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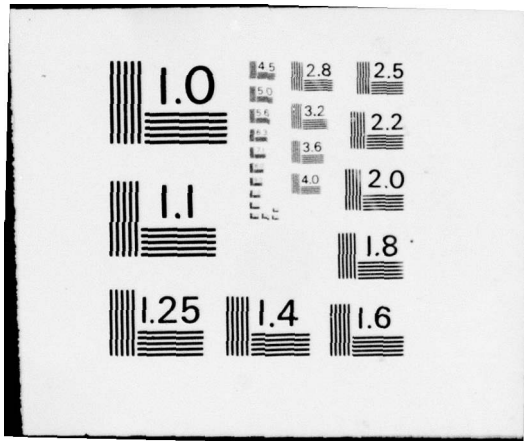
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# HYDRAZINE ANALYSIS USING CHEMILUMINESCENCE

AeroChem Research Laboratories, Inc.  
P.O. Box 12  
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September 1976

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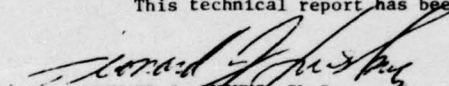
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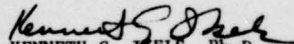
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This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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

  
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## HYDRAZINE ANALYSIS USING CHEMILUMINESCENCE

### INTRODUCTION

Safety and other factors necessitate the ability to monitor concentrations of the rocket propellants monomethylhydrazine (MMH), Aerozine-50 (a 50/50 mixture of 1,1-dimethylhydrazine and hydrazine), and  $\text{NO}_2$  (from  $\text{N}_2\text{O}_4$ ), at launch and storage sites. (Initially the three hydrazines were to be measured individually. During the project monitor's visit 5 Mar 1976, it was agreed that it would be preferable to measure MMH, Aerozine-50, and  $\text{NO}_2$ .) Preliminary studies at the Bioenvironmental Analysis Branch, USAF School of Aerospace Medicine, indicated that the hydrazines could be monitored by measuring the light output of their chemiluminescent reactions with ozone. The major objectives of this contract were to demonstrate the feasibility of this general approach and to define a specific method for carrying out these measurements. The concentration range of interest for these substances is approximately 1 to 1,000 ppm.

In addition to employing the chemiluminescent reactions directly to measure the hydrazines and  $\text{NO}_2$  (i.e., using differences in their spectral outputs), other approaches were investigated. These included using (1) differences in the rates of the various reactions, (2) converters, and (3) chemical scrubbers.

From these studies, the method developed to measure  $\text{NO}_2$  and the hydrazine fuels utilizes all these approaches and, because the reactions take place at a relatively high pressure (200-300 Torr), may ultimately result in a portable instrument.

### APPARATUS AND PROCEDURES

A number of sampling systems and measuring devices were used. These and the tests performed with them are described in this section. Figure 1 depicts the equipment used for most of this work.

#### Sampling Sources

Essentially two sampling systems were employed: (1) a "bubbler" (and a modification thereof) for continuous sampling, and (2) an exponential dilution flask for calibration purposes and where samples were required for short time periods. With the bubbler, continuous samples of the three hydrazines were obtained by bubbling  $\text{N}_2$  through liquid hydrazine,<sup>1</sup> passing the hydrazine-containing gas stream through a

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<sup>1</sup>Maahs, H. G. Interference of oxygen, carbon monoxide, and water vapor on the analysis for oxides of nitrogen by chemiluminescence. NASA TM X-3229, Aug 1975.

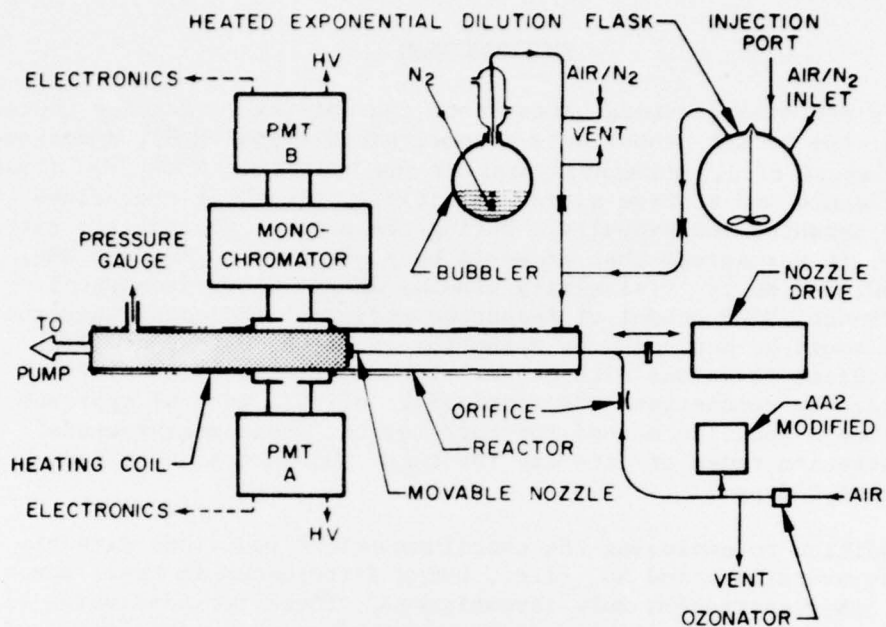


Figure 1. Test apparatus.

temperature-controlled condenser to define vapor pressure (assuming the  $N_2$  is saturated with the hydrazine), and diluting the resulting gas stream with excess air or  $N_2$ . This system was used for the constancy of the concentration available, not as a calibration source.

A related low-concentration gaseous source of a liquid sample was obtained at times by placing the liquid in a test tube immersed in an ice bath and sampling from a small tube extending part way into the test tube.<sup>2</sup> The concentration of the sample so obtained depends on the sample itself, the distance between the tip of the sampling tube and the surface of the liquid, and the sampling flow rate; the latter can be used to vary the concentration.

For calibration purposes, the well-known exponential dilution flask technique was used. Samples were obtained by injecting a known amount of liquid or pure gas into a heated ( $\sim 40^\circ C$ ) Pyrex flask of known volume. Sampling from one inlet of this vessel while supplying air or  $N_2$  to another inlet results in an exponential decrease in concentration with time.

<sup>2</sup>Sigsby, J. Environmental Protection Agency, personal communication, 1976.

For many of the interference tests performed (see Interferences section), both sampling systems were used simultaneously. For the lifetime test of the scrubber (Filters and Converters section), a continuous dilution system was set up that supplied 150 ppm methylamine at 20 ml/sec.

### Reactors and Measuring Devices

Most measurements reported here are performed with a flow tube reactor coupled to a monochromator. Some of the initial tests, however, were made with a large (1ℓ) spherical reactor approximating a stirred reactor in performance; some of the scrubber tests were made with our commercial NO<sub>x</sub> analyzer.

Flow Tube Reactor--The apparatus designed for making rate measurements was automated to some extent for both increased accuracy and more efficient data collection. The flow tube reactor is constructed with 26-mm-i.d. 304 stainless steel tubing (Teflon-coated stainless steel and Pyrex were also used) about 50 cm long with a 50-mm section of 26-mm-i.d. quartz (see Fig. 2).

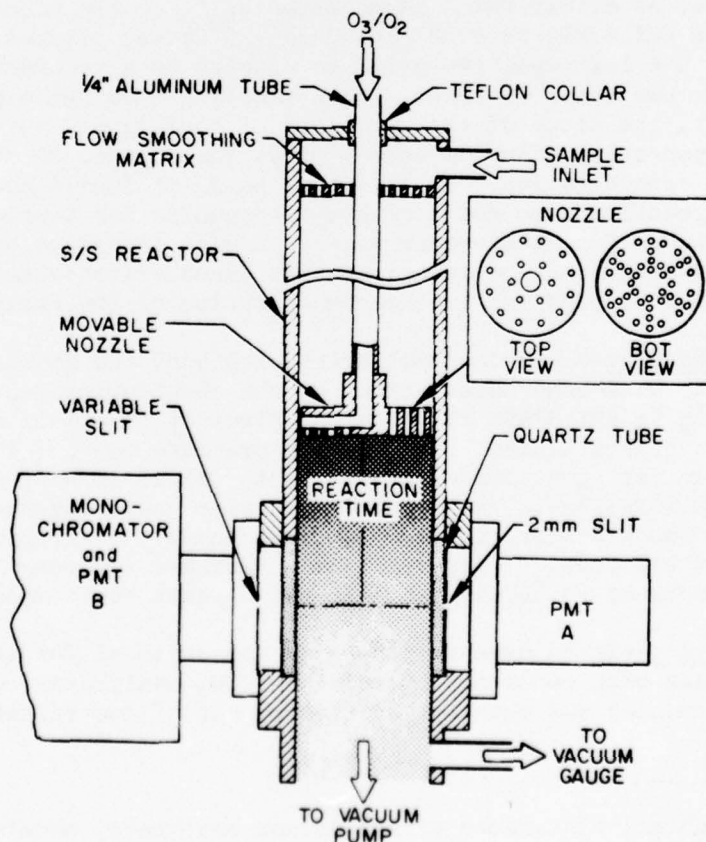


Figure 2. Flow Tube Reactor.

The position of the nozzle, which along with the gas flow velocity defines the reaction time, is adjusted either by manually moving the 6-mm ( $\frac{1}{4}$ " ) aluminum tube attached to the nozzle or by driving it (linearly) with a variable speed motor. In later tests a heating coil was wound around the reactor.

A photomultiplier tube (PMT A in Fig. 2) is used to monitor the total chemiluminescence while spectral scans are made with the monochromator to allow "effective" rate measurements over the 200-600-nm region. (With the heating coil around the reactor, PMT A was not used because of its excessive dark current.) The 2-mm slit defines the reaction zone viewed. The variable slit on the opposite side of the reactor defines the observation zone for PMT B (due to the monochromator geometry, it is about twice the slit width) and also serves as the monochromator entrance slit (the performance of the monochromator is only slightly altered by having the slit moved 5 cm from its usual position).

The ozone supply for this reactor is monitored by an  $\text{NO}_x$  analyzer<sup>3</sup> (AeroChem model AA2) modified to measure 0-10%  $\text{O}_3$  or NO on its highest range. Pressures are measured with 0-20 and 0-400 Torr Wallace Tiernan pressure gauges, and flows are measured with inverted burettes.

The output of either PMT A (Hamamatsu R212) or the monochromator PMT (either an EMI 9789Q or 9958 cooled to  $-20^\circ\text{C}$ ) was compressed for some tests with a log amplifier prior to display on a recorder. This was useful for two types of tests. When sampling from the exponential dilution flask, the slope of the recording of  $\log(\text{signal})$  vs. time (the log of the exponential dilution curve) gives the dependence of the signal on the concentration. On the other hand, if  $\log(\text{signal})$  is recorded vs. reaction time for a constant-concentration sample, linear plots are obtained for first-order reactions with the slope proportional to the rate constant for the reaction. For pseudo-first-order reactions, the proportionality constant is the concentration of the excess reactant.

Stirred Reactor--To gain familiarity with both the apparatus and the hydrazines, wide-band observations of the chemiluminescent reactions were made using an EMI 9789Q PMT attached directly to a  $\sim 1\ell$  spherical reactor with a quartz window. The reactor pressure was  $\sim 5$  Torr with both sample (in nitrogen) and ozone ( $\sim 3\%$  by volume in oxygen) flow rates of  $\sim 4$  ml(STP)/sec. This reactor was also used, together with a Spex Minimax monochromator, to make spectral scans. A stepping motor and associated electronics (removed from a Heathkit recorder) were added to the monochromator to permit variable speed scans to be made.

$\text{NO}_x$  Analyzer--Tests made in preparing the proposal for this contract were carried out with two AeroChem model AA3  $\text{NO}_x$  analyzers. Qualitative spectral information was obtained by placing one of two filters between

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<sup>3</sup>"AeroChem chemiluminescence air-pollution analyzers, models AA-1,-2 and -3," AeroChem TB-73-1, 1973.

the reactor and the PMT. Estimates of reaction rates were obtained by substituting a variable-output ozone source for the internal ozonator of one of these instruments and measuring the light output of the chemiluminescent reactions as a function of ozone concentration. Measurements were made in both the NO and NO<sub>x</sub> modes.

During the program, our NO<sub>x</sub>/O<sub>3</sub> analyzers were used to measure ozone concentrations in the kinetic studies and amine concentrations in the lifetime studies of the scrubber. A model AA2 analyzer was modified to measure up to 10% ozone by internally diluting the sample concentration by a factor of  $\sim 30$  (using two sample inlets to the reactor, with flows of 0.7 and 20 cm<sup>3</sup>/sec) and by using a factor of 2 higher reactant (NO) concentration than standard. For the ozone calibration of the instrument,<sup>4</sup> oxygen was used as carrier for the second reactant.

To measure amines in the lifetime tests of the scrubbers, the conversion efficiency of our NO<sub>2</sub>-to-NO converter was determined for each amine used (i.e., the instrument was calibrated in the NO<sub>x</sub> mode) using the exponential dilution system.

## RESULTS AND DISCUSSION

### Spectral Information

Qualitative spectral data were obtained in the proposal tests using our commercial NO<sub>x</sub> monitors. Both hydrazine and UDMH showed some response in the NO measuring modes; relative to NO, the responses were 2%-3% for hydrazine and 5%-15% for UDMH. Removing the red filter of the analyzer (Corning 2-60, transmits above 600 nm) increased the sensitivity toward both hydrazine and UDMH. Although the exact amount was not determined, it is less than a factor of 2. More accurate measurements were made with and without a blue filter (Corning 4-94, transmits below 600 nm). With the filter in place, the response to hydrazine dropped to approximately 20% of what it was without the filter. These results are consistent with the assumption that the observed chemiluminescent reaction in the NO/O<sub>3</sub> reaction shifts to the blue, possibly as a result of excited NO taking part in the reaction.

The first tests under the contract were also of a qualitative nature, intended to confirm the above results. Measurements were made with both hydrazine and UDMH, using the 1ℓ stirred reactor operating at  $\sim 5$  Torr. All samples were simultaneously monitored with an NO analyzer (AeroChem model AA2). Using heated 316 stainless steel sample lines resulted in erratic analyzer readings more than an order of magnitude larger than had been observed before for hydrazine. Less erratic measurements were obtained when shorter Teflon sample lines were used. The large analyzer readings may have been due to partial conversion of

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<sup>4</sup>Gould, R. K. Method of calibrating a quantitative analytical instrument. U.S. Patent Application Nos. 338,212, 5 March 1975, and 586,958, 16 June 1975.

hydrazine to NO by the heated stainless steel tubing. The response of the test system to hydrazine was large and stable, 2 nA/ppm, and to UDMH, about 0.2 nA/ppm. MMH was not used in this test. Placing a Pyrex disc between the reactor and the PMT resulted in a factor of  $\sim 2$  decrease in signal, indicating the presence of UV emissions and the need for quartz optics in future tests. The assumption that the chemiluminescence was due solely to the NO/O<sub>3</sub> reaction was thus false.

Spectral scans over the 200- to 900-nm range confirmed the presence of UV emissions for all three hydrazines. These scans were first made (for hydrazine and MMH only) with the stirred reactor. Better quality spectra were obtained when the scans were repeated with the flow tube reactor. The spectra of the hydrazine/ozone and MMH/ozone chemiluminescent reactions are shown in Figures 3 and 4. Note that two PMTs, each optimized for a different region of the spectrum, are used. The spectrum of UDMH is very similar to that of MMH.

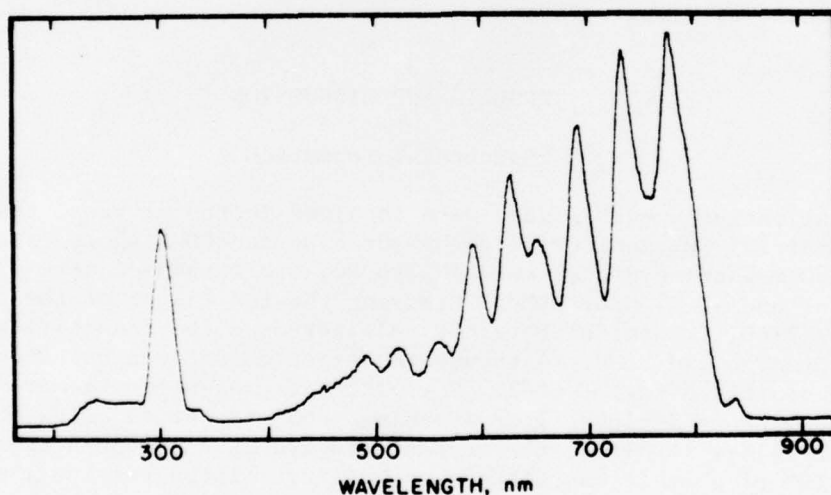


Figure 3. Hydrazine/O<sub>3</sub> emission spectrum.  
[Hydrazine]  $\approx 2[O_3] = 5 \times 10^{-6}$  moles/liter.  
P = 4.5 Torr; reaction time = 0.03 sec;  
resolution = 10 nm. PMT: below 550 nm,  
EMI 9789Q; above 550 nm, EMI 9558.

Little attempt was made to assign the observed emissions, although some of the hydrazine emissions appear to be the same as those observed in the hydrazine/O atom reaction; i.e., NO emission at 200-300 nm and the OH emission at  $\sim 310$  nm.<sup>5</sup> The emission at 350-500 nm for UDMH and

<sup>5</sup>Becker, K. H. and K. D. Bayes. A study of the chemiluminescence from oxygen atom-hydrazine flames. J Phys Chem 71:371-377 (1967).

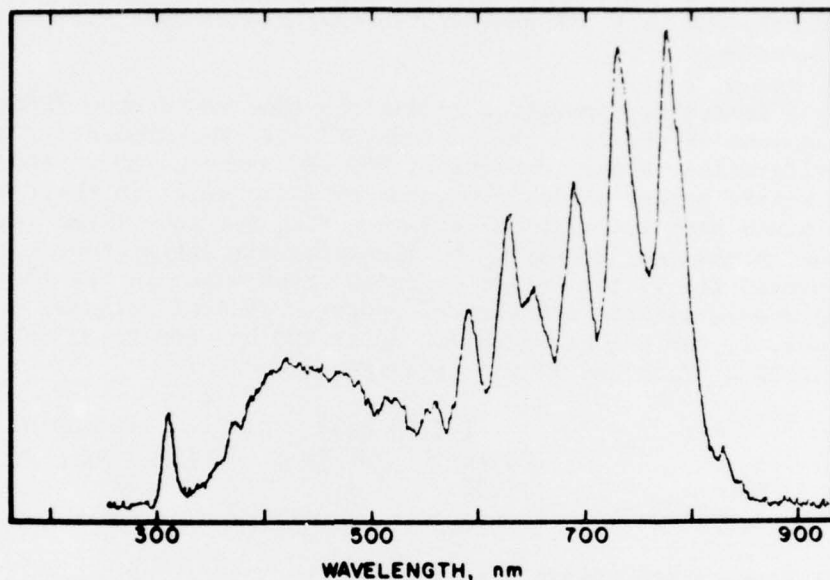


Figure 4. MMH/O<sub>3</sub> emission spectrum,  
 $[MMH] \sim [O_3] \sim 5.6 \times 10^{-6}$  moles/liter.  
 P = 4.5 Torr; reaction time = 0.02 sec;  
 resolution = 10 nm. PMT: below 380 nm,  
 EMI 9789Q; above 380 nm, EMI 9558.

MMH also occurs for the tertiary amines and the ethylene/ozone reactions; they may all have the same origin (CHO). (Tripropyl and triethylamine were briefly looked at since the triethylamine/ozone reaction is known<sup>6</sup> to emit in the 350-500 nm range.)

To achieve high light output, both the hydrazines (in N<sub>2</sub>) and ozone (in O<sub>2</sub>) concentrations were in the percent range for these scans. The data obtained at those high concentrations, however, were not useful in predicting the behavior of the reactions at the much lower concentrations of interest (in the ppm range); also, the oxygen content of the reacting mixture affected the course of the reactions. The concentrations of both the hydrazines and ozone samples were therefore lowered, and the reactions were carried out in air. These changes resulted in a loss in the light output, which was compensated for by operating the monochromator without slits (resolution  $\sim$  50 nm) and looking at a larger area (18-mm diameter) of the reaction zone than before. In subsequent tests

<sup>6</sup>Pitts, J. N., et al. Chemiluminescent reactions of peroxyacetyl nitrate and ozone with triethylamine. Environ Sci Technol 7:550-552 (1973).

spectral measurements were restricted (except for the sensitivity determination) to recording the light intensity at two wavelengths (400 and 760 nm), and only MMH and Aerozine-50, rather than all three hydrazines, were used.

In a search for operating conditions that would show differences in the reactions of the three hydrazines (Kinetic Measurements), we found that differences in the response of MMH and Aerozine-50 at 400 nm or 760 nm are mostly masked at low pressures by differences in their reaction rates (since peak intensities were measured, not integrated intensities). At higher pressures, however, where essentially integrated intensities are measured (i.e., the entire reaction takes place in the 18-mm diameter viewing area), sizable differences appear. Typical relative peak responses,  $I$ , for MMH and Aerozine-50 at 100 and 200 Torr, 80°C, 5 ml/sec 0.8% O<sub>3</sub> flow and 23 ml/sec sample flow are:

	I (760 nm)		I (400 nm)	
	100 Torr	200 Torr	100 Torr	200 Torr
MMH	1.89	1.13	1.89	2.74
Aerozine-50	3.11	2.36	0.85	1.00

Similar results are obtained at 130°C.

	I (760 nm)		I (400 nm)	
	100 Torr	200 Torr	100 Torr	200 Torr
MMH	4.25	2.36	4.25	4.15
Aerozine-50	7.55	4.91	2.08	1.60

Most of the increase in signal at 130°C over that measured at 80°C is due to the increase in reaction rate. This causes more of the reaction to occur in the 18-mm length of the reaction zone monitored through the monochromator.

A method based on these spectral differences at 200 Torr and 80°C between MMH and Aerozine-50 has been chosen for their measurement and has been investigated in some detail.

#### Kinetic Measurements

Rate measurements for the hydrazine(s)/ozone reactions are needed for two reasons. If a measuring method for monitoring the hydrazines is developed that differentiates between the hydrazines by using differences in their reaction rates, these rates must certainly be known. But even if complete differentiation can be effected by purely spectroscopic means (using a number of filters), rate data will be needed to design an instrument; i.e., to determine reactor size, flow rate, and the ozone concentration required.

Our initial goal was to determine the reaction mechanisms from detailed rate measurements, which would then allow us to calculate the behavior of the hydrazine(s)/ozone system for all conditions. Failing

this, we would have to make measurements at all conditions that might ultimately be useful.

With the initial goal in mind, we proceeded to make rate measurements (with MMH) for each emission (310, 400, and 760 nm) using relatively high spectral (20-nm) and spatial resolution. In these rate measurements, the validity of the experimental setup was confirmed using NO as sample. From the slope of the recording of  $\log(\text{signal})$  vs. reaction time, the known rate constant for the  $\text{NO}/\text{O}_3$  reaction ( $1 \times 10^7$  liters/mole-sec) was reproduced within experimental error (10%-20%).

To obtain usable signals for the tests with MMH, high concentrations of both samples (up to 2% MMH in  $\text{N}_2$ ) and ozone (up to 4% in  $\text{O}_2$ ) were used. A typical recording of one of these runs ( $\log$  intensity vs. nozzle distance) is shown in Figure 5. For this and most other runs the nozzle was driven at 25 mm/min. No single rate constant can be determined from this recording. The same general behavior was observed at other wavelengths where measurements were carried out (310, 400, and 760 nm).

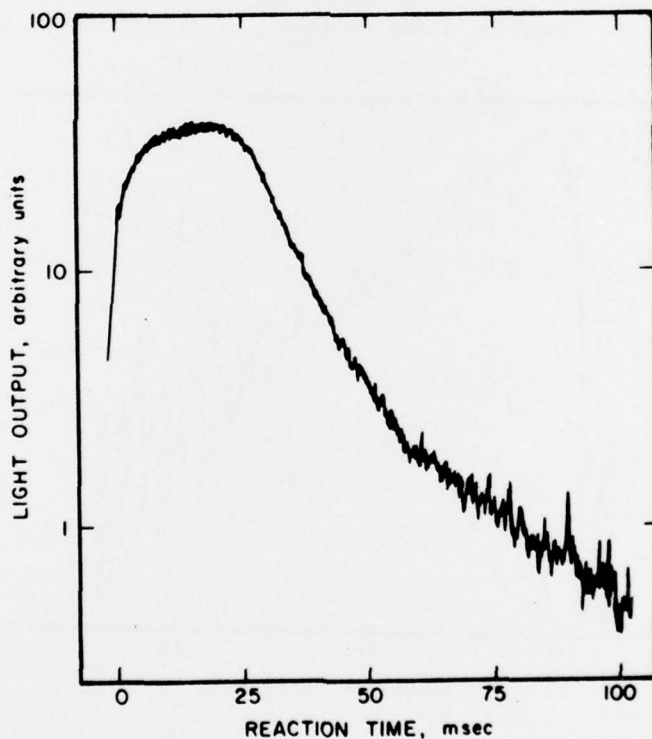


Figure 5.  $\text{MMH}/\text{O}_3$  chemiluminescent reaction at 400 nm.  $[\text{MMH}] \sim 5 \times 10^{-6}$  moles/liter.  $P = 4.5$  Torr; sample flow rate = 2.8 ml/sec; ozone flow rate = 2.8 ml/sec; resolution = 20 nm.

Since MMH is a more complex molecule than hydrazine, it was expected that the hydrazine/O<sub>3</sub> reaction would be simpler to characterize and the information obtained from its study could be used to analyze the MMH reaction. This was not so; all three hydrazine/O<sub>3</sub> reactions appeared equally complex.

In all subsequent tests, reactions were carried out in air since that would be the case for a practical instrument. Substituting air for oxygen to make ozone reduced the maximum ozone concentration attainable to ~ 1%. To keep ozone in excess, hydrazine concentrations were also kept low--generally less than 2,000 ppm.

An additional complication developed when it was determined that a product of the hydrazine/ozone reaction, a white powder, rapidly coats the reactor walls--affecting not only the transmission characteristics of the windows, but the reaction itself. Heating the reactor to 80°C or higher prevents this deposit from forming. At this temperature and with low-concentration samples, the reactions appeared to be simpler than at ambient temperatures and higher concentrations.

A recording of the log of the measured light output at 400 nm with 20-nm resolution vs. reaction time is shown in Figure 6 for UDMH. From

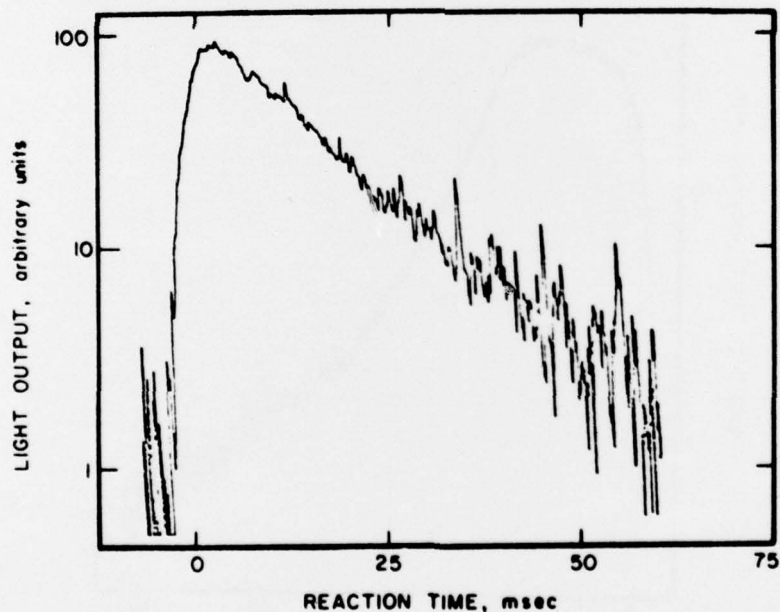


Figure 6. UDMH/O<sub>3</sub> chemiluminescent reaction at 400 nm. [UDMH] = 1 x 10<sup>-6</sup> moles/liter; [O<sub>3</sub>] = 2.8 x 10<sup>-6</sup> moles/liter. P = 15 Torr; T = 90°C; sample flow rate = 7 ml/sec; ozone flow rate = 5 ml/sec; resolution = 20 nm.

the slope of the decay curve in similar tests, an effective second-order rate constant of  $2 \times 10^7$  liters/mole-sec can be calculated. For MMH a similar curve is obtained, but with the maximum occurring about 20 msec later than it did for UDMH and the slope corresponding to a rate constant of  $1.1 \times 10^7$  liters/mole-sec.

This difference in rate constants could be the basis for MMH and UDMH measurements. However, because the method inherently would not be very sensitive and because the inclusion of hydrazine resulted in an unexpected behavior, another more sensitive method was sought. To this end a search was made over a wide range of conditions in an attempt to find conditions that would result in differences in behavior of the three hydrazines. Measurements were made over a pressure range of 7 to 400 Torr, ozone concentrations (entering the reactor) of 0.2% to 1.5% in air and at 80° and 130°C, with the concentration of the hydrazines between 100 and 3,000 ppm. Two broad emissions--one at 400 nm, the other at 760 nm--amounting to  $\sim 90\%$  of the total light output (see Figs. 3 and 4) were monitored with  $\sim 50$ -nm resolution. MMH was studied in more detail than hydrazine and UDMH, but qualitatively, the observations apply to all three hydrazines. Because of the relatively large observation area (18-mm diameter), details in the reaction zone of smaller dimension than this cannot be resolved. This limits the accuracy and the range of conditions over which rate and intensity measurements can be made. These measurements can be summarized as follows:

1. The order of the reactions with respect to ozone is not 1 but between  $\sim 0.5$  and 1 over the range investigated.
2. The reaction rates are inversely proportional to pressure.
3. The intensity of both emissions drops as pressure increases; the blue (measured at 400 nm) as pressure  $^{-1}$ , the red (measured at 760 nm) as pressure  $^{-2}$ .
4. The reaction rates increase by a factor of  $\sim 1.5$  for a temperature increase from 80° to 130°C. The increase is greatest for UDMH, least for hydrazine.
5. The ratios of the responses at 760 nm and 400 nm are different for MMH and Aerozine-50, and change with pressure.

This last observation was more fully investigated and is the basis for a measuring method for MMH and Aerozine-50.

Adding hydrazine to MMH resulted in a much larger increase in the 400-nm emission than expected from the very small intensity of the 400-nm emission for hydrazine. This effect is very nonlinear in concentration, decreasing rapidly at low hydrazine concentrations. The response of MMH and Aerozine-50, however, is additive.

## Filters and Converters

Because it is desirable to measure  $\text{NO}_x$  concentrations in addition to MMH and Aerozine-50 concentrations, means of removing hydrazines from a gas sample without affecting the  $\text{NO}_x$  present were sought. We considered reacting the hydrazines with ozone and passing the resulting sample through a converter. Since  $\text{NO}_2$  does not appear to be a significant product of the hydrazine(s)/ozone reaction (little response is obtained with an  $\text{NO}_x$  analyzer in the  $\text{NO}$  or  $\text{NO}_x$  mode when measuring the products of the hydrazine(s)/ozone reaction), the  $\text{NO}$  coming from the converter would be due to the  $\text{NO}$  and  $\text{NO}_x$  in the original sample. This approach was not investigated further since, from an engineering viewpoint, it appeared difficult to incorporate into an instrument; also, the interference of amines in the  $\text{NO}_x$  measuring mode could still pose problems. Attempts at absorbing hydrazines on a cold Pyrex surface proved difficult for MMH (only  $\sim 50\%$  absorption at  $0^\circ\text{C}$ ) and were also abandoned.

A chemical scrubber would have the disadvantage of a limited lifetime, but it could also be expected to remove ammonia and amines. A scrubber made by coating  $\sim 800$  3-mm beads (in a 15-mm-diameter column, 13 cm long) with a 5% phosphoric acid solution, followed by drying, removed all ( $> 99\%$ ) of the MMH and Aerozine-50 passing into it. The lifetime at a 3 ml/sec flow rate and at a  $\sim 800$ -ppm MMH concentration is approximately 4,000-ppm hours. For methylamine the lifetime is  $\sim 1,000$ -ppm hours; and for propylamine, 1,400-ppm hours. This is the same scrubber we use to eliminate  $\text{NH}_3$  from gas samples when measuring  $\text{NO}_x$  with our commercial  $\text{NO}_x$  analyzers.

$\text{NO}_2$  can be measured by passing the sample first through the scrubber to remove hydrazines, amines, and ammonia, and then through an  $\text{NO}_2$ -to- $\text{NO}$  converter, and measuring the  $\text{NO}/\text{O}_3$  chemiluminescence at  $\sim 700$  nm.

## A METHOD FOR MEASURING MMH, AEROZINE-50, AND $\text{NO}_2$

### Choosing a Method

Because of their relatively large light output, the emissions at 400 and 700 nm were considered most suitable for monitoring the hydrazines. The OH emission at  $\sim 310$  nm was weak and common to all three hydrazines, and the  $\text{NO}$  emission for hydrazine between 200 and 300 nm appeared too weak to utilize. These weaker emissions may, however, still be useful in view of the increased sensitivity attainable as a result of the nonlinear response of the system to the hydrazine (see Linearity section). The extent of the nonlinearity was determined too late in the program to allow reinvestigation of these weaker emissions. Under different operating conditions (higher concentrations), the signal is proportional to the concentration raised to a power greater than 1. This has the effect of making the sensitivity calculated on the basis of a high-concentration measurement less than what it would be if the

signal were proportional to the concentration raised to the first power. For this reason, these weaker emissions were not considered as a basis for the hydrazine(s) measurements.

In selecting a measuring method we had essentially two choices, one of which (making use of differences in rates of the MMH and UDMH ozone reactions) was considered only briefly because of its insensitivity. The other method, based on differences in the emission spectra of the MMH and Aerozine-50 reactions with ozone, was chosen and tested for linearity and interferences, and a sensitivity was determined.

The optimum operating conditions for an instrument such as the one considered here will depend on the use to which that instrument is put. Among other factors, they will depend on: which of the substances to be measured is of most interest, which potential interferences might be present and to what extent, the sensitivity and accuracy required, and the size and weight restrictions of the instrument.

We chose the following set of conditions for further testing. They are easily realizable and offer adequate selectivity, sensitivity, and potential for ultimate portability (a small pump can be used):

Operating pressure:	200 Torr
Flow rates, sample:	3 ml/sec
ozone:	20 ml/sec
Ozone concentration	
at reactor:	0.1%
Reactor temperature:	80°-100°C

#### Sensitivity

The normalized responses for MMH and Aerozine-50 at 400 and 760 nm given in the Spectral Information section can be used to calculate concentrations (in arbitrary units):

$$[\text{MMH}] = 4.18 I (400 \text{ nm}) - 1.77 I (760 \text{ nm}) \quad (1)$$

$$[\text{Aerozine-50}] = 4.85 I (760 \text{ nm}) - 2.01 I (400 \text{ nm}) \quad (2)$$

To obtain an estimate of the sensitivity attainable with this method, the spectral range of each of the two main emissions was determined by using the pressure dependence of each of these emissions. Recording the spectrum at low (13 Torr) and high (~ 300 Torr) total pressure and dividing the intensities of the high-pressure spectrum by the corresponding intensities of the low-pressure spectrum (at 25-nm intervals), results in only two distinct numbers if two nonoverlapping emissions are responsible for the radiation. A gradual change (observed here) from one number to another indicates overlap. Figure 7 shows a plot of these ratios as a function of wavelength. The change near 300 nm probably indicates that the OH emission intensity is proportional to pressure<sup>-2</sup>. From this analysis the optimum wavelength ranges for monitoring these emissions

were determined to be approximately 350-450 nm for the emission measured at 400 nm, and  $> 550$  nm for the emission measured at 760 nm. A measurement at 400 nm through the monochromator, followed by a measurement without the monochromator, resulted in a signal increase corrected for the bandpass of the monochromator (350-450 nm) of a factor of 175. For the measurement without the monochromator, the face of the PMT was moved 120 mm from the center of the 25-mm-i.d. reactor through an 18-mm-diameter opening. With a 50-mm PMT closely coupled (as near as practical with the reactor at 80°C) to a reactor of approximately the same area, an additional factor of 10-20 increase is expected. Since we can currently detect MMH concentrations lower than 10 ppm with a 3 ml/sec flow rate diluted with 20 ml/sec zero air, the sensitivity for a measurement is expected to be better than 0.01 ppm. Because concentrations are obtained from the weighted differences of two measurements, a factor of  $\sim 3$  in sensitivity will be lost in the electronic subtraction, making the sensitivity somewhat better than 0.1 ppm.

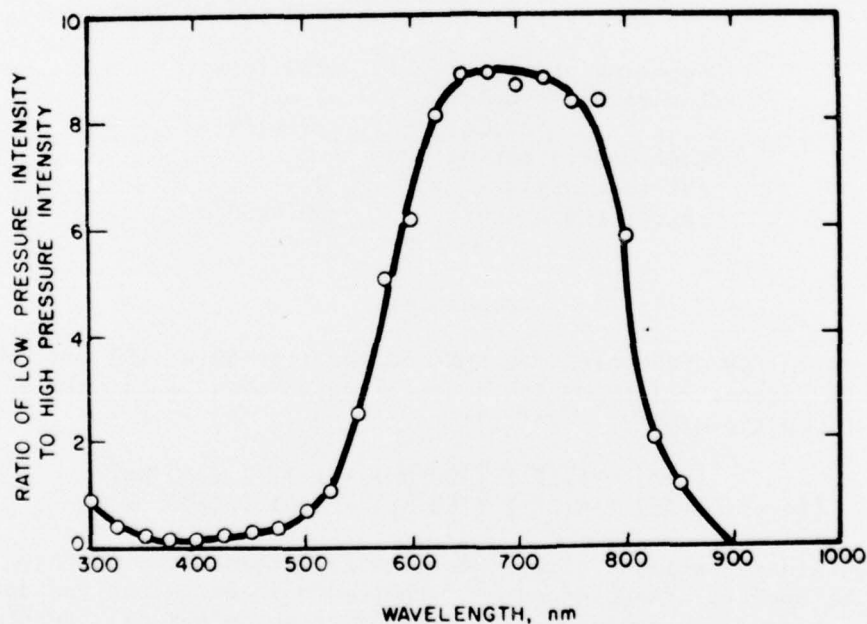


Figure 7. Wavelength range of emissions for MMH/O<sub>3</sub> reaction.

The sensitivity towards NO<sub>x</sub> in the NO<sub>x</sub> measuring mode should be at least as good for an instrument optimized for the hydrazines as for the NO<sub>x</sub> analyzer. In these experiments the sample was diluted by a factor of  $\sim 7$  to reduce interference effects of water and other substances. A slightly greater dilution ratio may be desirable, however, reducing the sensitivity somewhat.

### Linearity

For the hydrazines, the signal dependence on concentration was determined by comparing the slopes of the logs of the exponential dilution curves for the hydrazines in air with the slopes of NO in N<sub>2</sub>. Essentially the same ratio of slopes (0.70) is obtained within experimental error (~ 10%) for MMH and Aerozine-50 at both wavelengths monitored, 400 and 760 nm.

The light emission, I, is therefore related to concentration by

$$I = k(\text{concentration})^{0.70}$$

The total range of concentrations covered was ~ 1 to 10,000 ppm. The measurements at 760 nm for MMH had the exponential 0.70 concentration dependence up to ~ 10,000 ppm, while at 400 nm both MMH and Aerozine-50 had this dependence only up to ~ 2,000 ppm; above that the exponent increased. At 760 nm, Aerozine-50 was tested only at concentrations below 2,000 ppm. A typical recording of the log of the exponential dilution curve for MMH at 400 nm is shown in Figure 8, where the signal is plotted against concentration rather than time.

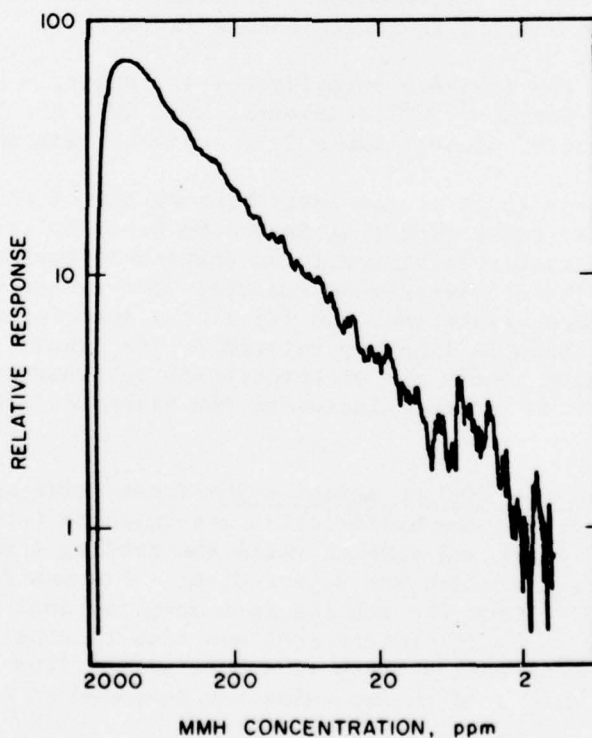


Figure 8. Linearity determination for MMH.

Because hydrazine is "stickier" than MMH and UDMH, the exponential dilution flask is only useful for concentration changes of about a factor of 10 for samples containing hydrazine.

The fact that intensity is proportional to concentration raised to a power less than one, adds some minor electronic complexity (see Proposed Instrument Design) to an instrument. This is far outweighed, however, by the considerable increase in sensitivity (i.e., lower concentrations can be measured) over what is predicted from the high-concentration measurements assuming perfect linearity. For the present case, this increase in sensitivity amounts to a factor of 8, or a 1,000-to-1 range of concentration.

### Interferences

Measured Alone--Several potential interferents have been tested individually. The extent of interference was determined by injecting a known amount of the substance into the exponential dilution flask and measuring the peak response. Simple amines (methyl, ethyl, propyl, butyl) show less than 2% the response of equal amounts of MMH. The interference is larger for aniline and N-methylaniline,  $\sim$  5% and 4% respectively. The signal due to aniline persists for several minutes after the sample line is disconnected. Because of this stickiness, the interference due to aniline is larger than measured.

As expected,<sup>7</sup> the ethylene interference is larger,  $\sim$  20%; and that due to H<sub>2</sub>S is very large,  $\sim$  200%. Ammonia, NO<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub>O do not interfere when measured alone. Table 1 summarizes these measurements.

The interference in an actual instrument of any of these substances will probably be different from that indicated here for two reasons: (1) The larger reaction zone viewed in an instrument would favor slow reactions such as the ethylene/ozone reaction (it was qualitatively compared to the MMH/O<sub>3</sub> reaction); and (2) if the interference of any of these substances is linearly related to its concentration, the interference relative to the MMH or Aerozine-50 response will decrease with decreasing concentration relative to the high-concentration measurements.

In Combination with MMH or Aerozine-50--These tests were carried out in two ways. Either the hydrazine(s) was injected into the exponential dilution flask and sampled until the reading started to decay, at which time the interferent was injected; or (this was done for MMH only) MMH was sampled from the bubbler (see Sampling Sources) at a 3-ml/sec flow rate while the interferent was simultaneously sampled (using a T) from the dilution flask at a  $\sim$  20 ml/sec flow rate. This second method was also used to determine the response of Aerozine-50 (in

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<sup>7</sup>Kummer, W. A., et al. Chemiluminescent reactions of ozone with olefins and sulfides. Environ Sci Technol 5:1045-1047 (1971).

TABLE 1. INTERFERENCES

Extent of interference<sup>a</sup> (as % of substance measured)

<u>Interferent</u>	<u>MMH mode</u>	<u>Aerozine-50 mode</u>
Ammonia	0	0
Methylamine	0.5	-0.3
Ethylamine	0.3	-0.2
Propylamine	0.6	0.6
tert-Butylamine	0.9	1.1
Diethylamine	0.5	0.9
Aniline	5.4	-2.7
N-methylaniline	3.7	-0.2
Ethylene	27.4	-13.7
Hydrogen sulfide	263.0	-107.0
CO <sub>2</sub>	0	0
NO <sub>2</sub>	0	0
N <sub>2</sub> O	0	0

<sup>a</sup>Interference measurements at 400 and 760 nm are used with Eqs. 1 and 2 relating MMH and Aerozine-50 concentrations to responses at 400 and 760 nm. All concentrations  $\sim$  5,000 to 15,000 ppm.

the dilution flask) in the presence of MMH. Electronically zeroing out the MMH signal resulted in an exponential dilution curve for Aerozine-50 identical to that (within experimental error) observed in the absence of MMH.

1. Water--Water poses a serious problem in measuring MMH and Aerozine-50 (and to a much less extent in measuring NO<sub>2</sub>). The effect of water has been tested in the presence of both MMH and Aerozine-50, and its presence drastically reduces both the 400- and the 760-nm intensities for both substances. In the reacting mixture, 1% water causes a  $\sim$  20% decrease in signal at 400 nm and a  $\sim$  50% decrease at 760 nm for Aerozine-50, and slightly less for MMH. This larger effect at 760 nm may be related to the stronger pressure dependence of that emission. A number of possible solutions to this problem include:

- a. Removing the water from the sample.
- b. Saturating the sample at some well-defined temperature to make the interference constant.
- c. Diluting the sample with zero air to reduce its water content.
- d. Calibrating the instrument with a sample having the same water content as the sample of interest (by adding a small amount of high-concentration hydrazine to the sample being measured).
- e. Measuring the sample at two water concentrations--one as is, the other diluted by some small amount--and electronically obtaining the corrected hydrazine concentrations.
- f. Generating curves and using them together with humidity measurement to correct the hydrazine concentrations.

For our testing procedure we chose to dilute the sample with zero air. Since other substances also interfere (especially NO and NO<sub>2</sub>), we recommend this procedure for a prototype instrument as well.

2. NO and NO<sub>2</sub>--Both NO and NO<sub>2</sub> have a large negative effect on measurements at 400 nm for MMH and Aerozine-50. The NO interference for a 2,000-ppm MMH sample at 400 nm is shown in Figure 9 as a function of NO concentration. For NO<sub>2</sub> the interference is about twice as large. NO does, of course, contribute to the 760-nm intensity. Since the NO/ozone reaction rate is more than 10 times greater at 200 Torr than the reaction rates of the hydrazines, it will be relatively easy to separate their reactions and either eliminate the NO contribution to the measured intensity at 760 nm or account for it.

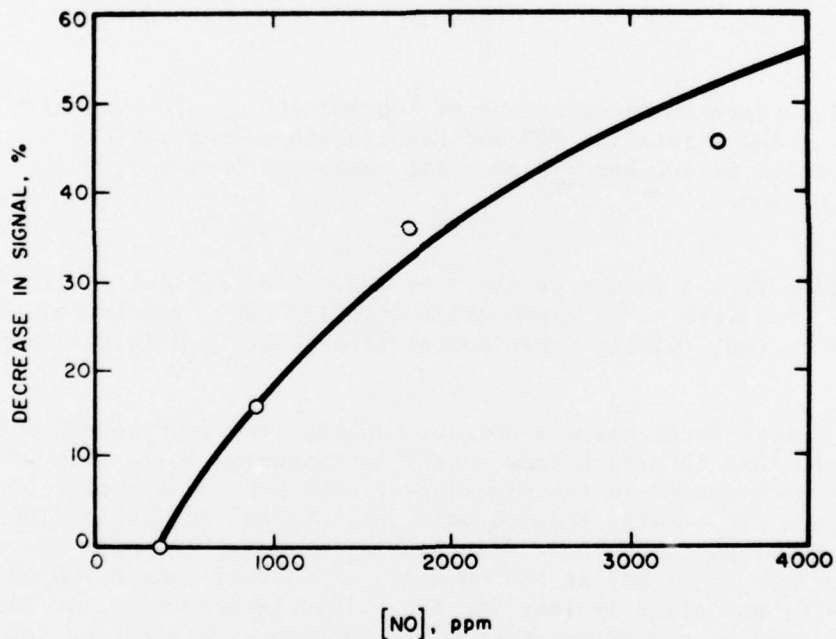


Figure 9. NO interference on MMH measurements at 400 nm.

Again the recommended solution to reduce the effect of both water and the N-oxides is to dilute the sample, possibly by an additional factor of 3 or 4. This would also eliminate interference by amines and reduce the water and NO<sub>2</sub> interference to manageable levels.

3. Amines--Ammonia and the organic amines tested cause a small increase in both emission intensities in the presence of MMH over intensities measured for the amines alone. This is small in all cases for a dilution factor of 3 or 4, making the interference for the amines essentially that given in Table 1.

4. Other Substances--The interference of both ethylene and hydrogen sulfide is increased in the presence of MMH over that given in Table 1. For a 3,000-ppm MMH concentration, adding 7,000-ppm  $C_2H_4$  increases the 400-nm emission by 100%; no change at 760 nm. The corresponding numbers for  $H_2S$  are 7500% (!) and 2000% for the 400- and 760-nm emissions, respectively. Neither of these compounds is expected to be present in high enough concentrations to be important.  $CO_2$  and  $N_2O$  do not interfere in MMH measurements.

#### PROPOSED INSTRUMENT DESIGN

Outlined below is one possible design of an instrument, based on the findings presented in this report, that will measure MMH, Aerozine-50, and  $NO_2$  in the range of 0.2 to 1,000 ppm. Operating conditions and specifications are similar to those used in our tests.

Pressure:	200-300 Torr
Flow rates sample:	1 ml/sec (from a flow of 20 ml/sec)
Ozone:	20 ml/sec
Ozone concentration:	0.1% in reactor
Reactor temperature:	90°C
Materials in contact with sample:	Teflon and glass for all samples; stainless steel, ceramic, and platinum for $NO_x$
Sensitivity:	0.2 ppm for all samples. Less for any one component when any other is in great excess.
Linear range:	Linearized electronically from 1 to 1,000 ppm
Interference:	See Interference section

Figure 10 is a schematic of the proposed instrument. If the proposed low sample flow rate (1 ml/sec) is a problem, the air intake for the ozonator can serve as a sample inlet to achieve rapid movement of the sample from the sampling point to the instrument. To do this, points X and Y are connected and the sample intake is closed. The dilution mentioned in the Interferences section is accomplished by having a large dried-air flow through the ozonator instead of adding a separate diluting filtered-air stream to the sample. The activated alumina filter removes enough of the water,  $NO_2$ , and hydrazines (only MMH was specifically tested) to prevent their interference from being important.

In the hydrazines measuring mode, the sample passes directly into the reactor while the ozone enters the reactor at point H. Any  $NO$  in the sample will have essentially reacted by the time the reacting mixture passes in front of the PMTs. The slower hydrazine reactions occur mainly in front of the PMTs. The light intensities in the two spectral ranges are measured by the two PMTs, whose outputs are linearized and weighted differences taken to yield the MMH and Aerozine-50 concentrations.

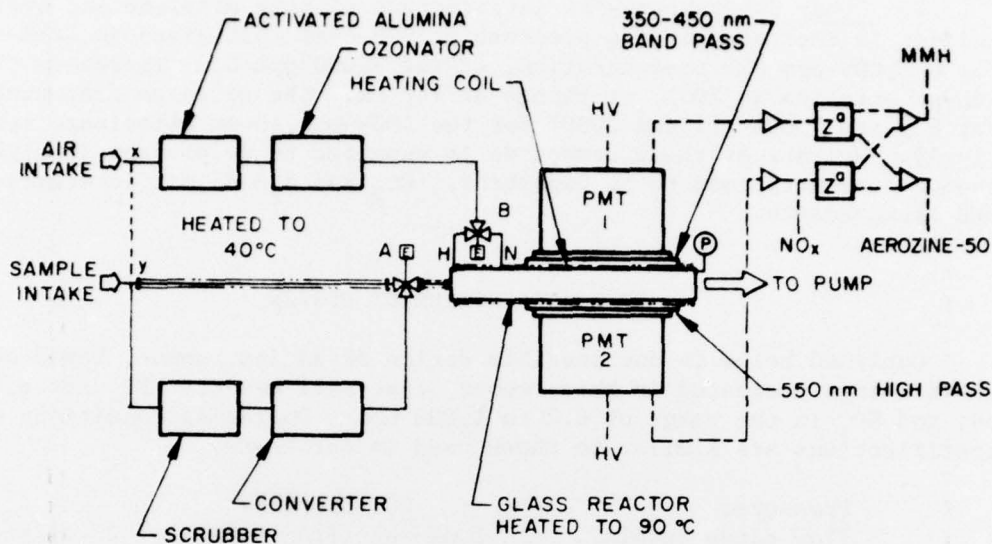


Figure 10. Schematic of proposed MMH/Aerozine-50/ $\text{NO}_2$  monitor.

To measure  $\text{NO}_x$ , the sample flow is passed through a phosphoric acid scrubber, through the converter, and into the reactor. Using ozone inlet N on the reactor allows the  $\text{NO}/\text{O}_3$  reaction to take place in front of PMT 2. The resulting current is amplified and displayed. If NO measurements are also desired, an additional measuring mode can be added which, except for bypassing the converter, is identical to the  $\text{NO}_x$  mode. If there are high NO levels, this extra measurement may be required to correct for the small NO interferences in the hydrazines measuring mode at 760 nm. This would add some minor complexity to the electronics because the  $\text{NO}_x$  measuring mode is linear in concentration and the hydrazine mode is not.

Although a portable instrument is the ultimate goal, a prototype should be large enough that changes can be made readily; also, it should be only as complex as necessary to perform its function, which is to demonstrate the capability of the method. For these reasons we suggest using two PMTs and manual-mode selection, all in an oversized enclosure giving ready access to all internal components. The internal layout is not at all critical if ample room is available for mounting parts.

The flow rates and operating pressure chosen are compatible with the performance of an MB 155 metal bellows pump. The selection of other components is somewhat biased towards those used in the AeroChem  $\text{NO}_x$  analyzers. If high sensitivity is desired, the only critical item is the PMT housing. Cooled commercial housings are generally highly inefficient because of the large distance separating the reactor from the PMT face. This is minimized in our housing, on which the sensitivity calculation is based.

The reactor should be designed to provide good mixing and should have a volume of  $\sim 20$  ml exposed to the PMT, with an additional  $\sim 5$  ml not exposed. Since all the reaction rates of interest are temperature sensitive, as is the light output of the  $\text{NO}/\text{O}_3$  reaction, the reactor temperature should be controlled to  $90^\circ \pm 5^\circ\text{C}$ . To minimize residence times and absorption of sample on the lines, they should be kept short and heated to  $\sim 40^\circ\text{C}$ .

Many other embodiments of the basic measuring scheme proposed here can be put forward, such as using one PMT with movable filters or switching samples around in a number of reactors monitored by one PMT. For a prototype, however, we believe the simplest, most direct approach is the best and the one most likely to succeed in testing the method.

#### ACKNOWLEDGMENTS

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