the combustor-exit gas properties. The combustor exit flow field was arbitrarily divided into a number of concentric streamtubes (Fig. 11), each of which had a different set of average flow properties. The combustor wall heat transfer was included as an energy loss term in the wall streamtube. Each tube was assumed to be in pseudo-equilibrium at an effective equivilence ratio of $ER \cdot \eta_c$—that is, a portion of the fuel $(1 - \eta_c)\ \dot{w}_f$, where $\dot{w}_f$ is the local fuel mass flow rate, remained in its unreacted state at the temperature and pressure of the remaining combustion products which were in local equilibrium. Slight perturbations in the assigned values of static and pitot pressure in each streamtube were made to obtain the best balance in the measured and calculated mass, momentum, and energy balances. In the typical test reported, the summation of the mass, stream thrust, and energy of the streamtubes all agreed with the measured air and fuel rates, inlet stream thrust plus integrated wall pressure and shearing force, and the calorimetrically determined heat release, respectively, to within 1%.

Finally, in a study of interaction and penetration of gaseous jets in supersonic flow,[9] extensive gas sampling was used to determine the effects of fuel injector shape and other parameters on jet penetration. Figure 12 compares the jet cross-sections from a 4 to 1 rectangular slot with circular ends, aligned with the supersonic cross flow, and a circular injector of equivalent area. In both cases the jet-air pressure ratio (p_{t_j}/p_b), momentum ratio (q_j/q_a) and, consequently, mass flow ratio were the same. As demonstrated by the figure, gas sample measurements taken at a distance of ten "equivalent" injector diameters downstream from the point of injection $(x/d_j^* = 10)$ showed that, except for minor variations in the contours, the initial penetration (y/d_j^*) and lateral spreading (z/d_j^*) were essentially the same. In other penetration tests using similar gas sampling techniques, parametric evaluation of injector performance was made.

[9] R. C. Orth, J. A. Schetz, and F. S. Billig, *The Interaction and Penetration of Gaseous Jets in Supersonic Flow*, NASA CR-1386, Jul. 1969.

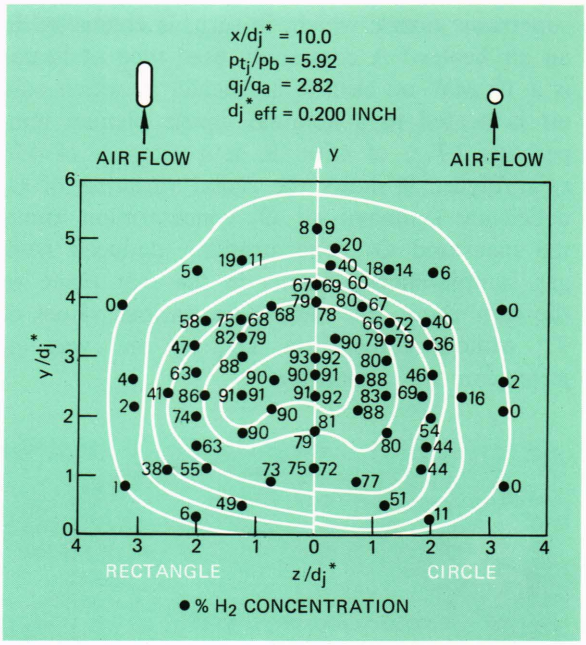

Fig. 12—Concentration profiles for underexpanded sonic injection into a Mach 2.7 stream.

Significant insight concerning the complex flow field behind the injector ports of a gaseous fuel injector was obtained, thus enabling definition of the controlling variables.

Conclusions

Considerable progress has been made in the development of a sophisticated gas sample and gas chromatographic analysis instrumentation. Numerous and varied demonstrations of the accuracy and reliability of the analysis techniques as applied to propulsion research have been made. Even with this instrumentation, precise control of carrier gas flow, column temperature, detector current and temperature, along with careful calibration with known gases and careful sample handling are essential for successful analysis of combustion gas samples.

Acknowledgement

The author wishes to gratefully acknowledge the valuable assistance of Mr. H. B. Land for his consistent ingenuity and diligence in the development, operation, and maintenance of the PRL Combustion Gas Analyzer. Sincere thanks are expressed to Dr. G. L. Dugger and Dr. F. S. Billig for technical guidance and encouragement in this work.