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FOR HYDROGEN-REACTION
COMBUSTION PRODUCTS

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The results of testing an on-line quadrupole gas analyzer system are reported. Gas samples were drawn from the exhaust of a hydrogen-oxygen-nitrogen rocket which simulated the flow composition and dynamics at the combustor exit of a supersonic combustion ramjet engine. System response time of less than 50 milliseconds was demonstrated, with analytical accuracy estimated to be ±5 percent. For more complex chemical systems with interfering atom patterns, analysis would be more difficult. A cooled-gas pyrometer probe was evaluated as a total temperature indicator and was also the primary gas sampling element.

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SUMMARY

An on-line gas analyzer system was developed for the rapid analysis of combustion products of a hydrogen-air propulsion system. A commercially available quadrupole residual gas analyzer with sample-hold circuitry was adapted for dry-gas analysis of hydrogen, oxygen, and nitrogen. Water was simultaneously measured by mass-flow measurement.

In order to test the analyzer, the nozzle flow of a rocket, located 7.6 meters (25 ft) from the sensor, was sampled through a cooled-gas pyrometer probe. The probe was evaluated as a total temperature indicator and as the primary mass flow measuring element for total sample flow rate. Overall system response time to source gas composition was less than 0.1 second.

INTRODUCTION

This report describes the design of an on-line gas sampling system and presents the results of tests under conditions simulating supersonic ramjet engine tests.

Gas analysis is a useful and convenient tool frequently utilized in combustion research. It provides supplementary data to support and extend the conventional performance parameters to include local combustion efficiency, fuel distribution, and mixing processes. Such data cannot otherwise be obtained from the parametric test measurements ordinarily made.

Frequently, analytical data of this type are obtained from batch samples extracted from the system, stored in gas bottles, and analyzed at a later time. Samples so
obtained are subject to possible composition changes. They also are time-averaged, rather than instantaneous, samples. The averaging period is dependent upon the test conditions and sample size requirements. Furthermore, batch sampling generally precludes the immediate availability of the analytical results. On-line gas analysis can eliminate many of the problems encountered with batch systems and also has the potential of higher analytical speed, computer control, and immediate availability of test results (ref. 1).

A particular application of on-line gas analysis was a series of performance tests of a hypersonic research engine (HRE).

Sampling of the supersonic exhaust stream of the HRE at five different locations to obtain a real-time gas analysis for oxygen, nitrogen, hydrogen, and water vapor content was required. Constraints on the analytical system included a 7.6-meter-(25-ft-) long sample line and a 3-second cycle time limit.

The system consisted of five probes and five diverter valves to direct the sample flow streams to either a commercially available quadrupole residual gas analyzer (RGA) or to a dump. The tests reported herein used a single probe in a hydrogen-oxygen-nitrogen (H-O-N) rocket exhaust stream to simulate the HRE flow conditions.

The capabilities to rapidly analyze for hydrogen, oxygen, nitrogen, and water in an on-line, real-time mode are discussed, together with the problems and apparent limitations of this analytical scheme.

The tests reported herein were conducted in the U.S. customary system of units. The International System of Units (SI) is included for reporting purposes only.

ANALYTICAL SYSTEM

System Design Constraints

The analytical and sampling system design was severely constrained by the requirements of the engine tests. It was required that (1) gas samples be drawn from the engine flow downstream of the combustor exit through five separate cooled-gas probes (refs. 2 and 3) over a total time period of 3 seconds; (2) stream temperature and pitot pressure be continuously measured; and (3) the gas samples be consecutively analyzed in an on-line mode. For each probe, a maximum time period of 0.3 second was allowed to obtain steady-state analyses for oxygen, nitrogen, hydrogen,
and water. In order to obtain multiple analyses, an analytical system response time of less than 0.3 second was thus required. A quadrupole gas analyzer was selected which had a 0.1-second sweep speed, a variable mass range, and also the capability of computer-controlled operation. Water vapor was to be measured separately and simultaneously by the sample mass-flow-rate difference before and after water condensation (ref. 4), since water vapor condensation in the sample lines could not be prevented.

Mass Analyzer

A Process Analyzers, Inc., quadrupole residual gas analyzer, Model 1100-A, with an associated eight-channel sample-hold module and accessory programmer was acquired for the analysis of the hydrogen, oxygen, and nitrogen content of the sample. Only a small portion of the 300-atomic-mass-unit scan capability of the instrument was utilized. Sweep rate was variable from 0.1 to 100 seconds, but all data were obtained at the maximum sweep rate.

The accessory programmer overrides the scan control and replaces the scan function by a time division of eight channels per sweep. It also provides a mass selector, or focus voltage control, for each channel which replaces the normal function of the center mass control. During the time period of a single sweep, the programmer steps the mass selector through each of the eight selected channels. When carefully focused, each channel will contain only the peak value of a single selected mass so that the signal output when viewed on a cathode ray tube would resemble a bar graph. The peak value of the selected mass is obtained only if the focus voltage is carefully set and maintained within the limits of the finite peak width. In order to minimize the effect of voltage drift on signal output, the mass resolution was sacrificed to broaden the width of the mass peaks. The width at the top of the peak could be broadened to only 3 to 4 millivolts (5 percent of peak width at its base); thus, electronic stability of the circuits and careful focusing of the spectra were imperative to assure maximum signal output. The sample-hold module stored the signals as a capacitor charge for each signal channel and updated the signal level once during each sweep. Synchronization of the data recording system to the sweep rate was not required for normal data readout. With operation in the sample-hold mode, capacitor leakage can introduce appreciable analytical error with a low sweep rate.
Low signal levels would be especially subject to this error. However, the use of a fast sweep rate eliminated such error since recharge rates were effectively greater than signal leakage rates.

All mass analyses were obtained at the maximum sweep rate of 0.1 second (12.5 msec/channel), 70-volt ionizing voltage, and 0.9-milliampere emission current. The analyzer control and signal readout was located approximately 15 meters (50 ft) from the sample point. The ionizer and analyzer electronic components were located at the sample line termination, 7.6 meters (25 ft) from the probe position. An eight-channel recorder was used for data readout. For these tests, sampling and instrument control were manual.

Gas Sampling System

A schematic of the gas sampling system is shown in figure 1. For these simulation tests, only one of the five sample lines was used. Sample line length from probe to gas analyzer was 7.6 meters (25 ft). Tubing with an inside diameter of 0.79 centimeter (0.31 in.) was determined to be small enough for high response and large enough to permit choked flow in both sample line flow nozzles. Sample flow through the probe and sample line was continuous to eliminate the necessity for line purge prior to analysis. A three-way transfer valve diverted flow either to a vacuum reservoir for dump or to the analyzer. Residual water was removed in an ice trap prior to measurement of the dry-gas flow rate. The flow nozzle diameter was 0.41 centimeter (0.161 in.). A small orifice extracted a portion of the dry sample flow for the analyzer. The analyzer head pressure was adjusted by sizing the double orifice system to the interstage pumping speed. The first orifice was the equivalent of a 0.18-millimeter (0.007-in.) hole, and the second was the equivalent of a 0.33-millimeter (0.013-in.) hole. Sample pressure at the first orifice was approximately 100 torr (0.13 atm), interstage pressure was $9 \times 10^{-2}$ torr, and the analyzer head pressure was approximately $4 \times 10^{-6}$ torr. Interstage and head pressures were relatively insensitive to rather wide pressure excursions at the first orifice. An identical flow system was used for calibration as shown.
Probe Flow Calibration

The water-cooled probe used for these tests is shown in figure 2. Gas temperature, after convective cooling, was measured by a platinum/platinum - 13-percent-rhodium alloy thermocouple located upstream of a nozzle. Nozzle flow was choked. Although not originally intended as a flow measuring element, for this application nozzle flow was used to measure the total sample flow rate. The nozzle total and throat static pressure were measured, and the nozzle was calibrated with air at ambient pressure. For flow measurement at run conditions, it was necessary to empirically relate an effective nozzle flow temperature to that indicated by the thermocouple since the data indicated nozzle flow temperatures that were appreciably lower than thermocouple indications. These low nozzle flow temperatures were assumed to be the result of the combined effect of the probe flow temperature profile and rapid cooling of the probe flow in the region of the nozzle entrance. The nozzle flow temperature was calculated from dry-sample flow rate, dry-gas composition, and theoretical water content calculated from the propellant flow ratios. The correction to the indicated temperature was pressure dependent and was assumed to be linear over the probe pressure range of 2 to 4 atmospheres. For indicated probe temperatures greater than 1110 K (2000° R), the effective gas total temperature at the nozzle was assumed to be

\[ T_1 = T_2 \left( \frac{1}{1.87 - 0.060 P_0} \right) \]

where \( P_0 \) is the total pressure in atmospheres at the nozzle inlet, \( T_2 \) is the measured probe temperature, and \( T_1 \) is the effective sample total temperature at the probe nozzle. From choked flow calibration data corrected to a specific-heat ratio of 1.3 and a gas molecular weight of 24.5, the total sample flow rate \( \omega_0 \) passed by the probe nozzle can be expressed as

\[ \omega_0 = 6.83 \times 10^{-2} P_0 \sqrt{\frac{1}{T_1}} \]
The error in $\omega_0$ is estimated to be near 3 percent.

**PROCEDURE**

In order to develop and test the gas sampling and analyzer system at flow conditions closely approaching those to be experienced in the hydrogen-air propulsion system test, a H-O-N rocket was employed as a hot-gas source. Nozzle exit Mach number at the sampling point was either 2.0 or 2.75. In order to vary reaction temperature over a range of 670 kelvins (1206 deg R) propellant oxygen-fuel weight ratio (O/F) was varied from 6 to 10, and nitrogen diluent was added. Table I compares the calculated rocket nozzle exit conditions with the equilibrium conditions expected for the near-stoichiometric hydrogen-air tests of the HRE. The exit pitot pressure reported varied somewhat with propellant flow variables, but it was determined primarily by the nozzle exit Mach number. The chamber pressure of the rocket was nearly constant at 690 kN/m$^2$ (100 psia).

All test runs were nominally limited to 10 seconds. The probe was inserted to the stream centerline, with the probe tip 0.6 centimeter downstream of the nozzle exit. The probe insertion occurred 3 seconds after ignition to eliminate probe exposure to flow transients. Stream pitot pressure and total temperature were calculated from probe measurements. Rocket performance was calculated from propellant flow rate and rocket chamber pressure.

**RESULTS AND DISCUSSION**

**Gas Temperature Measurements**

Reference 3 reports the results of tests of a prototype of the probe used in these tests. For a single test condition, good agreement between a stream temperature calculated from probe measurements and a direct thermocouple measurement was reported. The test conditions of reference 3 were near the lower temperature limit of the Mach 2 data reported herein, and probe flow Reynolds number was in the linear region of the empirical correlation curve reported in reference 2. The present test data were obtained at pitot pressures near 170 and 450 kN/m$^2$ (25 and 65 psia) at total temperatures ranging from 2000 to 2900 K (3700$^\circ$ to 5200$^\circ$ R).
Much of the lower pressure data were in the nonlinear region of the Reynolds number - temperature correlation function. For these data the sample total temperature at the probe inlet $T_0$ was calculated from the probe temperature $T_i$ and the coolant temperature $T_w$ according to

$$\ln \left( \frac{T_0 - T_i}{T_i - T_w} \right) = -4.89 + 7.35 f(a) - 3.07 [f(a)]^2 + 4.24 [f(a)]^3$$

where $f(a)$, the abscissa of the correlation curve, is defined in reference 2 as

$$f(a) = f(m_2, \gamma_2) = \left[ \frac{P_0}{\left( \frac{\mu_2}{\mu_R} \right)^{T_2 - T_1 \times 10^{-3}}} \right]$$

The function $f(m_2, \gamma_2)$ is an adjustment for the gas stream molecular weight and is defined in reference 2. The bulk gas temperature of the probe flow was used for $T_i$ and is defined in reference 4 as a function of the gas temperature (measured temperature corrected for radiation and recovery). For the temperature range of these data, $T_i$ was approximately 84 percent of the probe-indicated temperature. Probe flow viscosity $\mu_2$ (ref. 5) was based on the theoretical molar composition of the probe flow and was referenced to the viscosity of air at 556 K (1000° R).

For data within the linear region of the correlation, the total temperature relation is

$$\ln \left( \frac{T_0 - T_i}{T_i - T_w} \right) = 1.25 [f(a)]^{-0.3}$$

The total temperature $T_0$ calculated from the probe measurements was compared to the theoretical exhaust gas temperature $T_{\eta}$ calculated from propellant flow rate and adjusted for combustion efficiency. The temperature ratio is shown in figure 3 for bulk gas temperature at the probe nozzle ranging from 1000 to 1500 K (1800° R to 2700° R). The temperature ratios plotted were calculated as outlined by using...
two different base temperatures for determining probe gas viscosity \( \mu_2 \). For the data represented by the circular symbols, \( \mu_2 \) was calculated for an average gas film temperature \( T_{\text{avg}} \) (average of wall and gas temperatures) at the midpoint between the thermocouple and entrance planes. The data represented by the square symbols were calculated by using the corrected thermocouple indication for the determination of \( \mu_2 \). This latter procedure is the method used in reference 2.

Appreciable data scatter is indicated in the figure. Catalytic recombination on the thermocouple, reacting mixtures within the probe, or steep temperature profiles in the probe flow would contribute to deviations from the correlation of reference 2. It is apparent, however, that the calculated total gas temperature is quite sensitive to probe flow conditions and to the gas viscosity relation assumed for the calculation. For the higher pressure conditions of the Mach 2 tests, better data agreement was obtained by using the probe-indicated temperatures for the viscosity in the temperature range below 1150 K (2100\(^\circ\) R). The Mach 2.75 data showed greater scatter, reflecting the sensitivity of the method for use at low-Reynolds-number flow conditions. However, the data indicate that over the temperature range of interest, 1000 to 1500 K (1800\(^\circ\) to 2700\(^\circ\) R), the total temperature of the stream can probably be determined within \( \pm 10 \) percent by using the average film temperature for the determination of the gas viscosity. In all cases, for the calculation of gas viscosity the exhaust gas composition was not corrected for combustion efficiency.

**System Response**

The sample flow system was designed to provide fast analyzer response. The 7.6-meter (25-ft) sample line length with choked nozzle flow demonstrated a response time to a step change in gas composition at the probe inlet of about 0.3 second. However, since the system design provided a continuous purge of the lines with fresh sample to the three-way flow transfer valves, the response time of the lines could be neglected. The effective system response was determined only by the flow downstream of the three-way valve and the analyzer inlet flow system. By inducing a step change in flow composition past the primary sample orifice of the analyzer inlet system, the response time for the analyzer was determined to be approximately 30 milliseconds. Therefore, it was conservatively assumed that the
analyzer would respond to the sample flow within 50 milliseconds of the transfer valve closure.

Recorder traces of the analyzer signal output illustrate the response time of this system. The traces are reproduced in figure 4. For these data, all of the five transfer valves were utilized. Exhaust gases passed through one valve and air through the other. The response time for the composition change is typical of the system response between valve and analyzer. Figure 4(a) shows the analyzer response to masses 32 and 28 when the valves were cycled between the rocket exhaust sample and air. The oxygen peak responded to the valve change in less than 50 milliseconds, and the nitrogen peak follows shortly. (Because of the programmer circuitry, the readout time period between the start of the signals of masses 32 and 28 was 25 msec.) The analyzer response is further illustrated in figure 4(b), which includes the time history of other variables. Similar rapid response between the air and sample traces can be noted. Also a flow perturbation evident as a short sharp rise in the exhaust temperature was reflected as a sharp decrease in hydrogen concentration about 0.25 second later. A change in the level of the mass 32 peak can also be detected.

Analytical Method

In order to compensate for electronic instabilities, the analyzer was calibrated with known gas mixtures immediately before and after the exhaust samples were run. Hydrogen and oxygen were determined as ratios to nitrogen to simplify the analysis. In practice, however, signals were normalized to the mass 14 peak to increase the signal ratio. An analytical accuracy of 3 percent was estimated for the analysis of H-O-N mixtures. Including water, however, analytical accuracy more closely approached ±5 percent.

Analyzer Problems Encountered

In the course of adapting the analyzer for rapid, remote, on-line gas analysis, a number of problems became apparent. Many of them were inherent to the analyzer, so it was necessary to adopt an analytical method which would eliminate or minimize
their effects. The instability of the electronic circuits over long periods made it imperative that calibration data be obtained very close to the time of the run in order to eliminate peak drift and sensitivity change. The focus of mass peaks was especially sensitive to the temperature of the radiofrequency generator. Improper focus resulted in noisy signals with a possible error to 5 percent of full scale. A temperature-controlled shield minimized this problem. Other problems associated with ionizer variables were largely eliminated by operation at constant pressure and fixed electron emission current. A single range linear amplifier was used to amplify the electron multiplier output since range switching in the short available time periods could not be accomplished. For this reason it was necessary to normalize mass signals to the 14 peak to increase the signal ratios and analyzer sensitivity. Even so, component concentrations which are very low in comparison to nitrogen would be difficult to determine accurately.

Problems associated with the programmer and sample-hold circuitry were numerous, but their effects could be largely eliminated by selective operating procedures. Errors from signal noise arising from the gate components of the sample-hold circuits were more difficult to circumvent. However, by utilizing two adjacent channels of the circuitry for each mass, the second channel signal was relatively noise free and was used for the data.

CONCLUDING REMARKS

The results of these tests have demonstrated the feasibility of rapid on-line gas analysis for a limited number of noninterfering components. For more complex chemical systems where mass interference occurs, the analysis would be more difficult. Multiranging of the signal amplifier would have improved analytical accuracy. Similarly, a positive calibration of the probe flow nozzle at operating temperature would have improved the accuracy of the measurement of water vapor in the exhaust sample. It is probable that the effect of catalytic recombination on the surface of the thermocouple is small, but a thermocouple coating to eliminate such
error would be advisable. In spite of such shortcomings, on-line analysis will
provide greater convenience and more readily accessible data than batch sample
methods.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 30, 1974,

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   and Jaffe, Irving: Selected Values of Chemical Thermodynamic Properties.
### Table 1. Comparison of Exhaust Gas Conditions

<table>
<thead>
<tr>
<th></th>
<th>Expected equilibrium conditions for hypersonic research engine</th>
<th>Calculated rocket nozzle exit conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mach number at nozzle exit</td>
<td>1.0 to 2.0</td>
<td>2.0, 2.75</td>
</tr>
<tr>
<td>Pressure at nozzle exit, kN m²</td>
<td>110 to 480</td>
<td>170 to 450</td>
</tr>
<tr>
<td>Total temperature, K</td>
<td>2660 to 2890</td>
<td>2220 to 2890</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>20 to 24</td>
<td>22 to 26</td>
</tr>
<tr>
<td>Gas composition, mol %:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>0.003</td>
<td>0 to 0.053</td>
</tr>
<tr>
<td>N₂</td>
<td>0.65</td>
<td>0.37 to 0.72</td>
</tr>
<tr>
<td>H₂</td>
<td>0.007</td>
<td>0 to 0.15</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.33</td>
<td>0.25 to 0.46</td>
</tr>
</tbody>
</table>

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**Figure 1.** Schematic of gas sampling and analyzer flow systems.
Figure 2. - Cooled-gas pyrometer and gas sampling probe. (All dimensions are in cm.)
Figure 3. - Ratio of total temperature calculated from probe measurements to theoretical equilibrium total temperature corrected from combustion efficiency as function of bulk temperature.

Figure 4. - Typical analyzer response to composition step change.
Rocket chamber pressure.

Probe temperature.

Mass 2 (H2).

Mass 14 (N).

Mass 32 (O2).

Sample orifice pressure.

Flow nozzle pressure.

Analyzer sample pressure.

Flow system time history

Figure 4. Concluded.