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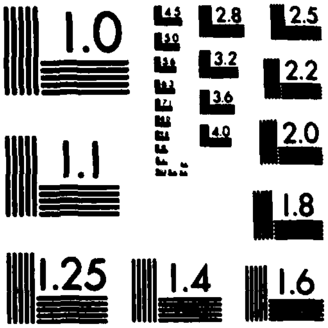

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PROTOTYPE CHEMILUMINESCENT ANALYZER FOR MEASUREMENT OF HYDRAZINES AND NITROGEN DIOXIDE

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Prepared for
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Brooks Air Force Base, Texas 78235

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NOTICES

This final report was submitted by AeroChem Research Laboratories, Inc., P.O. Box 12, Princeton, New Jersey, under contract F33615-81-C-0621, job order 7930-11-56, with the USAF School of Aerospace Medicine, Aerospace Medical Division, AFSC, Brooks Air Force Base, Texas. Dr. Leonard J. Luskus (USAFSAM/VNC) was the Laboratory Project Scientist-in-Charge.

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The Office of Public Affairs has reviewed this report, and it is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Five prototype instruments have been built which will measure concentrations of hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine in the range of 0.05 to 100 ppm in air, and nitrogen dioxide in the range of 1 to 100 ppm in air. The performance of the instruments is described, and tests results are given.

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EDITOR'S NOTE: For the convenience of the reader, all figures have been grouped at the close of this report.

PROTOTYPE CHEMILUMINESCENT ANALYZER FOR MEASUREMENT OF HYDRAZINES AND NITROGEN DIOXIDE

I. INTRODUCTION

Necessary for safety and other reasons is the ability to monitor, at launch and storage sites, the concentrations of the rocket propellants, monomethylhydrazine (MMH), 1,1-dimethylhydrazine (UDMH), and hydrazine (Hz), as well as nitrogen dioxide (NO_2). Preliminary studies at the USAF School of Aerospace Medicine Crew Protection 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 (No. F41609-76-C-0029) with the USAF Air Force Systems Command (USAF/AFSC), Aerochem Research Laboratories, Inc., confirmed these preliminary conclusions and obtained the information needed to design an instrument (1). A breadboard instrument, based on that information, was built (2,3) under Contract No. F33615-76-C-0602; and three prototype analyzers (4,5) were subsequently built under Contract F33615-79-C-0607.

The objective of the present contract was to design, construct, and test five prototype analyzers that would measure the concentrations of MMH, UDMH, Hz, and NO_2 in air. As before, our approach was to build instruments, and then to determine their performance as functions of such easily varied parameters as pressure and temperature.

The basic design for the five instruments was established in the feasibility study (1) and in the previous construction programs (2-5); and this design was further refined in the present program, prior to construction, to incorporate changes specified in the contract. The design was also modified somewhat during testing. (The final design is presented in Section III.) A more detailed set of drawings, including electronic schematics, is given in the instrument Manual (6).

Results are discussed in Sections IV and V; and possible future improvements or modifications, in Section VI.

II. PRINCIPLE OF MEASUREMENT

Concentration measurements of the three hydrazines rely on monitoring the light output of their direct chemiluminescent reactions with ozone. NO_2 concentration is measured by reducing it to NO, which is then measured similarly to hydrazines. For hydrazine measurements, the chemiluminescent light intensity is a function of the ozone and hydrazine concentrations, and of the pressure, temperature, and reactor geometry; but the functional relationship of these parameters is not known. The behavior of the instrument cannot be adequately predicted mathematically, as a function of operating conditions, without a detailed study of the fundamental reactions involved. Hence this behavior has been determined experimentally for a limited number of representative operating conditions. The results of these determinations are presented in Section IV. The NO/O_3 reaction is very well understood; so, when the instrument has been calibrated, instrument performance under any conditions when measuring NO_2 can be adequately predicted (5).

III. INSTRUMENT DESIGN

The basic instrument design is shown schematically in Figure 1. These instruments are very similar to AeroChem NO/NO_2 analyzers (7) and are, in fact, also designed to measure high levels of NO_2. They require higher reactor temperatures than does an NO analyzer, both to enhance the hydrazine-ozone reaction rate and to prevent reaction products from depositing on the reactor walls.

Referring to Figure 1, the air being monitored (sample) is drawn into the instrument at ≈ 13 cm^3(STP)s^{-1}. Additional air is: drawn in at 13 cm^3(STP)s^{-1}; passed through a Perma Pure permeation dryer to reduce its water content to less than about 0.5%; scrubbed in an activated alumina trap to remove remaining H_2O, amines, and hydrazines; and, finally, passed through a discharge ozonator and into the ozone inlet of the reactor. For NO_2 measurements, the sample is passed through a phosphoric acid-containing scrubber to remove hydrazines, and through a high temperature catalytic converter to reduce the NO_2 to NO; then the sample is passed into the reactor.

After exiting the reactor, the gases pass first through a thermal scrubber, and then a chemical scrubber to remove the ozone effectively. The resulting ozone-free gas stream at ≈ 300 Torr is used as the counterflow in the Perma Pure dryer. Manufacturer's specifications call for this counterflow to be dry air at a flow rate twice that of the air to be dried. Since the air used as counterflow cannot be completely dry, a lower pressure of slightly wet counterflow is used. Tests indicate that this arrangement reduces the water content of the air to $< 0.5\%$ at 25°C.

Approximate kinetic measurements (1) indicated that, at 80°C, a 20-cm^3 reactor volume would be required to achieve complete reaction of the hydrazines under the conditions used in the breadboard instrument (2,3). That instrument utilized a Pyrex reactor with a volume of about 10 cm^3. Similar Pyrex reactors are used in the present instruments.

In all the previous instruments, cooled trialkali photomultiplier tubes (PMTs) served as detectors; these tubes have useful response to wavelengths of 800 nm. Because large background readings, which consisted mainly of red and infrared (ir) radiation, were obtained in these instruments (2-5), optical filters were used to restrict the detector response to below ≈ 600 nm. In the present instruments, bialkali PMTs--with useful response to ≈ 600 nm--were therefore used. This choice eliminated both the need for optical filters and the need to cool the PMTs (since bialkali tubes have much lower dark currents than trialkali tubes); and it reduced the sensitivity toward NO to a few percents that of Hz (i.e., reduced the NO interference in hydrazine measurements).

Two other refinements to the design of the previous prototypes were made: (a) to increase the time between servicing of the activated alumina dryer; and (b) to improve span and zero stabilities. To increase the lifetime of the chemical dryer, a Perma Pure permeation predryer was installed upstream of it. In the permeation predryer, water passed through the semipermeable walls of the drying tubes from a region of high water concentration to one of lower concentration. In the present instruments, as compared with past types, the low water concentration air flow (counterflow) consists of air at about half the ambient humidity (the result of mixing equal volumes of dry and ambient air) and at a reduced pressure of ~ 300 Torr, thus achieving an effective humidity of about 25% of ambient. This permeation predryer extends the lifetime of the chemical dryer by a factor of 3 to 4 at high humidities (expected lifetime, at 50% relative humidity and 25°C, is 1 - 2 months).

To achieve zero and span stabilities, the following operating conditions must be held constant:

1. flow rates (sample and ozonator air)
2. reactor pressure
3. ozone concentration
4. reactor temperature.

Constant flow was achieved with critical flow orifices, and the diaphragm pump maintained a sufficiently constant reactor pressure. To achieve stable ozone concentrations and constant reactor temperature, some effort was required. The ozone concentration varies with ozonator conditions. It decreases with increasing air flow, water content of the air, and ozonator temperature--and increases with ozonator voltage increases. Again, critical orifices are used to yield a constant air flow. By use of a dryer with constant flow rates, variations due to changing water content were minimized. Temperature effects were reduced by operating the ozonator in a thermostated enclosure at ~ 35°C. Finally, to minimize the effect of line voltage variation on ozone concentration, the ozonator was initially powered from constant voltage supplies. When three of the five supplies failed after a short running time, we decided to replace all five with the standard transformers used previously. The effect of ozonator voltage variations that might thus occur due to changes in line voltage can be judged from the test results (in the next report section); e.g., <5% in response for a 10% change in ozonator voltage. These transformer failures and their replacements necessitated obtaining an extension in contract duration.

IV. TEST RESULTS

Testing of the instruments was divided into three parts: (A) testing of the separate functions of the instruments, including detection and temperature control electronics, and plumbing; (B) determination of their overall performance under various experimental conditions (interference tests are included in this category); and (C) environmental tests. The test results are discussed in the following paragraphs.

A. Function Tests

All separate function tests were passed with no unusual observation.

B. Performance Tests

All five instruments were initially calibrated for concentrations of one of the hydrazines, Hz; then, when MMH was measured, we found that the response toward the second hydrazine was different for each instrument. These differences do not pose a practical problem, because each instrument is calibrated for each hydrazine and the responses are equalized electronically. Additional tests were nevertheless conducted to determine the reasons for the differences; but no single dominant cause could be found. The variations appear to result from cumulative effects of small differences in the following parameters: PMT spectral response, ozone concentration, reactor temperature and pressure, flow rates, reactor geometry, and possible others. The respective effect of most of these parameters was determined.

Spectral response of the PMTs was tested by passing the light from an incandescent lamp through a monochromator onto the PMT cathodes. Over the 400- to 600-nm region, the responses of the four PMTs (normalized at 500 nm) varied by only 10%-20%. Ozone concentrations were estimated to be essentially identical for three of the four instruments tested.

Flow rates, reactor temperatures, and reactor pressures also were not (individually) sufficiently different to cause the differences in relative responses. More extensive temperature and ozone concentration tests were performed on two instruments. Each instrument showed a unique response with temperature and ozone concentration; fortunately, the differences between the instruments were small. The results are as follows:

1. Tests of Sensitivity Toward the Hydrazines As a Function of Reactor Temperature and Ozone Concentration

The effects of reactor temperature and ozone concentration are displayed in Figures 2-5. Figures 2 and 3 show the response of two instruments towards Hz and MMH, respectively, as a function of reactor temperature at a constant ozonator voltage of 115 V. Figures 4 and 5 illustrate the variations in response with varying ozonator voltage for Hz and MMH (UDMH behaves similarly to MMH) at a constant reactor temperature of 120°C. In these tests, the sample and ozone air flow rates were 13 $cm^3(STP)s^{-1}$, which corresponds to a reactor pressure of $\approx$ 300 Torr.

2. Sampling Sources

Test samples of Hz and MMH were prepared in two ways (a-b):

(a) Continuous constant concentration samples of the hydrazines were obtained (ref. 1) by placing the liquid in a test tube with a side arm, and immersing the tube in a constant temperature bath at 0°C. A small flow ($\approx$ 1 cm^3 s^{-1}) of air entered the test tube through a 3-mm o.d. Teflon tube, extending to within a few centimeters from the liquid surface. The air coming from the side arm of the test tube therefore was saturated with the hydrazine. This mixture was diluted with air and supplied to the instrument.

(b) To calibrate the instrument and to carry out the linearity tests, the well-known (ref. 5) exponential dilution flask technique was used. Samples were obtained by injecting a known amount of liquid or pure gas into a well-stirred and heated (≈ 40°C) 3.2-liter Pyrex flask, through which a constant flow of air passes. This procedure gives an exponential decrease in sample concentration with time. The exponential dilution flask was calibrated by injection of a known volume of pure NO, and by measurement of the response with a NO calibrated instrument.

3. Background Signal

As with the breadboard and prototype instruments, a sizable temperature dependent background signal is obtained with no hydrazines or NO_2 in the sample flow. The effect of temperature on background is shown in Figure 6; and the variation in background with ozone concentration (obtained by changing the voltage to ozonator transformer) is shown in Figure 7. Relative ozone concentrations as a function of ozonator voltage are shown in Figure 8 (3). The magnitude of this background appears to be proportional to the ozone concentration in the reactor (Figs. 7 and 8), and increases exponentially with temperature.

4. Sensitivity Optimization

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

As can be seen from Figures 2-8, different conditions maximize the sensitivity for different hydrazines. Maximum ozone concentrations give best results for MMH and UDMH. A much higher sensitivity for hydrazine occurs at a lower ozonator voltage of, for example, 75 V.

Operating conditions chosen were a 120°C reactor temperature, and an ozonator input voltage of 115 V (direct line voltage).

5. Interferences

Because these instruments are very similar to the breadboard instrument (they use basically the same Pyrex reactor and ozonator), interference tests were only carried out for the two gases not previously tested: SO_2, and a Freon. For the substances of interest (refer to Section V. Specifications) the interference is less than that specified.

C. Environmental Tests

The temperature inside the instrument enclosure is ≈ 5°C higher than ambient; therefore, no humidity problems (i.e., associated with condensation) are anticipated or have been observed. Temperature tests were made over the

15-35°C range. The PMT-ozonator enclosure temperature remains constant to within ≈ 2° with a 10°C change in ambient temperature. At larger than 10°C changes, corresponding changes occur in the enclosure temperature. The instruments were set to operate over an ambient temperature range of ≈ 20-30°C. From Figures 2 through 7, the estimate is that temperatures outside this set range will result in approximately 1% change in response and background per degree Centigrade change in temperature. The Manual describes the procedure for changing this range (6).

V. SPECIFICATIONS

The design goal specifications of the hydrazines analyzers (Table 1) have been essentially achieved. The instruments will operate from 5-35°C, although temperature control of the PMT, reactor, and ozonator is maintained only over a 10°C range (20-30°C was selected). Beyond that range, reactor temperature reflects changes in ambient temperature; and response can be estimated from Figures 2-7. Accordingly, from 30-35°C, the reactor temperature will rise by ≈ 5°C, thus increasing response by approximately 5%; and, from 20 to 5°C, a ≈ 15°C decrease in reactor temperature will cause an approximate 20% decrease in response (Figs. 2 and 3). Similarly, zero d[illegible]s from 30 to 35°C will be approximately 20 ppb in the Hz and MMH mode (≈ [illegible] of the ≈ 100 ppb background), and from 20 to 5°C zero will change by ≈ 30 [illegible] (Fig. 6).

The design goal for MMH sensitivity was considerably surpassed. The actual sensitivity varied, in the five instruments, from <10 ppb to about 20 ppb vs. the goal of 100 ppb.

VI. DISCUSSION

The instruments resulting from this work are very similar in performance to the breadboard instrument. The much larger Hz response relative to MMH, observed in the prototype instruments but not in the breadboard, was also absent here. This finding could mean either that the aluminum used to build the reactors in the previous prototypes had some effect on the response of the hydrazines, or that the larger volume of the aluminum reactors resulted in a larger increase in response for hydrazine than for MMH and UDMH.

The reason for the variation in response among the five instruments is not known, but is probably the result of the cumulative effect of a number of variables. Thus, small differences--in reactor temperature, reactor volume, reactor position relative to the PMT, ozone flow rate, ozone concentration, sample flow rate, reactor pressure, and PMT spectral response--can combine to make the relative response for the three hydrazines different for the five instruments. These differences are, of course, calibrated out and do not affect the performance of the instruments.

TABLE 1. SPECIFICATIONS

	Parameter	Design goals
1.	Contaminants to be measured	Hz MMH UDMH NO_2
2.	Sensitivity (minimum detectability)	0.05 ppm Hz 0.1 ppm MMH 0.1 ppm UDMH 1.0 ppm NO_2
3.	Range (multi)	0-0.1,0-0.25, 0-1, 0-2.5, 0-10, 0-25, 0-100 ppm
4.	Precision	3% full scale
5.	Accuracy at 0.1 ppm Hz	10% full scale
6.	Noise	Less than 1% on 1-ppm range
7.	Span drift	1% per day
8.	Zero drift	1% per day
9.	Rise time (90% of reading at 0.1 ppm Hz)	Less than 90 s
10.	Fall time (90% of reading at 0.1 ppm Hz)	Less than 90 s
11.	Specificity (Concentration of interference (Hz)[a])	Ammonia (100:1) Nitrogen dioxide (100:1) Sulfur dioxide (100:1) Carbon monoxide (1000:1) Carbon dioxide (1000:1) Freons (1000:1)
12.	Temperature range of operation	5-35°C
13.	Humidity range during operation	10 to 95% R.H.
14.	Mode of operation	Continuous, real-time
15.	Size	Less than 2 cu ft
16.	Weight	Less than 65 lb

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[a] Analyzer need not differentiate between hydrazines.

VII. FUTURE IMPROVEMENTS

The major shortcoming of the instruments is the limited range of temperature over which they are stable without being adjusted. This shortcoming is the result of more heat input than anticipated to the PMT from the reactor and through the insulation. The major result of operating beyond the set (20-30°C) temperature range is a change in background signal. Because the background is low to begin with (≈ 100 ppb for Hz), a small change would not pose serious problems. To alleviate this effect in future instruments, however, two steps should be taken: (a) a separate active temperature control should be used for the reactor, instead of relying on the indirect control of a constant surrounding temperature and heat input; and (b) additional insulation and two cooling chips, instead of one, should be used to control the PMT-ozonator enclosure temperature.

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FIGURE NOS. 1 - 8

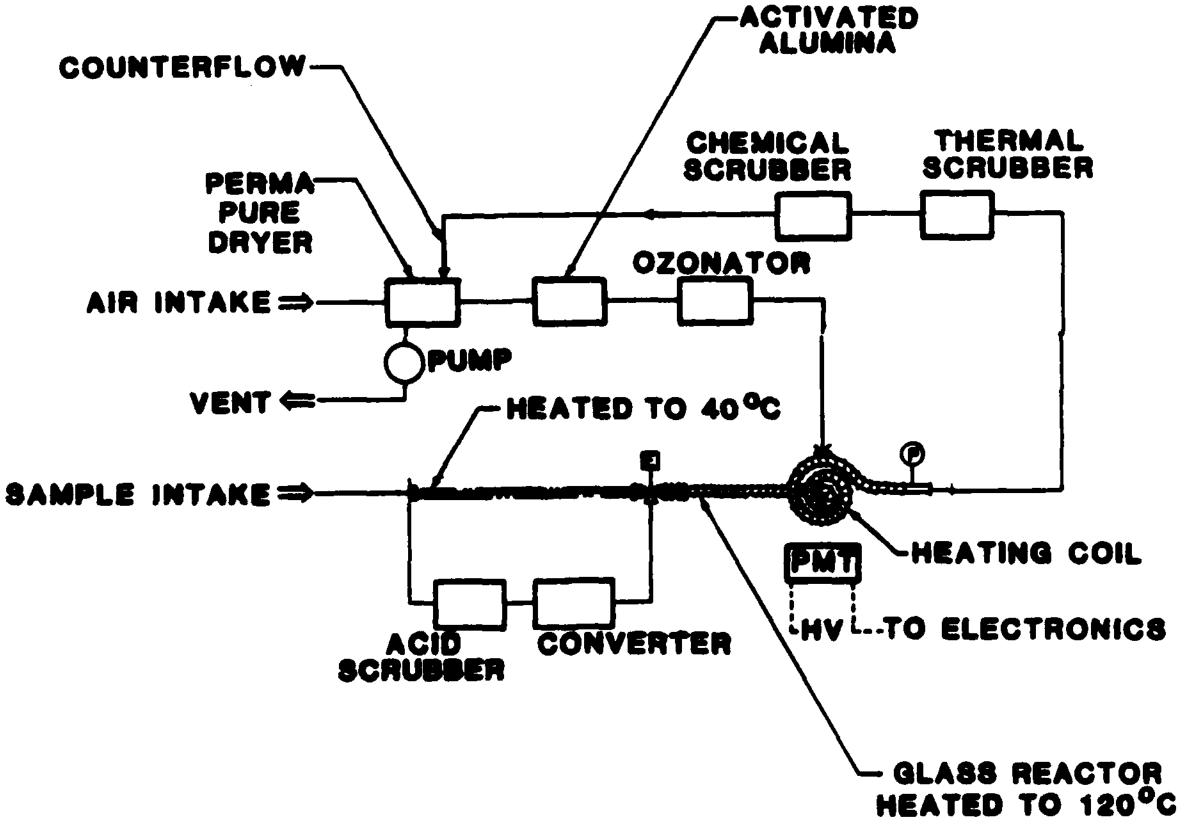

Figure 1. Basic instrument design of the hydrazines/NO_x analyzer.

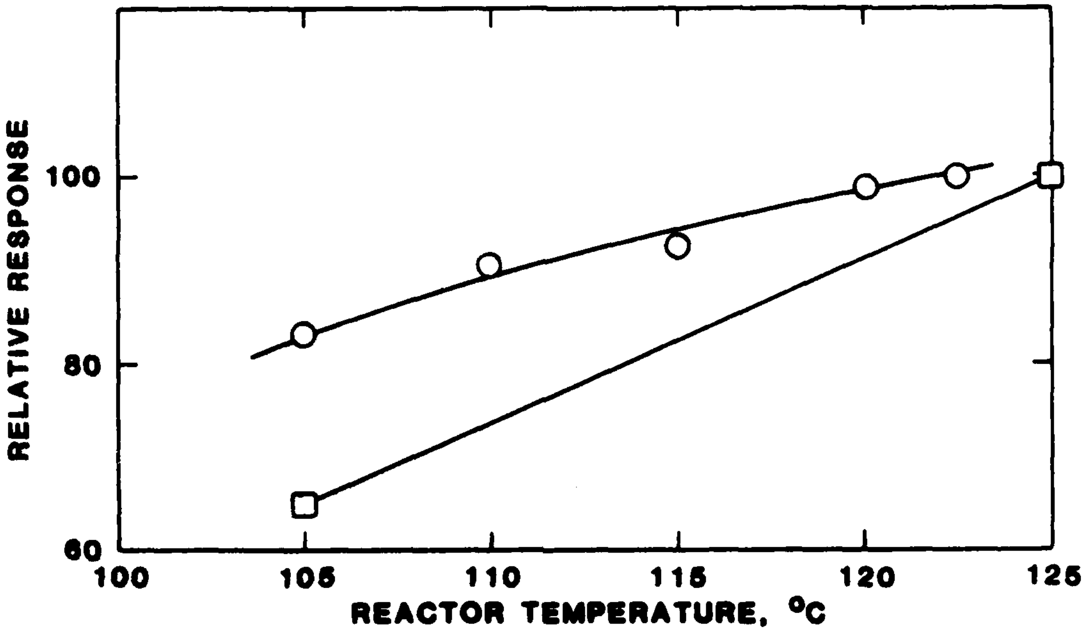

Figure 2. Hydrazine response at 115-V ozonator voltage.

○ Serial No. 2; □ Serial No. 4.

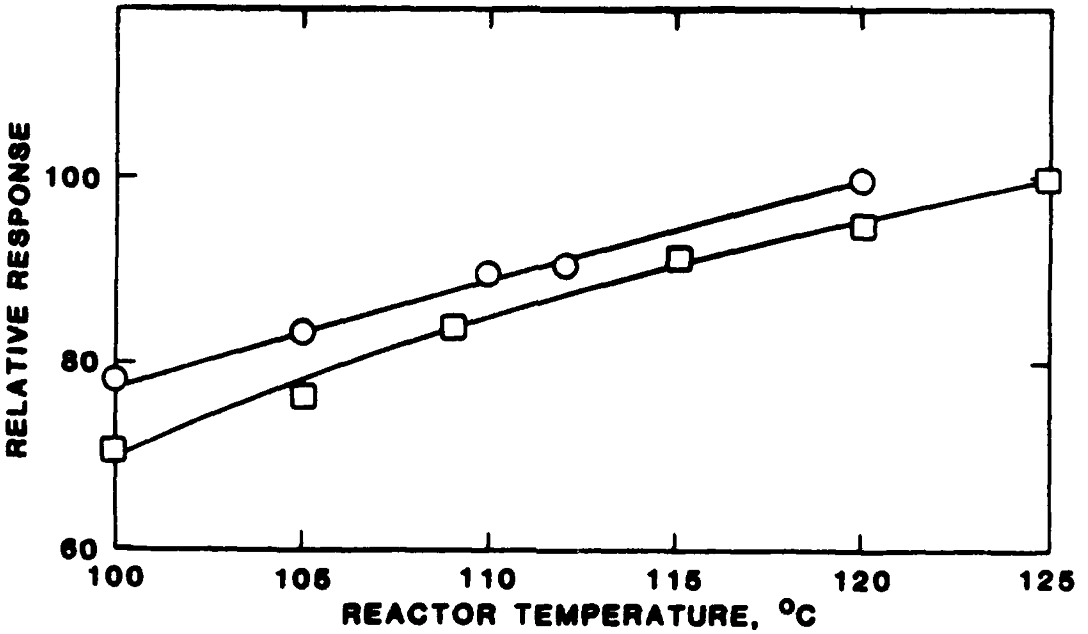

Figure 3. Monomethylhydrazine response at 115-V ozonator voltage.

○ Serial No. 2; □ Serial No. 4.

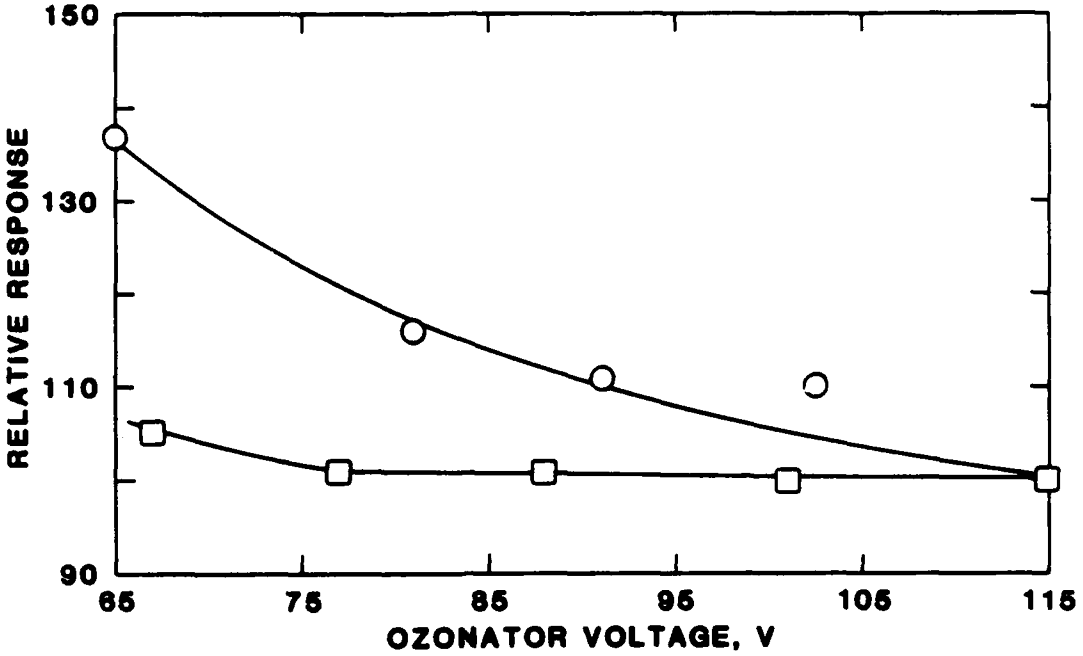

Figure 4. Hydrazine response at 120°C reactor temperature.

○ Serial No. 2; □ Serial No. 4.

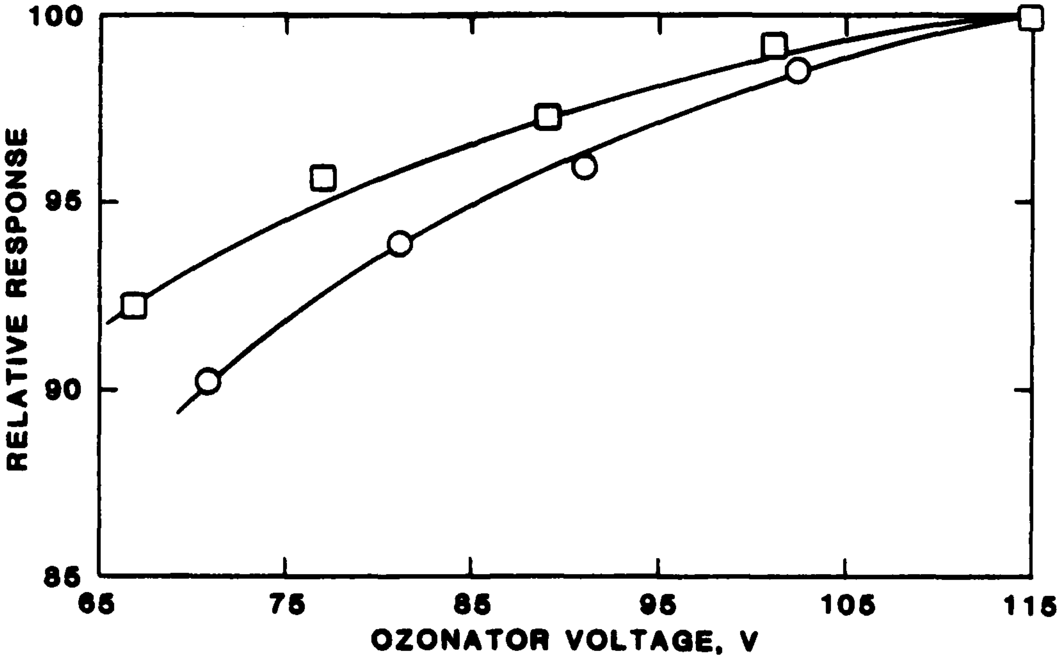

Figure 5. Monomethylhydrazine response at 120°C reactor temperature.

○ Serial No. 2; □ Serial No. 4.

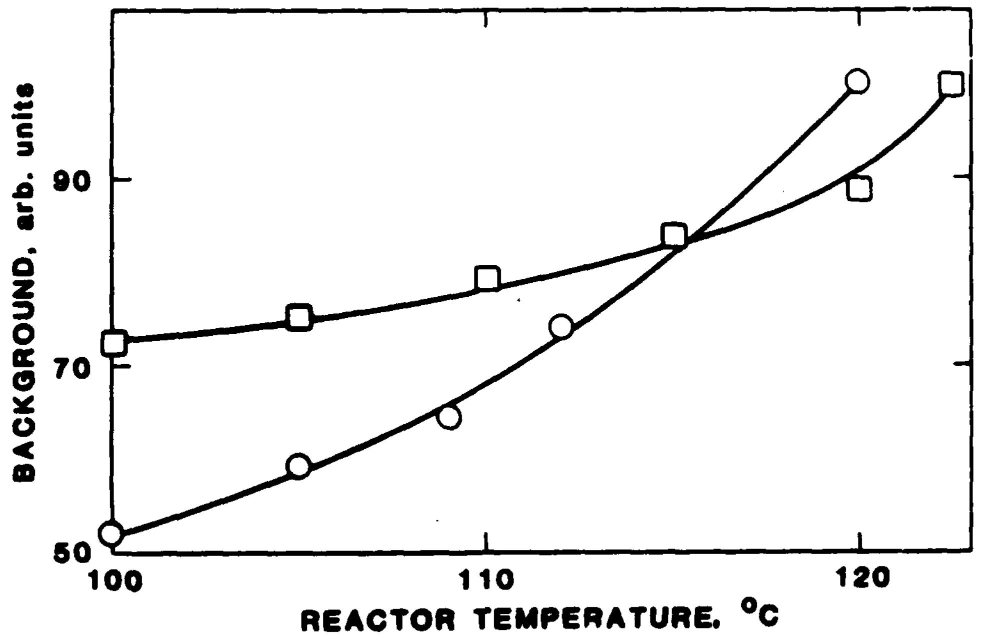

Figure 6. Background at 115-V ozonator voltage.

○ Serial No. 2; □ Serial No. 4.

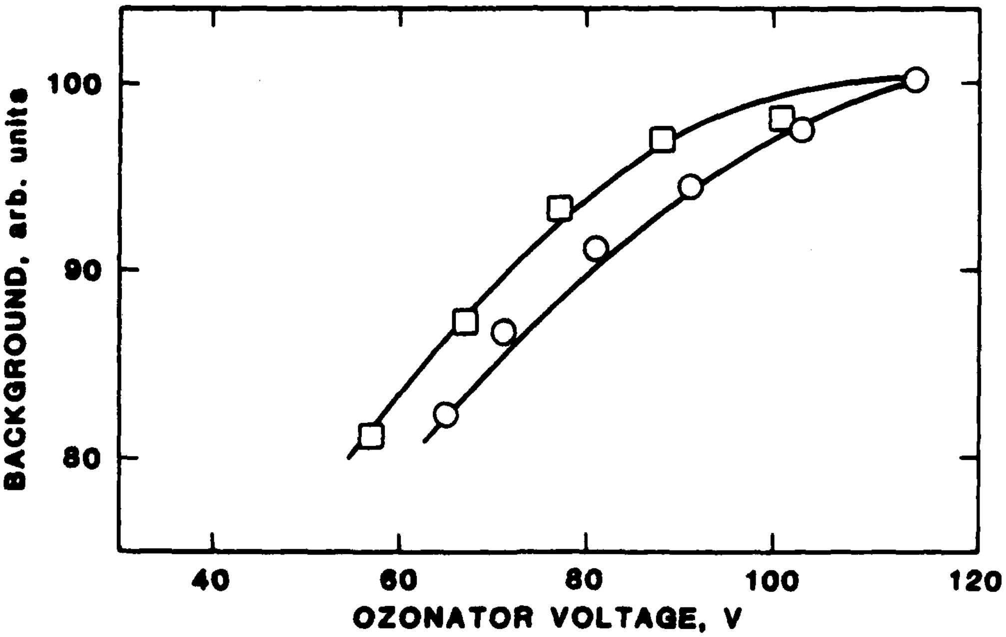

Figure 7. Background at 120°C reactor temperature.

○ Serial No. 2; □ Serial No. 4.

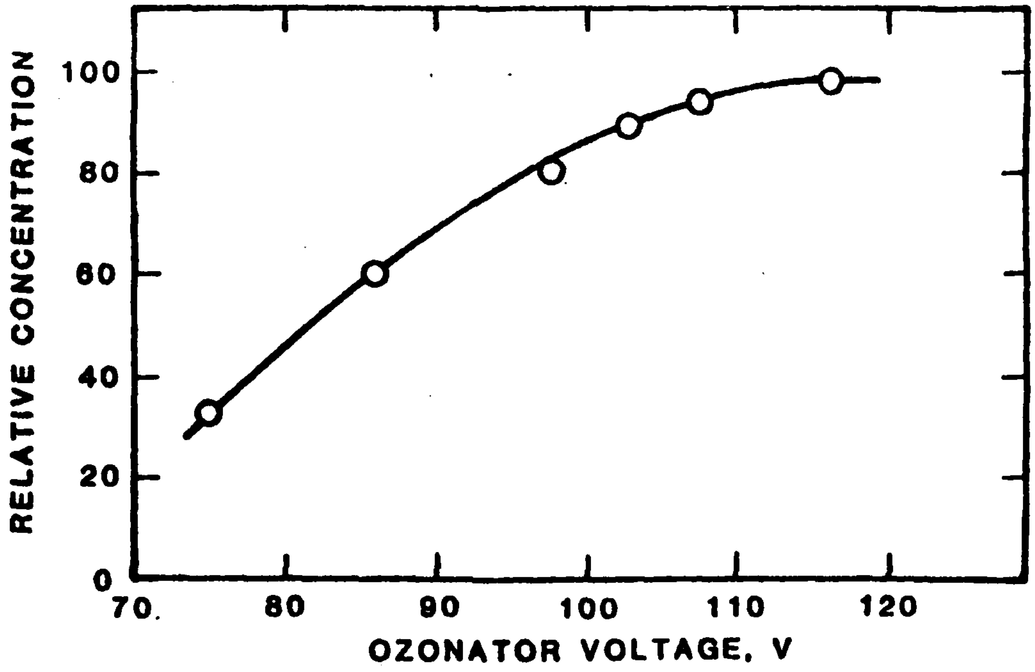

Figure 8. Relative ozone concentration at reactor. 100 corresponds to ≈ 0.2%. Ozonator air flow: 20 cm^3 (STPS)s^{-1}; and sample flow: 2 cm^3 (STP)s^{-1}.