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AMPEROMETRIC PROPELLANT-COMPONENT DETECTOR

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FOREWORD

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The contract was under the technical monitorship of the Aerospace Medical Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. Philip Diamond, Toxic Hazards Section, Physiology Branch, Biomedical Laboratory, was the contract monitor. Dr. A. A. Tamas, Chief, Toxic Hazards Section, initiated the contract.

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ABSTRACT

The data obtained in production of an improved multipurpose detector capable of measuring low airborne concentrations of nitrogen tetroxide (N_2O_4), ozone (O_3), hydrazine (N_2H_4), unsymmetrical dimethylhydrazine (UDMH), and hydrogen fluoride (HF) is presented.

The concept of "forward and reverse polarization" was applied and considerable specificity was obtained for oxidizing and reducing substances. Sensitivities were obtained of 100 microamperes per part per million of nitrogen tetroxide, 52 microamperes per part per million of ozone, 40 microamperes per part per million of hydrazine, and 20 microamperes per part per million of unsymmetrical dimethylhydrazine.

PUBLICATION REVIEW

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I. INTRODUCTION

Detecting the presence of dangerous concentrations of boranes, hydrazines, ozone, nitrogen tetroxide, hydrogen fluoride, and other related materials in laboratories, manufacturing areas, and handling and storage areas is an important personnel safety problem (refs. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10). The problem of nitrogen tetroxide detection is of great importance, since considerable amounts of nitrogen tetroxide can be inhaled without discomfort, and a delayed action symptomatic response is very often observed (ref. 8). The detection of nitrogen tetroxide was stressed in these researches to obtain sufficient warning at the 2.5 parts per million (PPM) level (ref. 7), the threshold value as nitrogen tetroxide. The threshold value for the monomer (NO_2) would be 5.0 PPM. At room temperature, nitrogen tetroxide is an equilibrium mixture of N_2O_4 and NO_2 (ref. 8).

The problem of pentaborane detection was essentially solved in studies on the construction of prototype borane monitors (ref. 11). The high sensitivity, compactness, and relative simplicity of operation of the Olin Mathieson prototype borane detectors indicated the desirability of adapting this instrument for the detection of other vapors normally encountered in fuel and oxidizer work.

Several methods have been reported in the literature for the detection of nitrogen tetroxide in air (ref. 12 and 13), ozone (ref. 14 and 15), hydrazine (ref. 16 and 17), and hydrogen fluoride (ref. 18 and 19). Most of these methods require time consuming collecting procedures, titrating procedures, etc., with the exception of the continuous ozone detector (ref. 15). Previous experience with the prototype borane monitors has indicated that these instruments are adaptable to the detection and determination of many other substances, both oxidizing and reducing types (ref. 11).

The purpose of this research was to adapt the highly sensitive Olin Mathieson prototype borane detectors to the detection and determination of nitrogen tetroxide, ozone, hydrazine, unsymmetrical dimethylhydrazine and hydrogen fluoride on a continuous, or semi-continuous basis. The objective for sensitivity was the reliable, continuous detection of 2.5, 0.1, 1.0, 0.5, and 3.0 PPM of the above-mentioned substances in air, respectively. In addition, studies were to be made of adsorbents and/or absorbents for specificity of action in removal and nonremoval of the various agents. The baseline stability was to be studied for the purpose of better zero stability.

The objectives set forth for this research project have been met and, in some cases, surpassed. Zero point stability has been improved by use of a split air flow system. Nitrogen tetroxide detection has been studied intensively and results have been exceptionally good, with sensitivities of 80 to 100 microamperes per PPM. Although the search for specific absorbents for removal of oxidizing and reducing substances has been inconclusive, the electrical device of forward and reverse polarization current has provided an invaluable way of selectively increasing the sensitivity in the oxidative or reductive direction.

II. METHOD

A. Construction of Amperometric Propellant-Component Detector (Figures 1, 2, 3, 4, 5, and 6).

The detector, when assembled, weighs about 23 pounds. This weight includes its nickel cadmium storage batteries, air pump motor, and rectifier system. The unit is capable of operating for about 4 hours without external power, or it may be operated indefinitely with the wall-plug attachment. Caution: Do not leave the wall plug attached to line voltage for more than 6 hours at a time (without using the air pump motor). It is permissible to leave the plug in a wall receptacle while operating the instrument thereby fully charging the batteries (the air pump motor must be on to prevent overcharge of the batteries).

The split air flow system and the generalized polarizing network are shown in Figures 4 and 5. The polarizing network as installed in the original instrument does not have provision for reversing the current, or for changing the total polarization current. Therefore, to obtain reverse polarization one must reverse the polarizing battery. Reverse polarization is defined as electron flow that results in the external electrode becoming more negative. Forward polarization is defined as electron flow that results in the external electrode becoming more positive. Reverse polarization was found to be best for detection of oxidizing substances; e.g., nitrogen tetroxide and ozone. Forward polarization was found to be best for the detection of reducing substances; e.g., pentaborane, hydrazine, unsymmetrical dimethylhydrazine, hydrogen sulfide, etc.

The polarization current was changed by "jumpering" another resistor across the limiting resistor (in this case a 100K ohm resistor). The resistors used in this study were 33K ohms and zero ohms (shorted out). Polarization currents were observed as follows:

100 K ohms	limit	R..... 4 microamps	(μA)
33 K ohms	limit	R.....15	(μA)
0 K ohms	limit	R.....30	(μA)

The platinum-platinum type of sensing cell was found to be easily polarized in either direction. The platinum vs. silver/silver chloride cell could be polarized only in the forward direction and therefore cannot be used for reverse polarization (which is best for detecting oxidizers).

The input resistance of the push-pull transistor circuit is approximately 10 K ohms. The D. C. resistance of the polarized platinum vs. silver/silver chloride cells is 5 K ohms each. Therefore, the sensing cells and the input resistance of the amplifier are suitably matched. The D. C. resistance of the polarized platinum-platinum electrodes is about 7 K ohms, and this is sufficiently matched to the push-pull transistor circuit. The D. C. resistance of the cells is measured as $R = \frac{\text{Delta E}}{\text{Delta I}}$.

The germanium 2N 214 or 2N 35 transistor was used in the final circuit. Silicon NPN transistors give an input resistance of 60 to 100 K ohms and are not

closely matched for these cells. It is possible to increase cell D.C. resistance by decreasing the surface area of the sensing electrode material, but this will decrease the total power output. Since the germanium transistors show the best matching characteristics, they were chosen for use. Furthermore, germanium transistors are priced at about 1/15th the price of silicon transistors. One disadvantage of germanium transistors, however, is that they are extremely sensitive to temperature differentials. This can be controlled by proper circuit design, and keeping the push-pull transistors at the same ambient temperature by mounting them close to one another. An effective current gain of 35 was observed for this particular instrument; that is, for each 1 microampere input, the output meter indicates 35 microamperes.

This particular instrument was provided with an X 100, X 10, and X1 range switch. A more desirable arrangement would be X 20, X 10, X 5, X 2, and X1. The proper shunt resistors to use for the five-range switch are 56, 120, 290, 1200, and infinity, respectively. The upper half of the X 100 range is beyond the linear range of the amplifier and cannot be used for calibration purposes.

A Philco 50 watt Zener diode with 7.8 volt firing characteristics was used to regulate the voltage of the rectifier circuit. Fully charged batteries would still gas somewhat even with this Zener diode protection. Better protection against overcharge may result from use of a 7.2 or 6.8 volt Zener diode. The Zener diode of 7.8 volt firing characteristics was better protection for the batteries than no regulation at all since, with no regulation, voltages as high as 8.75 volts were observed (this high voltage can damage the batteries irreversibly if allowed to continue for long periods of time). Inasmuch as there is no OFF-ON switch provided for the rectifier, the wall plug must never be allowed to remain in a 120-volt A.C. outlet for more than 6 hours consecutively in order to prevent damage to the batteries.

Complete drawings for constructing the Amperometric Propellant-Component Detector are shown in Figures 1, 2, 3, 4, 5, and 6. Lists of parts and sources of supply are given in Tables I, II, and III.

B. Construction of Sensing Cells (Figure 3).

a. Platinum vs. Platinum Type (General Purpose).

1. Polyethylene tubing (5/16-inch outside diameter) is cut to 13-cm. lengths, and one end is sealed.

2. Two 2-millimeter holes are drilled near the open end, and two 2-millimeter holes are drilled at a distance of 8.0 centimeters from the first set of holes.

3. An 11-inch wrapping of 3-inch wide surgical gauze is wrapped around the polyethylene and is fastened with thread.

4. A 3x4 cm. piece of No. 1 platinum gauze (52 mesh) is wrapped around the surgical gauze (centered).

5. A 6 inch length of 0.008 inch diameter platinum wire (or platinum 90 Rhodium 10 per cent alloy) is used to truss the platinum gauze, and a three inch

lead is allowed for electrical connections.

6. An 8 inch wrapping of 3-inch wide surgical gauze is wrapped around the inner platinum electrode, and is fastened with thread.

7. A platinum external electrode of 7.0 by 4.0 cm. (pure No. 1 platinum gauze of 52 mesh) is wrapped around the external layer of surgical gauze, and is trussed with 0.008 inch diameter platinum wire with provision for a three inch lead.

8. No. 8 cotton thread is spiraled tightly around the platinum gauze electrode with spacings of about 2 mm. between windings.

9. Both platinum electrodes are "brightened" by electrolyzing chlorine on their surfaces for 3 to 5 minutes. This is accomplished at 3.10 volts (platinum electrodes positive) in a 0.10 N hydrogen chloride solution. A separate platinum electrode was used as the negative electrode.

10. The cells are washed several times with the Carbitol, water, hydrogen chloride electrolyte solution, and are allowed to age for several days at ambient temperature.

b. Platinum vs. Silver/Silver Chloride Cell (See ref. 11 for complete instructions).

c. Aluminum vs. Silver/Silver Chloride Cell

1. Polyethylene tubing (5/16 inch outside diameter) is cut to 13 cm. length, and one end is sealed.

2. Two 2-millimeter holes are drilled near the open end, and two 2-millimeter holes are drilled at a distance of 8.0 centimeters from the first set of holes.

3. An 11 inch wrapping of 3-inch wide surgical gauze is wrapped around the polyethylene and is fastened with thread.

4. A 100 cm. length of pure silver wire of 28-gauge (0.012 inch diameter) is evenly wrapped around the gauze, with allowance for a 3-inch lead at the top.

5. An 8 inch wrapping of 3-inch wide surgical gauze is wrapped around the silver wire layer and is fastened with thread.

6. A 100 cm. length of aluminum wire (0.012 inch diameter) is evenly wound around the surgical gauze with provision for a 5 inch lead.

7. The silver chloride is electroplated onto the silver electrode by immersing the electrode into 0.1 N hydrogen chloride and using a voltage of 1.55 volts for one-half hour.

8. Solder connections could not be made to the aluminum lead, even with acid core solder. Therefore, a 6 inch tinned No. 22 reinforcement wire was used and a mechanical contact was made to the pin plug.

9. The sensing cells were washed well with 0.2 M acetic acid and were stored in the plastic containers until used.

d. Aluminum vs. platinum sensing cells

Construction is very similar to the above cell, except that the silver internal electrode was replaced with a piece of platinum gauze (No. 1 purity, 3x4 cm., 52 mesh). The external aluminum electrode was 0.125 inch diameter aluminum of 30 cm. length. This increased size of aluminum electrode was necessary since the finer aluminum wire collapsed in about a month because of corrosion.

e. Other electrode combinations

Inner electrodes of gold, tungsten, platinum-rhodium alloy, etc., are also possible. The best material for general purpose type of cells for external electrode material appears to be No. 1 purity platinum gauze (52 mesh), 99.9 + per cent pure platinum, catalytic grade.

Inner electrodes serve only as a carrier for polarization current. Occasionally, (especially when pure platinum is used), a tapering off of response is noted, due to diffusion of the active agent (nitrogen tetroxide, ozone, etc.,) through the layers of gauze to the inner electrode. Therefore, it is desirable to have a "poisoned" or deactivated inner electrode. This tapering response is especially noticeable at the lower polarization current levels, and occasionally actual backlashing of response was observed.

A triode system of electrodes was studied in a beaker of standard electrolyte solution. This system consisted of a silver/silver chloride electrode versus a platinum electrode, and the platinum electrode was polarized externally through another platinum electrode. This combination makes it possible to measure the e.m.f. output across the silver-platinum leads without passing current through the silver/silver chloride electrode. Such a system would be useful with a high impedance voltage device. This triode system could also be built directly into a similar cell system now in use. Its prime advantage would be increased zero stability because the silver/silver chloride reference electrode draws very little current. Another advantage of this system is that the platinum-platinum part of the circuit can be polarized in either direction (forward or reverse polarization with reference to the position of the external platinum electrode).

Another triode system would be a platinum-platinum-platinum system with two external polarizing networks. Such a system may make it possible to determine both oxidizers and reducing substances with the same cell(two output meters and/or amplifiers would be required).

A good system to use with a diode type of sensing cell would be a platinum external electrode with a gold internal electrode. This system has the advantage of sustaining polarizing current in both directions. The inner electrode (gold) would be relatively insensitive to detectors, thereby enabling a better choice of polarizing current operation. Undesirable "backlashing" type of responses would be prevented. In addition, the gold-platinum system is corrosion proof.

A tetrode system is possible using two external platinum electrodes and two internal references (gold or silver/silver salt).

A hexode system is also possible by combining two triode units into one sensing cell. Such a unit can be made to operate to detect both oxidizing and reducing substances. Two output meters and/or amplifiers would be required in this system.

The platinum external (sensitized) electrode may be replaced by other metals having sensitivity to oxidation-reduction systems (e.g., palladium nickel alloys). The corrosive action of the electrolytes must be considered, however, and this immediately excludes nickel. Other metals, such as tantalum, have been suggested but it is doubtful that they would function as oxidation-reduction sensors.

C. Formulation of Electrolyte Solutions (Table III)

Electrolyte solutions were essentially the same mixtures described in a previous report (ref. 11). The electrolytes studies are listed in Table III.

One problem encountered in calibration studies of the various gases was that the first response to 1-2 PPM of the agent would not return completely to zero. This led to the investigation of the addition of small amounts of nitric acid or hydrazines to the mixtures. It was found that 0.01 to 0.02 vol. per cent of these additives did substantially reduce this effect. One may also "set" the zero point by discarding the first calibration run and resetting the zero. Calibration studies after this initial "setting" were found to give excellent return to zero. The error caused in the initial incomplete return to zero is small and equivalent to about 0.05 to 0.10 PPM, in terms of nitrogen tetroxide.

The major problem of the electrolyte solutions is drying out, loss of hydrogen chloride and change of conductance with drying out. It may be advantageous to add a simple "humidifier" section to the air flow system before entering the sensing cell chamber. A simple polypropylene container (such as houses the sensing cell) may be used with a wick of gauze around the sides, and a reservoir of water in the bottom. A bubbler type of humidifier would be undesirable and should be avoided, because of excessive absorption effects and entrainment of water droplets.

The standard electrolyte described in Table III appears to be the best general-purpose electrolyte mixture. Studies with nitrogen tetroxide were conducted up to 48 hours with no redipping required, with reliable, repeatable results. Generally, however, a redipping every 24 hours is recommended.

D. Studies on Nitrogen Tetroxide

A large high-purity nitrogen tank was used to prepare a mixture of nitrogen tetroxide in nitrogen by the method described in a previous report (ref. 11). By absorption in two bubblers containing 0.1 N sodium hydroxide and back titrating with 0.1 N hydrogen chloride, a value of 3,800 PPM was obtained for the nitrogen tetroxide concentration. This value was used for calibration purposes.

The best results for detecting nitrogen tetroxide were obtained with platinum-platinum sensing cells with a high, reverse polarization current of 30μA per cell. A series of 10 runs in the 0-5 PPM range of nitrogen tetroxide

gave a sensitivity of 97.1 $\pm$ 10 per cent. Sensitivity is defined as microampere output per one PPM chemical input. The output is a linear function of concentration of nitrogen tetroxide in this range. These runs were considered excellent.

Another series of experiments was conducted in the 0-15 PPM range of nitrogen tetroxide. Platinum vs. platinum cells were utilized with a reverse polarization of 15 A. In a series of 20 experiments a sensitivity of 11.8 $\pm$ 17.3 per cent was obtained. This range was essentially linear, although there was some decrease in sensitivity at the higher concentrations.

In a system using the silver-silver chloride vs. platinum cells, with forward polarization of 4μA, a series of 22 experiments yielded a sensitivity of 3.4 $\pm$ 9.1 per cent. In the range of 5 to 10 PPM of nitrogen tetroxide this system was a linear function of concentration.

The platinum-silver/silver chloride system was studied in the range of 10 to 50 PPM and was found to be non linear in this higher range. The results, however, were repeatable and consistant. The sensitivity became lower in the higher concentrations.

A typical response-recovery curve for nitrogen tetroxide is shown in Figure 7. Response time constants in the range of 20 to 30 seconds were observed, and recovery time constants in the range of 45 to 75 seconds were observed. These constants are the logarithmic (1/e), or 63 per cent of "infinite time" responses.

Standardization charts for nitrogen tetroxide are shown in Table IV. Note that response output is a function of polarization direction and amount of polarization. The best conditions for highest sensitivity are reverse polarization of approximately 30 A per cell.

Drift was found to be about 2-3 microamperes per 4 hours, and is equivalent to approximately 0-05 PPM of nitrogen tetroxide per 8 hours.

Tabulations of the sensitivity data are as follows:

Pt-Pt Cell
(30 μ A Reverse Polarization)
0-5 PPM N_2O_4

Sensitivity (μA/PPM)	Deviation
83	-14.1
91	- 6.1
83	-14.1
93	- 4.1
100	+ 2.9
92	- 5.1
92	- 5.1
107	+10.0
113	+16.0
117	+20.0
10/971	10/97.5

97.1 plus or minus 10%

Pt-Ag/AgCl Cell
(4 μA Forward Polarization)
5-10 PPM N_2O_4

Sensitivity (μA/PPM)	Deviation
5.2	+0.8
3.4	+0.0
3.1	-0.3
2.9	-0.5
3.1	-0.3
3.3	-0.1
3.2	-0.2
2.9	-0.5
3.1	-0.3
3.0	-0.4
3.0	-0.4
2.9	-0.5
3.0	-0.4
3.4	0.0
3.6	+0.2
3.6	+0.2
3.6	+0.2
3.7	+0.3
3.7	+0.3
4.2	+0.8
3.5	+0.1
3.5	+0.1
22/74.8	22/ 6.8

3.4 plus or minus 9.1 per cent

Pt-Pt Cell
(15 μA Reverse Polarization)
0-15 PPM N_2O_4

Sensitivity (μA/PPM)	Deviation
7.5	-3.3
8.8	-3.0
10.2	-1.6
12.7	+0.9
10.7	-1.1
10.7	-1.1
12.7	+0.9
11.0	-0.8
12.3	+0.5
15.3	+3.5
15.3	+3.5
15.3	+3.5
12.7	+0.9
12.7	+0.9
8.7	-3.1
8.7	-3.1
15.3	+3.5
13.7	+1.9
11.5	-0.3
9.3	-2.5
20/ 235.1	20/40.0

11.8 plus or minus 17.3 per cent

Pt-Ag/AgCl Cell
(4 μA Forward Polarization)
10-30 PPM N_2O_4

Sensitivity (μA/PPM)	Deviation
3.3	+0.4
3.3	+0.4
3.6	+0.7
3.1	+0.2
2.7	-0.2
2.6	-0.3
2.5	-0.4
2.5	-0.4
2.5	-0.4
2.5	-0.4
2.9	0.0
3.8	+0.9
12/ 35.3	12/ 4.6

2.9 plus or minus 13 per cent

Pt-Pt Cells
(15 μA Reverse Polarization)
15 to 50 PPM N_2O_4 Range
Sensitivity at
Peak (μA/PPM) (1) Deviation

4.0	-1.3
4.0	-1.3
5.1	-0.2
5.3	0.0
4.8	-0.5
4.8	-0.5
6.1	+0.8
6.1	+0.8
7.4	+2.1
9/ 47.6	9/ 7.5
5.3	0.83

5.3 plus or minus 15.7 per cent
(System appears fairly linear)

Pt-Pt Cells
(15 μA Reverse Polarization)
15 to 50 PPM N_2O_4 Range
Sensitivity at
Equilibrium (μA/PPM) Deviation

2.4	-1.4
2.6	-1.2
3.8	0.0
4.0	+0.2
2.9	-0.9
3.0	-0.8
4.8	+1.0
4.8	+1.0
6.1	+2.3
9/ 34.4	9/ 8.8
3.8	0.98

3.5 plus or minus 25.6 per cent
(This system is non-linear)

Pt-Pt Cells
(15 μA Reverse Polarization)
0-15 PPM N_2O_4 Range

Sensitivity (2)	Deviation
8.0	-6.4
8.3	-6.1
12.1	-2.3
15.5	+1.1
13.1	-1.3
13.1	-1.3
22.0	+7.6
22.8	+8.2
8/ 114.91	8/ 34.3
14.4	4.3

14.4 plus or minus 30 per cent
(This system is non linear)

(1) "Peaking" is observed with Pt-Pt cells at the higher N_2O_4 concentrations followed by a drop off to "equilibrium" readings. This is believed to be due to diffusion of N_2O_4 to the inner electrode, thereby setting up a reverse current. This peaking can be reduced by increasing the polarization current, or by use of an inert inner electrode; e.g., gold.

(2) Note that no peaking occurs at the 0-15 PPM level of N_2O_4 even with only 15 μA of reverse polarization.

E. Studies on Ozone

Ozone was generated as needed by use of an ultraviolet lamp. A large Pyrex glass tank was used as the generating tank, the ultraviolet lamp being suspended into this tank, and an air pump (Diaphragm type) pumped out the ozone-air mixture at a rate of 4.5 liters per minute. Air was allowed to diffuse back into the tank to replace the ozone-air mixture that was removed.

Analysis of the air-ozone mixture obtained from this system indicated the presence of 40-50 PPM of ozone. This analysis was performed by absorbing the ozone into an aqueous sodium bicarbonate-potassium iodide mixture. The iodine generated was back-titrated with standard thiosulfate using a starch-indicator for the end point.

The proper dilutions for calibration studies on ozone were obtained by utilizing this source of ozone and mixing with more pure air filtered through activated charcoal. The recording charts showed very jagged responses in the tracings. This was due to concentration gradients of ozone forming in the generating tank and mixing gradients caused by air diffusing back into the generating tank. The jagged edges could be reduced considerably by insertion of a fan into the generating tank.

The standard electrolyte solution was utilized. When platinum-platinum cells were used a high sensitivity was obtained for ozone, namely, 52 ± 17.9 per cent (per PPM of ozone). A reverse polarization of 30 A was used. When platinum vs. silver/silver chloride cells were used with a forward polarization of 4 A, a sensitivity of 2-3 A per PPM was obtained. Reverse polarization is the system of choice for detecting ozone.

Response time constants of 30 to 60 seconds were observed, and recovery time constants of 5 to 10 seconds were obtained. The rate of decomposition of ozone is very rapid as shown by the very short recovery time constant.

A platinum-platinum system using hydrogen bromide rather than hydrogen chloride as the acid material in the electrolyte should give better results and possibly a higher sensitivity (for ozone, and also many other oxidizers). Hydrochloric-hydrobromic acid mixtures should give improved responses.

The mixing system utilized Neoprene rubber tubing exclusively, since Neoprene has considerable resistance to attack by ozone. In spite of this, some cracking of the tubing occurred at the inlets to the mixing manifold and had to be replaced. Neoprene is apparently attacked by ozone in areas where the synthetic rubber is under stress. Natural rubber tubing is completely unsatisfactory for use. Tygon may possibly show usefulness for this application.

Tabulations of the sensitivity data for ozone are as follows:

Pt-Pt Cells
Reverse Polarization of 30 A
0-5 PPM Ozone Range

Sensitivity (μA/PPM)	Deviation
40	-12.0
55	+ 3.0
71	+19.0
58	+ 6.0
38	-14.0
50	- 2.0
6/312	6/56.0

52 plus or minus 17.9 per cent

Pt. vs. Silver/Silver Chloride Cells
Forward Polarization of 4μA
0-5 PPM Ozone Range

Sensitivity (μA/PPM)	Deviation
2	-
3	-

2-3 (Insufficient data for averaging)

F. Studies on Hydrazine

A fresh sample of hydrazine hydrate (85 per cent) was obtained and placed into a small bubbler. A study of the weight loss was done at nitrogen flow rates of 10 to 50 ml. per minute. The calculated concentrations of hydrazine generated by this method were in the 3,000 to 4,000 PPM range at a temperature of 20-22°C. By further dilution with pure air, the required amounts of hydrazine were obtained.

Studies on hydrazine were conducted in the 1 to 10 PPM range. The standard type of electrolyte was used with platinum-platinum sensing cells having forward polarization of 20μA per cell. A sensitivity of 40μA/PPM of hydrazine was observed. At somewhat higher concentrations of hydrazine (20-30 PPM), a "backlashing" type of response was observed. This appears to be due to diffusion of hydrazine to the inner platinum electrode followed by a subtractive response. This effect can be reduced by reducing the size of the inner platinum electrode, using an "inert" inner electrode such as gold, or by using a silver/silver halide inner electrode.

In studies conducted on hydrazine in the 1-10 PPM range using platinum-silver/silver chloride cells, a sensitivity of 20-25μA per PPM of hydrazine was obtained. A forward polarization of 4μA was used.

Hydrazine showed response times of 1 to 1 1/2 minutes, and recovery times of 1 1/2 to 2 1/2 minutes. There was a considerable "memory" effect in which, when the source of hydrazine was shut off, some response could be demonstrated for 10 to 15 minutes by switching the activated charcoal switch on and off. This "memory" effect is due to absorption of hydrazine on the Neoprene tubing, polyethylene tubing, and possibly the glass walls of the manifold. This "memory" effect is sufficiently noticeable to require further correction. Correction of this effect would necessitate the replacement of all Neoprene and polyethylene tubing with Teflon or Kel-F material. The air pump would require the replacement of one diaphragm and two valves with suitable non-absorbing type of materials.

G. Studies on Unsymmetrical Dimethylhydrazine

A fresh sample of pure, anhydrous unsymmetrical dimethylhydrazine

was obtained and placed into a small bubbler. A study of the weight loss at nitrogen flow rates of 10 to 50 ml. per minute showed the presence of 30,000 to 35,000 PPM of unsymmetrical dimethylhydrazine in the exit stream (at ice-bath temperatures). Further dilution of this stream gave the required amounts of unsymmetrical dimethylhydrazine in air.

Studies were conducted in the 5 to 10 PPM range. The standard type of electrolyte was used, with platinum-platinum sensing cells having forward polarization of 20 μA per cell. Sensitivity of 20 microamperes per PPM of unsymmetrical dimethylhydrazine was obtained. The first calibration usually would not quite return to zero but after re-zeroing, this problem was eliminated.

Studies were also made at 10 PPM of unsymmetrical dimethylhydrazine using the platinum-silver/silver chloride cells with 4 μA forward polarization. Sensitivity of 10-15 μA/PPM of unsymmetrical dimethylhydrazine was observed.

Studies were conducted in the 5-10 PPM range using a strongly alkaline electrolyte (potassium hydroxide). When using platinum-platinum cells with forward polarization of 30 μA per cell, a sensitivity of 10-15 μA per PPM of unsymmetrical dimethylhydrazine was observed. A severe disadvantage of alkaline solutions is that the baseline is severely disturbed by traces of acid or carbon dioxide changes in the air. Alkaline electrolytes do not seem to be practical unless there is an alkaline pre-filter for removing acid and carbon dioxide before the sensing cell. An alkaline pre-filter might require frequent and troublesome maintenance.

Unsymmetrical dimethylhydrazine also showed a similar "memory effect" as was obtained with hydrazine. This undesirable effect should be correctable by upgrading the materials of construction to Teflon or Kel-F.

Small amounts of unsymmetrical dimethylhydrazine added to the standard electrolyte solution reduced the effect of the first calibration not returning to zero. This small amount must be held to 0.01 to 0.02 per cent (by volume).

H. Studies on Hydrogen Fluoride

Two sets of cells were constructed using 0.012 and 0.125 inch diameter aluminum wire as shown in the section on sensing cell construction. The small aluminum wire electrode was coupled with a standard silver/silver chloride internal reference electrode. The larger aluminum wire was coupled with a small platinum gauze internal electrode.

The smaller aluminum wire was found to corrode and collapse after being used for one month in the presence of 0.2 M acetic acid (about 5 vol. per cent). The larger aluminum vs. platinum electrodes were used in calibration studies in aqueous 0.2 M acetic acid medium. Since the steel tanks reacted with the hydrogen fluoride gas originally placed in them, it was not possible to generate hydrogen fluoride air flow systems for study. Monel tanks should be used for such work but could not be acquired in time.

The data obtained with hydrogen fluoride in aqueous 0.2 M acetic acid is as follows:

Concentration of HF (PPM)	Voltage change in volts
5.0	0.260
10.0	0.390
15.0	0.50
30.0	0.61

(Vacuum Tube Voltmeter, 1 M ohm input). (Two minutes allowed to reach stability)

Concentration of HF ($1/PPMX10^{-2}$)	Voltage change in volts
20	0.260
10	0.390
6.7	0.50
3.33	0.61

A plot of concentration versus voltage change on the logarithmic portion of semi-log paper gives a straight line relationship.

These voltages were easily reproducible to 0.01 volts thereby allowing the detection of 0.01 to 0.02 PPM of hydrogen fluoride (in fluid system).

Although no data was obtained in an air flow system, it is believed that a Carbitol-water-organic acid mixture would allow the detection of a few PPM of hydrogen fluoride on a continuous basis.

I. Studies on Absorbents

Silica gel (with indicating color) was an excellent absorbent for nitrogen tetroxide and the hydrazines in the 1-10 PPM range. Its disadvantage, however, is that the efficiency drops off after saturation with water vapor normally found in the air. It would have to be repacked daily to obtain proper function. Another disadvantage of the silica gel is that a water-loss, water-gain phenomenon causes an instability of the baseline when the charcoal switch is turned off and on. Activated charcoal still appears to be the best absorbent since it will last for a long period of time, does not absorb water, gives the best baseline, and does not lose its efficiency in the presence of water normally present in the air.

Activated charcoal was ideally suited for all the substances tested. Although no air flow data was obtained with hydrogen fluoride, it is believed that activated charcoal would be useful in the 1-10 PPM range. Another absorbent for hydrogen fluoride would be sodium fluoride pellets.

The hydrazine filter was tested with 10-20 PPM of hydrazine and unsymmetrical dimethylhydrazine and found to remove about 95 per cent of these substances. A hydrazine filter should be retreated with 6 N sulfuric acid about every two weeks to keep it in good absorbing condition.

Soda-lime was ineffective in removing 10 PPM of nitrogen tetroxide from an air stream. Ascarite removed about 75 per cent of the nitrogen tetroxide

in the instrument air stream. It suffers from the disadvantage that water vapor causes the absorbent to cake and plug. Carbon dioxide in the air is also an interfering material with this absorbent. Activated alumina was found to be poor for removing nitrogen tetroxide from an air stream.

"Drierite" absorbed 25 per cent of the nitrogen tetroxide. "Drierite" suffers from a baseline shift caused by removal of water vapor from the air stream.

"Anhydrone" was ineffective in removing nitrogen tetroxide from an air stream. It is efficient, however, for the removal of water vapor, hydrazines, and ammonia.

Sodium Fluoride pellets were ineffective in removing nitrogen tetroxide from an air stream.

Although no specific adsorbents could be found to selectively remove oxidizers and/or reducing substances, the fact that specificity can be gained by forward and reverse polarization makes it possible to determine oxidizers and reducing materials in the presence of one another. Although the specificity is not 100 per cent, polarization reversal does suppress the interference of reducing components when oxidizers are being detected. The suppression of oxidizers when reducing substances are being sought is not as pronounced. The search for specific oxidation-reduction adsorbents should be continued as a basic research project.

J. Studies on Improving Baseline Stability

The major sources of baseline instability was described in a previous report (ref. 11). These included junction corrosion, silver/silver chloride electrode instability, current density effects, and uneven drying out. The junction corrosion problem was solved by sheathing the lead-in wires with polyvinyl chloride. The silver/silver chloride instability was solved by electrodeposition and by increasing the surface area of the silver/silver chloride electrode. Uneven drying was overcome by splitting the air flow into two equal parts in the instrument. The silver/silver chloride instability may also be handled by the use of an internal platinum electrode (or gold or other suitable material). The undesirable side responses of platinum-platinum cells (backlash type of response) can be partly controlled by increasing the polarization current. Another control of this undesirable side reaction is to decrease the size of the inner electrode by a factor of 5 to 10.

The platinum-platinum sensing cells described in the cell construction section gave good zero point stability with the standard electrolyte solution with forward and reverse polarization currents of up to 30μA per cell. Drift values of 2-3 microamperes per 4 hours were observed.

The drift is negligible as far as the detection of nitrogen tetroxide is concerned since it is equivalent to only 0.05 PPM of nitrogen tetroxide per day. Furthermore, the drift of 2-3 microamperes per 4 hours is indistinguishable from the drift inherent in the transistorized circuit.

Another form of drift is observable in which the first one or two calibrations (with any of the chemical agents) for a five minute period will show a characteristic incomplete return to zero. This type of "zero shift" may be controlled by simply testing the instrument with a few parts per million of the agent to be detected, followed by rezeroing while the air switch if on "charcoal". The incomplete return to zero may be partly alleviated by the addition of 0.1 to 0.2 vol. per cent of nitric acid (for the case of nitrogen tetroxide, or 0.01 to 0.02 vol. per cent of unsymmetrical dimethylhydrazine in the case of unsymmetrical dimethylhydrazine). The best results, however, were obtained by "setting the zero" by pretreating the instrument for about 5 minutes with a few parts per million of the reagent to be detected, followed by rezeroing while the air switch is on "charcoal." Even without the "setting" treatment the baseline shift would be equivalent to only about 0.05 PPM in terms of nitrogen tetroxide and, therefore, could be neglected.

In the case of ozone, however, the baseline shift of 2-3 microamperes per 4 hours becomes significant when one considers that a concentration as low as 0.1 PPM ozone is to be detected. In this case, the zero point must be checked hourly with the air switch on "charcoal."

Another way of reducing the effect of the zero drift would be to increase the output of the sensing cell for one PPM of ozone, for example, while keeping the zero drift at the same level. In the case of ozone, the use of mixtures of hydrogen chloride and hydrogen bromide in the standard electrolyte would probably double or triple the output, and the zero drift would remain approximately the same and, therefore, be of less consequence.

It is believed that a zero drift of 2-3 microamperes per 4 hours is the practical limit of zero control with the present type of system. Any further improvements to increase sensitivity must be made on the electrolyte mixture while keeping zero drift at the same level.

Another consideration in reducing drift due to drying out of the sensing cells would be the incorporation of a simple "humidifying" device in the polypropylene chamber before the air stream enters the sampling and reference chambers. This device would be an identical polypropylene tube (such as is used for housing the sensing cells) with a lining of gauze or wick-like material and a water reservoir on the bottom. A bubbler type device would be undesirable, and would probably absorb too much of the substances one desires to detect. If this humidifier would prove of sufficient advantage to reduce the drift level down to about 1 microampere per 4 hours, or less, it would be worth incorporating into the instrument.

III. RESULTS AND DISCUSSION

The Amperometric Propellant-Component Detector was shown to be readily adaptable for the detection of nitrogen tetroxide, ozone, hydrazine and unsymmetrical dimethylhydrazine. The instrument is a compact, portable unit with the desirable built-in, plug-in type of rectifier. It is self-powered and/or line operated. The new design with split air flow system has given better zero point stability. A range switch of X100, X10 and X1 is provided.

The most significant results to evolve from these researches was that considerable specificity could be obtained by a simple device of using forward and reverse polarization. The platinum-platinum type of sensing cell was adaptable for this general-purpose use.

Forward polarization sensitizes the cell for reducing substances; e.g., hydrazine, unsymmetrical dimethylhydrazine, pentaborane, hydrogen sulfide, hydrogen, etc.

Reverse polarization sensitizes the cell for detection of oxidizing substances; e.g, nitrogen tetroxide, ozone, fluorine, chlorine, interhalogens, interoxyhalogens, etc.

Sensitization for reducing substances appears to require only a small amount of polarization current. In the case of the platinum-silver/silver chloride reference cells, this small amount of forward polarization could easily be tolerated, and no "backlash" type of responses were observed at the higher concentrations of the reducing substances. In the case of the platinum-platinum sensing cells, however, the lower polarization current (4-5μA per cell) was insufficient to "deactivate" the inner platinum electrode, thereby eliciting undesirable reverse current effects in the inner electrode. Apparently, the platinum-platinum type of sensing cell (which is obviously the best system to use as current reversal is easily possible) has not been optimized in design. It is believed that the best type of design to use for general purpose detection is a moderately large external platinum electrode, and a considerably smaller internal electrode.

In lieu of an inner platinum electrode, a gold inner electrode may be suitable. In this case, a polarization reversal switch and a polarization control potentiometer would suffice to give a simplified, general purpose instrument. An optimized platinum-platinum cell design should also incorporate a polarization current control and reversing switch.

Although no data is available for optimum platinum-platinum cell design, electrochemical considerations have shown that an external electrode with ten times the surface area of the inner platinum electrode should give a good design for a general purpose detection cell.

Other considerations for optimum operating conditions would be the choice of electrolyte solution. To date, studies have shown that the standard type of electrolyte solution is suitable for general purpose use. This electrolyte contains Carbitol, water and hydrochloric acid. Another type of acid to use

with a platinum-platinum system is hydrobromic. It may have distinct advantages over hydrochloric acid in that it is less volatile, should give a better baseline, should give much higher sensitivities (bromide is much more easily oxidized to bromine than chloride to chlorine), and may give better response-recovery characteristics (bromine would have a greater residence time in the film coating on the external platinum electrode). Mixtures of hydrochloric and hydrobromic acids may give even better characteristics in the standard electrolyte mixture. Hydriodic acid would be too unstable for use in an acidic medium. In addition, iodine has too high a molecular weight, and would tend to give long, drawn-out recovery curves.

Further work is indicated for an electrolyte solution to give higher sensitivity, especially for detection of ozone. Present sensitivities obtained for nitrogen tetroxide are more than sufficient for detection of Threshold Limit Values (TLV), and baseline drift is negligible in this case. Ozone, however, has a marginal continuous detection characteristic at the 0.1 PPM level.

Sensitivity is defined as microampere output on the instrument meter per one PPM of chemical input (in air). A sensitivity of 100 was observed for nitrogen tetroxide at the higher reverse polarization current. A sensitivity of 52 was observed for ozone at higher reverse polarization currents. A sensitivity for hydrazine of 40 was observed with forward polarization. Sensitivity of 20 was observed for unsymmetrical dimethylhydrazine with forward polarization. The required TLV detection of nitrogen tetroxide was 2.5 PPM on a continuous basis. The required TLV detection of ozone was 0.1 PPM. The required detection of hydrazine was 1 PPM, and the required continuous detection of unsymmetrical dimethylhydrazine was 0.5 PPM. As can be observed, with a 2-3μA drift per 4 hours, the eight hour continuous detection of all substances except ozone is easily possible. To be used for ozone, the instrument must be rezeroed every 1 or 2 hours.

Although drift has been considerably improved by the use of a split air flow system, a value of 2-3 microamperes per 4 hours appears to be a practical limit of baseline drift under the present system. Further improvements must come by use of continuous flow electrolyte systems, by increase of sensitivity, and by keeping the baseline drift constant. The suggested use of mixed acids should increase the sensitivity for ozone to a point where the continuous detection of 0.1 PPM ozone should be possible with unattended operation.

Baseline stability is also affected by water vapor. The idea behind the current system is that the film covering the external platinum electrode comes into equilibrium with the relative humidity of the air stream passing through the sensing cell housing. This serves well as long as the sensing cell and reference cell lose (or gain) water at an exactly equal rate, but this is a difficult condition to actually approach. A noticeable effect is observed when a gross change of relative humidity occurs artificially. For example, a sudden change from 40 to 95 per cent relative humidity will displace the baseline to the right (reductive response) for a few minutes. Eventually, however, the reference cell "catches up" with this change of relative humidity. This delay of "catching up" is due to the time required for the fixed activated charcoal cartridge to come into equilibrium with the new relative humidity.

A way of reducing the relative humidity effect would be to place two

humidifiers in the air path before both the sensing cell and the reference. Such a humidifier could be a simple polypropylene tube with a wick-like gauze lining and a distilled water reservoir on the bottom. This wick system would keep the relative humidity at a fairly constant high level (80-85 per cent) and would be relatively insensitive to local external relative humidity changes.

Several adsorbents were studied and activated charcoal had the best characteristics for baseline stability, efficiency of adsorption, and effective lifetime. Silica gel, while an excellent adsorbent for nitrogen tetroxide, hydrazine and unsymmetrical dimethylhydrazine, showed undesirable baseline shift due to water adsorption from the air stream. It may be possible to eliminate this water-loss, water-gain effect by use of a humidifier in the air stream just before the sensing cell and reference cell. Another disadvantage with silica gel is that it tends to lose its efficiency after it becomes saturated with water, and would have to be repacked every day. The greatest advantage of activated charcoal is that it keeps its adsorption efficiency in the presence of water vapor. Although activated charcoal was utilized continuously for several months, it is suggested that it be repacked every two weeks as a precautionary measure.

Two types of adsorbents were studied: the physical type with a large surface area and intricate pore system, and the chemical type. Among the physical types were activated charcoal, silica gel, and activated alumina. As previously discussed, the activated charcoal was found to be the best general purpose adsorbent, and was not affected by water vapor.

Nitrogen tetroxide, hydrazine, unsymmetrical dimethylhydrazine and ozone were found to be easily and completely removed from the air streams used in the instrument over a fairly wide range of concentrations (up to 50 PPM). Silica gel was also found to remove these substances over a wide range of concentrations, but it also removed water vapor from the air and eventually lost its effectiveness. Activated aluminum also was studied, but the sample used showed very little adsorption characteristics and is suspected of being saturated with water vapor.

Among the chemical types of adsorbents were the hydrazine filter (sulfuric acid on Boileazers), soda-lime, Ascarite, "Drierite", "Anhydrone", and sodium fluoride pellets.

The hydrazine filter was found to be 90-95 per cent efficient in removing streams of 10 PPM of unsymmetrical dimethylhydrazine or hydrazine. The Boileazers should be retreated with 6 N sulfuric acid every two weeks and allowed to air dry to keep its efficiency high. If used for a month without retreatment, the efficiency decreases significantly. Ozone, nitrogen tetroxide, and pentaborane pass through the hydrazine filter.

The other adsorbents, while showing some special adsorption properties were found to be inadequate. Soda-lime was poor for removing even the acidic contaminant, nitrogen tetroxide. Ascarite, while showing about 75 per cent efficiency in removing nitrogen tetroxide, also removes water and carbon dioxide. "Anhydrone" shows fairly good characteristics for removing ammonia, and may be of special use for unsymmetrical dimethylhydrazine. No data was obtained for sodium fluoride because of difficulties in generating known air streams with trace amounts of hydrogen fluoride.

IV. SUMMARY

An Amperometric Propellant-Component Detector was constructed and tested for adaptation to nitrogen tetroxide (N_2O_4), ozone (O_3), hydrazine (N_2H_4), unsymmetrical dimethylhydrazine (UDMH) and hydrogen fluoride (HF) detection. The Amperometric Propellant-Component Detector features self-powered operation and/or line operation. It also has a built-in rectifier system. A split air-flow system was incorporated to reduce baseline shift, and a charcoal-sample air by-pass is utilized to give the best system for zero checking. The instrument has an effective current gain of 35, and has an input resistance of 10 K ohms. This particular instrument was provided with a range switch of X 100, X 10, and X 1. Resistor values for providing X 20, X 10, X 5, X 2, and X 1 operation were obtained by actual shunt substitution.

Adaptations for the detection of nitrogen tetroxide were highly successful. With forward polarization of 4 to 5 microamperes, the standard platinum vs. silver/silver chloride sensing cells were found to give an output of 4-5 microamperes per PPM of nitrogen tetroxide in the air stream. With reverse polarization of 30 microamperes, the platinum vs. platinum sensing cells were found to give an output of 100 microamperes per PPM of nitrogen tetroxide in the air stream. After a pre-treatment with a few PPM of nitrogen tetroxide, followed by re-zeroing, the return to the baseline was excellent for 10 to 12 hours of continuous use. Response time constants were in the range of 20 to 30 seconds, and recovery time constants of 45 to 75 seconds were observed. Over one hundred successful tests were made. Line adsorptior of nitrogen tetroxide is not noticeable.

Adaptations for the continuous detection of ozone were successful in the 0.1 to 5.0 PPM range. Sensitivities of 2-3 microamperes per PPM of ozone were obtained with forward polarization using the platinum vs. silver/silver chloride cells. With reverse polarization (30 microamperes per cell with platinum vs. platinum cells), sensitivities of 40-50 microamperes per PPM of ozone were observed. Although the detection of 0.1 PPM is relatively easy, drift considerations do not allow the detection of such a low level on a continuous basis. Methods are suggested for improving the low level detection of ozone. A response time constant of 1 to 1 1/2 minutes and a recovery time constant of 50 to 60 seconds were observed.

Adaptation for the detection of hydrazine and unsymmetrical dimethylhydrazine was successful in the 0.1 to 10 PPM range. Sensitivities of 40 and 20 microamperes per PPM of hydrazine and UDMH were obtained, respectively. Forward polarization of 15 to 20 microamperes was used with platinum vs. platinum electrodes. All electrolytes were of the standard Carbitol, water and concentrated hydrochloric acid type. A small amount of hydrazine (or unsymmetrical dimethylhydrazine) was necessary to stabilize the zero point and return to zero (0.01 vol. per cent).

Studies on hydrazine and unsymmetrical dimethylhydrazine were also conducted with strongly alkaline electrolytes and 30 to 40 microamperes of forward polarization, utilizing platinum vs. platinum sensing cells. The cells required an excessively long time to come into an operating condition, and the inner electrode continued to be sensitive, as was noted by additive and subtractive type of response curves (occasionally whiplash type of response-recovery curves were noted). Eventually, after several hours of polarization, the response

recovery curves became "normal". Further studies are needed for alkaline type of electrolytes. A severe disadvantage of the alkaline electrolyte is the disturbance caused by trace amounts of acid substances or carbon dioxide in the air.

Hydrazine and unsymmetrical dimethylhydrazine were rather troublesome due to moderately severe line absorption-desorption phenomena. Neoprene and polyethylene appeared to be contributing to the difficulties. Teflon or Kel-F parts are indicated for reducing this interference. The "memory" effect of the lines was observed to last 10 to 15 minutes. Response times for the hydrazines of 1 1/2 to 2 minutes and recovery times of 1 to 1 1/2 minutes were observed. The response-recovery times may be in error due to line absorption-desorption effect.

Hydrogen fluoride responses were studied in aqueous acetic acid in the 1 to 30 PPM range, using aluminum vs. platinum, and aluminum vs. silver/silver chloride. The Amperometric Propellant-Component Detector was not utilized in these studies because hydrogen fluoride could not be standardized in air streams in the time available (severe interference from cylinder metals and glassware in manifolds). Direct e.m.f. measurements were made using a vacuum-tube voltmeter. A plot of 1/PPM of hydrogen fluoride against millivolts change on semi-log graph paper gives a straight line relationship. Although these tests were conducted in the aqueous acetic acid phase, an air flow system should also be feasible using Carbitol-water-acetic acid mixtures. Aluminum electrodes were found to corrode at a measurable rate, and the smaller wire type of electrodes collapsed in about one month. A separate set of electrodes, with ten times the diameter, are still operable.

Four types of sensing cells were constructed and studied for the most desirable response to nitrogen tetroxide, ozone, hydrazine, unsymmetrical dimethylhydrazine and hydrogen fluoride. The first type was the standard cell having an external platinum gauze electrode with an internal silver/silver chloride reference electrode. The second type of cell was a platinum-platinum gauze type of electrode, with the internal electrode submerged below several layers of cotton gauze. The third type of electrode was an aluminum wire vs. a silver/silver chloride reference electrode. The fourth type was an aluminum wire vs. an internal platinum gauze electrode.

The concept of forward and reverse polarization is very important and considerable specificity can be obtained for oxidizing and reducing substances. Forward polarization is defined as electron flow in such a direction that the external platinum electrode becomes more positive. Reverse polarization is defined as electron flow in such a direction that the external platinum electrode becomes more negative. Reverse polarization enhances the detection of oxidizing substances; e.g., ozone, nitrogen tetroxide, fluorine, chlorine trifluoride, etc. Forward polarization enhances the detection of reducing substances; e.g., pentaborane, hydrogen, HEF-2, hydrazines, hydrogen sulfide, etc.

Activated charcoal was found to be the best general purpose adsorbent. Advantages are gained by use of activated charcoal since it allows the passage of water vapor normally present in air and gives the best baseline. Silica gel was also found to be an excellent adsorbent for nitrogen tetroxide, hydrazine and unsymmetrical dimethylhydrazine. Silica gel, however, shows a poor baseline

due to removal of water from the air stream, thereby upsetting the water equilibrium of the film on the sensing cells. Silica gel also loses some of its physical adsorption properties when it is saturated with water vapor (will last about 24-48 hours). Activated charcoal has been used for several months with no observable loss of activity. A chart of adsorbents studied is given in this report.

V. CONCLUSIONS

1. The Olin Mathieson Prototype Borane Monitor was adapted successfully for the detection of nitrogen tetroxide, ozone, hydrazine and unsymmetrical dimethylhydrazine on a continuous basis.

2. An input resistance of 10 K ohms is recommended for the transistorized amplifier. The input resistance must remain the same on all ranges. A floating type of input is recommended and a floating type of output stage is also recommended (a differential type of amplifier).

3. Sensing cell construction should be of such a nature that the cells are operated at approximately 5 K ohms D.C. resistance. D. C. resistance is measured by $R=\frac{\text{Delta E}}{\text{Delta I}}$, while the cells are polarized and in the presence of air.

4. A reversing switch and a polarization current control is recommended in a finalized instrument.

5. Considerable selectivity of sensing is obtained by use of forward and reverse polarization.

6. A sensitivity of 100 microamperes/ppm is obtained for nitrogen tetroxide at the optimum polarization current level.

7. A sensitivity of 52 microamperes/PPM is obtained for ozone at the optimum polarization current level.

8. A sensitivity of 40 microamperes/PPM is obtained for hydrazine, and a sensitivity of 20 microamperes/PPM is obtained for unsymmetrical dimethylhydrazine.

9. Hydrogen fluoride is detectable in aqueous 0.2 M acetic acid at levels as low as 0.01 PPM, using a platinum-aluminum sensing system.

10. Activated charcoal was found to be the best general-purpose adsorbent, with the least amount of interference due to water vapor of the atmosphere.

11. Although no specific absorbents for oxidizing or reducing materials could be discovered, polarization reversal gives sufficient selectivity for oxidizing or reducing substances to make possible the determination of mixtures of these substances without special filters.

12. A finalized instrument design must have a polarization current reversal switch, and a polarization current control device.

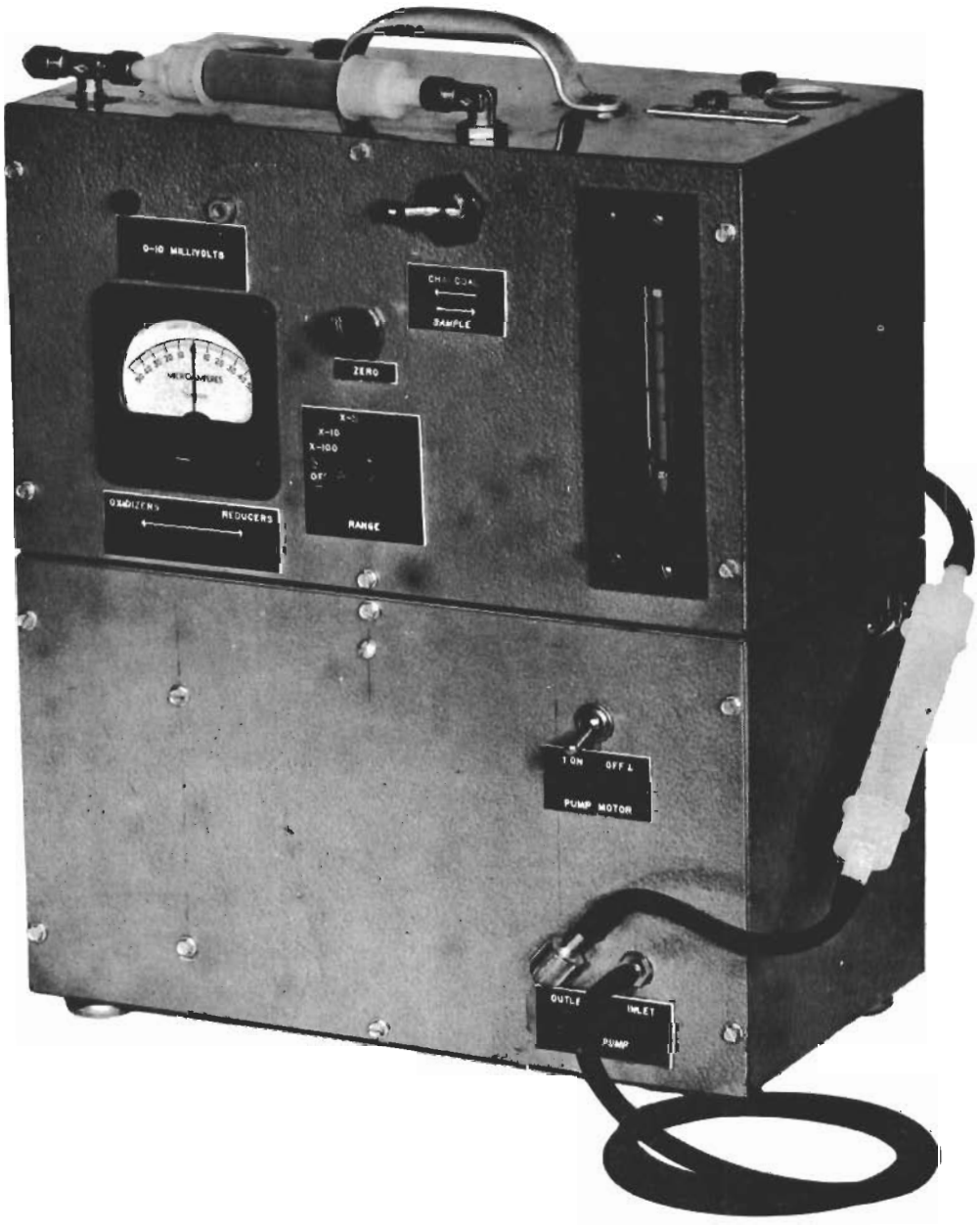


Figure 1 - Amperometric Propellant-Component Detector
(Front View)

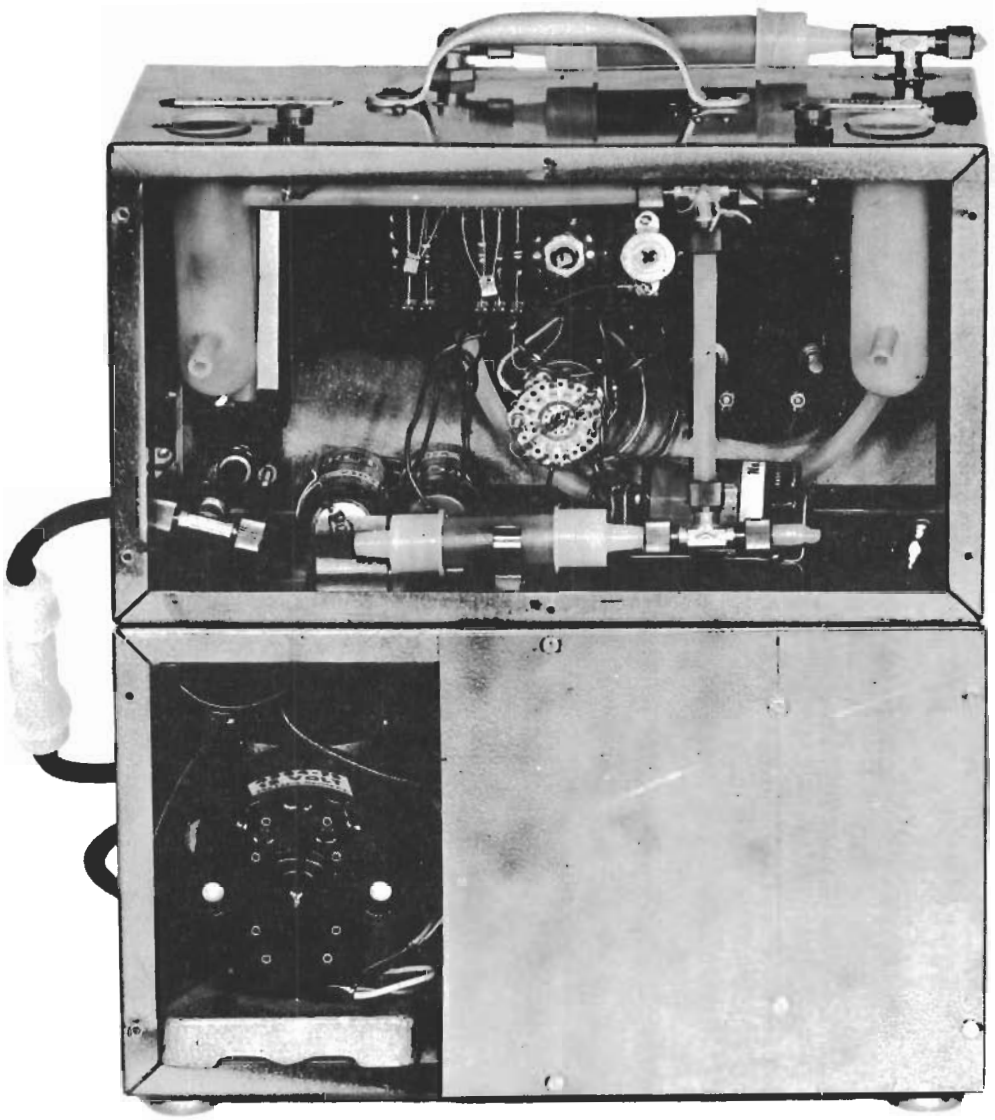


Figure 2 - Amperometric Propellant-Component Detector

(Back View)

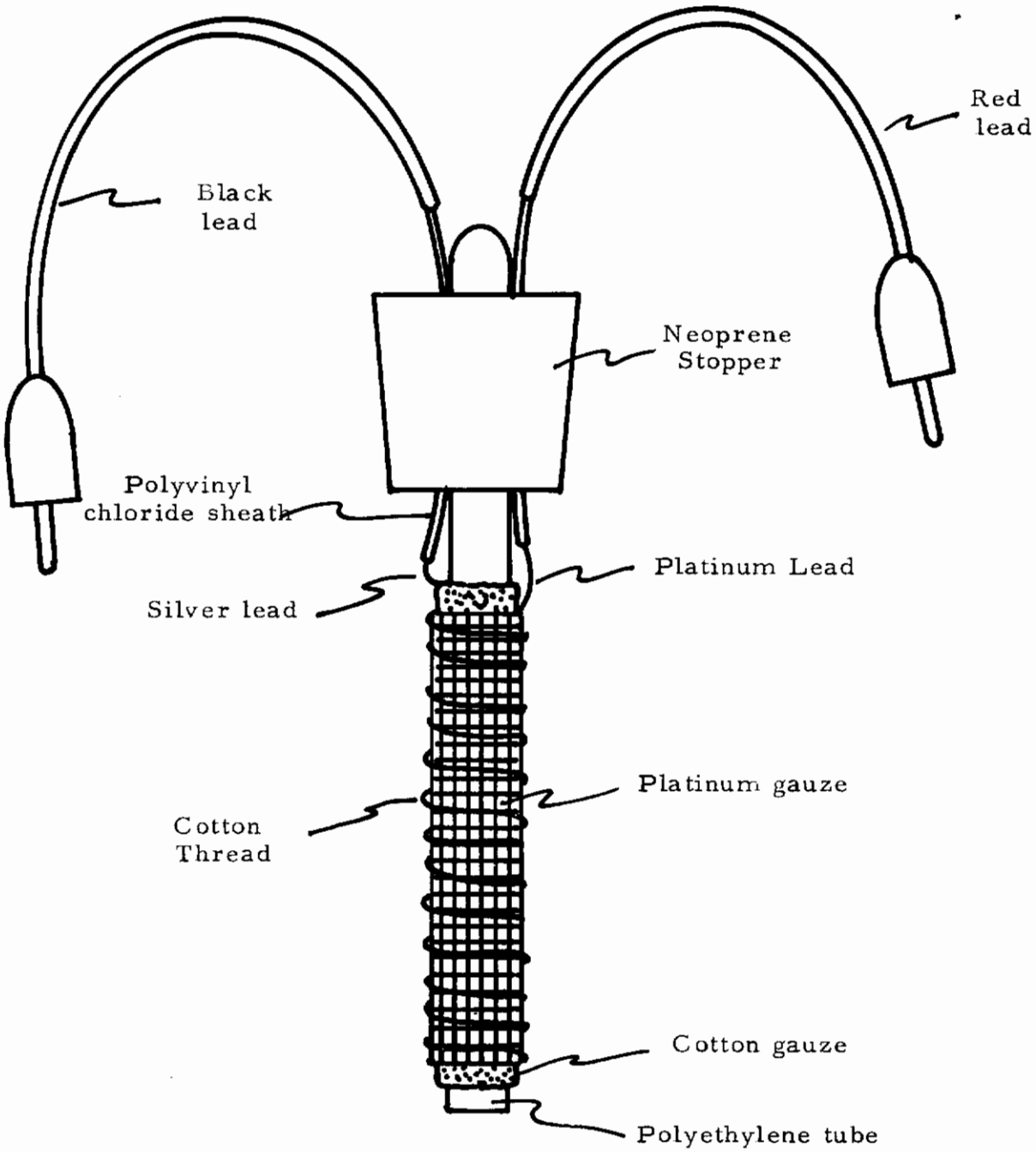


Figure 3 - Sensing Cell - To Scale

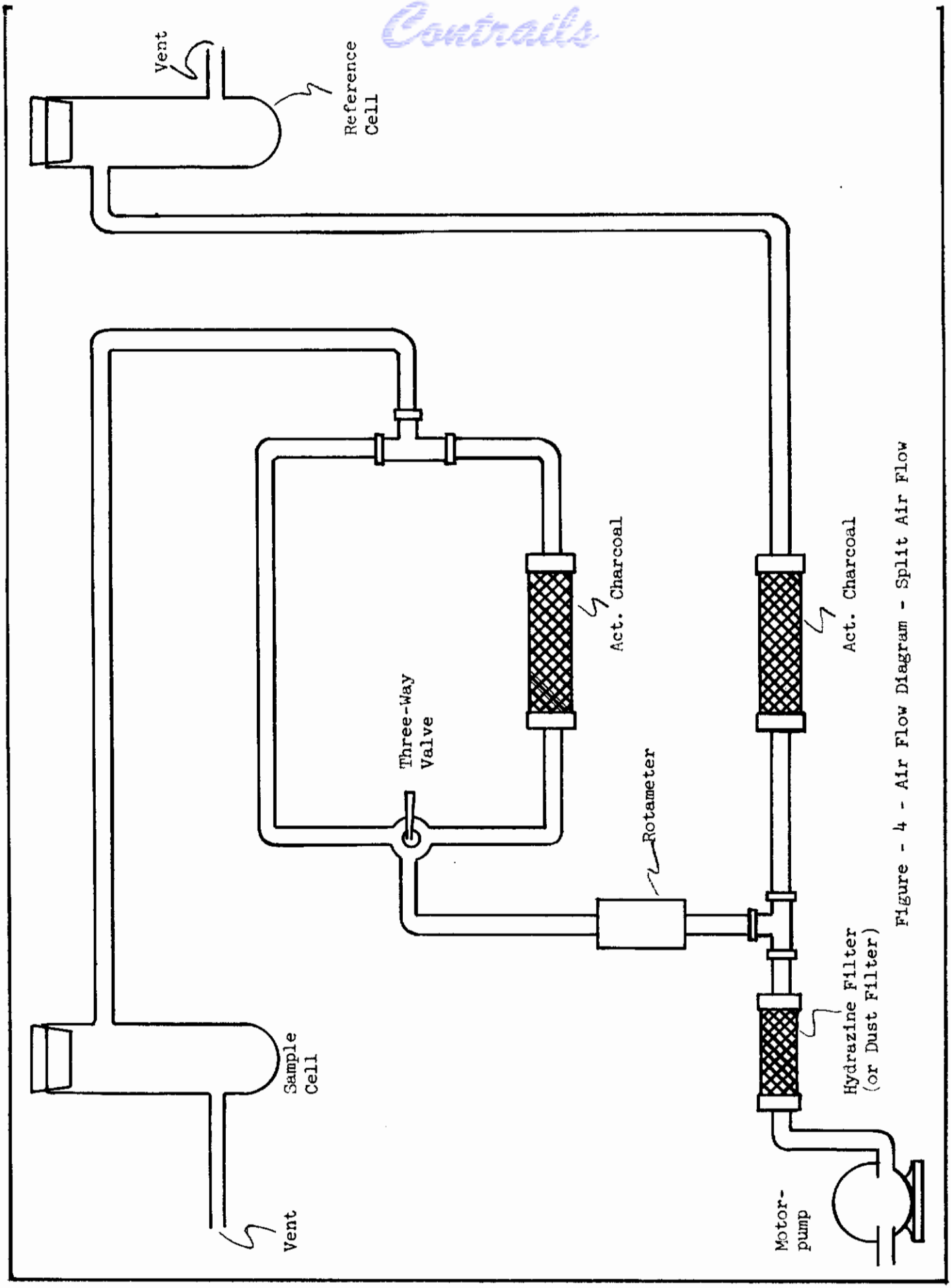
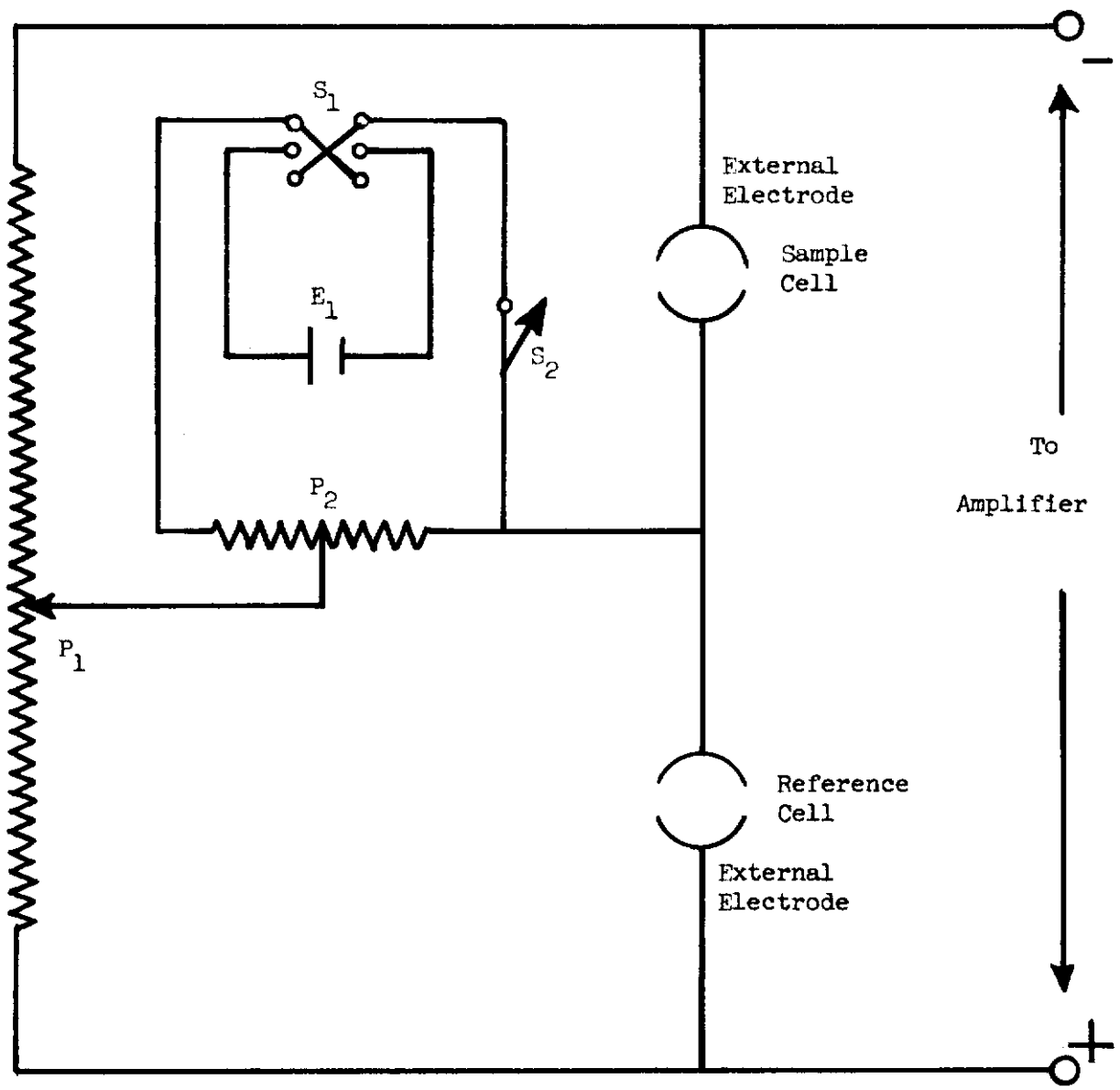
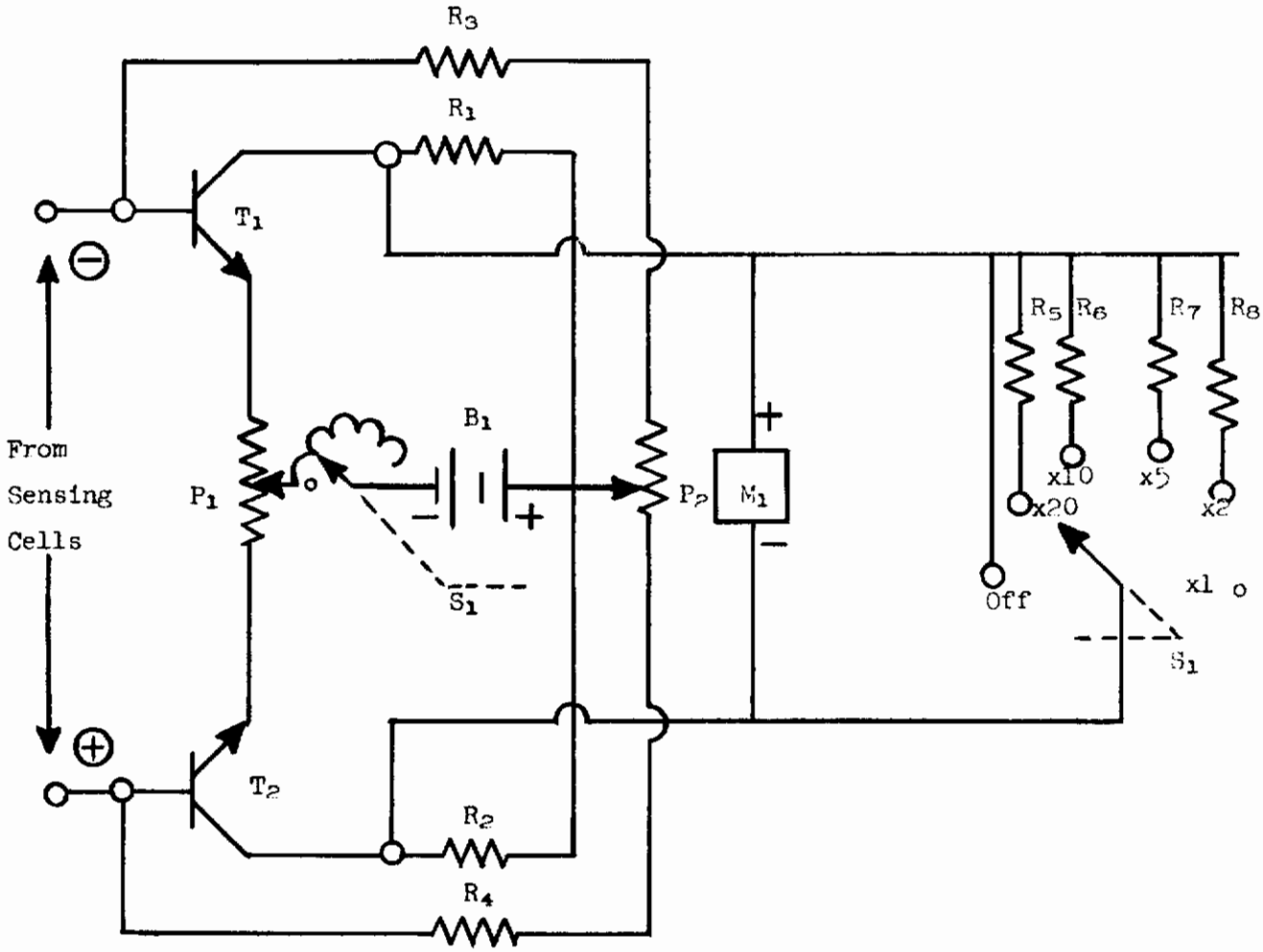


Figure - 4 - Air Flow Diagram - Split Air Flow



P_1 50 K Ohm, 10-Turn Miniature Linear Potentiometer
P_2 50 - 100 K Ohm Miniature Linear Potentiometer
S_1 DPDT Reversing Switch
S_2 SPST Off-On Switch Attached to P_2
E_1 1.5 Volt Battery

Figure - 5 - Generalized Polarizing Network



M_1 50-0-50 uA, 2,000 Ohm Meter B_1 3.0 or 4.5 Volt Batteries
S_1 Miniature Steatite Switch, 2-Pole 6-Position, Shorting Type
P_1 100-Ohm Miniature Potentiometer (Screw Adjust Type)
P_2 50 K Ohm Miniature Potentiometer (Worm Screw Type)
$R_1 = R_2$ = 1200-Ohms $\pm$ 5 per cent
$R_3 = R_4$ = 47-83 K-Ohms $\pm$ 10 per cent
R_5 = 56 $\pm$ 5 per cent (Ohms) R_6 = 120-Ohms $\pm$ 5 per cent
R_7 = 290 $\pm$ 5 per cent (Ohms) R_8 = 1200-Ohms $\pm$ 5 per cent
$T_1 = T_2$ = 2N35 Sylvania or 2N214 Sylvania Transistors (or equivalent).

Figure - 6 - Amplifier Circuit (Transistorized) With Range Switch.

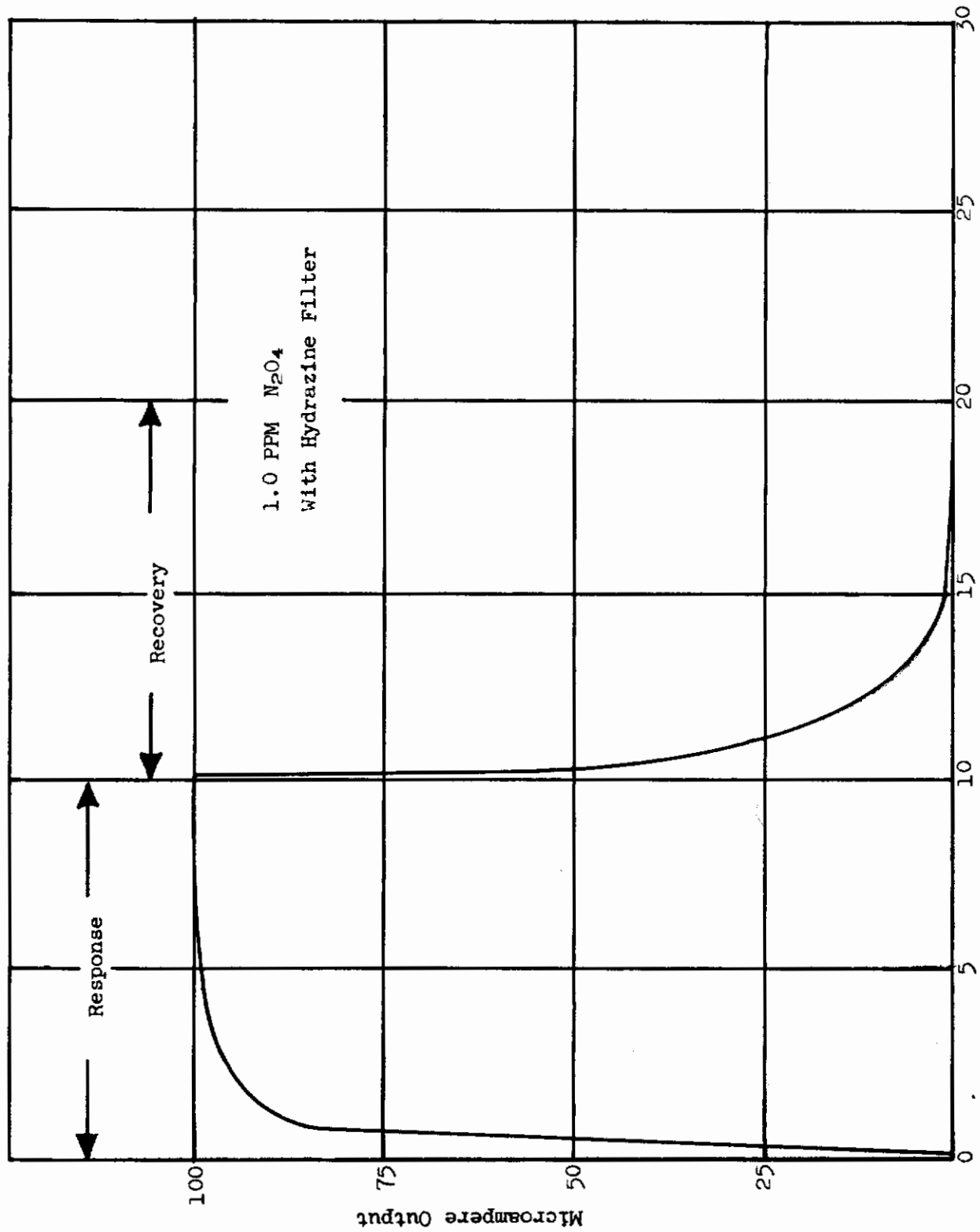


Figure - 7 - Typical Response-Recovery Curve for N_2O_4

TABLE I

MAINTENANCE AND PARTS LIST FOR AMPEROMETRIC PROPELLANT-COMPONENT DETECTOR

1. Re-dip sensing cells after 10-12 hours use.

2. Recheck zero point occasionally (about every two hours) by turning air switch to CHARCOAL for a few minutes, rezeroing if necessary, and turning air switch back to SAMPLE.

3. A procedure for checking calibrations is to prepare a source of about 1,000 to 5,000 PPM in high purity nitrogen. This can be conveniently diluted with air in a manifold to give nitrogen tetroxide in air and 1 to 10 PPM levels with great accuracy.

   a) The air pump is a Neoprene diaphragm air pump, manufactured by Neptune Products, Inc. This pump is obtainable under the trade name of DYNA-PUMP Model 2. Upgrading of the diaphragm and two valves to Teflon of Kel-F materials may be needed for reducing hydrazine absorption-desorption phenomena.

   b) The D.C. motor (replacing the original A.C. motor of the DYNA-PUMP) is a 12-volt Leece-Neville automobile blower motor. This motor is operated at 6 volts to obtain the proper r.p.m.

   c) The nickel-cadmium batteries are manufactured by the Sonotone Corporation. Two sets of 6 volts are operated in parallel. They are housed in a single 12 volt steel holder. Best results were obtained by getting cells individually and assembling when needed.

   d) The Budd aluminum cases, Simpson Model 27 microammeter, range switch (2-pole, six position, shorting type), plugs, jacks, resistors (1/2 watt plus or minus 10 per cent), 2N 35 transistors, and other accessories, are available from supply houses. The minature 10-turn potentiometer (50 K ohm) is manufactured by the Circuit Instruments Co.

   e) Tubing is 5/16 inch OD polyethylene, or Neoprene. Rubber is not satisfactory.

   f) The Rotameter is a 0-6 Cubic Feet/Hour meter from the Brooks Rotameter Co., Lansdale, Pennsylvania.

   g) The Schauer Model A-3 full-wave rectifier is a 6-volt commercial rectifier.

   h) The pipe, and POLY-FLO fittings are 5/16-inch OD obtainable from the Imperial Brass Company.

   i) The plastic cell holders are standard 150 ml. centrifuge tubes made of polypropylene. The inserts are 5/16 inch taps.

TABLE I (con't)

j) The polyethylene cartridges are calcium chloride tubes (double ended). These cartridges are cut down to size, and if necessary, the center hole size is increased to fit into the 5/16-inch brass fittings.

k) The three-way air switch is designated DEMI S-Brass plus P2 plus B10, three-way selector valve, obtainable from the George W. Dahl Co., Inc., of Bristol, Rhode Island.

l) The internal activated charcoal bracket is a broom holder.

TABLE II

PARTS LIST FOR SENSING CELLS (PER CELL)

1. Polyethylene tubing, 5/16 inch diameter, cut to 13 cm. length, and sealed at one end. 1/4 inch may also be used. Glass or other suitable materials compatible with Carbitol, acids and bases may also be used.

2. No. 6 gray Neoprene stoppers of low-sulfur content. These have a hole bored with a No. 4 cutter, and are heated for several days in a double boiler with the dip solution to remove all traces of sulfur. The stoppers are given a final boiling with distilled water, then are dried in an oven at 50°C.

3. Each finished cell is provided with a 29 x 105 mm. polypropylene tube for shippingand protection.

4. Platinum gauze, 52 mesh, 7 x 4 cm. piece of No. 1 purity metal[++]

5. Fine silver wire of 0.012 inch diameter, 100 cm. in length (or platinum gauze 52 mesh, 3 x 4 cm. piece)[++]

6. Two bare, tinned No. 22 hookup wires 6 inches in length.

7. One platinum wire, 0.0078 inch diameter, approximately six inches.

8. Two pieces of No. 18 polyvinyl chloride tubing 2-1/2 inches in length.

9. One red and one black miniature tip plug.

10. One red and one black piece of No. 14 spaghetti tubing approximately 4 inches long.

11. 3-inch wide surgical cotton gauze, as needed.

12. No. 8 cotton thread.

[++]Purity of platinum and silver is approximately 99.9+ per cent

TABLE III

ELECTROLYTE DIPPING SOLUTIONS

		Remarks
1.	Standard Solution	
	1 liter Carbitol	Good general-purpose electrolyte. Fast warm-up, and good for standardization studies.
	200 Ml. Water	
	8 Ml. conc. HCl	
2.	Basic Solution	
	1 liter Carbitol	Very sensitive to acid-fumes and carbon dioxide changes in air. Generally a poor choice
	200 Ml. Water	
	10 g. KOH	
3.	High Electrolyte Solution	
	1 liter Carbitol	Good zeroing, and fast warm-up. Not as much affected by acid fumes as the Standard.
	200 Ml. Water	
	8 Ml. conc. HCl	
	10 g. LiCl	
4.	Standard with Additives	
	1 liter Carbitol	Gives good results for nitrogen tetroxide and ozone detection. Helps stabilize baseline somewhat.
	200 Ml. Water	
	8 Ml. Conc. HCl	
	1-2 Ml. Conc. HNO_3 (or 0.1 Ml. UDMH)	

TABLE IV

STANDARDIZATION CHARTS FOR NITROGEN TETROXIDE, OZONE, HYDRAZINE, AND UNSYMMETRICAL DIMETHYLHYDRAZINE

Agent	Polarization Current (uA)	Cell Type	Sensitivity (Microamperes/PPM)	Electrolyte
N_2O_4	30 (Reverse)	Pt-Pt	97 ± 10%	Standard + HNO_3
N_2O_4	15 (Reverse)	Pt-Pt	11.8 ± 17.5%	Standard + HNO_3
N_2O_4	5 (Reverse)	Pt-Pt	"Backlash Response"	Standard + HNO_3
N_2O_4	5 (Forward)	Pt-Ag/AgCl	3.4	Standard + HNO_3
O_3	30 (Reverse)	Pt-Pt	52 ± 17.9%	Standard + HNO_3
O_3	5(Forward)	Pt-Ag/AgCl	2-3	Standard + HNO_3
N_2H_4	20 (Forward)	Pt-Pt	40	Standard
N_2H_4	4 (Forward)	Pt-Ag/AgCl	20-25	Standard
UDMH	20 (Forward)	Pt-Pt	20	Standard
UDMH	4 (Forward)	Pt-Ag/AgCl	10-15	Standard
UDMH	30 (Forward)	Pt-Pt	10-15	Alkaline
UDMH	20 (Reverse)	Pt-Pt	0-1	Standard

TABLE V

POTENTIOMETRIC RESULTS WITH HYDROGEN FLUORIDE IN AQUEOUS 0.2M ACETIC ACID (a, b)

Concentration of HF in PPM	Voltage Change in Volts	Concentration of HF ($1/PPM \times 10^{-2}$)
5.0	0.260	20
10.0	0.390	10
15.0	0.50	6.7
30.0	0.61	3.3

a) Sensing cells constructed of 30 Cm. of 0.125 inch diameter aluminum vs. 3 X 5 Cm. of 52 mesh No. 1 platinum gauze with lead.

b) All measurements made with a high impedance (1 M ohm) vacuum tube voltmeter.

BIBLIOGRAPHY

1. Comstock, C.C., Inhalation Toxicity of Diborane in Dogs, Rats, and Guinea Pigs, ibid, Report No. 258, March 1954.

2. Comstock and Oberst, The Median Detectable Concentration of Diborane, Pentaborane and Decaborane Odor for Man, Research Report No. 206, Chemical Corps Medical Laboratory, Army Medical Center, Maryland, August 1953.

3. Fairhall, L. T., Industrial Toxicology, 2nd Edition, Williams and Wilkins Company, 1957.

4. Jacobson, K. H., The Toxicity of Boron Hydrides, Third Light Metal Hydrides Meeting, p. 101, March 1953. Department of Defense, Research and Development Board.

5. Lawson, L. H., and Jacobson, K. H., The Median Lethal Concentration of Diborane Vapor for Rats and Mice, Chemical Warfare Laboratories Technical Report, CWRL 2031,

6. Mantell, C. L., Adsorption, Second Edition, McGraw-Hill Book Company, Inc., New York, 1951.

7. U. S. Government Industrial Hygienists, "Threshold Limit Values", A.M.A. Archives of Industrial Hygiene and Occupational Medicine, 1959.

8. Sax, N. I., Dangerous Properties of Industrial Materials, Reinhold Publishing Company, 1957.

9. McCabe, L. C., "Air Pollution", Proceedings of the United States Technical Conference on Air Pollution, McGraw-Hill Book Company, Inc., New York, 1952

10. Rozendaal, H. M., "Clinical Observations on Toxicology of Boron Hydrides", A.M.A. Archives of Industrial Hygiene and Occupational Medicine, Vol. 4, 257-60. 1951.

11. Poulos, N. A., MONITOR-1, Olin Mathieson Chemical Corporation Technical Report, 1 September 1960.

12. Beatty, R. L., Berger, L. B., and Schrenk, H. H., "Determination of the Oxides of Nitrogen by the Phenoldisulfonic acid Method", U.S. Bur. Mines, Rept. Invest. 3687. 1943.

13. Saltzman, B. E., "Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere", Anal. Chem. 26, 1949. 1954.

14. Heller, W., "Determination of Atmospheric Ozone by Fluorescein", Compt. Rend. 200: 1936, 1935.

15. Brewer, A. W. and Milford, J. R., "The Oxford-Kew Ozone Sonde". Proceedings of the Royal Society, No. 1287, July 19, 1960. Vol. 256.

16. McKennis, H., and Witkin, B., "Determination of Hydrazine in Air", Arch. Ind. Health 12:511. 1955.

17. Pesez, M., and Petit, A., "Recherche et dosage de l'hydrazine" Bull. Soc. chim. France 265:122. 1947.

18. Lamar, W. L., "Determination of Fluoride in Water", Ind. Eng. Chem., Anal. Ed. 17: 148, 1954.

19. Setterlind, A. N., Determination of Hydrogen Fluoride and Fluorides in Air, State of Illinois, Div. of Ind. Hyg. Lab. Manual. 1947.