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PROTOTYPE CHEMILUMINESCENT ANALYZER FOR MEASUREMENT OF HYDRAZINES

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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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Three prototype chemiluminescent instruments were built that will measure concentrations of hydrazine, MMH, and UDMH in the range of 0.01 to 100 ppm in air. Sensitivity of the instrument is 0.01 ppm hydrazine, 0.04 ppm MMH, and 0.07 ppm UDMH with an accuracy ±10%. Sensitivity toward the hydrazines as a function of various conditions is discussed along with the results of an interference study. Ways of decreasing cost, weights, and size of the units without adversely affecting sensitivity or reliability are suggested.

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CONTENTS

Page

LIST OF FIGURES

Figure

LIST OF TABLES

Table

PROTOTYPE CHEMILUMINESCENT ANALYZER FOR MEASUREMENT OF HYDRAZINES

INTRODUCTION

The ability to monitor concentrations of the rocket propellants, monomethylhydrazine (MMH), 1,1-dimethylhydrazine (UDMH), and hydrazine (Hz), at launch and storage sites is necessary for safety and other factors. Preliminary studies at the USAF School of Aerospace Medicine, Crew Environments Branch (USAFSAM/VNL), indicated that the hydrazines could be monitored by measuring the light output of their chemiluminescent reactions with ozone. In a previous contract with the USAF School of Aerospace Medicine (USAFSAM Contract No. F41609-76-C-0029) we confirmed these preliminary conclusions and obtained the information needed to design an instrument (1). A breadboard instrument based on the design was built under Contract No. F33615-76-C-0602 (2, 3).

The objectives of the present contract were to design, construct, and test three prototype hydrazine analyzers that will measure the concentrations of Hz, MMH, and UDMH in air. As before, our approach 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 and temperature. Since it had 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.

The basic design of the instrument was established in the feasibility study and in the prototype construction. This was further developed prior to the start of construction and modified somewhat during testing. The final design is presented in this report. A more detailed set of drawings, including electronic schematics, is given in the manual (4) for the instrument.

A discussion of results is presented, and possible future improvements or modifications are discussed.

PRINCIPLE OF MEASUREMENT

Measurements of the three hydrazines rely on monitoring the light output of their direct chemiluminescent reactions with ozone. This light intensity is a function of the ozone and hydrazine concentrations, 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.

INSTRUMENT DESIGN

The basic functions of the instrument are shown schematically in Figure 1. This instrument is very similar to an NO/NO_2 analyzer (5) and does in fact measure high levels of NO. It does, however, require a higher reactor temperature both to enhance the reaction rate and to prevent products from the hydrazine-ozone reaction from precipitating on the reactor walls.

As shown in Figure 1, the air (analyte) being monitored is drawn into the instrument at ≈ 13 ml(STP)s^{-1}. Air is also drawn in at 13 ml(STP)s^{-1} and 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.

Very rough kinetic measurements (1) indicated that at 80°C a 20-ml reactor volume would be required to achieve complete reaction of the hydrazines. The breadboard instrument used a Pyrex reactor with a volume of about 10 ml. Tests made during this work indicated that aluminum was also a satisfactory reactor material. Since aluminum is easier to shape, a somewhat larger volume of ≈ 15 ml was achieved with the aluminum. As in the breadboard instrument (3), a flat spiral reactor was made with the gas inlet in the center to achieve good mixing and efficient light transmission to the photomultiplier tube (PMT).

Initially the hydrazines were to be mixed with the ozone ≈ 4 ml upstream of the reactor entrance to allow any NO in the sample 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, and this could result in ambient NO levels causing significant interference in the hydrazines mode.) This approach was attempted and abandoned in the breadboard instrument since the optical filter required to reduce background also reduced NO interference to acceptable levels. It was attempted again in the present work because a potentially large increase in Hz sensitivity is obtainable by including the red emissions in the detection scheme (see Fig. 3 in ref. 1) and the background in the breadboard was ultimately reduced to very low levels, thus suggesting that the optical filter is not necessary for background reduction.

Based on the higher than expected background signal and response which were encountered in the prototypes, the optical filter again was the best choice for eliminating the NO interference. Therefore, a less expensive non-cooled bialkali PMT may be used rather than the cooled trialkali employed in these instruments. This possibility was investigated with good results (see "change in PMT").

TEST RESULTS

Testing of these instruments can be divided into three phases: (1) testing of the separate functions of the instruments, including detection and temperature control, electronics, and plumbing; (2) determination of the performance under various experimental conditions (interference tests are included in this category); and (3) environmental tests. The performance and

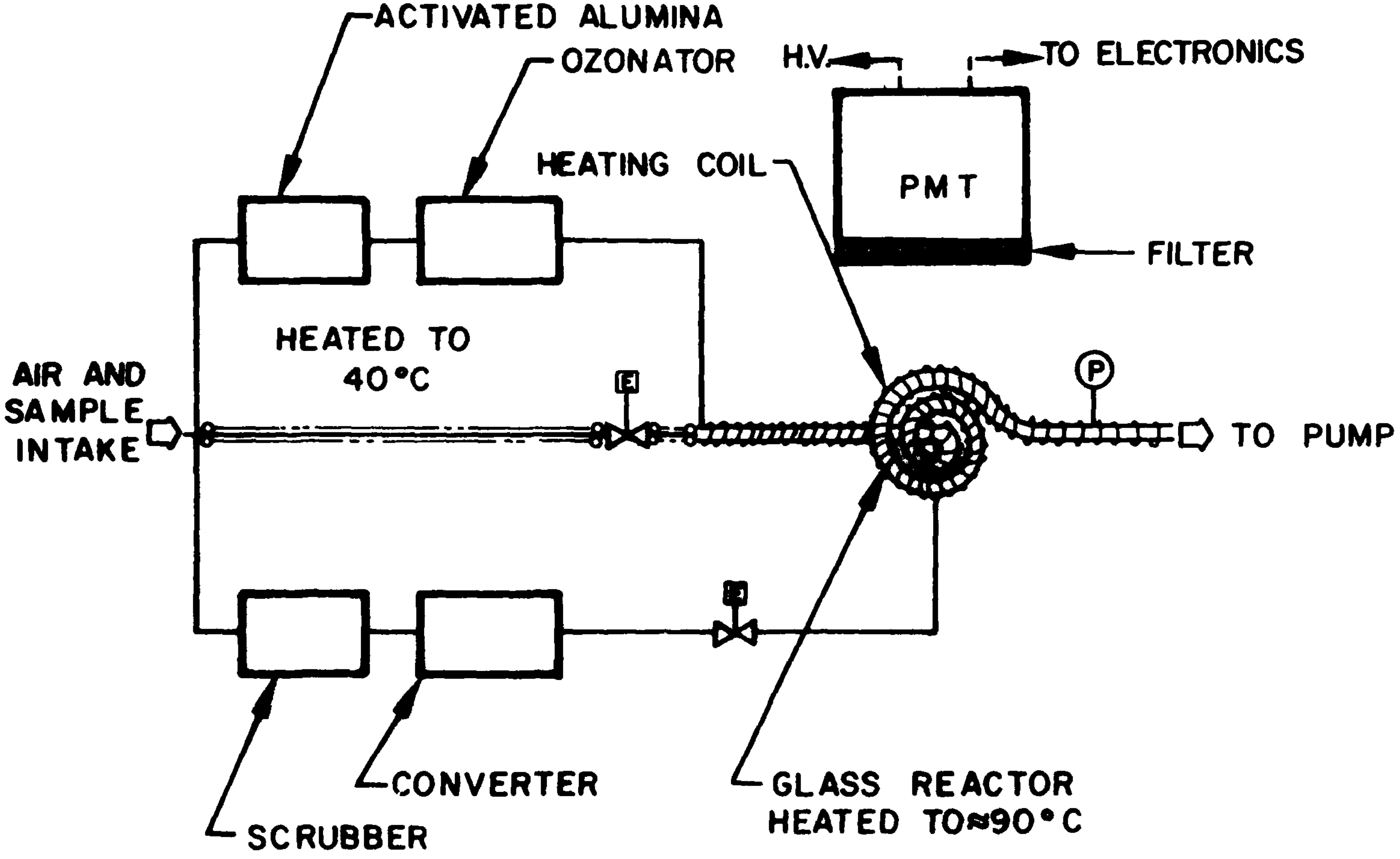

Figure 1. Schematic of hydrazine analyzer.

environmental tests are reported here; the functional tests were successfully passed.

Sampling Sources

Samples were prepared in one of two ways. Continuous samples of the hydrazines were obtained (1) 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 (< 1 ml s^{-1}) of N_2 entered the test tube through a 3-mm-o.d. Teflon tube extending to within a few centimeters from 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.

To calibrate the instrument and to carry out the linearity tests, the well-known exponential dilution flask technique was used (5). Samples were obtained by injecting a known amount of a liquid or pure gas into a well-stirred and heated (≈ 40°C) Pyrex flask of known volume (2 liters). 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.

Background

As was the case with the breadboard instrument, a sizable temperature dependent signal is obtained with zero gas as sample. The effect of temperature on background is shown in Figure 2, and the variation in background with ozone concentration (as input voltage to ozonator transformer) is shown in Figure 3. It appears that the magnitude of this background is proportional to the ozone concentration in the reactor and increases exponentially with temperature up to at least 170°C, the highest temperature tested. Relative ozone concentration as a function of ozonator voltage is shown in Figure 4 (from reference 3).

Sensitivity toward the Hydrazines as a Function of Conditions

The parameters varied were: reactor temperature and pressure, and ozone flow rate and concentration. The results of these tests are displayed in Figures 5-8. Figures 5-7 show the response of the instrument toward Hz, MMH, and UDMH, respectively, as a function of reactor temperature at an ozonator voltage of 115 V. Figure 8 illustrates the variations in response with ozonator voltage for Hz and UDMH (MMH is very similar to UDMH) at a reactor temperature of 100°C. A pressure effect was also observed, but it is small (and positive) for all three hydrazines, i.e., an increase in reactor pressure causes only a slight increase in signal. Unless indicated otherwise, the sample and ozone flow rates were 13 ml(STP)s^{-1} in the above tests which

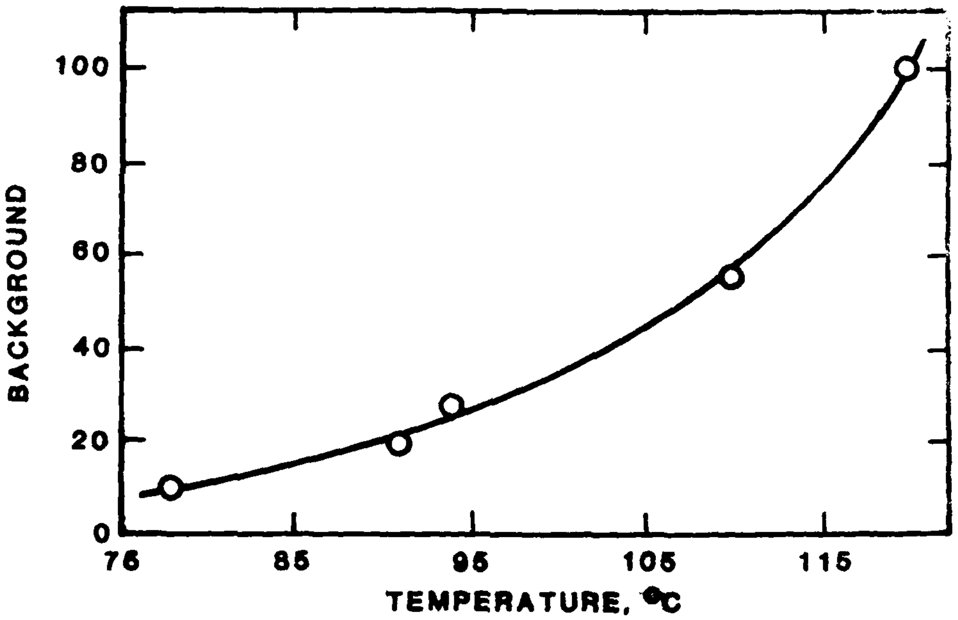

Figure 2. Background at 115-V ozonator voltage.

Sample and ozone flows: 13 ml(STP)s^{-1}

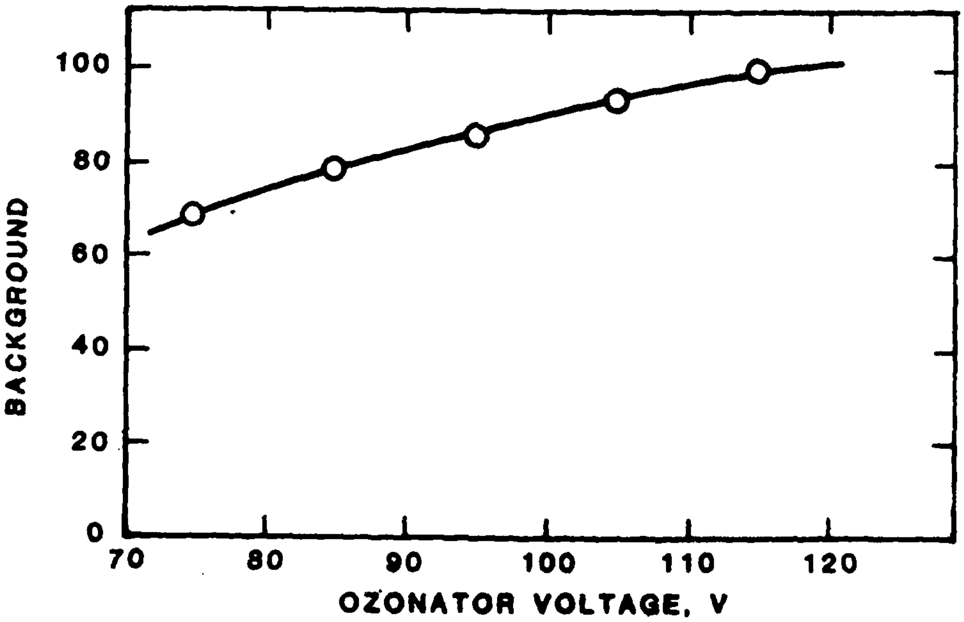

Figure 3. Background at 100°C.

Sample and ozone flows: 13 ml(STP)s^{-1}

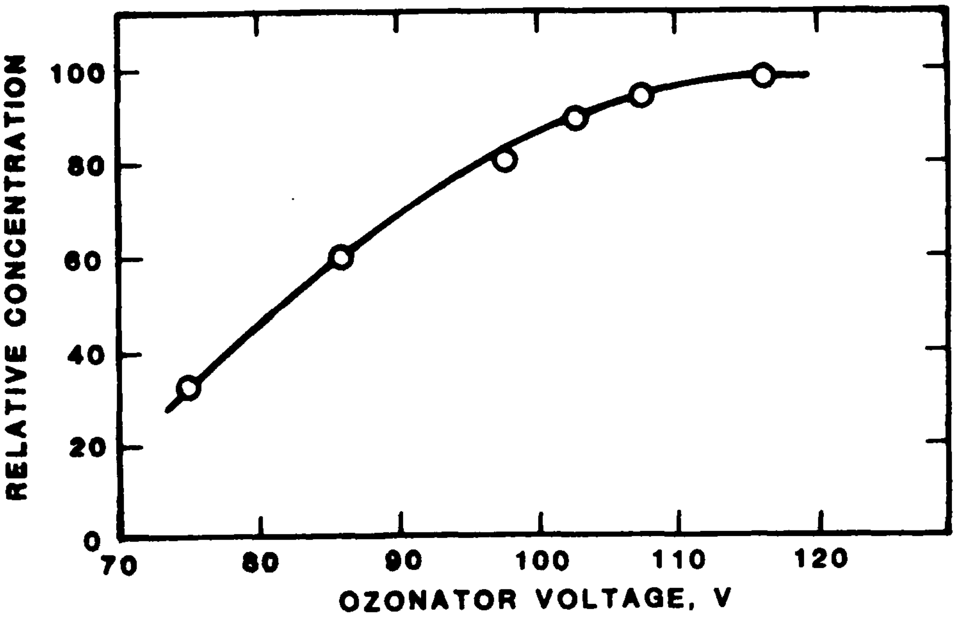

Figure 4. Relative ozone concentration at reactor.

100 corresponds to ≈ 0.2%. Ozone flow: 20 ml(STP)s^{-1};
Sample flow: 2 ml(STP)s^{-1}.

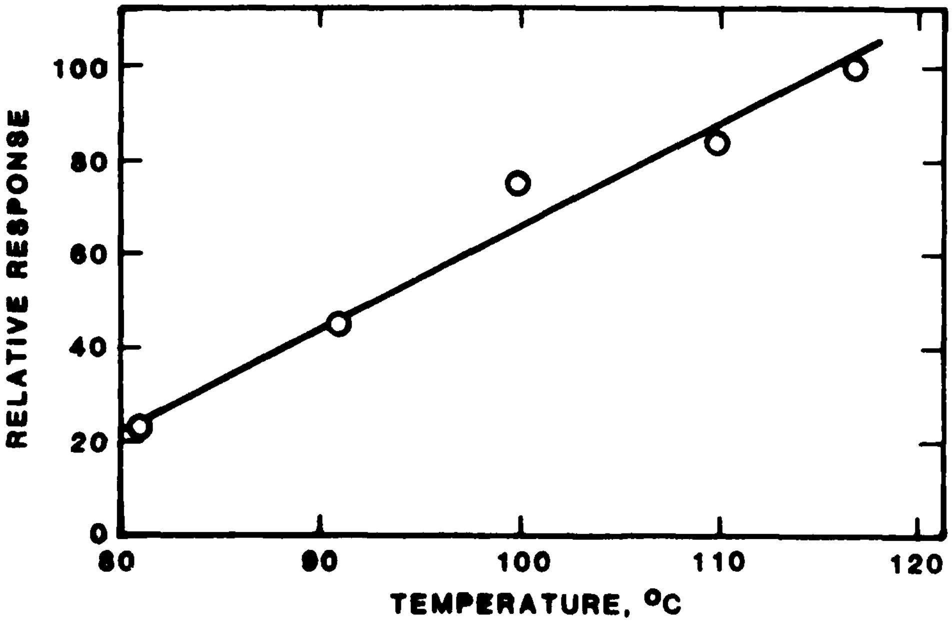

Figure 5. Hydrazine response at 115-V ozonator voltage.

Sample and ozone flow rates: 13 ml(STP)s^{-1}

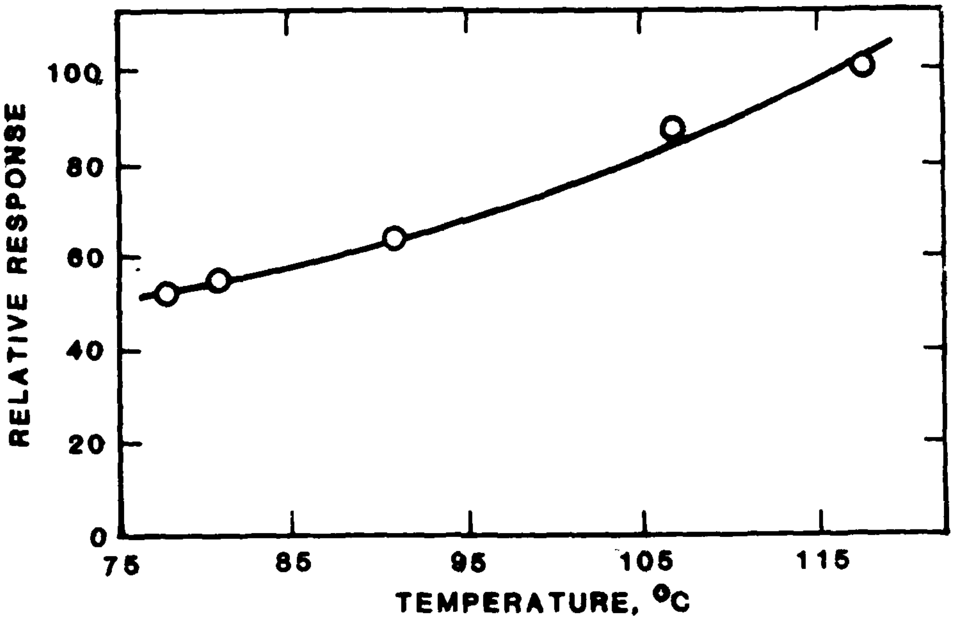

Figure 6. MMH response at 115-V ozonator voltage.

Sample and ozone flow rates: 13 ml(STP)s^{-1}

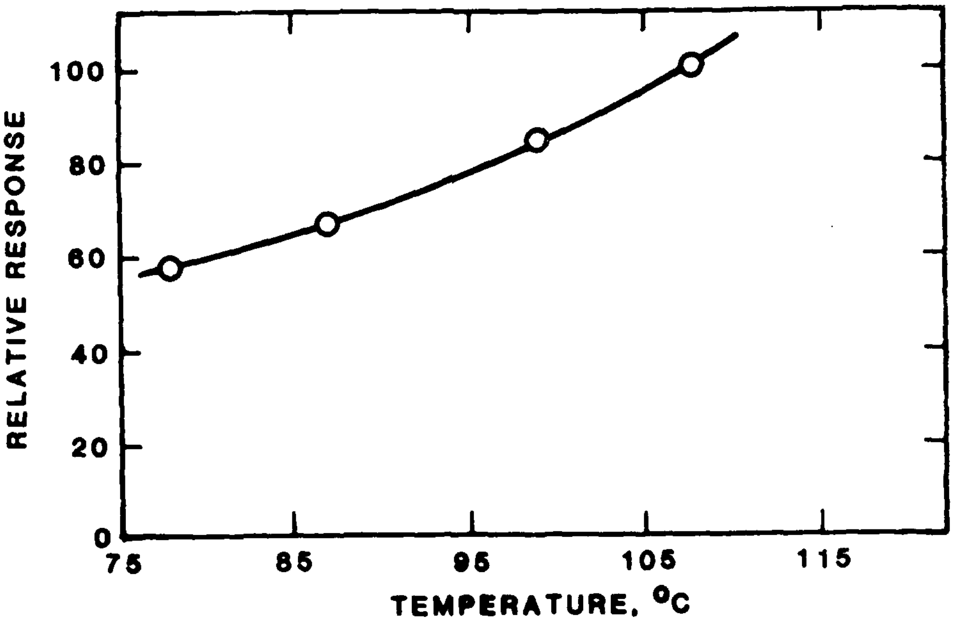

Figure 7. UDMH response at 115-V ozonator voltage.

Sample and ozone flow rates: 13 ml(STP)s^{-1}

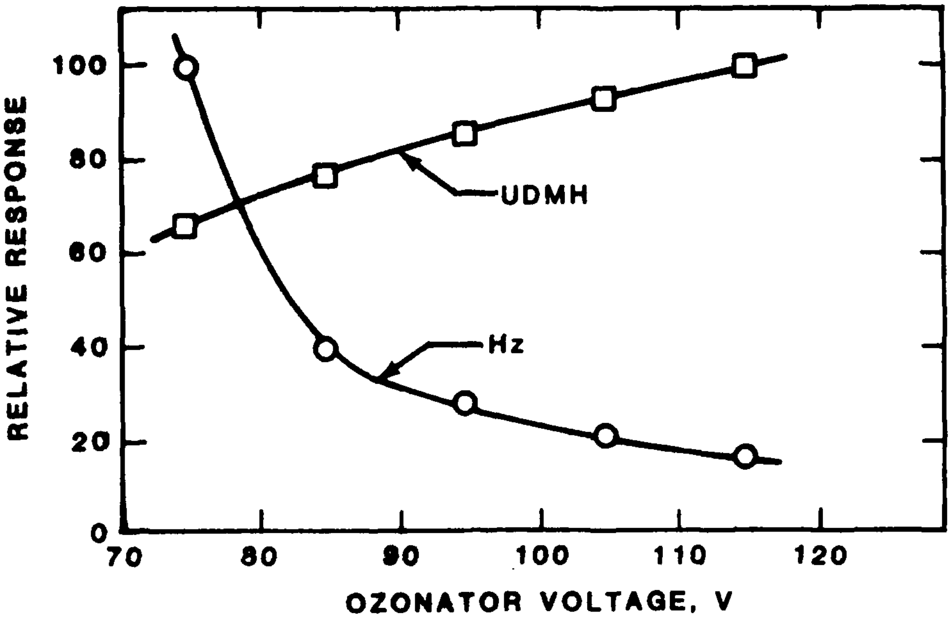

Figure 8. Hz and UDMH response at 100°C.

corresponds to a reactor pressure of ≈ 200 Torr. Higher pressure measurements were made by throttling the pump.

To maximize the sensitivity of the instrument, the largest signal to background must be chosen. In this case the factor limiting sensitivity is not due to the limited number of PMT pulses observed (as in the case for PMT dark current) but is due to the noise (instability) in the background. This instability in the background, possibly due to small temperature fluctuations, is roughly proportional to the background signal itself (rather than its square root). The PMT dark current contributes negligibly to the noise in the background.

It can be seen from Figures 4-7 that different conditions maximize the sensitivity for different hydrazines. A relatively low temperature, e.g., ≈ 85°C, and maximum ozone concentrations give best results for MMH and UDMH. A much higher sensitivity for Hz compared to these conditions occurs at a lower ozonator voltage of, e.g., 75 V and a higher temperature (probably greater than the maximum of 125°C actually used in testing). The conditions that maximize the MMH and UDMH response were chosen since even there the response toward Hz is almost a factor of 5 greater than for the others.

Interferences

The interferences of interest are possible positive interferents that can give false alarms, such as amines, and negative interferents such as water.

Also of interest are NO and C_2H_4 which, while not expected to be present in high enough concentrations to cause problems, could be considered as possible calibration gases for field use. Because Hz and the other two hydrazines behave differently with changing instrument conditions, it is clear no substitute calibration sample can be found. NO or C_2H_4 can, however, be used to indicate changes in instrument performance and whether a more complete calibration is required. The responses to NO, C_2H_4, H_2O, and several amines are shown in Table 1. The interference levels of the aliphatic amines are roughly the same as measured in the breadboard instrument while aniline shows a much higher response. Fortunately, aniline is not expected to be present.

TABLE 1. INTERFERENCES

Interferent	Extent of interference (% of response in MMH mode)
Diethylamine	<2
Propylamine	<2
Aniline	≈30
C_2H_4	3
NO	10
per % H_2O[a]	2

[a] For UDMH multiply by 0.5; for hydrazine by 4.

Environmental Tests

The 5-15°C higher internal temperature of the instrument relative to ambient eliminates humidity problems. Effects of ambient temperature variations were investigated by placing the instruments in a sealed enclosure that can be maintained at temperatures from ≈ 15°C to 50°C; test temperatures were limited to a maximum of ≈ 35°C. Although the internal instrument temperature is controlled, it varies with changes in external temperature, by somewhat less than half of the external temperature change. Thus, the internal temperature should be in the range of 30-40°C for ambient changes from 5-35°C. The separate temperature control on the reactor maintains it constant to within about 2°C over the 5-35°C ambient range.

The factor affecting performance most is the drift in background, the temperature variation of which amounts to about +1/2% per °C external increase.

Linearity

Problems similar to those described before (1) were again experienced in determining linearity, i.e., adsorption of sample on tubing walls and in the exponential dilution flask and reaction of the hydrazines (especially Hz) with air. The latter problem was minimized by passing nitrogen through the dilution flask and then diluting that sample with a large amount of air. It appears from these tests that the signal is proportional to the hydrazines concentration raised to the power of 1 ± 0.05, as was concluded from the breadboard tests.

Specifications

Table 2 shows the specifications of the instrument.

The dark current and background are 0.4 and 2.2 ppm, respectively, relative to MMH.

TABLE 2. SPECIFICATIONS OF HYDRAZINES ANALYZER

Contaminants	Hz, MMH, UDMH
Range	Hydrazines: 0.1, 0.25, 1, 2.5, 10, 25, 100
Linearity	See "Linearity" in text
Accuracy	± 10%
Span drift	± 5% (accuracy of preparing samples)
Sensitivity	Hydrazine[a]: 0.01 ppm MMH[a]: 0.04 ppm UDMH[a]: 0.07 ppm
Noise	< 0.5% on 2.5 ppm scale Hz
Response	Selectable 3, 10, and 30 s for 95%
Environmental stability	5-35°C
Size	0.07 m^3
Weight	≈ 30 kg
False alarm	See "Interferences" in text

[a] Twice peak-to-peak noise.

Change in PMT

Because only the visible region of the emissions is viewed (to reduce NO interference and background), a less expensive PMT than the cooled trialkali used should perform adequately. This was tested and found to be true. The response toward a given concentration of Hz's, NO, and C_2H_4, and the background are compared below for the cooled trialkali (Centronics 4283) and a noncooled bialkali (Centronics 4242).

	Centronics	
	4283	4242
	Response[a]	
MMH	1	1.4
UDMH	1	1.5
Hz	1	1.2
NO	1	1.1
C_2H_4	1	1.2
Background	1	.75
Dark current	1	.8

[a] Arbitrary units

DISCUSSION

The instruments resulting from this work are very similar to their predecessor, the breadboard hydrazine analyzer, with the major exception being the significantly higher sensitivity toward hydrazine. In view of the fact that the reactor temperature used in these instruments is lower than that in the breadboard, a lower hydrazine response was expected, but it was found to be a factor of ≈ 5 higher. The only difference that could cause this (assuming the aluminum used as reactor material does not affect the reactions) is the increase by a factor of about 2 in reactor size. The much larger aniline interference may be related to the larger Hz response for the same reason.

IMPROVEMENTS

The major change suggested by the results presented in this report is to replace the relatively expensive red-sensitive trialkali PMT and its cooled housing with a noncooled bialkali tube. This change alone would almost halve the parts cost of the instrument without affecting performance much. Nearly 100 W would be saved as well by not having to cool the PMT.

While the metal bellows pump used in these instruments is very rugged, power, weight, and cost savings could be realized with a smaller pump. The higher resulting reactor pressure would, if anything, improve sensitivity, but some reliability would be lost.

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