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BREADBOARD CHEMILUMINESCENT ANALYZER FOR MEASUREMENT OF HYDRAZINES

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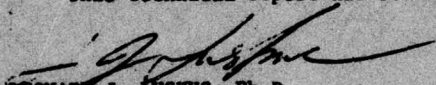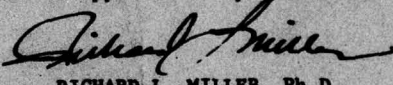Approved for public release; distribution unlimited.

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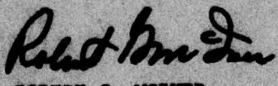
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This technical report has been reviewed and is approved for publication.

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An instrument was built that will measure concentrations of hydrazine, MMH, and UDMH in the range of 0.07 to 100 ppm and NO$_2$ in the range of 1 to 100 ppm. The performance of the instrument is described and test results are given.

REPORT DOCUMENTATION PAGE

BROADBAND CHEMILUMINESCENT ANALYZER FOR
MEASUREMENT OF HYDRAZINES

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BREADBOARD CHEMILUMINESCENT ANALYZER FOR
MEASUREMENT OF HYDRAZINES

INTRODUCTION

Monitoring airborne concentrations of the rocket propellants, monomethylhydrazine (MMH), 1,1-dimethylhydrazine (UDMH), hydrazine, and NO_2 (from N_2O_4), at launch and storage sites is necessary for safety and other factors. Preliminary studies at the Crew Environments Branch, USAF School of Aerospace Medicine, indicated that the hydrazines could be monitored by measuring the light output of their chemiluminescent reactions with ozone. In a resulting contract with USAF/Air Force Systems Command, Contract No. F41609-76-C-0029, these preliminary conclusions were confirmed and the necessary information obtained to design an instrument (5).

The objectives of the present contract were to design, construct and test an instrument that will measure the concentrations of these three hydrazines and NO_2. The design was to be based on the results of the feasibility study (5) and to result in an instrument that will meet the specifications given in "Results and Discussion."

The approach used was to build a functioning instrument and then to determine its operation as a function of the values of easily varied parameters such as pressure, temperature, etc. Since it has been established that certain deficiencies could be minimized at the expense of other desirable features (e.g., H_2O interference vs. sensitivity), knowing the behavior of the instrument as a function of conditions would permit the selection of those conditions that achieve the best performance for a given application.

For NO_2 (NO) measurements, the relative response of the instrument can be accurately calculated from the known rate constants of the NO/O_3 reactions, and the conditions under which the measurements are made. These calculations are presented in "Background."

Since the reaction mechanisms of the hydrazine(s) ozone systems are not known, the response of the instrument toward the hydrazines could not be accurately calculated and was therefore measured under a variety of conditions. These measurements are presented in "Results and Discussion."

The basic design outline of the instrument was established in the feasibility study (5). This was further developed prior to the start of construction and modified under testing. The final design is presented in "Experimental Procedure." A more detailed set of drawings including electronic schematics is given in the manual (6) for the instrument.

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BACKGROUND

Measurements of the three hydrazines rely on monitoring the light output of their direct chemiluminescent reactions with ozone. NO_2 is measured by its reduction to NO in a high temperature catalytic converter followed by monitoring the light output of the NO/ozone reaction. The NO/ozone reaction can follow two paths (2).

$$NO + O_3 \xrightarrow{k_1} NO_2^* + O_2 \tag{1}$$

$$NO + O_3 \xrightarrow{k_2} NO_2 + O_2 \tag{2}$$

where $k_1 = 7.6 \times 10^8 \exp(-4180/RT)$ and $k_2 = 4.3 \times 10^8 \exp(-2330/RT)$ ℓ mole^{-1} sec^{-1}.

The excited NO_2 can then either emit

$$NO_2^* \rightarrow NO_2 + h\nu \tag{3}$$
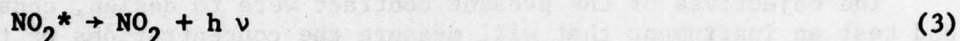
or it can be deactivated by collisions with other molecules

$$NO_2^* + M \rightarrow NO_2 + M \tag{4}$$
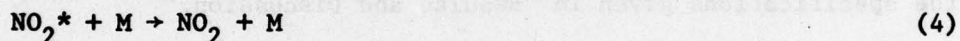
At pressures above a few Torr the light intensity, I, resulting from these reactions is (2)

$$I = k_1 a_t b_t/P \tag{5}$$

where

k_1 = rate constant for Reaction (1)
a_t = ozone concentration
b_t = NO concentration
P = pressure

For a given geometry, reactor, and gas flow rate, the extent of the reaction occurring in front of the photomultiplier tube (PMT) determines the sensitivity of the instrument.

By integrating the second-order rate equation (1) it can be shown that for a flow tube reactor (used in this instrument), the extent of the reaction occurring in time t is given by

$$\frac{x}{b} = \frac{e^{akt(1 - (b/a))} - 1}{e^{akt(1 - (b/a))} - (b/a)} \tag{6}$$

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where x is the concentration of NO that has reacted in time t, b is the initial NO concentration and a is the ozone (O_3) concentration; k is the effective rate constant for the reaction. For small values of b relative to a, the expression reduces to

$$\frac{x}{b} = 1 - e^{-akt} \tag{7}$$

Sensitivity, in addition to its relationship to the extent of the reaction occurring in view of the PMT, will also be a function of the pressure in the reactor (equation 5), the flow rate, and a geometric factor relating to the configuration of the reactor and its separation from the PMT.

For the instrument considered here, the pressure, P, is related to the volume flow rate, Q, by $P = P_o + cQ$, where $P_o \simeq 150$ Torr, is the minimum pressure attainable with the pump used and c is a constant. In terms of the volume, V, of the reactor, the reactant flow rate, Q_b, and the second reactant flow rate, Q_a, the quantities a and t of equation 7 become

$$a = a' \frac{Q_a}{Q_b} \frac{P_o + cQ}{760} \qquad\qquad t = \frac{V}{Q} \frac{P_o + cQ}{760}$$

and the sensitivity, S (PMT current per unit NO concentration) becomes

$$S \propto \frac{k_1}{k_1 + k_2} \frac{GQ_b}{P_o + cQ} [(1 - e(-a'VQ_ak(P_o + cQ)^2/Q^2)] \tag{8}$$

where G is the geometric factor, a' is the ozone concentration at the ozonator and $k_1/(k_1 + k_2)$ is the fraction of the reaction going through the excited state of NO_2. Since the reactor volume (approximately 10 ml) was chosen to allow a large fraction of the slow hydrazines/O_3 reaction to take place in view of the PMT, all of the relatively fast NO/O_3 reaction will take place in this volume for all reasonable conditions. This results in a large akt (> 10) and a sensitivity related only to the term preceding the brackets in equation 8, i.e., $1 - e^{-10} \simeq 1$.

For the hydrazine ozone reactions, the light intensity is also a function of the ozone and hydrazine concentrations, the pressure, temperature, and reactor geometry, but the functional relationship is not known. Since the behavior of the instrument cannot be adequately predicted mathematically as a function of operating conditions, it has been determined experimentally for a limited number of variables. The results of these tests are presented in "Results and Discussion."

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EXPERIMENTAL PROCEDURE

The basic functions of the breadboard instrument are shown schematically in Figure 1. This instrument is very similar to an NO/NO_x analyzer (3) and is in fact designed to measure both NO (assumed absent in sample) and NO_x. It does, however, require a higher reactor temperature both to enhance the reaction rate and to prevent products of the hydrazine ozone reaction from precipitating out on the reactor walls; it uses a scrubber to remove hydrazines and amines in the NO_2 measuring mode.

Referring to Figure 1, the air (analyte) being monitored is drawn into the instrument at approximately 19 ml(STP) sec^{-1}, 6 ml of which is treated as sample while the remaining 13 ml is scrubbed in an activated alumina trap to remove H_2O, amines, and hydrazines before passing through a discharge ozonator and into the ozone inlet of the reactor. Depending on the measuring mode, the 6 ml sec^{-1} sample is either passed directly into the sample inlet of the reactor for the measurement of hydrazines or through a phosphoric acid scrubber and NO_x converter prior to entering the reactor for NO_x measurement.

Very rough kinetic measurements (5) indicated that at $80^{\circ}C$ a 20-ml-reactor volume would be required to achieve complete reaction of the hydrazines. Because of the erratic behavior we experienced early in the feasibility study with the standard aluminum reactor and the stainless steel tubing used in our NO/NO_x analyzers, it was decided to make the reactor for this instrument out of Pyrex. To achieve good mixing and to have the initial reaction occur in the center of the PMT, a 7-mm-o.d. (5-mm-i.d.) flow tube curled into a spiral was chosen for the reactor geometry. The largest practical volume achievable with this design is about 10 ml. Heating of the reactor tube was accomplished by winding 0.13-mm (5-mil) platinum along the length of the spiral.

Initially the hydrazines were to be mixed with the ozone approximately 4 ml upstream of the reactor entrance to allow any NO in the sample test to react with the ozone prior to entering the reactor and thus not be detected (the instrument was expected to have higher sensitivity to NO than to the hydrazines, which would possibly result in ambient NO levels causing significant interference in the hydrazine mode). Because of the background problem outlined in "Results and Discussion," this was not done; instead both NO and the hydrazines flow into the same reactor inlet and the other inlet is used for ozone.

Sonic orifices control both sample and ozone flow. The operating pressure of the instrument is about 220 Torr.

The detection system consists of a 5-cm-diameter trialkali PMT (Centronics 4283) and an electrometer type amplifier. Zeroing and calibration potentiometers are provided for independent adjustment of the three hydrazines and the NO_2 measurements.

Results of the feasibility study (5) indicated that the response of the instrument would not change linearly with concentration (response = (concentration)$^{0.7}$). A circuit to linearize the response was therefore incorporated into the detection system, but not used because the feasibility study results proved to be erroneous.

RESULTS AND DISCUSSION

During the initial testing of this instrument many qualitative observations were made on which instrument modifications were based. These modifications in turn were followed by more tests. For example, when a background problem was discovered, a major effort was undertaken to eliminate or reduce it. There were essentially three phases in the background investigation. During the first phase, the background was equivalent to approximately 20 ppm MMH with test results obtained under those conditions not reported here. In the second phase the background was reduced by approximately a factor of 10 and sensitivity tests run as a function of conditions (see Figs. 2-6 and the following discussion). Prior to performing the interference tests, it was discovered that an additional reduction by a factor of 2 could be achieved by a higher reactor temperature; during the water interference tests, the sample flow was increased by a factor of 3 resulting in a like decrease in the background. All interference tests were performed at the higher sample flow rate and the higher reactor temperature.

Testing can be divided into the following four main categories: (1) investigation of background; (2) sensitivity towards the hydrazines as a function of conditions; (3) linearity; and (4) interferences. These will also be discussed.

Investigation of Background

In our first attempt at determining the linearity of the instrument, we discovered a residual signal which persisted indefinitely in the absence of sample once the reactor was exposed to a hydrazine. Apparently the reactor is coated with a transparent film, which, in the presence of ozone, gives off light. Measurements of this background, relative to a given concentration sample, showed that it could be reduced by the proper choice of reactor temperature, ozone concentration and optical filtering. A rather severe reduction in sensitivity (PMT current per unit concentration) resulted from minimizing the background with a decrease in the lowest detectable concentration as well as the stability of the instrument.

Use of filters to reduce the background relative to signal due to sample was investigated using only MMH and NO as samples. Since the MMH spectral output is in the 400-600 nm region, only blue filters (blocking the red) were tried.

Three filters were used. In each case the signal due to an arbitrary fixed MMH concentration was measured as was the signal due to an NO concentration and the background. The results are:

Filter used	MMH signal	MMH signal/ background	NO signal	NO signal/ background	Background signal
None	24	4.8	1500	300	5.0
Corning 4-74	12.2	13.6	22	24	0.9
Corning 4-72	10.5	12.1	9	10	0.87
Corning 5-56	8.5	2.7	550	18	3.0

The Corning 4-72 filter was selected for the instrument because of its greater reduction of the NO signal. This is important because the inherent higher sensitivity of the instrument toward NO would, without the use of the filter, cause a positive NO interference even for ambient NO levels. Our attempt to premix the hydrazine-containing sample with the ozone stream approximately 4 ml upstream of the reactor to eliminate the NO interference was abandoned, because mixing at the lower temperature prevailing outside the reactor (the fittings used on the reactor limit the temperature of the external lines) aggravated the background problem.

The effect of temperature and ozone concentration on the background signal was investigated. The results are shown in Figure 2, which also shows the dark current of the PMT as a function of reactor temperature. The variation of ozone concentration in the reactor as a function of ozonator voltage is shown in Figure 3. Flow rate and reactor pressure had little effect on these measurements.

Measurements were not made above a reactor temperature of $120^{\circ}C$ because the background rose more rapidly at that temperature than did the response towards MMH. The background signals measured in Figure 2 (amounting to about 2 ppm relative to MMH measurements) resulted from operating the reactor between $80^{\circ}C$ and $120^{\circ}C$. When the reactor was cleaned and operated at $150^{\circ}C$, a smaller but also stable background signal resulted which was only 0.1 ppm relative to the MMH measuring mode.

Sensitivity Toward The Hydrazines As A Function of Conditions

The varied parameters were: reactor temperature and pressure, and ozone flow rate and concentration. The results of these tests are displayed in Figures 4-6 which show the relative sensitivity toward hydrazine, MMH, and UDMH, respectively, as a function of ozone concentration (2) at three temperatures and ozone flow rates of 20 ml(STP)sec^{-1} and 13 ml(STP)sec^{-1}. At an $80^{\circ}C$ reactor temperature, hydrazine shows only a small erratic response (these measurements are not given in Figure 4 because of their limited usefulness). The sample flow rate in

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all these cases is approximately 2 ml(STP)sec^{-1}. The effect of changing the sample flow rate will be, to a first approximation, to obtain a like change in signal. This was not measured quantitatively.

The effect of pressure changes is small for all three hydrazines—less than 1/2% per 1% pressure change.

The above tests were not carried out with NO since the results are accurately predictable using the equations presented in "Background."

From the results presented in Figures 2 and 4-6, the operating conditions that maximize sensitivity (ratio of signal-to-background) would appear to be an intermediate temperature and a low ozone concentration. Since the slope of signal vs. ozone concentration (related to ozonator voltage, see Figure 3) at low ozone concentrations is greater for the background than for signals due to hydrazine, the ratio of hydrazine signal to background signal increases as ozone concentration decreases. The PMT dark current also contributes to the signal and would limit the extent to which ozone concentration could be lowered. Since operating the reactor at 150°C appears to prevent a large background from forming (it is about 1/8 as large as the dark current at an ozonator voltage of 120 V) a 150°C reactor temperature was chosen together with 120 V ozonator voltage, 13 ml (STP)sec^{-1} ozone flow rate and 6 ml(STP)sec^{-1} sample flow rate as operating conditions.

Linearity

Tests performed in the feasibility study indicated that the light emitted from the reactions of all three hydrazines with ozone was proportional to the concentration of the hydrazines raised to the 0.7 power (p = 0.7). The first linearity tests performed with the finished instrument, using an exponential dilution flask, indicated an exponent between 0.5 and 1.0 which changed with concentration and reactor pressure. This unexpected behavior was thought to be at least in part the result of the background, and to be incorrect due to unknown experimental problems.

A more systematic study showed two causes for the difficulty in making linearity measurements. One results from the ease with which the three hydrazines (especially hydrazine itself) adsorb on the walls of the dilution flask and associated tubing. The other cause appears to be a background-related memory effect.

At 120°C reactor temperature the apparent non-linearity for MMH and UDMH as determined from the slope of the exponential dilution curve corresponds to a p of 0.8 to 0.9. When the reactor temperature is raised to 140°C, p approaches 1 (between 0.95 and 1) for all three hydrazines. Apparently the entrance of the reactor is at a somewhat lower temperature than the average reactor temperature because the

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sample lines are cooler than the reactor. This lower temperature may result in a memory effect which makes the slope of the dilution curve smaller than it would otherwise be. The effect is nearly eliminated at the higher reactor temperature.

At both $120°$ and $140°C$ reactor temperatures, the slopes of the log (p) of the dilution curves decrease as the concentrations decrease. If, however, initial maximum readings are measured as a function of the amount of injected sample, the readings increase faster than the size of the samples, indicating an exponent greater than 1.

These results are assumed to be due to a given amount of the hydrazine adsorbing on the walls of the dilution flask during the time the sample is allowed to evaporate and, as the concentration drops while sampling, coming off the walls. Assuming simple adsorption theory applies and the system is at equilibrium, there are two terms affecting the concentration, C, in a flask of volume, V, with flow rate Q through it

$$\Delta C = -k_1 C \Delta t + k_2 \Delta \theta \tag{9}$$

where

$k_1 = \dfrac{Q}{V}$

k_2 = constant related to internal area of flask

$\Delta \theta$ = fraction of surface of flask becoming uncovered as a result of decrease of concentration in flask

From the Langmuir adsorption isotherm (4)

$$\Delta \theta = \frac{\theta}{C} (1 - \theta) \Delta C \tag{10}$$

Using only the first term of equation 9 (valid since the second term is a small correction) to determine $\Delta \theta$, equation 9 gives an exponential dilution decay with a variable decay constant k'

$$k' = \frac{Q}{V} \left(1 - \frac{k_2 b}{(1 + bC)2} \right) \tag{11}$$

where b is the adsorption coefficient. This expression agrees qualitatively with experimental results.

Since the slope of the dilution plot predicts signal $\propto$ (concentration)^p with p < 1, and the maximum readings vs. sample size and measurements predict p > 1, the true value of p must be somewhere between these values and is very likely equal to 1, especially since at $140°C$ p is greater than 0.95. In addition, after a minimum amount of sample is injected into the dilution flask, increases in injected sample size result in corresponding increases in maximum signal, thus also indicating linearity.

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The major consequence of this result is a considerable decrease in sensitivity over that predicted based on p = 0.7 since the predicted sensitivity was calculated from a measurement at 200 ppm. For a value of p = 0.7, a concentration of 0.2 ppm would result in a signal only 125 times less than that due to a 200 ppm concentration, i.e., a factor of eight greater than is the case for a linear system (p = 1). To achieve a 0.2 ppm sensitivity it therefore becomes necessary to increase the sample flow rate and thus to increase the negative water interference. This can in principle be corrected for, however, since the extent of the water interference is known (see "Interferences"). Instead of the 20 to 1 ratio of ozone to sample flow rate suggested in the feasibility study a 13 to 6 ratio is used in the instrument.

Interferences

The response of the instrument toward other substances was measured under the following conditions:

Reactor temperature: 150°C
Reactor pressure : 220 Torr
Ozone flow : 23 ml(STP)sec^{-1}
Sample flow : 6 ml(STP)sec^{-1} (note this is higher than for the data of Figs. 2-6)
Ozone concentration: 0.2% at the reactor

The measurements obtained are presented in Table 1 relative to an MMH calibration.

TABLE 1. INTERFERENCES

Interferent	Extent of Interference (% of response in MMH[a] Mode)
Ethylamine	3.7
Diethylamine	3.4
tert-Butylamine	4.7
Propylamine	5.8
Analine	20.8
NO	10.4

[a]For UDMH multiply by 1.4; for hydrazine divide by 2.7.

The water interference is -2%/% water for UDMH, -4%/% water for MMH and -8%/% water for hydrazine. The higher sample flow (6 ml sec^{-1}) was chosen for these measurements because at 2 ml sec^{-1} the interference was less than -1%/% water for MMH with a signal enhanced by a factor of three by the increased sample flow. The lower than expected water interference is probably due in part to discrimination against the red

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emission which showed a much larger water interference in the feasibility study.

NO_x Converter Efficiency

By the proper choice of operating voltage, the NO_x converter efficiency has been set to 96%.

Specifications

Table 2 shows a comparison between the desired specifications (4) and those measured.

The dark current and background are 1.0 and 0.12 ppm, respectively, relative to MMH.

Reliability

The instrument described above was in continuous operation for 4 months (24-hr. days, 7 days a week). The only failure that occurred during that time was the burning out of a transformer which resulted from the accidental shorting of two wires during testing.

Intervals between normal maintenance are predicted to be about a week for the dryer and scrubber. Operating without a sample filter did not require cleaning of the sample orifice during the last 3 months of operation. The reactor required cleaning once after many high concentration (200-300 ppm) measurements of the hydrazines and amines equivalent to at least 10,000 ppm hrs. including measurements at 90°C.

It is suggested that significantly higher background readings than given above indicate the reactor requires cleaning.

Sampling Sources

Samples were prepared in one of two ways. Continuous samples of the hydrazines were obtained (5) by placing the liquid in a test tube equipped with a side arm and immersing the tube in a constant temperature bath (adjustable from -4° to 50°C). A low flow rate (less than 1 ml sec^{-1}) of N_2 was passed into the test tube through a 3-mm-o.d. Teflon tube extending to within a few centimeters of the liquid surface. The N_2 coming from the side arm of the test tube contained the hydrazine at a concentration which depended on the temperature of the liquid, the distance of the N_2 inlet tube from the liquid surface, and the N_2 flow rate. The N_2/hydrazine mixture was diluted with air and supplied to the instrument.

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TABLE 2. SPECIFICATIONS OF HYDRAZINES/NO_2 ANALYZER

Measurement	Design goal	Achieved
Contaminants	Hydrazine, MMH, UDMH, NO_2	Same
Range	Hydrazine: 0-1, 0-10 0-100 ppm	Hydrazines: 0-1, 0-2.5, 0-10, 0-25, 0-100
	NO_2: 0-10, 0-100 ppm	NO_2: 0-10, 0-25, 0-100
Linearity	1% (full scale)	Same (see "Linearity" section)
Accuracy	± 10%	Same
Span drift	1% per day	± 5% (accuracy of preparing samples)
Sensitivity	Hydrazines: 0.2 ppm	Hydrazine[a]: 0.015 ppm
	NO_2: 5 ppm	MMH[a]: 0.04 ppm
		UDMH[a]: 0.07 ppm
		NO_2: 0.35 ppm
Noise	0.5% (full scale)	<0.5% of 10 ppm scale
Response	10 seconds (show) 60 seconds (90%)	Selectable 3, 10 and 30 sec for 95%
Specificity	Hydrazines, NO_2	Same
Environmental stability	$-20°$ to $150°F$ (40 to $100°F$)	$40°$ to $100°F$
Size	1 ft^3 (0.028 m^3) (2.5 ft^3)[b] (0.07 m^3)	2.5 ft^3 (0.07 m^3)
Weight	30 lb (13.6 kg) (100 lb)[b] (45 kg)	75 lb (34 kg)
Readout/ control features	Meter readout Recorder output Flashing light alarm with manual set override	Same
Calibration	External zero and span calibration controls	Same
False alarm	Negligible	(see interferences above)

[a]Twice peak-to-peak noise.
[b]Relaxed goals.

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To calibrate the instrument and carry out the linearity tests, the well-known exponential dilution flask technique was used. Samples were obtained by injecting a known amount of a liquid or pure gas into a well-stirred and heated ($40^{\circ}C$) Pyrex flask of known volume (2ℓ). Sampling from one inlet of this vessel while supplying air to another results in an exponential decrease of concentration with time. The exponential dilution flask was calibrated by injecting pure NO and comparing the response against a continuous standard NO sample. For the linearity tests, the slopes of the recordings of the log (signal) vs. time for the hydrazines were compared to the slope for NO samples (run in both air and N_2 to exclude errors due to NO oxidation in air). The linearity of the instrument towards NO was determined by comparing it against a commercial NO/NO_x analyzer whose linearity had been established previously.

CONCLUSIONS AND RECOMMENDATIONS

From the results of our tests it is apparent that some simplification of the instrument is possible. Since the response toward the hydrazines is a much weaker function of pressure than anticipated, there is little need for a pressure gauge. The linearization circuit and dual range switch can also be eliminated. To make the instrument more rugged, an aluminum reactor should be evaluated. The aluminum reactor was found to be unacceptable at low temperatures; a high temperature test was not made.

Because it was possible to reduce the background to approximately 0.1 ppm the optical filter used may not be necessary. Its elimination would yield a factor of 3 increase in signal and a factor of 6 increase in background (to about 0.2 ppm). The NO (and NO_x) sensitivity would go up by a factor of about 150 and possibly become a real interference in the hydrazines measuring modes. The reactor inlet design of the feasibility study (5) would eliminate this problem. Higher reactor temperatures may yield additional sensitivity although as is the case with the elimination of the optical filter, interferences should be rechecked.

To reduce the higher water interference for hydrazine, some of the extra sensitivity available in its measurement could be sacrificed, i.e., by having a different (smaller) sample flow rate for hydrazine measurement than for MMH and UDMH measurement.

If a smaller instrument is desired, sensitivity and probably stability must be sacrificed. A smaller and lighter pump would mean lower flow rates and higher pressures, both reducing the sensitivity. At the expense of a larger water interference, only the ozone flow rate could be reduced. This would yield an increase in sensitivity comparable to the decrease resulting from the pressure increase. No specific pump is considered here but a pressure of about 400 Torr is assumed. The signal loss because of the smaller reactor and PMT will be approximately proportional to the decrease in PMT area, i.e., a factor of four.

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Since a sensitivity higher than expected was realized and prospects are good for further increases, a portable instrument with the original specifications appears to be a reasonable goal, but would require further study.

To minimize power requirements in a miniature instrument, a low temperature chemical converter could be used for NO_2 to NO conversion (7).
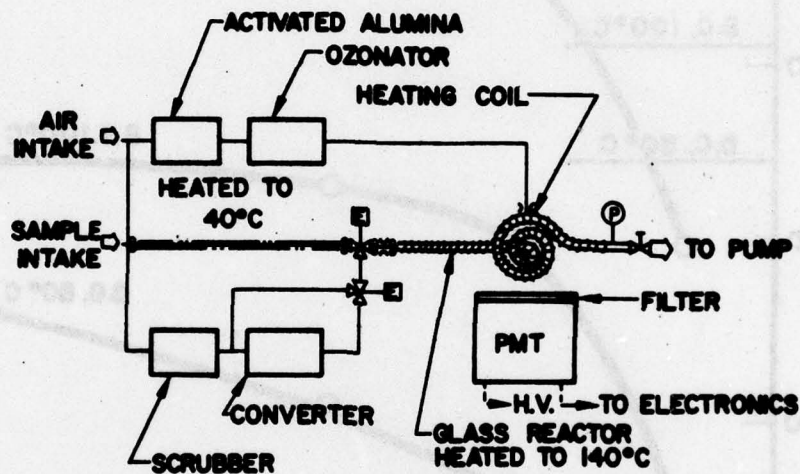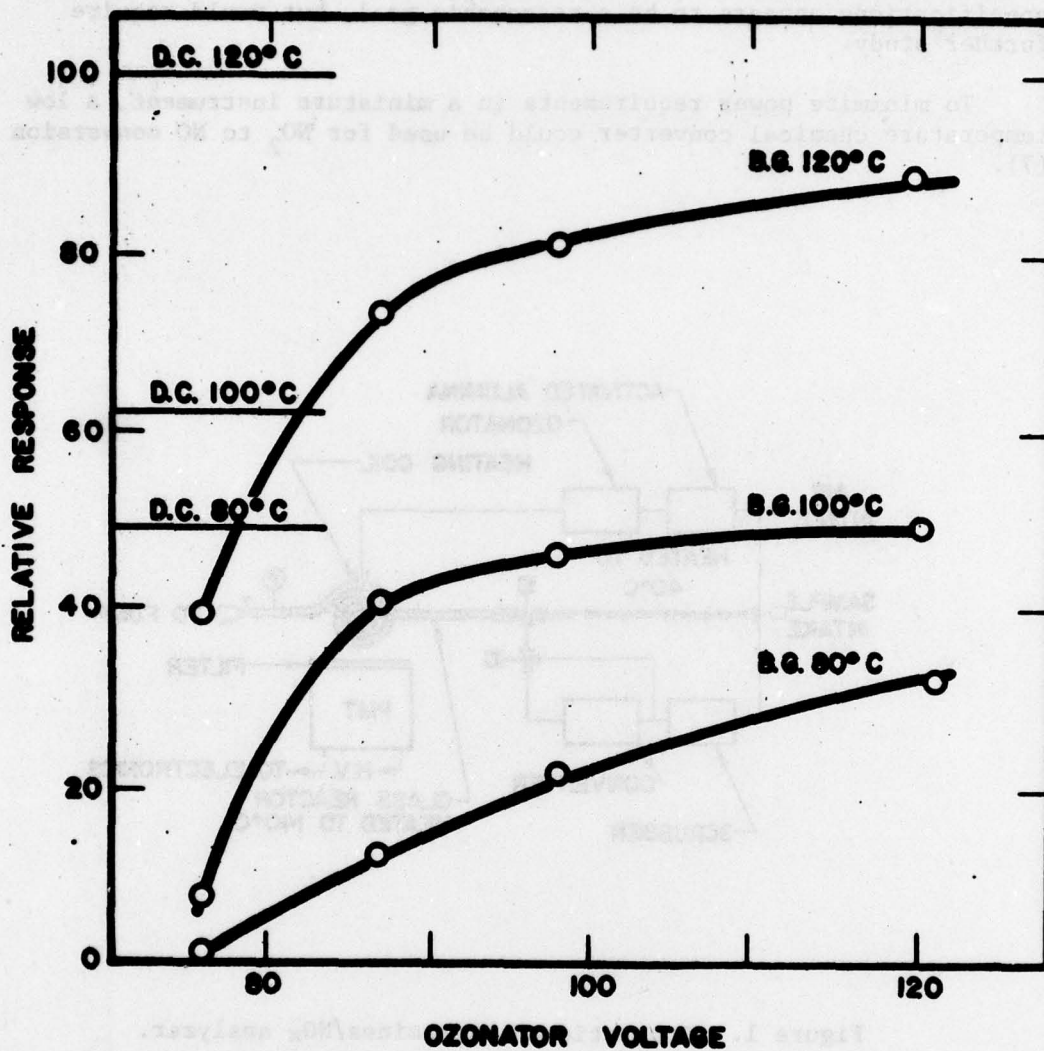
Figure 1. Schematic of hydrazines/NO_x analyzer.

Figure 2. Background (B.G.) and dark current (D.C.).
Ozone flow: 13 ml(STP)sec^{-1}; Sample flow:
2 ml(STP)sec^{-1}; Reactor temperatures as
indicated.

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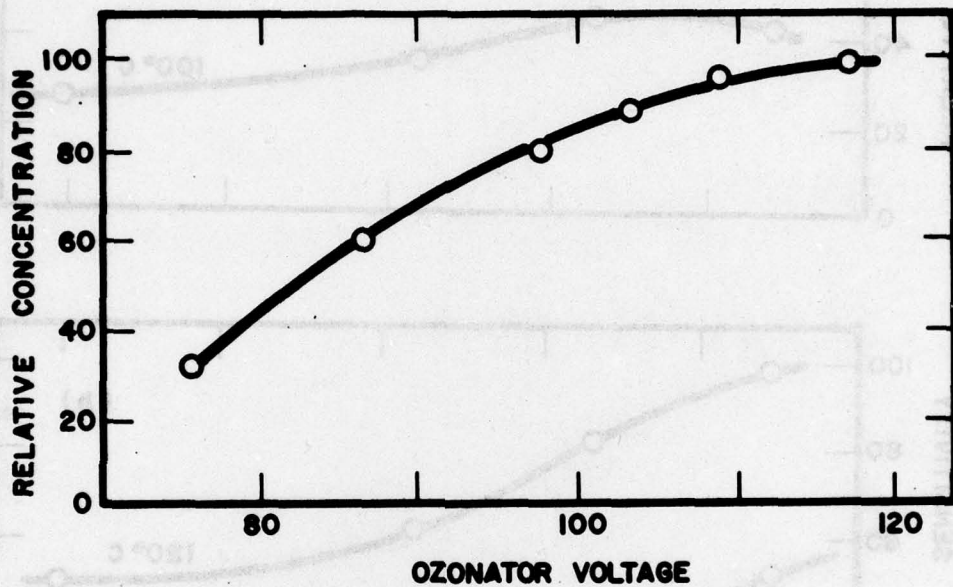**Figure 3.** Relative ozone concentration at reactor. 100 corresponds to ≈ 0.2%. Ozone flow: 20 ml(STP)sec^{-1}; Sample flow: 2 ml(STP)sec^{-1}.
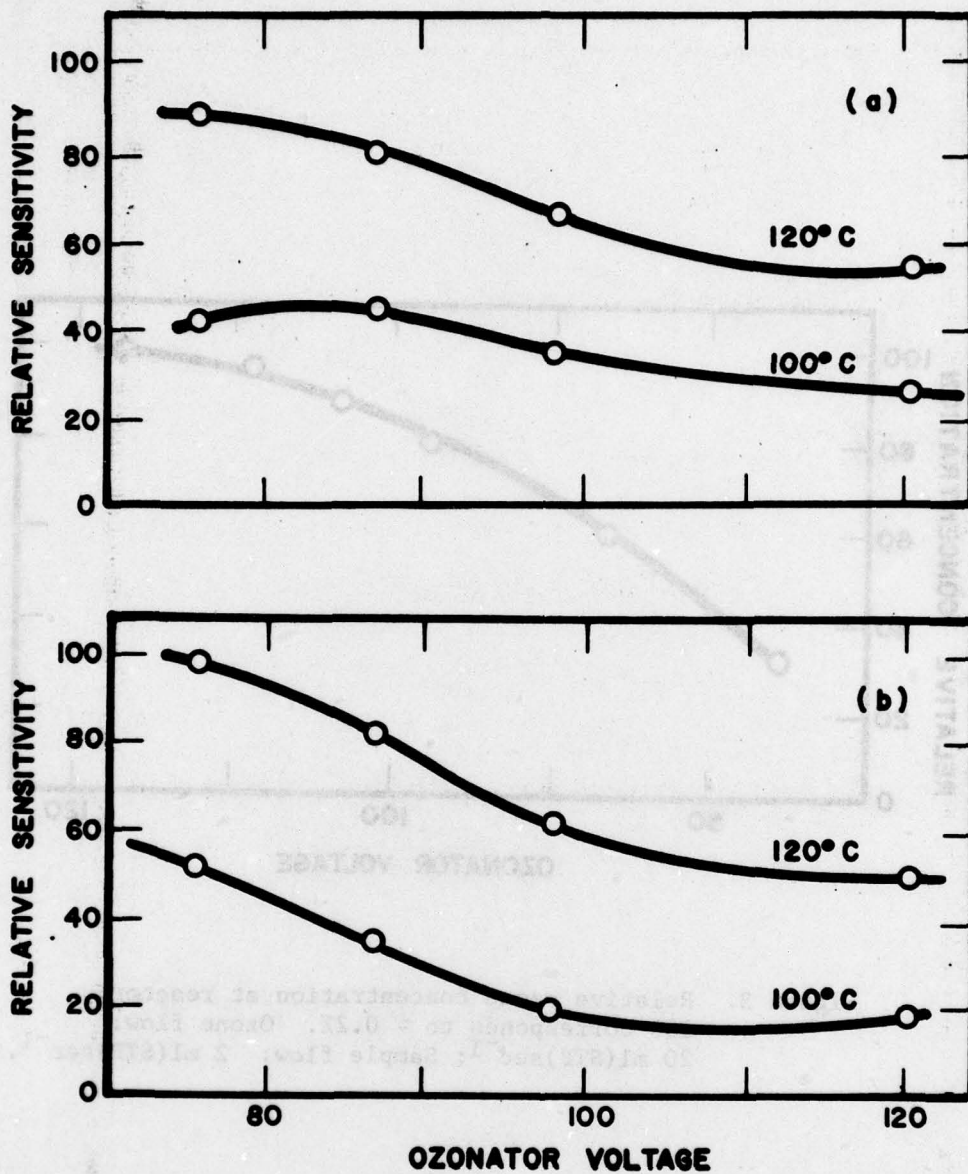
Figure 4. Relative sensitivity toward hydrazines.

Sample flow: 2 ml(STP)sec^{-1}. Ozone flow:
(a) 13 ml(STP)sec^{-1}; (b) 20 ml(STP)sec^{-1}.
Reactor temperatures as indicated.

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REFERENCES

1. Benson, S. W. The foundations of chemical kinetics, p. 19. New York: McGraw-Hill, 1960.

2. Clough, P. N., and B. A. Thrush. Mechanism of chemiluminescent reaction between nitric oxide and ozone. Trans Faraday Soc 63:915 (1967).

3. Fontijn, A., A. J. Sabadell, and R. J. Ronco. Homogeneous chemiluminescent measurement of nitric oxide with ozone. Implications for continuous selective monitoring of gaseous air pollutants. Anal Chem 42:575 (1970). See also, AeroChem chemiluminescence air pollution analyzers. Model AA-1 for NO, Model AA-2 for NO and NO_x, Model AA-3 for NO, NO_x, and O_3. AeroChem TB-73-1, 1973.

4. Moore, W. J. Physical chemistry. 3rd ed; pp. 303-309. New York: Prentice-Hall, Inc., 1962.

5. Volltrauer, H. N. Hydrazine analysis using chemiluminescence. SAM-TR-76-37, Sept 1976.

6. Volltrauer, H. N. Manual for breadboard chemiluminescent analyzer for measurement of hydrazines. AeroChem TP-354, Mar 1977.

7. Winfield, T. M. A method for converting NO_2 to NO by ferrous sulfate prior to chemiluminescent measurements. Presented at 173rd National Meeting, American Chemical Society, New Orleans, La., 20-25 March 1977.