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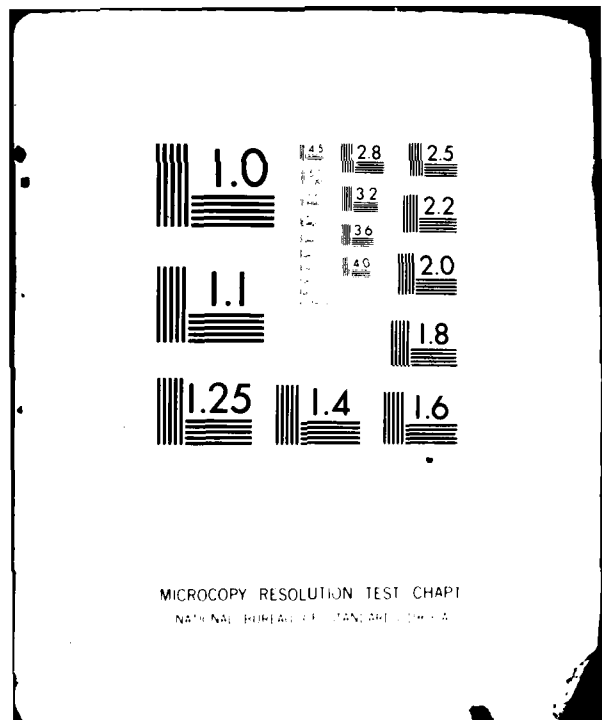
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# BREADBOARD GAS FILTER CORRELATION SPECTROMETER FOR ATMOSPHERIC MEASUREMENT OF HYDRAZINES AND NITROGEN DIOXIDE

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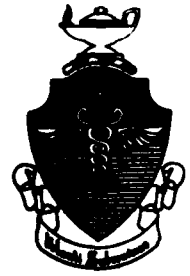
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NOTICES

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This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

  
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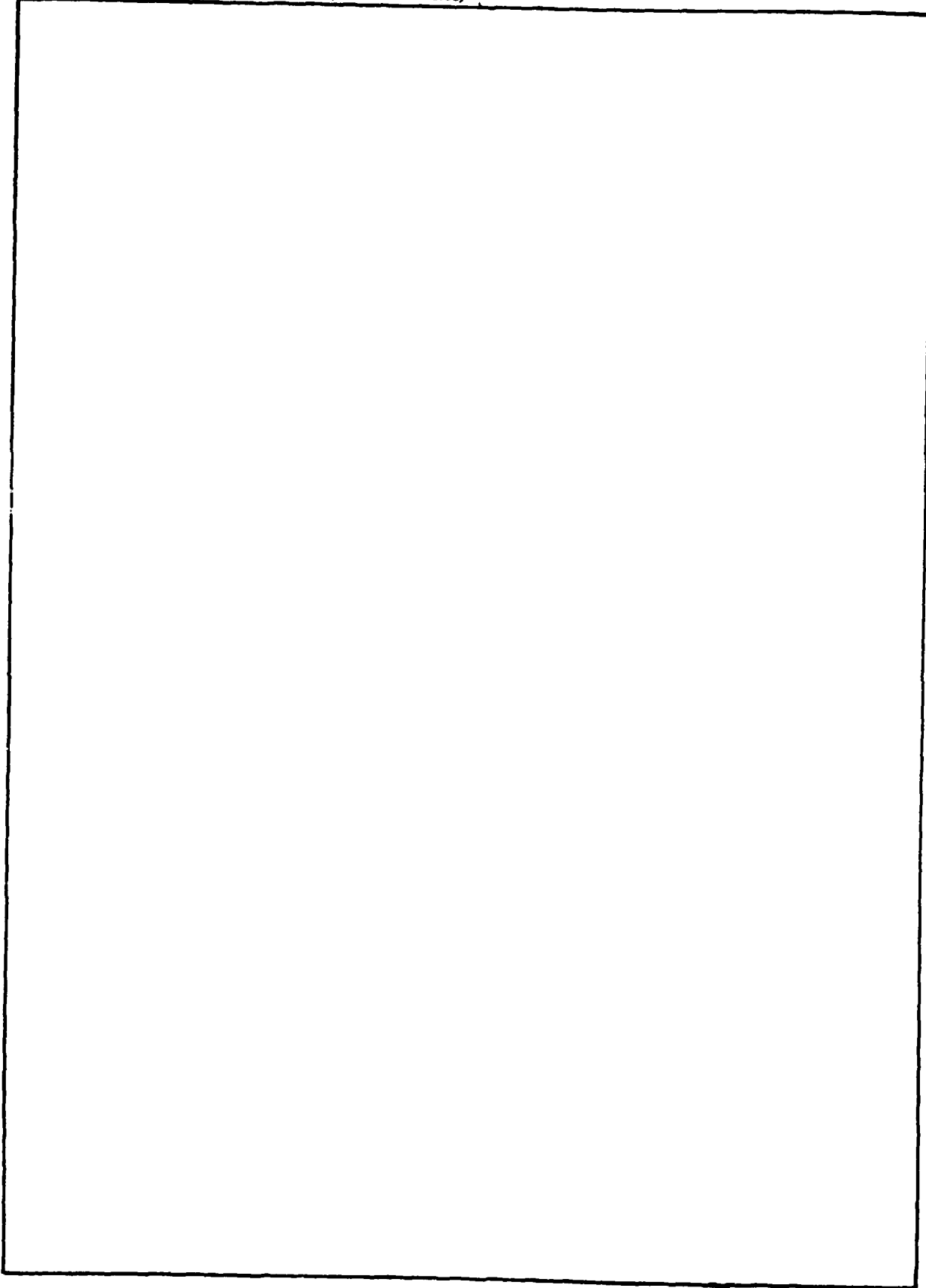
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# BREADBOARD GAS FILTER CORRELATION SPECTROMETER FOR ATMOSPHERIC MEASUREMENT OF HYDRAZINES AND NITROGEN DIOXIDE

## INTRODUCTION

The present contract arose from a need to measure, in real time, various hydrazines and nitrogen tetroxide (nitrogen dioxide) used by the U.S. Air Force in many of its propulsion systems. When hydrazines are used or stored, their extreme toxicity requires that the quality of the environment be monitored to satisfy requirements established by specific agencies responsible for air quality control.

The GASPEC, in previous applications, had demonstrated an ability to measure numerous gases in the atmosphere with reasonable accuracy and good specificity. Thus, a program was initiated to build a GASPEC to provide an analytical method for measuring the concentration of hydrazines and nitrogen dioxide in the ambient air. The instrument was to be configured for use as an ambient monitor, with the possibility of conversion to a remote sensor by addition of a telescope.

## THEORY OF OPERATION

### Radiative Transport

The GASPEC was originally designed as a remote sensor to be used to detect atmospheric pollutants. In switching from the remote-sensing to the ambient-monitor mode, the only significant change for the basic instrument is the source. In the remote-sensing mode any convenient thermal source can be used; for example, in the upward mode, the sky; and in the downward mode (as when looking from an airborne platform), the ground. The ambient monitor, on the other hand, has its own source, whose temperature can be adjusted to maximize the radiant energy in the band of interest.

Neglecting radiation scattered into the field of view (FOV) of the sensor, we can write the radiation reaching the sensor from a given source (s) as\*

$$N(\nu) = \epsilon_s(\nu) B_s(\nu, T_s) T_r(\nu, L) \quad (1)$$

This represents a very simple formulation of radiation transfer since multiple scattering and reradiation along the path of interest have been omitted.

\* Symbols used in equations are defined in the List of Symbols at the end of this report.

These effects are difficult to treat theoretically, although some complicating factors have been considered. Reviews of these problems and summaries of recent work have been published (1,2). The error introduced by neglecting scattering is far less serious in the infrared region of the spectrum than in the visible or ultraviolet.

The fundamental vibration-rotation bands of many compounds appear in the thermal spectral region and consist of a distribution of separate lines whose locations provide unambiguous fingerprints of the target molecule in question. The sum of the strengths of the lines detected by the sensor leads to the quantitative determination of gas burden in the sensor's FOV (3).

### Optical Design

The instrument to be described here is a nondispersive gas filter correlation spectrometer (GASPEC) that was developed initially for use as an airborne remote sensor for sensing vapor plumes near Earth's surface. The sensor has since been used also as an upward-looking device and an ambient monitor, as in the present situation. The hydrazine/nitrogen dioxide GASPEC is unique in that it incorporates a White cell, which serves to contain the sample and increase the instrument's sensitivity by increasing the distance the radiation must travel through the gas.

A nondispersive analyzer, or gas filter correlation spectrometer, has been in use for many years. Several versions are described in the literature (4-6). The basic theories of operation of these instruments are similar; differences occur in arrangement of optical components, methods used for moderating the incoming signal, and electronic signal processing.

The principle of operating a gas filter correlation spectrometer is illustrated in Figure 1. The main feature of a GASPEC is a pair of gas cells. One cell, referred to as the sample gas cell (Gas cell 1), contains a selected quantity of the target gas to be sensed. The second cell, the reference gas cell (Vac cell), contains a spectrally inactive gas. (This cell is often omitted because the reference gas is usually nitrogen which is present in the instrument atmosphere.) The optical depth of target gas in the sample cell is optimized for a maximum product of the modulation of the target gas energy and average transmission. Incoming radiation characteristic of the target gas is selectively filtered by being absorbed in the sample cell, but is readily transmitted through the reference cell. Thus, radiation transmitted through the sample cell is largely independent of the presence of target signature in the received spectrum, whereas the radiance transmitted through the reference cell is strongly dependent on the target gas. The difference in spectral transmittance between the two cells is thus a sensitive indicator of the amount of target gas signature in the radiation received by the sensor.

Some types of gas filter correlation spectrometers have used single detectors, and the differential transmittance was derived by time-sharing the incident energy through the two gas cells. These designs have inherent sensitivity and thermal-drift problems that are eliminated by the unique GASPEC two-detector design. The detectors receive amplitude-shared source signals at

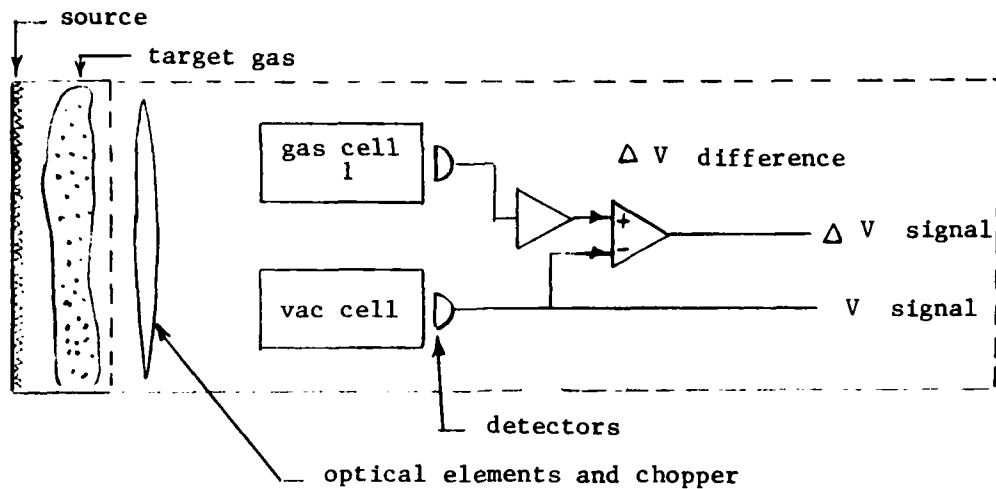


Figure 1. Instrument concept.

the source-chopping frequency. Thermal radiation within the instrument is not chopped and does not contribute to the source signals because the chopper disc is located near the sensor field stop. In the remote-sensing mode (without the multipass cell), only radiation originating at the objective lens contributes coherently with radiance originating outside the sensor. Because of the low lens emissivity, only a small amount of radiation is emitted, and the flat spectral character of this radiation does not correlate with the sample-gas transmission spectrum. Thermal changes within the instrument are thus overcome.

Additionally, the use of a common field stop and chopper results in simultaneous sampling of source radiance through both sensor arms. This enables the sensor to operate effectively even in the presence of rapidly changing source radiance. Radiance from two internal blackbodies at two temperatures is alternately chopped to provide a constant reference signal. A single reflective chopper disc with a double set of annular holes is used to modulate both the reference blackbodies and the scene radiance. This produces signals at two frequencies with a fixed frequency ratio. The reference and source signals are optically combined and then follow a common path through the sensor to the detectors. Coherent detection is used to separate electronically the two signal frequencies. The reference signals derived from the detectors are fixed to a constant ratio to provide a precise and continuous optoelectronic gain stabilization.

An additional feature of this GASPEC design is the use of a common blackbody for both the source and the source-reference blackbody. During the half-cycle when the source radiance exiting from the multipass cell is blocked by the chopper, the reflective inner side of the chopper views radiance from the source as seen over the top of the cell and delivered to the instrument by two focussing mirrors. This ensures that the reference blackbody will always be comparable in radiance to the source blackbody, which greatly facilitates the

electronic signal processing by keeping the chopped radiance to a minimum. This arrangement also means that any instabilities in the source are compensated for by matching fluctuations in the reference blackbody.

A schematic GASPEC optical layout is shown in Figure 2. The source radiance leaves the multipass cell and enters the sensor via objective lens L1. (In this instrument the lens also serves as a window on the multipass cell.) The radiance from the source is imaged in the objective focal plane, where a sensor field stop common to all detectors is located. A 45° reflective chopper is located adjacent to the field stop.

A relay lens, L2, images the objective lens at the aperture stop. L2 also images the sensor field stop through the interference filter, IF, and the gas cells onto field lenses L4, L5, and L6 via beam splitters BS2 and BS3. The field lenses image the aperture stop and the objective onto the detectors, thus avoiding imaging any scene hot spots onto the detectors. A second relay lens, L3, images the reference stop, via beam splitters BS1, onto the field lenses, coincident with the sensor-field-stop image.

The sensor's three optical paths (three detectors) are combined in two pairs to give two gas channels, with reference detector D2 common to each gas channel. The D1 and D2 detectors combined comprise the hydrazine channel, while D2 and D3 form the nitrogen dioxide channel. With the appropriate gas cells in position, the gas to be sensed is determined by the interference filter used. The pass band for NO<sub>2</sub> is centered around 3.4 μm, and that for hydrazine around 10.5 μm. (See Appendix A for transmission curves for the filters.) Both gases cannot be sensed simultaneously.

For either of the gas channels, the target-gas output signal, ΔS, from GASPEC may be written as the difference in the source signals of two gas-detector/amplifier arms:

$$\begin{aligned} \Delta S &= S_1 - S_2 \\ &= A\Omega t \int_0^\infty I_\nu(s) t_{c1} - I_\nu(s) t_{c2} F(\nu) d\nu \end{aligned} \quad (2)$$

i = 1,3

In the absence of target gas radiance, the GASPEC is "balanced" and insensitive to noncorrelating incoming radiance changes when  $S_1 = S_2$ . The electronic signal processing that maintains this balance is described in the next section. In the remote-sensing mode, the radiometer output,  $S_1$ , can be interpreted in terms of the background-source effective temperature.

Examination of equation 2 reveals several noteworthy characteristics of the instrument response. First, it is fully multiplexed; that is, all wavelengths are in phase at the detectors. Thus there is no signal power cancellation caused by phase shifts of different wavelengths of radiation, as occurs, for example, in an interferometer. Secondly, the device has a large etendue advantage, since the gas cell that determines the resolution limit has none of the spectrometer or interferometer angular restrictions, and the

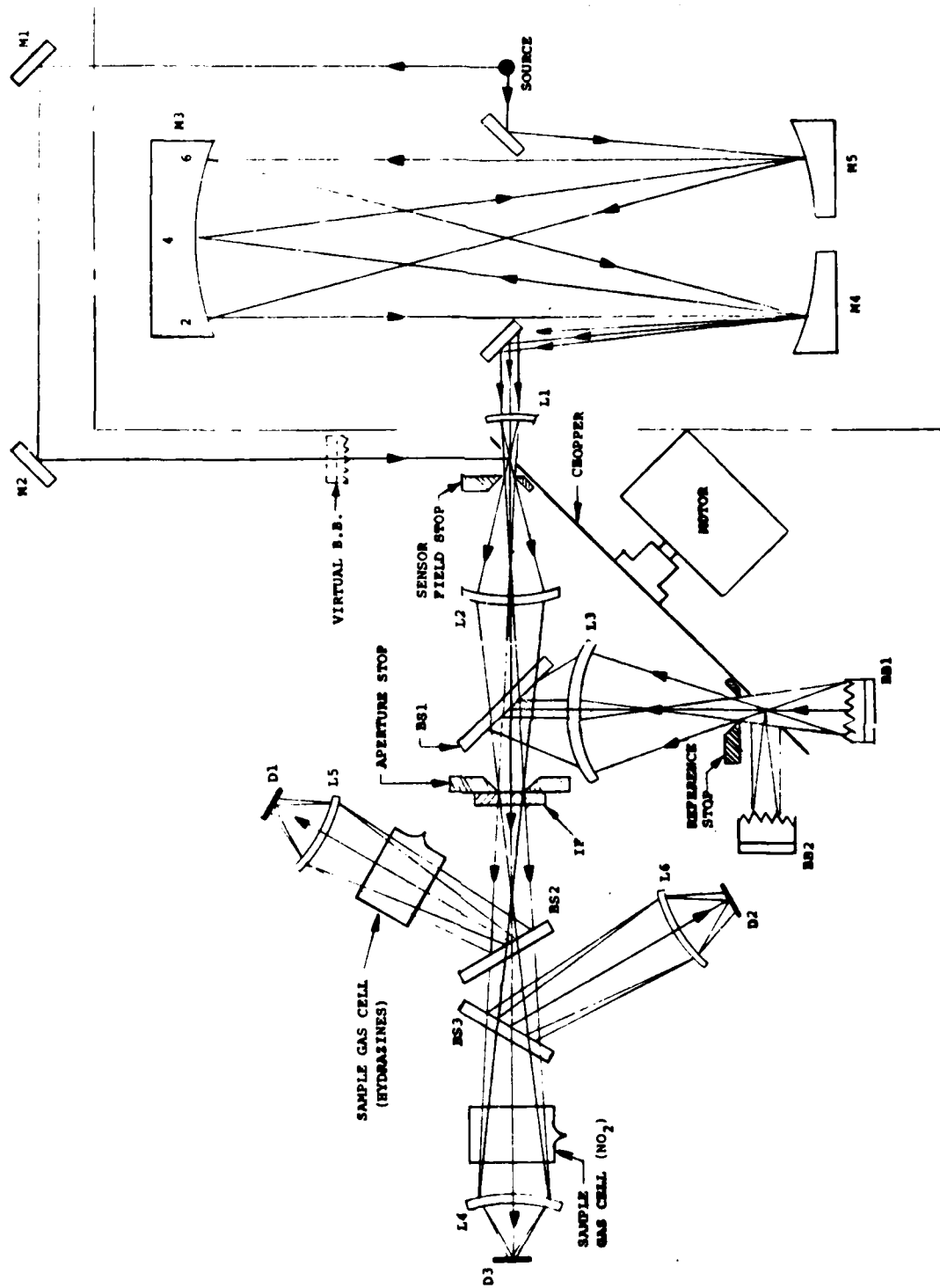


Figure 2. GASPEC optical layout.

diameter of the gas cells may be large without great expense or technical difficulty. The etendue limitation is determined by the required optical thickness in the sample cell, by the imaging optics, and by the interference filter. Further, the spectral resolution is limited only by the absorption line width of the gas in the sample cell. Finally, the chopping may be carried out at any convenient frequency to match detector responsivity requirements.

### Electronic Design

Figure 3 illustrates schematically the GASPEC electronic signal processing. The optoelectronic gain balancing and stabilization are achieved by synchronously detecting the frequency and phase of the signals derived from the two internal reference blackbodies and holding these reference signals at a fixed ratio for a given detector pair.

By using a feedback loop to preserve a fixed ratio for the signals from the reference blackbodies, we maintain a zero response in the presence of non-correlating radiance. This null is maintained for detector and electronic gain changes as well as optical gain changes within the loop. Only correlating radiance (i.e., target-gas modulated radiance) upsets this balance and provides the desired signal.

Referring to Figure 3 again, we trace the signal for gas channel one (detectors 1 and 2). Signals  $S_1$  and  $R_1$  (from the source and reference blackbodies respectively) arrive synchronously at detector D1. The two signals are chopped at two frequencies by two concentric rows of holes at different radii in the chopper disc. Similar signals,  $S_2$  and  $R_2$ , arrive at detector D2. The radiance arriving at D1 has passed through a sample cell containing some of the target gas, while energy arriving at D2 has been modulated only during the transit from source to sensor. The signals produced by the detectors are amplified by amplifiers 1 and 2 respectively.

The output of Amp 2 is then inverted by Inverting Amp 1 (I.A.1) and summed with the output of Amp 1 in Summing Amp 1 (S.A.1). The output of S.A.1 is fed to Product Detector 1 (P.D.1) which produces  $S_1 - S_2$  output. The  $S_{sync}$  signal is derived from a LED phototransistor assembly mounted in the chopper disc cover. The  $R_{sync}$  signal is produced in a similar fashion. The  $S_1 - S_2$  output is branched: one branch goes directly to a control panel, the other to a divider/scaler. This in turn produces the output  $\frac{S_1 - S_2}{S_2}$ . The  $S_2$  signal is divided from the output of Amp 2 through Amp 4 and P.D.2.

Similarly, the output of Amp 2 is routed through I.A.2 to S.A.2 where it is summed with the amplified signals to detector D2. Product Detector 3 produces  $R_1 - R_2$  which is fed back to the automatic gain control element AGC 1. This then controls the gain of Amp 2 so that the ratio of  $R_1$  to  $R_2$  is kept constant. This servoloop assures that optoelectronic gain changes within the system are compensated; thus, spurious outputs caused by factors such as detector responsivity changes and aging amplifiers are eliminated.

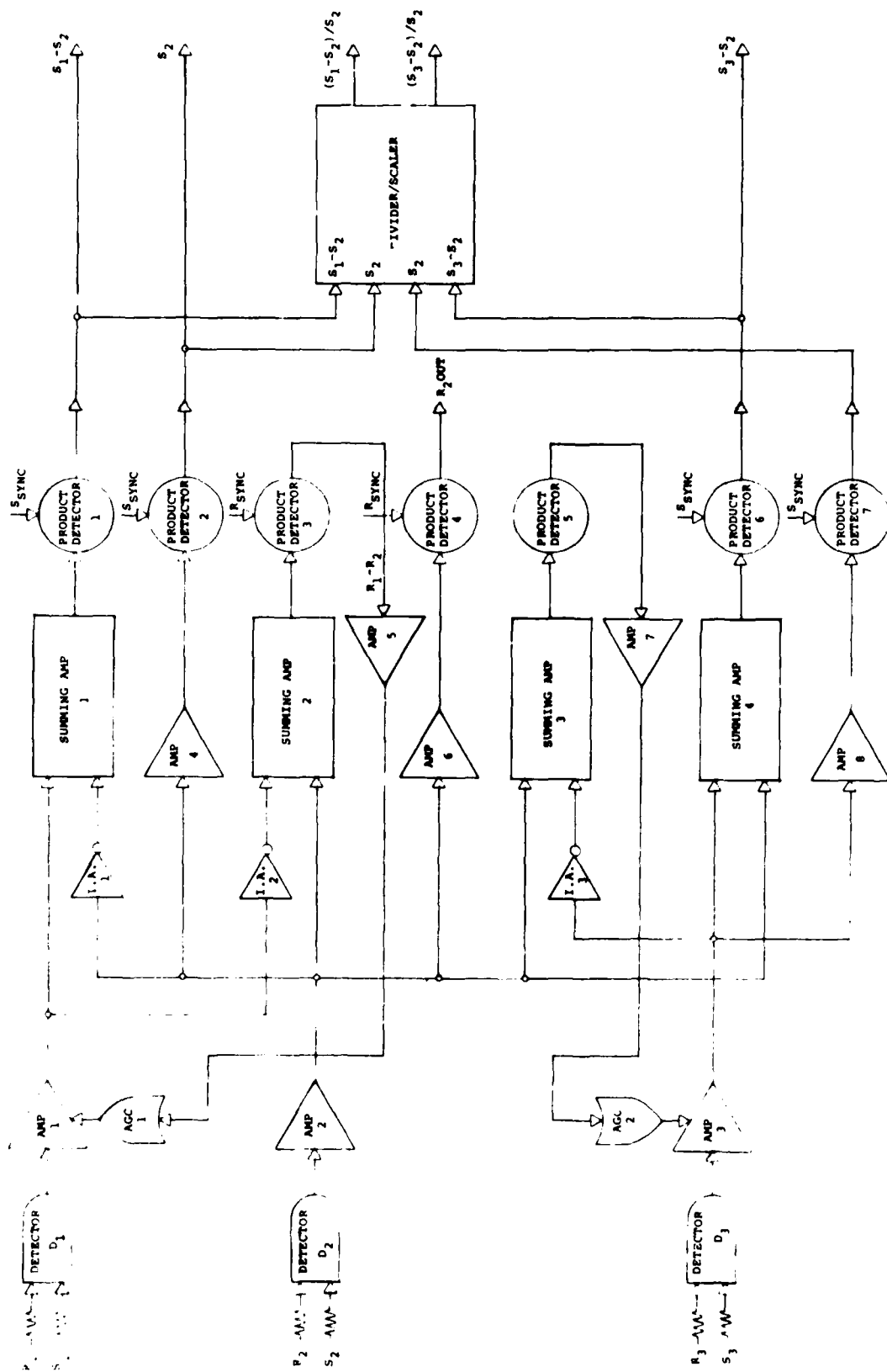


Figure 3. GASPEC electronic signal processing.

A similar description applies to the second gas channel, which consists of detectors D3 and D2.

### Multipass Cell

The multipass cell (or White cell) is illustrated schematically in Figure 2. The theory of operation of White cells has been described in detail by J. Strong (7). To achieve some space saving, the entrance and exit of the multipass cell are at 90° to the main axis. The beams are deflected internally by two 45° mirrors mounted just inside the ports. The main mirrors of the system will all have the same radius of curvature, with the two secondaries (M4, M5) cut from one blank identical to the primary (M3). Light enters the cell via the germanium window (source port) and reflects off the first plane mirror to the first secondary mirror. It traverses the cell 8 times before being deflected by the second plane mirror and exiting via the second port. The window of the second port is a lens that focuses the source radiation at the sensor field stop.

The source is also viewed over the top of the White cell by a focussing mirror (M1) mounted in the instrument. This light beam is relayed by another focussing mirror (M2) and deflected by the reflective chopper disc to focus at the same place as the primary beam. This second beam replaces the source-reference blackbody as described in the Optical Design section.

The multipass cell has been equipped with a series of micrometer adjustments that permit adjusting the mirror alignment from outside the cell in a precise and repeatable fashion. The optical alignment should not require adjustment during normal use, but it should be checked if the cell end flanges have to be removed and replaced. The micrometers are fitted with locking rings, and these should normally be kept locked (full right rotation).

The multipass cell is also a high-quality vacuum system. It is constructed primarily of standard stainless-steel UHV components and is capable, with suitable pumping, of achieving pressures of  $10^{-6}$  torr or less. The system comes equipped with a 200  $\mu$ /min rotary pump which will reduce the system pressure to less than  $10^{-3}$  torr.

The cell is also equipped with a high-vacuum port that enables the user to connect a diffusion pump or equivalent if desired. Conveniently located at the top of the cell is a port containing a pressure gauge-head and a bellows-sealed valve to which an inlet sample line may be connected. The system is bakeable to approximately 100°C, a useful feature considering the nature of the compounds to be studied. (Higher temperatures are possible if the O-rings are replaced with elastomers which will tolerate higher temperatures.)

### Radiometric Analysis

An expression for the radiation propagation through each optical arm of the instrument may be written and the instrument radiative transfer function



obtained for each signal output. By combining signals  $S_1$ ,  $S_2$ , and  $S_3$ , the transfer functions  $S_1 - S_2 = \Delta S$  and  $S_3 - S_2 = \Delta S'$  may be found. As the expressions for  $\Delta S$  and  $\Delta S'$  are similar, only  $\Delta S$  will be considered here:

$$\begin{aligned} \Delta S = A\Omega & \left[ \int_{\lambda} N_s \rho_m (T_1 t_{c1} t_G - T_2 t_G) d\lambda \right. \\ & + \int_{\lambda} N_{BRR} (T_2 - T_1 t_{c1}) d\lambda \left. \right] \quad (3) \\ & + \text{instrument self-emission} \end{aligned}$$

$$\text{when } T_1 = T_{BS1} T_{L1} T_{L2} T_{1F} T_{BS2} T_{BS3} T_{L4} R_{D3}$$

$$T_2 = T_{BS1} T_{L1} T_{L2} T_{1F} T_{BS2} \rho_{BS3} T_{L6} R_{D2}$$

$$\begin{aligned} \text{then } \Delta S = A\Omega & \left[ \int_{\lambda} N_s \rho_m T_1 t_G t_{c1} - t_G \frac{\rho_{BS3} T_{L6} R_{D2}}{T_{BS2} T_{L4} R_{D3}} d\lambda \right. \\ & + \int_{\lambda} N_{BRR} T_1 \left( \frac{R_{BS3} T_{L6} R_{D2}}{T_{BS2} T_{L4} R_{D3}} - t_{c1} \right) d\lambda \left. \right] \\ & + \text{instrument self-emission} \quad (4) \end{aligned}$$

All quantities within the brackets are wavelength dependent. To initially balance the instrument, the source energy,  $N_s$ , is injected into the instrument, ensuring that the amount of target gas in the FOV is below the instrument sensitivity ( $t_G=1$ ); then  $R_{D2}$  is adjusted until  $\Delta S = 0$ .  $N_s$  is chosen to be greater or less than the expected source radiance to ensure maximum accuracy. This balancing causes the instrument to be insensitive to variations in the source temperature around the  $N_s$  value selected.

Since the instrument uses coherent detection, the only self-emission terms that are coupled to the output are the chopper and the optical elements preceding the chopper. With the instrument at near-room temperature, the self-emission is one to two orders of magnitude below the other terms in the equation of the signal output (Fig. 4) and thus can be ignored.

#### INSTRUMENT DESCRIPTION

The system described in this report is composed of four main sub-units: the GASPEC, the White cell, the GASPEC power supply, and the vacuum pump(s).

## The GASPEC

The GASPEC proper contains the optical train and the signal-processing electronics. The optical elements are all mounted on a single rigid baseplate to eliminate relative movement of components. All transmitting elements are of germanium, antireflection coated for 10.6 and 3.6  $\mu\text{m}$ . Reflective elements are gold-coated glass substrates with a reflectivity  $>0.95$ . The chopper disc is fabricated to exacting specifications from aluminum and is gold coated for high reflectivity. It has two rows of concentric apertures, the outer row with seven holes and the inner with five. The outer row chops the source radiance, and the inner row chops the reference blackbodies' radiance, producing signals of different frequencies but with a constant frequency ratio. The chopper disc assembly is also equipped with two LED-phototransistor assemblies which generate the phase reference used in demodulating the various signals produced by the detectors.

The detectors are T-300 pyroelectric detectors supplied by Barnes Engineering Company. The detectors have a 2-mm<sup>2</sup> active area and respond well over a large region of the infrared. They were selected for this property since the detection wavelengths for NO<sub>2</sub> and the hydrazines are so widely separated. The detector assembly incorporates the field lens and the sample cell.

Two types of sample cells are supplied with the instrument, in two sizes. The short cells (0.9-cm body) are for NO<sub>2</sub>, and the long cells (3-cm body) are for the hydrazines. One type of cell has a double pinch-off glass stem extending from the body. These cells are intended to be refilled only infrequently. The other kind of cell is equipped with a bellows-sealed stainless steel shut-off valve. These cells are intended for use when experimenting with the amounts of the various gases in the instrument cells.

The cells are all constructed with a Pyrex body approximately 2.54 cm in diameter. The 2-mm-thick germanium windows are sealed to the cell with crushed indium O-rings. Pressure is maintained on the indium by the anodized aluminum clamping rings. Removing the tension from these clamps may destroy the seal and necessitate replacement of the O-rings.

### Multipass Cell (White cell)

The multipass cell is a variation of the standard White cell. It is made of UHV grade 304 stainless steel. The main body is formed from a 20-cm-diameter stainless steel tube approximately 50 cm long and equipped with standard UHV conflat flanges. The cell has been designed so that the primary optical surfaces are nominally 50 cm apart when the system is operational.

The three main mirrors are mounted kinematically on two 24-cm conflat flanges. The flanges are equipped with external micrometer adjusters so that the mirror alignment can be altered with the cell assembled. Vacuum integrity around the micrometer shaft is maintained with sliding O-ring seals.

The two side ports form the entrance and exit for the source radiation. Each assembly has a 45° mirror to deflect the beam quasi-parallel to the main

axis of the chamber. Each port has a germanium window; the window on the exit port is actually a plano-convex lens. The source assembly forms an integral part of the source port. The assembly is offset from the horizontal so that the source may be viewed over the cell to provide radiation for the reference blackbody as well as providing radiation for the path through the cell.

The multipass cell is equipped with two pump ports, one for a rough pump and the other for a high-vacuum pump. The high-vacuum port was sealed with a blank flange when shipped. There is also a port equipped with a 0.6-cm stainless-steel sample inlet valve and a Pirani gauge head.

#### Power Supply

The main d.c. power supply is located in a separate box. A keyed cable connects the power to the GASPEC and provides all basic voltages required by the instrument. It is fused on both the input and output to provide maximum protection for the power supply and the instrument.

#### Vacuum Pump

The vacuum pump is a standard 200-l/min two-stage rotary pump. It will reduce the system pressure to less than  $10^{-3}$  torr in less than 5 minutes. The pump is equipped with an activated alumina trap to reduce back streaming of oil and with a 2.54-cm isolation valve. The pump is connected to the system with a section of 2.54-cm stainless-steel bellows tubing.

#### SYSTEM OPERATION

The following instructions for start-up and operation of the system assume that the multipass cell is clean and free of contamination.

##### Start-up

1. Switch on power to the instrument and let it warm up for 15 to 20 minutes. This allows the source on the multipass cell and the reference blackbody to stabilize. If the vacuum pump is not operating, turn it on and pump on the vacuum chamber while the GASPEC is warming up. This helps remove impurities which may out-gas from the walls of the chamber.

2. After the instrument has equilibrated, balance the  $S_1 - S_2$  and  $S_3 - S_2$  outputs. If the compounds to be sensed will be observed undiluted (i.e., low pressures of pure vapor in the cell), balance the instrument with the cell evacuated. If the target is to be observed diluted in a carrier gas (i.e., nitrogen or air), valve-off the vacuum pump and back-fill the cell with the appropriate carrier to the pressure at which the measurements will be made.

3. When the preceding conditions have been established, balance the instrument by adjusting the appropriate potentiometer on the instrument panel.

The output of either  $S_1 - S_2$  or  $S_3 - S_2$  can be monitored on the digital panel meter (DPM) by selecting the correct "function switch" setting.

4. Once the instrument is balanced, measurements can be made by admitting the sample to the multipass cell. To determine the amount of target gas in the sample, compare the DPM reading to the appropriate calibration curve.

#### Changing Gases

Hydrazine to Hydrazine Derivative--The same interference filter (W1078-9) and the same gas cell (monomethylhydrazine, MMH) can be used for all three hydrazines. If, however, the cell needs to be changed for any reason, demount the cell currently installed in the instrument by removing the two retaining screws holding it to the detector assembly and fasten the new cell in its place. Take care to avoid finger marks or other contamination on the optical surfaces. Rebalance the instrument for start-up.

Hydrazine to Nitrogen Dioxide--To monitor nitrogen dioxide, change the interference filter to the one with the 3.5- $\mu$ m center wavelength (see Appendix A).

Since detector D3 is used exclusively for  $\text{NO}_2$ , the sample cell can remain mounted independent of which gas is actually being monitored. After the correct interference filter has been installed, rebalance the instrument for start-up.

#### Pump-Down (High-Vacuum Operation)

Assuming the vacuum chamber is at or near atmospheric pressure, start up the roughing pump and slowly open the main valve to the system. The pressure should fall rapidly (in less than 5 min) to a level below  $10^{-3}$  torr. If a diffusion pump (or other suitable high-vacuum pump) has been installed in the system, close off the valve to the roughing pump and slowly open the diffusion-pump isolation valve. (We are assuming that the operator is familiar with the operation of a diffusion pump and that the pump has previously been started.) The vacuum system is now operational.

NOTE: The roughing pump is equipped with an activated alumina trap to reduce the back streaming of oil from the pump. This trap should be checked every 3 to 6 months depending on the amount of use the pump gets. The alumina must be replaced when it becomes visibly contaminated, as oil back-streaming into the chamber will soon reduce the efficiency of the optical surfaces contained therein. If a diffusion pump is used, it must also be adequately trapped (liquid nitrogen) to prevent back streaming of its working fluid.

#### TESTING AND CALIBRATION - RESULTS AND ANALYSIS

All signal-processing boards were bench tested individually to check for connection faults. The electronics were then assembled, checked again, and

tested to ensure correct operation of the entire assembly. The output noise was measured, and the ratio of the measured NEP (noise equivalent power) to the value calculated from the component manufacturer's data was less than 2 for all detectors. The electronic noise output from each channel was significantly less than the detector noise contribution.

The multipass cell was aligned and checked according to the design to produce eight passes of the laser beam. The cell was then aligned so that the optical axis of the GASPEC was co-linear with the axis of the output port. A similar procedure was used to align the two mirrors that look at the source over the top of the cell. With the source in place, the mirror adjustments were fine tuned to maximize the outputs of each detector. (About this time, the original program funding was exhausted; however, testing was continued at Barringer Research Limited expense.)

Preliminary calibrations were made on a number of the gases in order to estimate instrument response and sensitivity. All tests were performed with pure target gas, in the multipass cell, at pressures less than 1 torr.

The first configuration to be considered was the response to hydrazine ( $N_2H_4$ ), with a  $N_2H_4$  instrument cell. The results of these measurements are displayed in Table 1. The minimum detectable amount (MDA) of  $N_2H_4$  with an average-signal to rms-noise ratio  $(S/N)_{rms}$  of 1 is approximately  $1.5E-4$  torr, corresponding to 0.2 ppm in 1 atm.

TABLE 1. RESPONSE OF INSTRUMENT TO  $N_2H_4$  CONCENTRATION WITH A  $N_2H_4$  INSTRUMENT CELL

Pressure of target gas in White cell (torr)	Concentration of target gas (ppm)	Output (MV)	Noise amplitude (MV)	MDA* (ppm) $(S/N)_{rms} = 1$
$1.1 \times 10^{-2}$	14	100	5	0.1
$3 \times 10^{-2}$	39	175	6	0.2

\*MDA = Minimum detectable amplitude.

The second system considered was the response to unsymmetrical dimethylhydrazine (UDMH) with a  $N_2H_4$  instrument cell. The results of these tests are shown in Table 2. The MDA for UDMH in this configuration is about  $3E-4$  torr (0.4 ppm).

The next system tested was the response to UDMH when the instrument was equipped with a UDMH instrument cell. These results are displayed in Table 3. The MDA for UDMH is about  $2.3E-4$  torr (0.3 ppm).

TABLE 2. RESPONSE OF INSTRUMENT TO UDMH CONCENTRATION WITH A  $N_2H_4$  INSTRUMENT CELL

Pressure of target gas in White cell (torr)	Concentration of target gas (ppm)	Output (MV)	Noise amplitude (MV)	MDA (ppm) $(S/N)_{rms} = 1$
$9 \times 10^{-2}$	118	210	5	0.5
$1.1 \times 10^{-1}$	145	235	5	0.5
$7.3 \times 10^{-2}$	94	160	4	0.4
$2 \times 10^{-2}$	26	60	4	0.3

TABLE 3. RESPONSE OF INSTRUMENT TO UDMH CONCENTRATION WITH A UDMH INSTRUMENT CELL

Pressure of target gas in White cell (torr)	Concentration of target gas (ppm)	Output (MV)	Noise amplitude (MV)	MDA (ppm) $(S/N)_{rms} = 1$
$4 \times 10^{-2}$	53	115	5	0.4
$7.5 \times 10^{-2}$	98	178	5	0.5
$1.1 \times 10^{-1}$	144	215	5	0.5
$5.2 \times 10^{-2}$	68	125	5	0.3
$2.5 \times 10^{-2}$	33	95	5	0.3
$1 \times 10^{-2}$	13	50	5	0.2
$2.8 \times 10^{-2}$	37	80	4	0.3
$3.3 \times 10^{-2}$	43	94	4	0.3

In each situation the instrument cell was filled to approximately 20 torr or to the maximum vapor pressure of the compound at room temperature. A problem was experienced with the MMH. It apparently reacted with the antireflection coating material on one cell window, producing a cloudy film and entirely depleting the cell of MMH. Since only one window was affected, the reaction with MMH is attributed to a defect in the coating of that window, perhaps due to water occluded during the coating process. A new window was fitted and the problem did not recur.

An attempt was then made to test the system with the samples in the multipass cell pressurized to atmospheric pressure with dry nitrogen, but pressurization (even with pure nitrogen and no hydrazine) produced a large offset in the instrument output. We concluded that this offset was most likely produced by--

(a) Changing illumination of the GASPEC optics by the multipass cell, due to displacement of the cell entrance and/or exit optics by the forces of pressurization and evacuation.

(b) Lack of congruence of the fields of view of the GASPEC detectors, causing each detector to see the changes in illumination differently.

However, a relatively simple modification to the cell, separating the means of mechanical location from that of vacuum sealing, should minimize the movement of the cell optics and, combined with careful realignment of the detectors for exact boresight, should greatly reduce if not eliminate the pressure-induced offset.

Thus, in view of the encouraging nature of the initial sensitivity measurements, we requested additional funding to carry out the necessary modifications of the multipass cell and to continue the atmospheric pressure testing. The request for additional funding was successful, and modification of the multipass cell was begun early in November 1978.

First, an elementary stress analysis was carried out to confirm that the changing optical alignment could not be due to flexing of the cell walls or end plates. Then the mounting arrangement for the input and output optics of the cell was redesigned so that the location was via a metal-to-metal contact with the cell body, rather than via the O-rings used for vacuum sealing. The required modifications were fabricated and installed.

The fields of view of the GASPEC detectors were mapped and the detector was realigned for maximum congruence, as measured by balancing  $S_1 - S_2$  and  $S_3 - S_2$  and minimizing the offsets produced by interrupting one-half of the input aperture.

The multipass cell was reinstalled on the instrument, and the effect of evacuation and refill to atmosphere was less than three times the RMS noise level of the system. Completely evacuating the cell changed the radiation reaching the detectors by less than 1 part in 2000, and pressure changes of the size that could occur in flow-through operation could not produce any detectable offset.

With the multipass cell operating correctly, testing was resumed. Calibrations were made for all nine possible combinations of the hydrazines--in atmospheric pressure nitrogen, in the multipass cell, and in the instrument cell.

In each case, the instrument was filled to the 15°C vapor pressure of the hydrazine concerned and back-filled with prepurified nitrogen to 700 torr.

Tests with lower hydrazine concentrations in the instrument cell showed lower responsivities. Measurements of the  $S_1$  and  $S_2$  channels individually, at the 15°C vapor pressure, showed that the  $S_1$  responsivity was in all cases less than 20% of the  $S_2$  responsivity; i.e., the instrument  $(S_1 - S_2)/S_2$  responsivity could be increased only 2% at the most by achieving the optimum hydrazine concentration in the instrument cell.

Increasing the concentration would have required using heated cells to prevent condensation, and this complexity was not justified by the marginal increase in responsivity that it would achieve.

We found that the best S/N for  $N_2H_4$ , UDMH, and MMH was achieved with MMH in the instrument cell. The resulting calibration curves are shown in Figures 4, 5, and 6. The concentrations required to give S/N = 1 for a 1-second time constant are:

<u><math>N_2H_4</math></u>	<u>UDMH</u>	<u>MMH</u>
0.3 ppm	0.23 ppm	0.22 ppm

Use of a 10-second time constant will reduce these noise-equivalent concentrations by a factor of 3.

The system was then calibrated for  $NO_2$ , as shown in Figure 7. The dependence of responsivity on  $NO_2$  partial pressure in the instrument cell had a very broad optimum centered about 600 torr. The noise-equivalent concentrations for  $NO_2$  are 9 ppm for 1-second and 3 ppm for 10-second integration.

Replacing prepurified  $N_2$  in the multipass cell with laboratory air produced no detectable signal, indicating that the instrument does not respond to ambient concentrations of  $CO_2$ ,  $H_2O$ , or  $CH_4$ . Neither  $NO$  nor  $CO$  have any spectra within the filter passbands used for hydrazines or  $NO_2$ .

#### REQUIREMENTS FOR CONVERSION TO A REMOTE SENSOR

The instrument can be converted to a remote sensor by replacing the multipass cell with a telescope whose output f/# matches the f/1.7 input cone of the GASPEC optics.

The GASPEC sensor field stop is the 0.52-cm aperture located just behind the chopper disc (see Fig. 2). This aperture should also be made the field stop for the telescope, to ensure that the scene viewed by the telescope is not imaged to points in the GASPEC optics that have nonuniform spatial properties. The telescope effective focal length must then be chosen so that the 0.52-cm field stop dimension subtends the desired field of view.

The telescope components must have adequate transmittance (or reflectance, as appropriate) in the instrument passbands. Reflective optics coated with gold over inconel or chromium probably provide the simplest and least expensive solution.



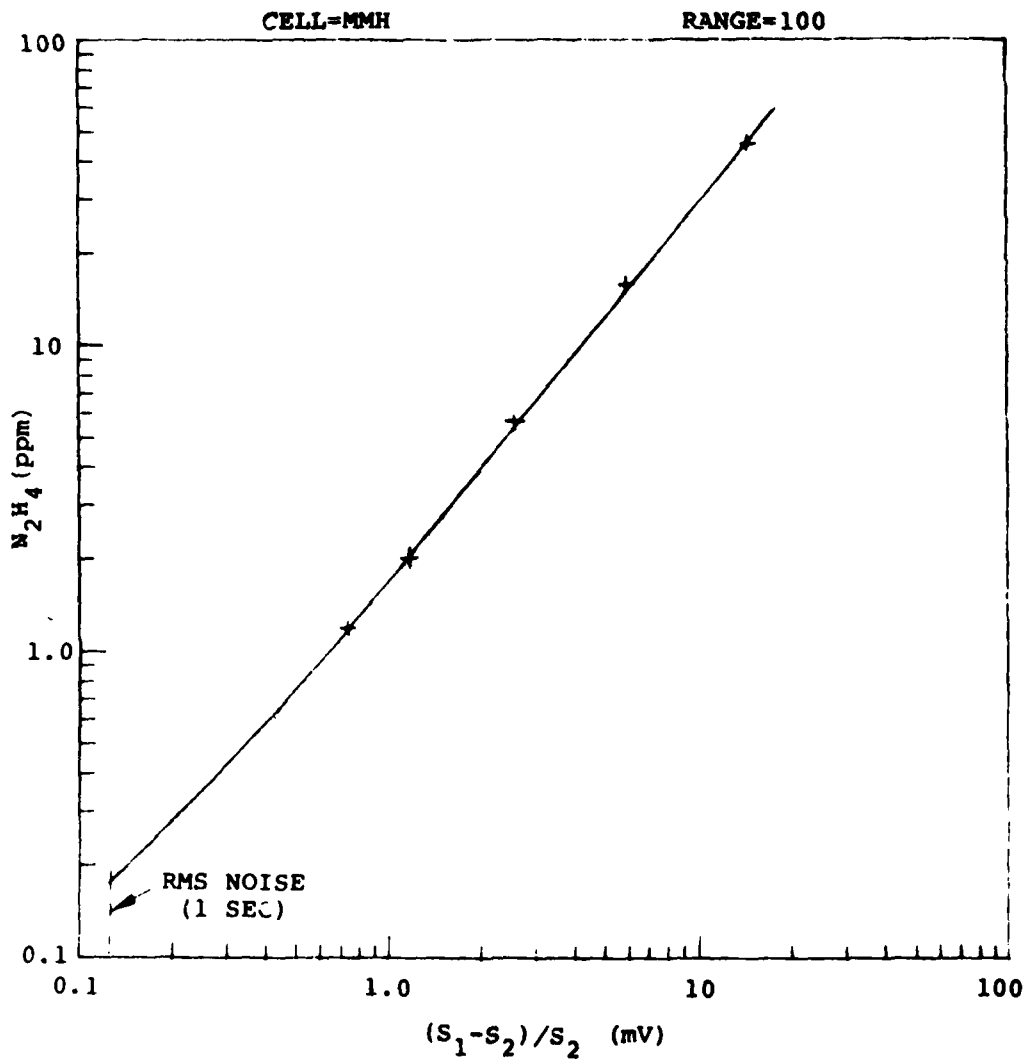


Figure 4. Instrument response to  $N_2H_4$ .

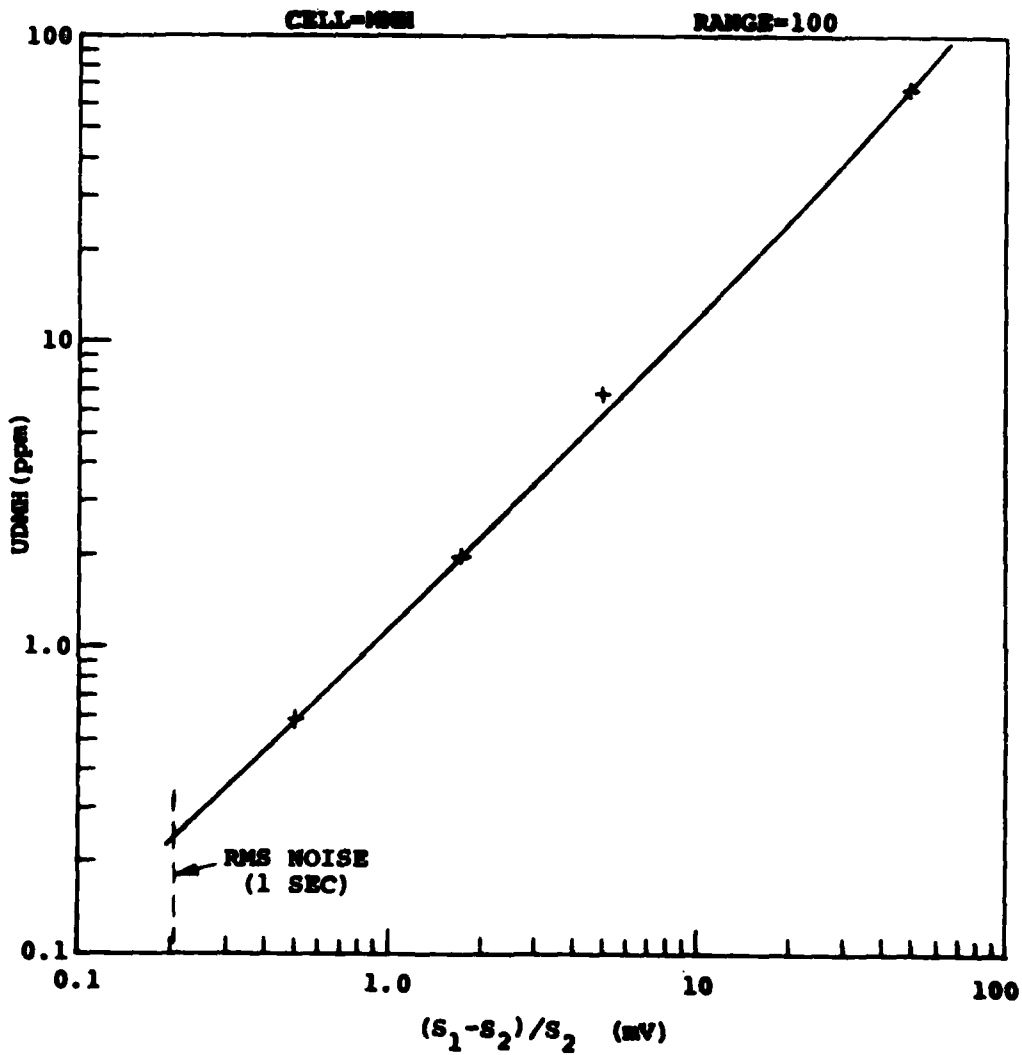


Figure 5. Instrument response to UDMH.

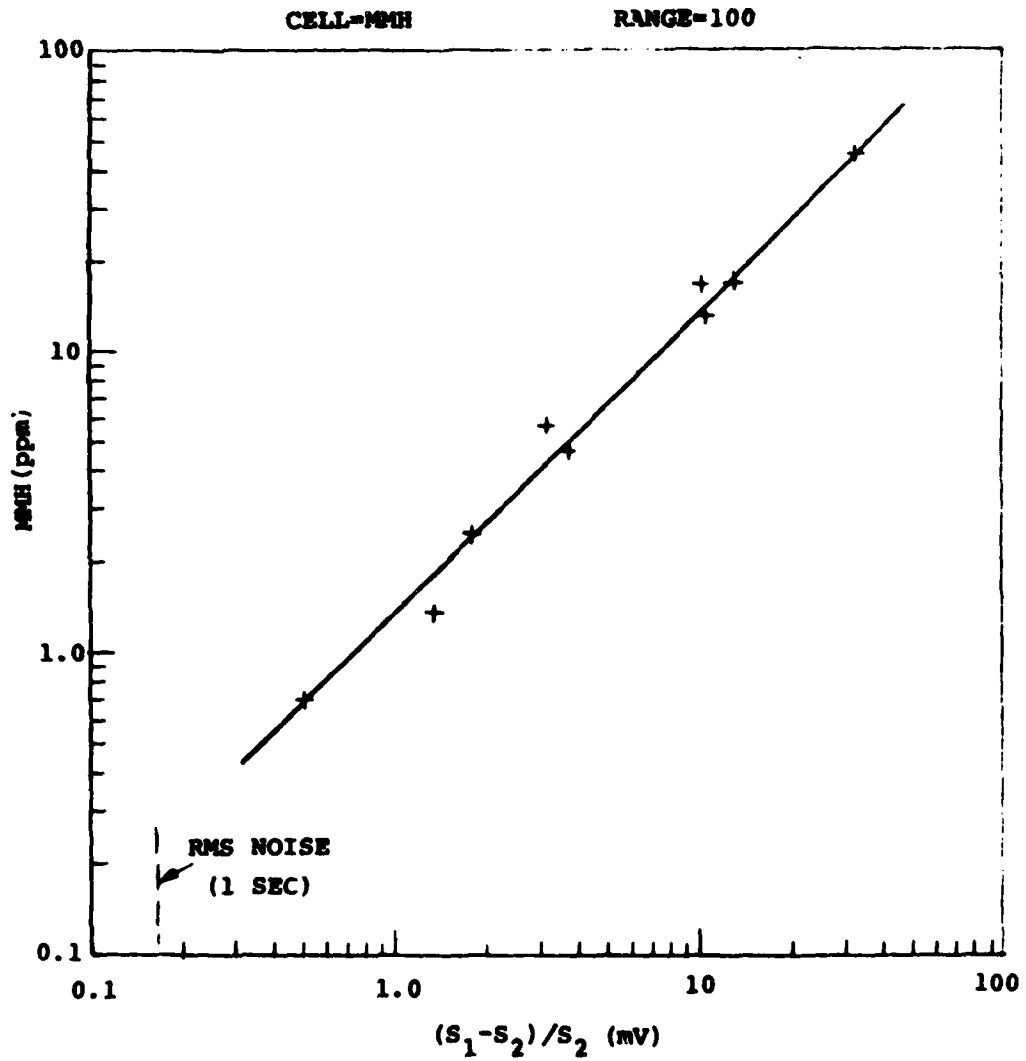


Figure 6. Instrument response to MMH.

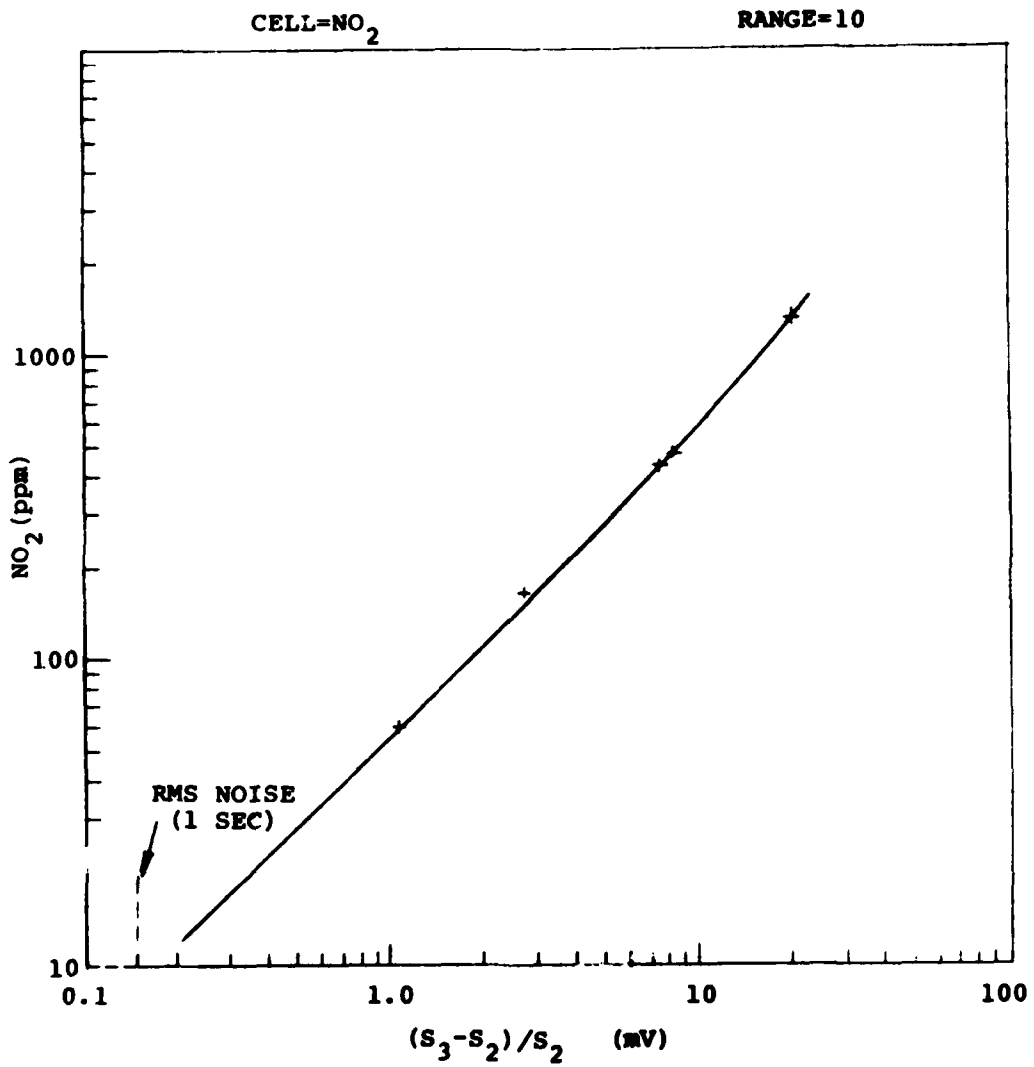


Figure 7. Instrument response to NO<sub>2</sub>.

When a telescope is fitted, the two mirrors that normally view the source over the top of the multipass cell should be removed, but the cover for this optical path should be retained.

The procedure for calibrating the system as a remote sensor will depend on the circumstances in which it is to be used, such as upward looking and downward looking.

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## APPENDIX A

### GASPEC INTERFERENCE FILTERS

Three interference filters are supplied with the GASPEC. The filter for the  $\text{NO}_2$  mode of operation has a quartz substrate and center wavelength of  $3.456 \mu\text{m}$ . The half bandwidth (HBW) is  $0.23 \mu\text{m}$ , and the peak transmission is about 70%.

Two germanium substrate filters are supplied for the hydrazines. One has a center wavelength of  $10.918 \mu\text{m}$  and a HBW of  $5.297 \mu\text{m}$ . The other has a center wavelength of  $12.143 \mu\text{m}$  and a HBW of  $2.8 \mu\text{m}$ . It is necessary to determine empirically which filter produces the best and most selective response to a particular target. In the tests described in this report, the wider filter was used exclusively.

Spectra of the three filters are given in Figures A-1, A-2, and A-3.

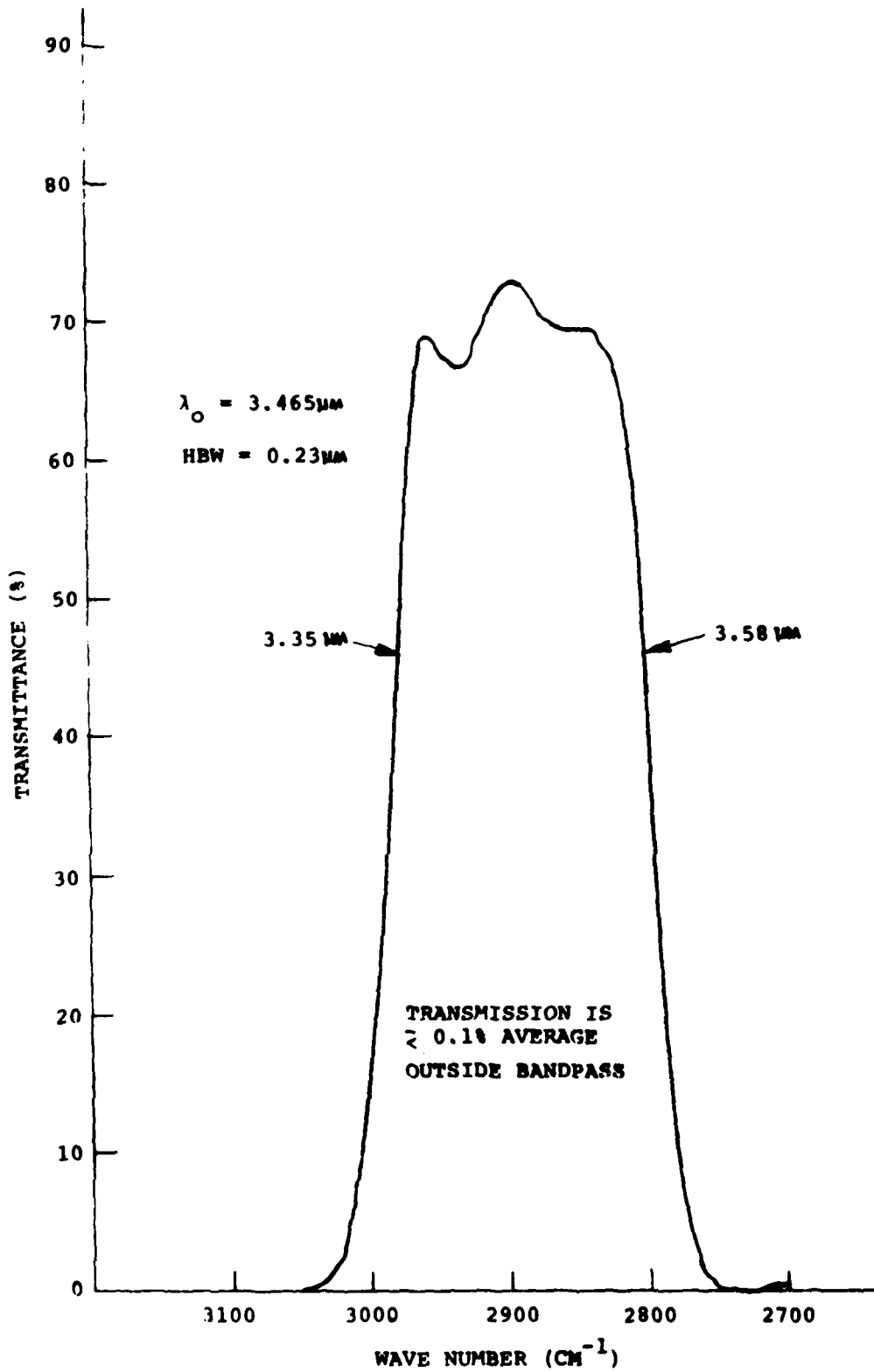


Figure A-1. Interference filter for NO<sub>2</sub> operation mode ( $\lambda_0 = 3.456 \mu\text{m}$ ; HBW = 0.23  $\mu\text{m}$ ).

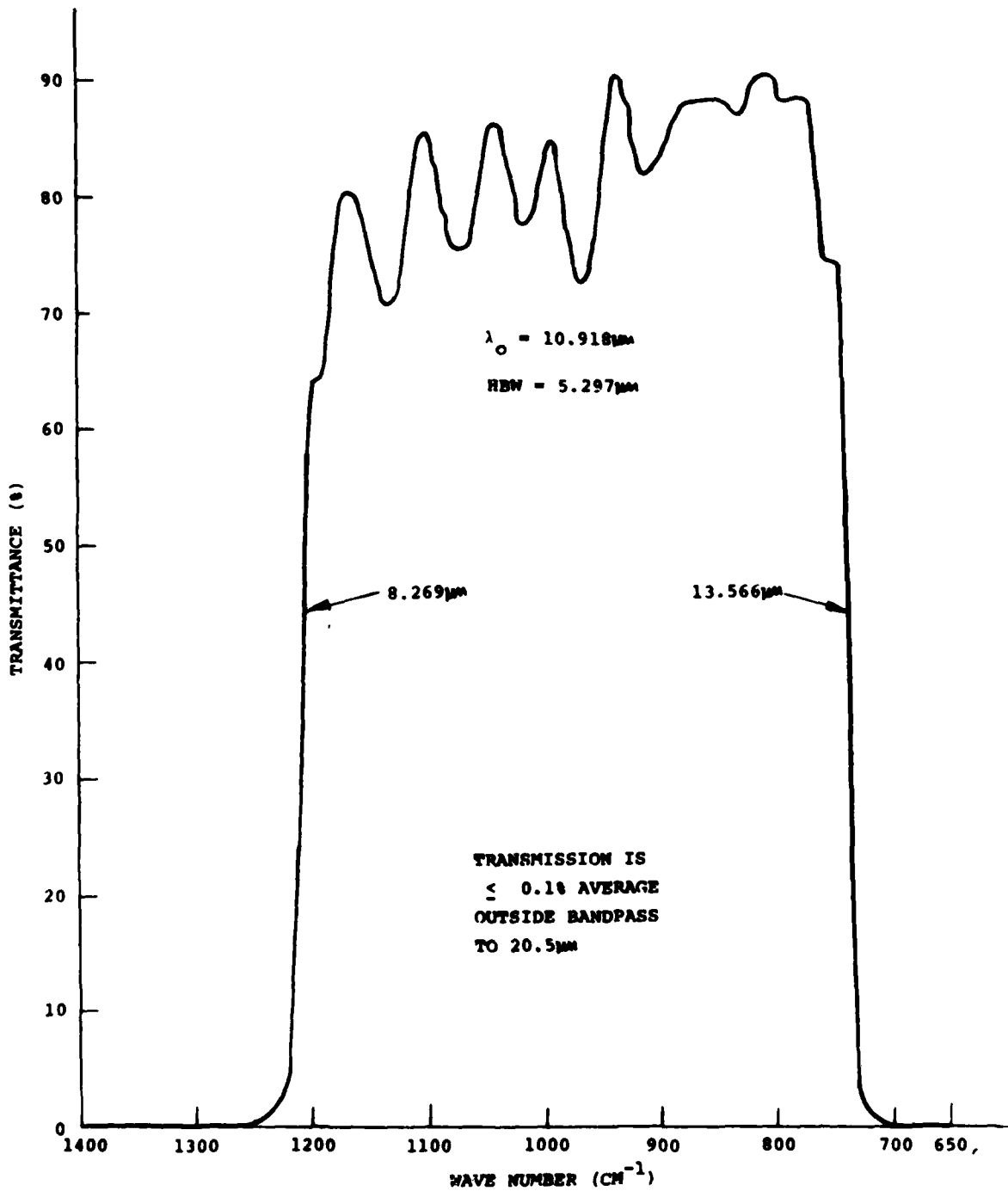


Figure A-2. Interference filter for hydrazines  
 ( $\lambda_0 = 10.918 \mu\text{m}$ ; HBW = 5.297  $\mu\text{m}$ ).



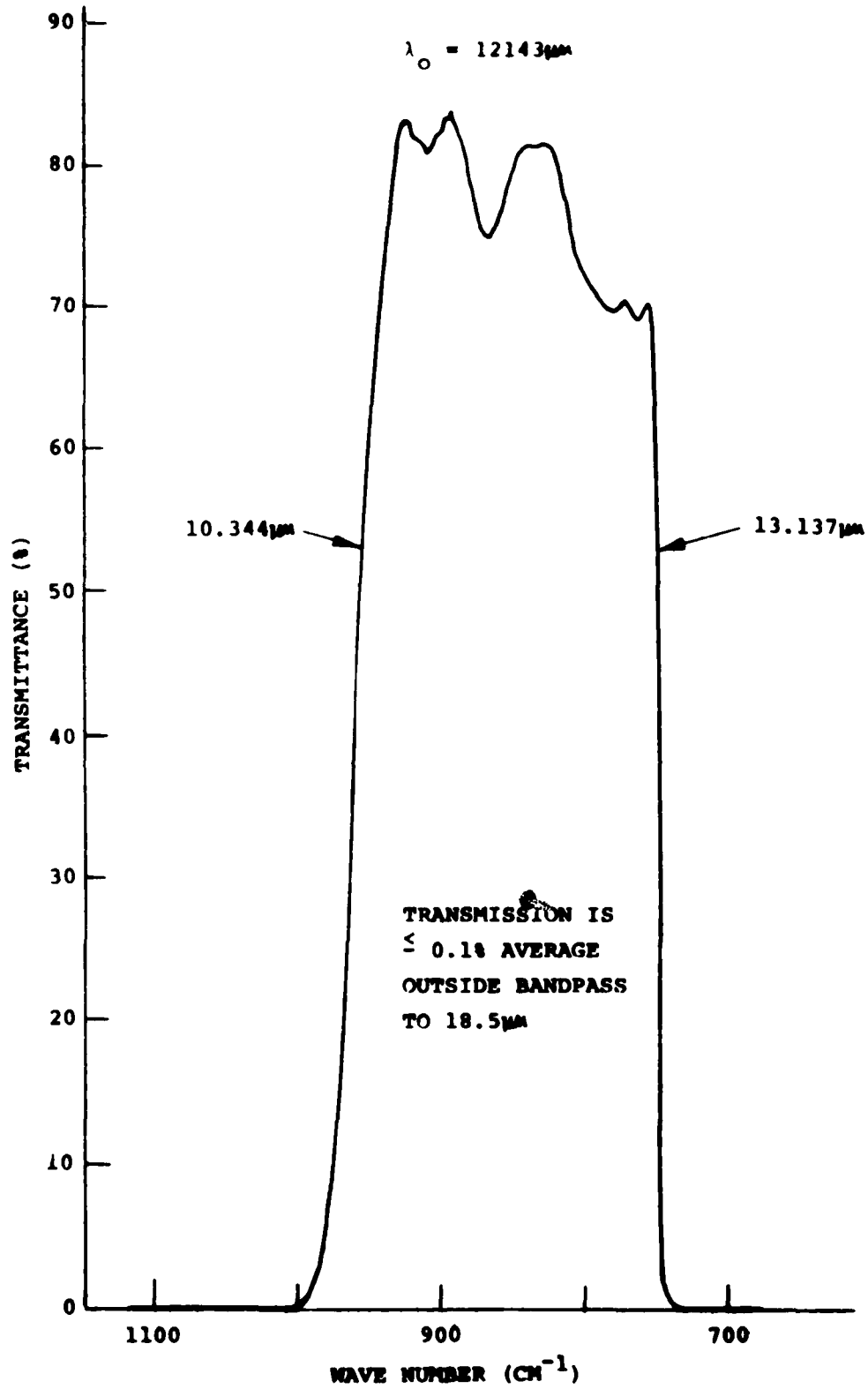


Figure A-3. Interference filter for hydrazines  
 ( $\lambda_0 = 12.143 \mu\text{m}$ ; HBW = 2.8  $\mu\text{m}$ ).

## LIST OF SYMBOLS

<u>Symbols</u>	<u>Definition</u>
$B(\nu)$	Plank radiance from source S at temperature $T_s$ at wavenumber $\nu$
T	Temperature
$\nu$	Wavenumber
$N(\nu)$	Radiance reaching sensor at wavenumber $\nu$
$\epsilon_s$	Spectral emissivity at wavenumber $\nu$
$T_r$	Transmittance of "atmosphere" between source and sensor
$t_o$	Spectrally constant part of the sensor optical transmission (including chopper efficiency)
$t_{ci}$	Normalized transmission through sample cell i
$I_\nu(s)$	Incoming source radiance
$A\Omega$	Sensor etendue
L	Path length
$F(\nu)$	Interference filter function
$S_i$	Source signal from channel i
$\Delta S$	Output signal ( $S_i - S_j$ ) $i \neq j$
$R_i$	Reference signal for channel i
$\rho_m$	Reflectivity of chopper disc
$\rho_{BSi}$	Reflectivity of beam splitter i
$N_{BRR}$	Radiance of reference blackbody
$N_s$	Source energy
$t_G$	Instrument sensitivity

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