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AFAPL-TR-67-123
Supplement I

DEVELOPMENT OF A HAZARDOUS VAPOR DETECTION SYSTEM FOR ADVANCED AIRCRAFT

Orlando Cucchiara, Philip Goodman and Thomas Donaghue
Panametrics, Inc.
Waltham, Massachusetts

TECHNICAL REPORT AFAPL-TR-67-123

SUPPLEMENT I

June 1968

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DEVELOPMENT OF A HAZARDOUS VAPOR DETECTION SYSTEM FOR ADVANCED AIRCRAFT

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FOREWORD

This report was prepared by Panametrics, Inc., Waltham, Massachusetts, on Air Force Contract AF 33(615)-3646, "Development of a Hazardous Vapor Detection System for Advanced Aircraft." The contract was initiated under Project No. 3048, Task No. 304807. The work was administered under the direction of Fuels, Lubrication, and Hazards Branch, Support Technology Division, Air Force Aero Propulsion Laboratory. Mr. Jon R. Manheim (APFL) served as project engineer for the Laboratory.

This supplementary report is divided into two parts. The first part concerns the field evaluation of a hazardous vapor detection system for advanced aircraft. The development and construction of this system has been described in detail in AFAPL-TR-67-123, "Development of a Hazardous Vapor Detection System for Advanced Aircraft." The second part of this report concerns the results obtained during the investigation of osmium Kryptonate as a potential sensor for the detection of oxygen in the ullage space of fuel tanks aboard advanced aircraft.

The studies presented here were conducted in the period 1 September 1967 through 31 March 1968, by the Chemistry Department of Panametrics, Inc., Dr. Philip Goodman, Director. Mr. Orlando Cucchiara was the principal investigator.

This report was submitted by the authors June 1968.

This technical report has been reviewed and is approved.

Arthur V. Churchill

Arthur V. Churchill, Chief
Fuels, Lubrication and
Hazards Branch
AF Aero Propulsion Laboratory

ABSTRACT

This report covers two separate and distinct efforts associated with the evaluation of hazardous vapors aboard advanced aircraft.

Part I is concerned with an experimental evaluation of prototype instruments based on a catalytic oxidation technique for the detection of hydrocarbon vapors aboard advanced aircraft.

Two hydrocarbon vapor probes were placed in the engine compartments of a JT-12 engine housed in a wind tunnel. The response of the probes to controlled leakages of JP-4 fuel under varying engine operating conditions was ascertained.

The prototype instruments operated completely satisfactorily. Reproducible results under identical engine operating conditions were attained. Response times were of the order of two seconds and the lower limit of detection was approximately 0.3% of the lower inflammability limit for JP-4.

Part II is concerned with the evaluation of osmium Kryptonate®* for the detection of oxygen in the ullage space of fuel tanks aboard advanced aircraft. Sensitivities adequate to cover the oxygen concentration range of interest (0.5% - 40.0% O_2v/v) were attained at a sensor operating temperature of 600°F. The response of the sensor to oxygen was independent of JP-6 vapor concentration. Lifetimes attained during this investigation were of the order of 140% O_2 - min to 300% O_2 - min. Methods for increasing this lifetime are indicated and are within the present state-of-the-art.

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*A registered trademark of Panametrics, Inc.

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PART I

EVALUATION OF A HAZARDOUS VAPOR DETECTION SYSTEM FOR ADVANCED AIRCRAFT

PART I

SECTION I

INTRODUCTION

During the period March 1966 through 1 September 1967, prototype instruments of a hazardous vapor detection system for advanced aircraft were designed, constructed and laboratory tested. These instruments were developed for the detection of JP-6 fuel in advanced aircraft engine compartments and for oxygen in the ullage spaces in the fuel tanks of such aircraft. Detection of both species is accomplished by the use of a catalyst coated thermistor sensor. Catalytic oxidation occurring at the catalyst surface liberates heat, which is sensed by the thermistor. The JP-6 detector is simple in concept requiring only a detecting probe and associated electronics, whereas the oxygen detector additionally requires a gaseous flow system, a trap to remove JP-6 vapor and the introduction of isobutane as the combustion fuel. These instruments have performed satisfactorily and reliably during the numerous laboratory experiments necessary for development, design and testing. The detailed results of this development phase are reported in AFAPL-TR-67-123.

The purpose of this report is to present the results obtained during the field testing of these instruments. Because of the additional complexity of the oxygen detection instrument, the lack of proper field testing facilities, and the lack of time, it was decided by the Wright-Patterson Project Engineer to field test the JP-6 instruments only.

The tests described in this report were conducted at National Aviation Facilities Experimental Center, Atlantic City, New Jersey, utilizing the available wind tunnel facilities. Two JP-6 probes were mounted at various locations within the engine compartment of a JT-12 jet engine. The JP-6 probes were connected via electrical cable to the auxiliary electronics and readout located in the control room of the wind tunnel. Over forty runs were conducted under varying conditions of engine speed, engine temperature, engine pressures, fuel leakage rates, etc. The results of these tests indicated that the JP-6 instrumentation operated extremely satisfactorily, indicating at all times the gaseous fuel concentration within the proximity of the probes.

SECTION II

TECHNICAL DISCUSSION

The evaluation of the JP-6 instruments was originally to be conducted by in-flight tests aboard selected aircraft. It was decided by WPAFB personnel not to conduct in-flight tests, but rather to utilize ground base installations in its stead. This decision was based primarily on two facts: the difficulty in obtaining test aircraft during the allotted test period, and second, further ground testing was desirable to insure that the detector probe itself did not consitute an explosive hazard at high ambient temperatures. As a restult, all tests were conducted at the wind tunnel site at NAFEC, Atlantic City, N. J., utilizing a JT-12 jet engine. This report presents the results attained during these tests.

A complete description of the hazardous vapor detection system is presented in AFAPL-TR-67-123 "Development of a Hazardous Vapor Detection System for Advanced Aircraft." However, for the purposes of clarity a brief description of the instrument including its operating principles and capabilities will be presented first. The report will then present the tests conducted, results of the tests and a discussion of the results.

A. Background

The hazardous vapor detection system developed operates on the principle of catalytic thermal detection. During the catalytic oxidation of a binary gas system, the heat liberated at the surface of a catalyst coated thermistor is proportional to the gas-phase concentration of the minor reactant. This principle was employed for the detection of both JP-6 vapors in engine compartments (oxygen in excess) as well as for oxygen in the ullage space of fuel tanks (isobutane in excess). However, this report will be concerned only with the detection of JP-6 vapors. For a complete detailed description on the employment and instrumentation necessary for the detection of oxygen, it is suggested that the reader refer to AFAPL-TR-67-123.

The JP-6 detector consists basically of a probe housing three thermistors, a control box for bridge circuits, temperature control, readout, etc., and an alarm box. These three units are interconnected by electrical cable to provide for a complete system. Important aspects of the operating principle and the instrument description are presented below.

1. Operating Principle

A number of gas-phase reactions proceed at extremely slow rates unless they are catalyzed by certain solid materials. Catalysts usually exert their effect by a selective adsorption process in which molecules of one or more of the gaseous species are held at particular sites in configurations which make them highly susceptible to reaction.

If such a reaction is exothermic, then heat will be liberated at the reaction site at a rate which is proportional to the reaction occurring. By measuring the liberated heat, it becomes possible to estimate the relative rate of reaction, and as often happens when one reactant is present in excess, this rate of reaction is directly proportional to the minor gas-phase concentration.

In gaseous hydrocarbon-oxygen mixtures, it is found that the oxidation rate of the hydrocarbon is usually quite low unless very high temperatures or an initiation process are present. However, by allowing the reaction to occur at a catalytic surface, reaction rate is greatly increased and a sizable amount of heat is liberated. Surprisingly large amounts of heat energy are available in even seemingly very dilute hydrocarbon-oxygen mixtures. If even a small fraction of this energy is tapped, a very sensitive detection technique would result.

By utilizing a thermistor, coated with a catalyst, the liberated heat due to catalytic oxidation can be measured conveniently. The instrument developed employs platinum black, a very finely divided form of platinum metal, as the catalyst. Thermistors typically have a relatively large negative temperature coefficient of electrical resistance, varying by several percent for a change of 1°C. The thermistors' large temperature coefficients allow extremely sensitive measurements of small temperature differentials. By employing two thermistors in a typical Wheatstone Bridge circuit, small changes in thermistor resistance are readily detected.

The above describes briefly the operating principle used in the hazardous vapor detection system developed.

2. Instrument Description

The sensing probes developed for the prototype instruments consist of three thermistors imbedded in a brass block. The block is heated by means of a small cartridge-type heater. Two of the three thermistors were "matched pairs," i.e., the selected pairs matched each other to within 0.5% over the temperature range 290°C to 310°C. The probe was designed always to operate in this region, and hence this is the only temperature range of concern as regards matching of the thermistor pairs. One of the matched thermistors is coated with the catalyst consisting of an equal mixture of platinum black and silica gel "G." The silica gel "G" serves to form an adherent coating to the thermistor surface. This coating will not shake off, although it can be rubbed off.

The third thermistor is utilized for controlling the cartridge-heater power, in order that the heated block will remain at constant temperature under varying ambient conditions. This thermistor is connected to a proportional controller, which automatically adjusts the heater power to maintain it at a constant resistance.

Indirect heating of the thermistors rather than resistive heating was employed in order to cover a greater range of signals at the high ambient temperatures and to eliminate the possibility of "hot spots," particularly at the thermistor-lead wire interface.

The sensing probe is connected by cable to a control box containing the temperature control, bridge circuits, visual readout, as well as a recorder output. An Oven Industries proportional temperature controller was used to regulate the power to the cartridge-heater. A Wheatstone bridge circuit was used to measure the imbalance of the matched thermistors caused by the reaction of the hydrocarbon vapors on the surface of the catalyst coated thermistor. A regulated power supply accepts a 115 volt 400 HZ input, yielding a dc output of 10 volts. The instrument sensitivity is determined by the portion of this voltage which is applied to the bridge; this is adjustable by means of a potentiometer. The bridge output signal is displayed on a 0-5μa meter relay which is also used to operate an alarm. The voltage developed across the meter is also available as a recorder output. The impedance of the meter is 10,000 ohms; therefore full scale (5μa) corresponds to a recorder output of 50 mv.

The control box serves as a dual unit, containing the necessary circuitry and controls for operating both a JP-6 detector and an oxygen detector simultaneously. The box contains two identical bridge circuits and readouts which operate, with individually adjustable input voltages, from a common dc power supply. Similarly, there are individual heater controllers for the two sensors. In the tests discussed below only the JP-6 portion of the control box with the corresponding JP-6 probe were used.

B. Test Facilities

Three complete hydrocarbon and oxygen vapor detection systems were constructed. One hydrocarbon and oxygen vapor detection system was delivered to WPAFB for in-house analysis. The remaining two instruments were delivered to the wind tunnel facility at NAFEC, Atlantic City, N. J., for testing their ability to detect hydrocarbon vapors in a JT-12 engine under actual operating conditions.

The Five-Foot Fire Test Tunnel Facility located at NAFEC is a fixed installation consisting of an open-circuit, induction-type wind tunnel; an engine room containing two turbojet aircraft engines; an operation area; and an instrumentation buildup area. The test tunnel is a subsonic wind tunnel powered by two Pratt and Whitney J-57-519W turbojet aircraft engines. This facility is used to fire-test small aircraft engines and aircraft components under conditions which simulate actual in-flight fires. It is also used to test and evaluate fire detection systems and fire extinguishing systems of the types used to extinguish in-flight fires that are subjected to high-velocity air movement. These tests are performed in a 5-foot diameter test section of the wind tunnel by using either the actual components or scale models.

A Pratt and Whitney JT-12 turbojet engine was mounted in the test section of the wind tunnel. This engine as well as the wind tunnel is instrumented to provide velocity, temperature, pressure, engine speed, etc. In addition, the JT-12 engine is provided with a JP-4 fuel flow system to simulate a leakage of fuel within the accessory compartment of the engine.

Two hydrocarbon detection probes were mounted at various locations within the JT-12 engine and their capability of detecting hydrocarbon fuel vapors under simulated flight conditions were ascertained.

C. Test Conditions

Two probes (Probe #2 and Probe #4) were mounted at several different locations within Zone II of the engine compartment of the JT-12 engine. Simple angle brackets with nut and bolt attachments were used to clamp the probes to the interior engine surfaces. The probes were connected by cable to their respective control boxes located in the control room of the wind tunnel. The engine itself is instrumented so that pertinent parameters (temperatures, pressures, engine speed, etc.), which might affect the response of the JP-6 sensors, could be monitored. The engine was also provided with equipment to enable injection of hydrocarbon fuel within the engine compartments. By changing the fuel injector nozzle, or increasing the time the fuel was left on, it was possible to vary the quantity of fuel being injected into the engine compartment.

The JT-12 engine operated on JP-4 fuel. Since the probes had been originally calibrated for JP-6 fuel, recalibration was necessary. The probes were calibrated using a bubbler arrangement from which saturated JP-4 vapor was attained. The concentration by weight of the JP-4 in the gas issuing from the bubbler was determined by condensation (in a cold trap) and subsequent weighing. Sensitivities of the instruments were set so that 50 mv (full scale) corresponded to 10% by weight of JP-4. Because of the variable molecular weight of JP-4, the volume percentage can only be estimated. Assuming an "average" molecular weight of 100 for JP-4, then 10% by weight corresponds to 2.9% by volume.

Prior to actual engine installation, the meter readings for both probes were nulled to zero. After installation, and without any engine power, a "background" reading of approximately 2-5 millivolts was observed, indicating a residual hydrocarbon vapor in the engine compartment prior to actual fuel injection. During engine operation, but still prior to fuel injection, this "background" reading decreased to 0-2 mv. When the desired engine power was attained, this "background" was nulled to zero. This nulling procedure was employed prior to each run.

During the tests, a high input impedance recorder compatible with the detector output was not available. As a result, manual recording of the signal as a function of time was necessary. The meter reading was recorded at 5 second intervals using a stopwatch as a timer. In general, this technique proved satisfactory. However, a certain amount of data was unavoidably lost, especially when rapid changes in signal, due to rapid concentration fluctuations, occurred.

D. Results

The results attained during the tests conducted at NAFEC are shown in the following tables. The first table in each set presents the engine conditions while the second set presents the signal attained with the probes as a function of time for each run. Pertinent notes regarding the data attainment and the results are provided at the conclusion of each set of tables.

Two probes were utilized throughout these tests. These probes were designated probe #2 and probe #4 associated with control box #1 and control box #2 respectively. Both probes were located within Zone II of the engine. The fuel injector nozzle was always located at a distance of ten inches forward of Zone II at 6 o'clock.

Table I

Engine Operating Conditions

RUN NO.	1	2	3	4	5	6	7	8	9	10	11	12
Mach No.	0.210	0.210	0.210	0.230	0.245	0.340	0.370	0.390	0.425	0.440	0.50	0.50
Engine Speed %	48	48	48	60	70	80	48	60	70	75	80	80
Air Inlet Temp. (°F)	41	41	41	41	41	41	41	41	41	41	41	41
Accessory Compartment Temp. (°F)	45	45	45	65	80	90	50	60	80	85	80	80
Louvre Compartment Temp. (°F)	45	45	45	70	88	110	50	60	80	90	105	105
Static Pressure in Zone II (in. of Hg)	-0.8	-0.8	-0.8	-1.10	-1.60	-2.46	-2.90	-3.40	-3.80	-4.0	-5.0	-5.0
Fuel Flow Rate (gal/min)	.421	.421	.421	.421	.421	.421	.421	.421	.421	.421	.421	.421
Fuel Time On (seconds)	5	15	35	15	5	10	10	10	2	2	3	2

Table I (cont.)

RUN NO.	13	14	15	16	17							
Mach No.	0.50	0.50	0.50	0.50	0.465							
Engine Speed %	48	48	60	70	95							
Air Inlet Temp. (°F)	41	41	41	41	41							
Accessory Compartment Temp. (°F)	50	50	55	70	120							
Louvre Compartment Temp. (°F)	45	45	60	80	93							
Static Pressure in Zone II (in. of Hg)	-5.0	-5.0	-5.0	-5.0	-4.5							
Fuel Flow Rate (gal/min)	.421	.421	.421	.421	.421							
Fuel Time On (seconds)	10	10	10	10	30							

Table II

Probe Response vs Time, mv

Time Sec.	Run #1		Run #2		Run #3		Run #4		Run #5		Run #6		Run #7		Run #8	
	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	4	0	3	0	10	0	15	1.5	27	1.5	10	-	13	1.5	15	-
10	5	0	4	2	20	1	30	2.0	32	1.0	23	2.5	33	1.0	45	2
15	3	0	3	2	20	2	43	2.5	24	-	18	1.8	32	2.0	> 50	-
20	2	0	13	2	18	2	37	1.5	17	-	19	1.5	-	-	33	1
25	5	0	6	1	9	3	32	0.5	32	1.0	19	1.5	15	-	-	-
30	3	0	0	0.5	12	3	27	0	28	-	19	.5	13	-	26	-
35	2	0	0	0	42	2	41	0	26	-	14	-	11	-	-	0
40	0	0	0	0	32	1.5	50	0	20	-	-	-	11		4	
45					26	0	47	1.0	14		10	-	10		15	
50					20	0	42	0	14		-		4		11	
55					19	0	13	-	13		7		3		10	
60					16	0	13	-	6		6		10		3	
65					15	0	9	0	5		-		7		0	
70					5		10		-		-		6		0	
75					1		11		10		6		4		-	
80					0		10		-		-		2		1	
85							-		0		-		0			
90							-				0		1			
95							-				0		1			
100							-						1			
105							0									
110																
115																
120																

Table II (cont.)

Time Sec.	Run #9		Run #10		Run #11		Run #12		Run #13		Run #14		Run #15		Run #16		Run #17	
	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	9	0	8	2	12	0	6	0	12	1	12	0	11	2	1	0	1	2
10	7	0	13	0	6	0	3	0	20	1.5	18	2	0	2	0	1	1	1
15	4	0	5	0	4	0	3	-	15	-	4	1	7	1	2	2	0	3
20	2	0	3.5	0	3.5	0	2		5	0	6	2	0	0	2	2	2	4
25	5	0	1	0	4				20	1.5	33	2	0	3	0	1.5	0	4.5
30	0		1.5		0				30	2.0	22	1	3	1.5	0	2.0	0	3
35	0		1.5		0				35	1.0	10	1.5	0	0		1.5	0	2
40	0		1.5						22	-	18	0	-			0		1
45	0								10	-	22	0	-			0		2
50	0								5	0	15		1					1
55	0								3		9		-					2
60	0								3		8		-					1
65									1		6							0
70									2		3							0
75									2		3							
80									1		0							
85									0		0							
90									0									
95									-									
100									-									
105									0									
110																		
115																		
120																		

NOTES TO TABLE I AND TABLE II

Probe #2 was located in the accessory compartment, aft, at 5o'clock a distance of 32 in. from the fuel injector nozzle. Probe #4 was located at the midpoint of the louvre at 12 o'clock. The probes were mounted horizontal to the longitudinal axis of the engine.

Runs #1 through #16 were conducted with the bleed valve opened. Since it was apparent that very little fuel was reaching the louvre area, an additional run was conducted with the bleed valve closed, in order to increase the JP-4 concentration in that area. At the conclusion of run #17, the probes were removed, inspected and tested with known concentrations of JP-4. Probe #4 had retained its integrity as well as its calibration. Probe #2 was found to be insensitive to JP-4 vapors. Close inspection revealed that the catalyst coating had washed off the surface of the thermistor and was the result of direct impregnation of liquid fuel into the probe housing. From the results, it appears that this "washing off" occurred during run #15. The results obtained with probe #2 from run #1 through run #14 are believed valid. Results obtained with probe #4 are believed valid for all runs.

Probe #2 was recoated with catalyst and recalibrated for future runs. Calibration was maintained at 0.2% by weight of hydrocarbon/millivolt, i.e., 10% by weight for full scale deflection.

Table III

Engine Operating Conditions

RUN NO.	18	19	20	21	22	23	24	25
Mach No.	0.365	0.365	0.500	0.500	0.500	0.500	0.500	0.500
Engine Speed %	48	48	50	60	70	70	80	80
Air Inlet Temp. (°F)	31	31	31	31	31	31	31	31
Accessory Compartment Temp. (°F)	40	35	35	50	75	75	85	85
Louvre Compartment Temp. (°F)	20	20	20	35	55	55	65	65
Static Pressure Zone II (in. of Hg)	-2.9	-2.9	-5.15	-5.15	-5.15	-5.15	-5.15	-5.15
Fuel Flow Rate (gal/min)	.421	.421	.421	.421	.421	.421	.421	.421
Fuel Time On (seconds)	10	10	5	5	5	10	5	15

Table III (cont.)

RUN NO.	26	27	28	29				
Mach No.	0.180	0.180	0.220	0.265				
Engine Speed %	49	49	60	70				
Air Inlet Temp. (°F)	36	36	36	36				
Accessory Compartment Temp. (°F)	40	40	62	80				
Louvre Compartment Temp. (°F)	25	25	45	60				
Static Pressure in Zone II (in. of Hg)	-0.85	-0.85	-1.15	-1.62				
Fuel Flow Rate (gal/min)	1.00	1.00	1.00	1.00				
Fuel Time On (seconds)	5	10	10	10				

Table IV

Probe Response vs Time, mv

Time Sec.	Run #18		Run #19		Run #20		Run #21		Run #22		Run #23		Run #24		Run #25	
	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4
0	0	0	0	0	0	0	0	7	0	8	0	9	0	0	0	0
5	30	2	3	22	4	10	2	13	2	15	2	15	3	4	2	5
10	50	6	4	49	4	15	3	1	3.2	11	6	15	3	8	4	6
15	50	4	5	47	3	12	2	2	1.5	4	3	12	2	8	5	10
20	48	4	3	46	2	15	1.2	3	1	3	3	6	1.5	4	4	11
25	40	3	3	35	1.8	17	1	2	1	2	2	6	1	5	2	4
30	30	2	2.5	28	1.5	21	1	2	1	2	1.5	2	1	3	1	2
35	25	2	2	24	1.2	17	1	2	1	3	1.5	6	1	3	1	4
40	16	2	2	19	1.0	14	1	3	1	4	1	4	1	4	1	2
45	20	3	2	19	1	13	1	2	1	4	1	4	1	2	1	5
50	23	2	2	16	1	11	.8	3	1	2	1	6	.8	1	1	5
55	18	2	2	16	1	8	.8	4	.5	1	1	7	.8	1	1	4
60	20	2.5	2	20	.5	7	.2	3	.5	2	1	6	.8	1	1	3
65	12	3	2	14	1	4	.2	2	.5	1	1	3			1	2
70	13	3	2	12	1	4	.5	2	.5	1	1	2			0	2
75	13	2	-	12	1	5	.5	1	.5	0	1	1			0	2
80	15	2	-	10	1	5	.2	1	.5	1	1	0			0	1
85	8	1.0	1.5	7	1	4	.5	0	.5	0	1	1			0	0
90	9	1.0	1.5	8	.8	3	0		0	0	1	1			0	0
95	15	2.0	1.5	8	.8	4										
100	17	1.0	1.5	10	.8	3										
105	14	1.5	1.5	8	1	4										
110	6	1.0		6	1	3										
115	8			5	1	3										
120	7			6	1	3										

Table IV (cont.)

Time Sec.	Run #26		Run #27		Run #28		Run #29		Run		Run		Run		Run	
	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe #2	Probe #4	Probe	Probe	Probe	Probe	Probe	Probe	Probe	Probe
0	0	0	0	0	0	0	0	0								
5	15	7	6	6	14	14	14	12								
10	11	6	18	14	22	21	30	28								
15	7	3	21	11	18	17	20	23								
20	4	4	10	7	11	18	20	18								
25	3	3	6	3	6	7	7	10								
30	2	3	4	1	4	1	5	7								
35	1.5	4	3	3	3	3	3	2								
40	1.2	2	2	2	3	7	3	3								
45	1	1	2	4	2.5	8	2.5	5								
50	1	2	2	4	2	7	2	7								
55	1	2	1.5	2	2	5	2	5								
60	1	1	1.2	2	2	5	1.5	6								
65			1.2	3	1	5	1.5	5								
70			1.2	3	1	5	1.5	5								
75			1.2	2	1	0	1.5	5								
80			1.2	2	1	0	1.5	3								
85			1.0	2	1	0	1.5	0								
90					1	0	1.5	0								
95																
100																
105																
110																
115																
120																

NOTES TO TABLE III AND TABLE IV

For runs #19 through #29, probe #2 was located in the accessory compartment, aft, at 7 o'clock, probe #4 was located in the accessory compartment, aft, at 5 o'clock. The probes were separated by a distance of 18 inches, and mounted horizontal to the longitudinal axis of the engine. For run #18, probe #2 was located at the 5 o'clock position while probe #4 was located at the 7 o'clock position. This probe substitution was used to ascertain the reproducibility of the two probes when located at the same position.

In runs #26 through #29, the injector nozzle was changed so that a fuel leakage rate of 1.00 gal/min could be attained.

Table V

Engine Operating Conditions

RUN NO.	30	31	32	33	34	35	36	37	38	39	40
Mach No.	0.180	0.220	0.265	0.320	0.320	0.340	0.340	0.445	0.260	.500	.500
Engine Speed %	48	60	70	80	80	48	48	80	70	95	95
Air Inlet Temp. (°F)	38	38	38	38	38	38	38	38	38	38	38
Accessory Compartment Temp. (°F)	45	60	80	100	100	60	60	80	85	100	100
Static Pressure in Zone II (in. of Hg)	-0.8	-1.15	-1.62	-2.15	-2.15	-2.60	-2.60	-4.05	-1.64	-5.15	-5.15
Fuel Flow Rate (gal/min)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Fuel Time On (seconds)	10	10	10	10	20	10	20	20	20	20	30

Table VI

Probe Response vs Time, mv

Time Sec.	Run 30	Run 31	Run 32	Run33	Run34	Run35	Run36	Run37	Run38	Run39	Run40
	Probe #4	Probe #4	Probe #4	Probe #4	Probe #4	Probe #4	Probe #4	Probe #4	Probe #4	Probe #4	Probe #4
0	0	0	0	0	0	0	0	0	0	0	0
5	2	3	2	4	3	1	1	1	3	3	5
10	3	5	6	8	4	1.5	1.5	2	5	7	10
15	1.5	4	8	6	6	1.5	2	2	7	10	14
20	1	2	10	7	12	1	3	2	9	14	12
25	.5	1.5	11	6	17	1	4	1.5	12	15	10
30	.2	1.5	10	5	16	.5	5	1.5	14	14	10
35	0	1	9	5	15	.5	4	0	15	14	9
40	0	1.5	8	4	14		3	0	13	14	10
45	0	1.5	7	4	13		3	0	13	10	12
50		1.5	6	3	12		3		12	9	15
55		1.5	5	2	13		3		12	8	15
60			5	1	11		2		13	8	14
65			5	1	11		2		12	8	13
70			5		11		2		12	8	12
75			4		8				11	8	11
80			4		7				11	8	10
85			4		7				9	9	9
90					7				7	10	8
95					7				6	8	5
100									6	6	4
105									6	5	2
110										3	1
115											
120											

NOTES FOR TABLE V AND TABLE VI

Probe #4 was located in the accessory compartment, aft, at 5 o'clock. The probe was mounted vertical to the longitudinal axis of the engine.

Probe #2 was not utilized in these runs. A thermistor lead from probe #2 was accidentally broken during installation and the probe was thus inoperative.

Run #40 was conducted with the bleed valve closed, runs #30 through #39 were conducted with the bleed valve opened.

Probe #4 was removed from the engine and its calibration checked. No change in calibration had occurred.

E. Discussion of Results

A complete and detailed discussion of the results is not feasible without a thorough knowledge of the jet engine operation; specifically, the air flow paths, flow rates, and leakage fuel mixing characteristics under various engine conditions must be known. This information was not available. A detailed analysis of the data is left to those personnel who are experienced with the characteristics of jet engines, specifically of the JT-12 engine, as regards internal gas flow conditions.

However, the data does indeed indicate that the hydrocarbon vapor probes operated satisfactorily and did indeed determine the actual concentration of the hydrocarbon vapors in the immediate vicinity.

Runs #1 through #16 indicate that relatively large amounts of JP-4 vapors were present in the accessory compartment after fuel injection. The actual vapor concentration being a function of the total fuel injected as well as the engine speed, temperature, etc. However, by the time these vapors reached the louvre area, they were considerably diluted to the order of 0.4% by weight. This value is considerably below the lower inflammability limit of JP-4 (0.8% by vol.).[1] That the concentrations attained were at least of the right order of magnitude was confirmed by NAFEC personnel who routinely use this JT-12 engine in various fire tests. NAFEC personnel indicated that a fire cannot be started in the louvre area, and ignition of the fuel always occurs in the accessory compartment. Hence, the JP-4 vapor concentration in the louvre area must be lower than 0.8% by vol. (~2.8% by weight) and greater than this value in the accessory compartment. The results obtained with the test JP-4 probes are in agreement with these observations.

During actual fuel injection, a fine spray of liquid fuel is formed, evaporates, and enters the flowing air stream passing through the engine. However, a considerable quantity of fuel is not vaporized and falls as a liquid within the accessory compartment. Thus, one or more "puddles" of liquid fuel are formed during fuel injection. In almost every run, the results obtained show two or more concentration peaks indicating the presence of these "puddles." The first peak in the run is due to the direct spray injection of the fuel, while subsequent peaks indicate the presence of puddles. These puddles eventually run off through a drain provided in the engine or are evaporated completely by the onrushing air stream. Hence, although actual fuel injection was maintained for a time period not exceeding 35 seconds, a considerable amount of hydrocarbon vapors persisted, due to these puddles, for almost two minutes.

Thus it would not be expected that a single hydrocarbon peak would result, and indeed the data verifies this expectation.

As one would expect, the longer the time that the fuel is injected, the greater will be the concentration of hydrocarbon vapors. For the runs in which the monitored engine parameters were kept constant and the fuel injection time, only, was varied (e.g., Runs 1-3), the signal (peak signal as well as total quantity of vapor) increases with the increasing amount of fuel injected (see Figure 1). The maximum peak signal increases approximately linearly with increasing amount of fuel.

Reproducibility of the probes under identical engine operating and fuel injection conditions was satisfactory. Runs #13 and #14 were duplicate runs using the same probe. Although run #14 indicates three peaks while run #13 indicates only two (see Figure 2) maximum peak heights for run #13 are 7.0% and 4% by weight JP-4 and for run #14, 6.6% and 3.6% respectively. In addition, the total amount of JP-4 seen during each run (the area under the curve) is almost idential, i.e., 192% HC-sec for run #13 and 193% HC-sec for run #14. The fact that three peaks are seen in run #14 vs only two for #13 is not surprising in view of the difficulty in reproducing exactly the same engine conditions.

Runs #18 and #19 were obtained under identical engine operating conditions. However, run #18 was conducted with probe #2 located at 5 o'clock aft in Zone II, while run #19 was conducted with probe #4 in exactly the same location. These two runs demonstrate excellent reproducibility between probes under identical engine conditions (see Figure 3).

Runs #18 through #29 were conducted with both probes located in the accessory compartment aft at 5 o'clock and 7 o'clock respectively. The probes were separated by a distance of 18 inches. Using the small fuel injector nozzle (.421 gallons per minute), the 5 o'clock position consistently results in a higher JP-4 vapor concentration than the 7 o'clock position, whereas with the large injector nozzle (1.00 GPM) the reverse is true. It would appear that the mixing ratio as well as the gas flow path is different for each nozzle.

In runs #30 through #40 the probe (only one probe was used during these tests) was mounted at 5 o'clock in Zone II of the engine, however the probe was mounted normal to the assumed gas flow stream contrary to the

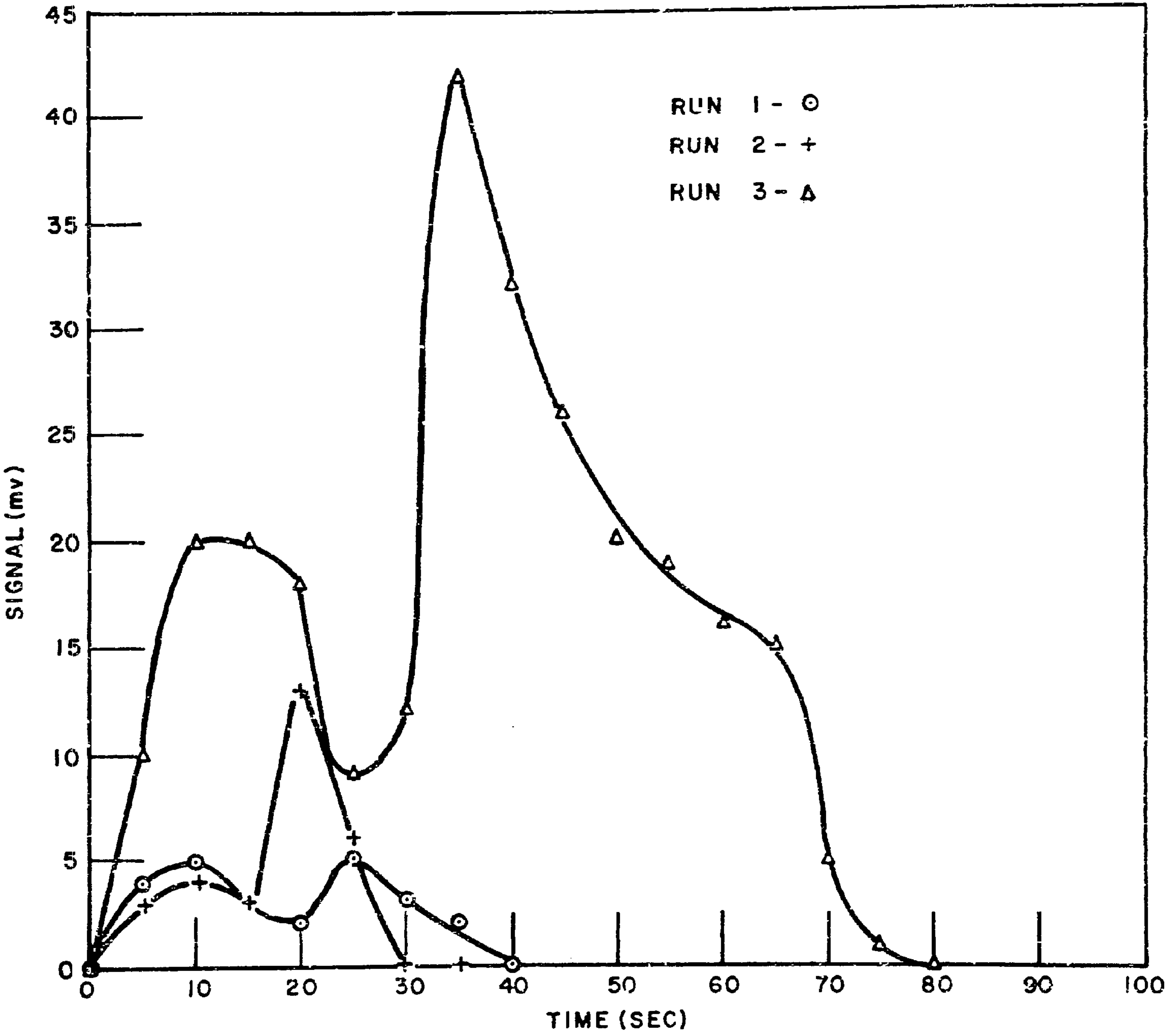

Figure 1 Signal vs Time for Run Nos. 1, 2 and 3

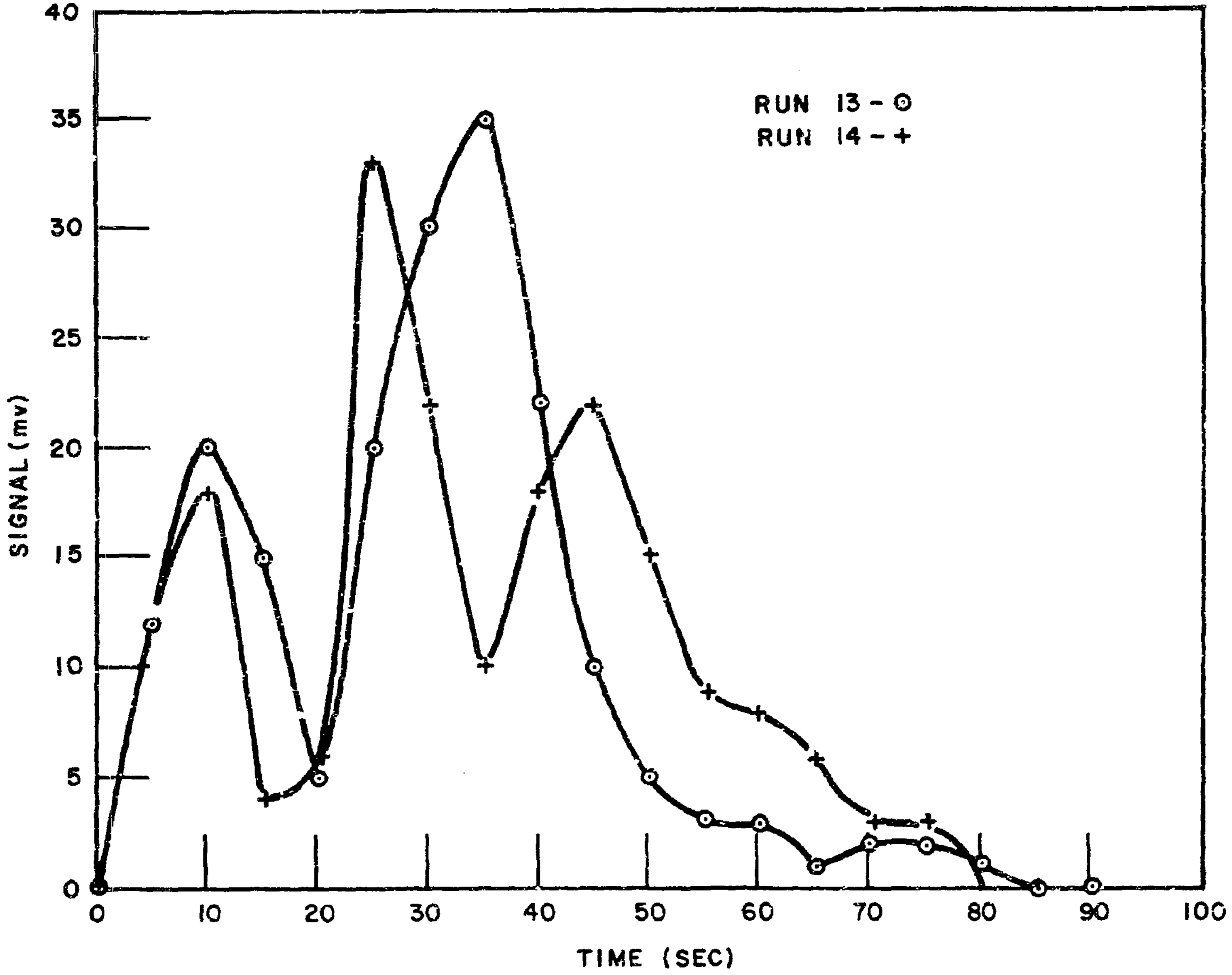

Figure 2. Signal vs Time for Run Nos. 13 and 14

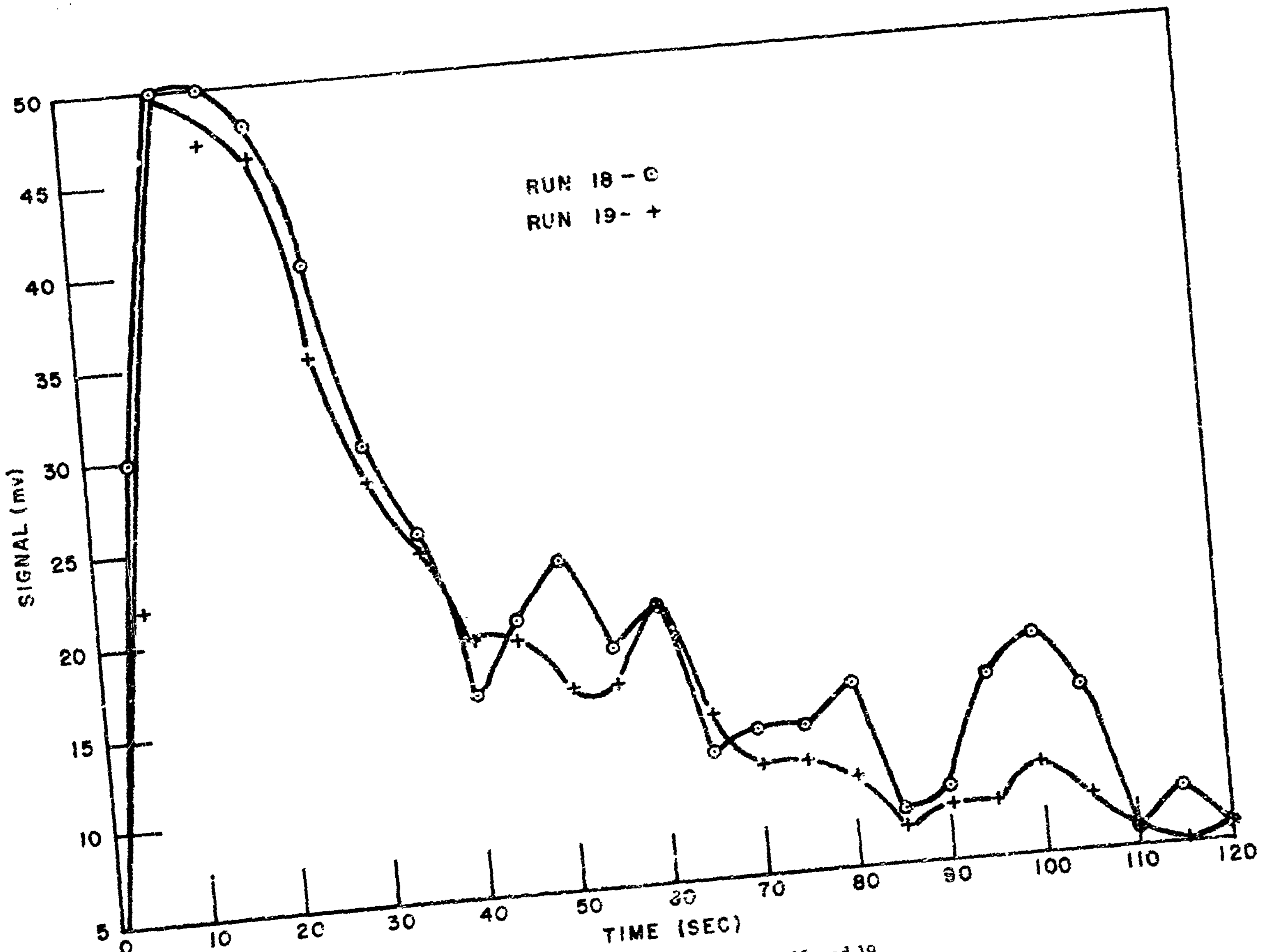

Figure 3. Signal vs Time for Run Nos. 18 and 19

horizontal position used in prior runs. This relatively small change in position resulted in approximately a factor of four less in signal (compare runs #30 through #32 with runs #27 through #29). This would indicate a steep concentration profile of the fuel in the gas stream. However, the fact that the probe sensitivity may be directional cannot be rule out at the present time. Laboratory tests have indicated that the signal is independent of the probe position. However, these laboratory tests were conducted at moderate flow rates (1-2ℓ/min), and further testing at the high flow rates attained in an engine is believed warranted to elucidate this effect.

It is important to note that during the performance of the tests that not a single fire or explosion resulted. Thus it can be concluded that at concentrations greater than the LEL and at environmental temperatures up to 100°F that the probe will not initiate an explosion or fire. Indeed, fire was not attained even though the probe itself became saturated with sufficient liquid fuel to actually wash off the catalyst coating from the thermistor surface. However, it is strongly suggested that the probe be further tested at environmental temperatures up to 600°F to insure that the probe will be explosion free for actual deployment in advanced aircraft with a Mach 3 capability.

Response time of the instrument appears to be limited only by the gas transport time. During these tests, a meter readout only was used. The time constant of the meter is approximately 2 seconds full scale; thus a full scale response of less than this value cannot be attained. A recorder output is provided with the instrument which by-passes the meter. Using a recorder as a readout which can have a time constant of one second or less, the meter time constant could have been eliminated. Unfortunately a suitable recorder was not available during the performance of these tests. The fact that the response time is limited by the gas transport time can be seen from runs #19 through #23. The time for the first peak signal decreases with increasing engine speed (flow rate through engine). For example, first peak signal during run #19 was attained in 10 seconds (engine power 48%) while first peak signal for run #22 was attained in 5 seconds (70% engine power). Considering that the signal-time data was attained manually without service of a recorder, an error in the 5 second increments of ±2 seconds is quite probable. Referring to run #22, it is seen that the "0" time signal, which should, of course, be zero is recorded as 8 mv. Since the meter is known to have a response time of 2 seconds, the sensor response time must be considerably smaller, i.e., one second or less.

SECTION III

SUMMARY AND RECOMMENDATIONS

Prototype instruments for the detection of hydrocarbon fuels were evaluated under simulated flight conditions. These tests were conducted at the wind tunnel facilities at NAFEC, Atlantic City, N. J., using a Pratt and Whitney JT-12 turbojet engine. A complete data analysis of the data is not possible without a thorough knowledge of the flow paths, mixing ratios, etc., of the gas stream within the engine. Nevertheless, the data indicate that the hydrocarbon fuel detectors operated extremely satisfactorily under actual aircraft engine operating conditions.

The sensitivities of the prototype instruments have been shown to be more than adequate for detecting 10% of the lower inflammability limit of JP-4 (0.8% by volume or ~2.8% by weight). An easily readable signal of 0.5 mv on the meter readout corresponds to .01% by weight of JP-4. This value is approximately 0.3% of the lower inflammability limit of JP-4. Still higher sensitivities are possible by simply increasing the supply voltage to the bridge circuit. A control is provided for this purpose. The minimum detectable quantities for the prototype instruments are estimated to be less than 2% of the LEL for JP-6. (The hydrocarbon fuel for which the instruments were originally intended.)

The response and recovery times of the sensors are independent of concentration, and by bypassing the readout meter and using the recorder output a response time of less than 1 second can be achieved.

Although the prototype instruments operated satisfactorily during the wind tunnel tests, there are several areas which should be investigated prior to the development of final instrumentation. These are:

1. Saturated concentration of hydrocarbon at 100°F in the presence of a large excess of oxygen did not explode or ignite when in contact with the hot catalytic surfaces of the thermistor probes. Nevertheless, tests using hydrocarbon vapors at concentrations greater than the LEL and at ambient temperatures up to 650°F should be conducted to confirm that the probes will not initiate an explosion aboard advanced aircraft with a Mach 3 capability.

2. A difference in signal of approximately a factor of four was achieved when at the same engine location the probe was mounted in a vertical position as compared to a horizontal position. It is not known at the present time whether this signal was actually due to a concentration gradient or due to the probe sensitivity being directional. A lack of directionability was demonstrated during laboratory tests, but such tests were performed at gas flow velocities much lower than those encountered in the engine. Therefore, it is recommended that the probe should be tested at various angles to the flowstream and at flow rates comparable to those within an aircraft engine to determine whether this effect does exist and to characterize the effect if, indeed, it is present.

3. In only one instance did a break in the thermistor lead wire occur. This break occurred due to mishandling while inserting the probe in the engine. No malfunction of the probes or the control boxes occurred during actual engine operation. Nevertheless, it is recommended that the probe be ruggedized by a redesign of the thermistor and cable connectors, to prevent such an occurrence in the future.

4. In one instance, the catalyst was found to have been physically removed from the thermistor surface due to "washing" by liquid hydrocarbon fuel. This effect can be prevented by using suitable baffles or by using a porous metal plug in place of the perforated plate of the present probes. It is believed that this change will eliminate any "washing" effect; however, such an arrangement may affect the response time as well as probe directionality. The effect of such a change on these parameters should be investigated.

PART II

DETECTION OF OXYGEN VIA OSMIUM KRYPTONATE

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PART II

SECTION I

INTRODUCTION

During the initial phase of this contract, a brief investigation was conducted to determine if the Kryptonate technique could be developed into an instrument for the detection of hydrocarbon and oxygen vapors aboard advanced aircraft. From prior work,[2] it was known that JP-6 fuel could be detected with platinum dioxide Kryptonate at concentrations as low as 0.01 percent by volume at ambient temperatures from 0°F to 750°F. However, preliminary results obtained during the contract indicated that the detection of oxygen via the Kryptonate technique would require a considerable effort. This effort would be involved not with the general technique itself, but rather would require the development of a specific sensor for oxygen which would be capable of continuous operation. A number of candidate materials were investigated as to their ability to detect oxygen. Such materials as copper, zinc, carbon and boron Kryptonates were found to be unsatisfactory due to either the formation of protective oxide layers (e.g., copper oxide on copper) or because of the extremely high sensor operating temperatures required for adequate sensitivity (e.g., boron required an operating temperature of 1800°F).

Because of the lack of a suitable Kryptonate sensor for oxygen, the catalytic combustion technique was selected to be developed into prototype instruments for the detection of hydrocarbons and oxygen. However, the thermistor oxygen sensor had become more complex than originally anticipated, and utilization of a Kryptonate sensor appeared to be ultimately more attractive. Hence, supplementary funds were allocated for further evaluation of this technique.

The most likely candidate material for the detection of oxygen appeared to be osmium Kryptonate. Osmium is a fairly hard metal with a melting point of 4900°F. Osmium will react with oxygen directly at 392°F to form the oxide, osmium tetroxide, OsO_4. This oxide is volatile at 214°F and hence, at the formation temperature, osmium tetroxide would be continuously vaporized, leaving a clean metal osmium surface for further unimpeded reaction with oxygen.[3]

Instrumentation based on this technique would consist of a sensor cell, counting chamber, pump and associated electronics. The sensor cell containing the Kryptonate can be located directly within the compartment of interest. The ambient gas is drawn through the sensor cell and then through the counting chamber by means of the pump. Reaction of the gas of interest (hydrocarbon vapors or oxygen) with the Kryptonate occurs in the sensor cell releasing Krypton-85. The effluent activity released is detected by means of a radiation detector mounted in a chamber (the counting chamber). The signal from the radiation detector can be read directly on a meter in gas concentration units or can be used to actuate an alarm at predetermined alarm concentrations.

This part of the report is concerned with the preparation and evaluation of osmium Kryptonate as a potential oxygen sensor for use aboard advanced aircraft.

SECTION II

TECHNICAL DISCUSSION

A. Preparation of Osmium Kryptonate

There are two general techniques by which Kryptonates can be prepared, viz., ion-bombardment and high-pressure, high-temperature diffusion. Both these techniques were employed in an attempt to prepare homogeneous osmium Kryptonate.

1. Ion-Bombardment

Kryptonates can be prepared by ion bombardment with krypton ions under the influence of a potential drop. From prior work[4] it was known that if the solid is heated to high temperatures during the actual bombardment process that much higher specific activity and greater penetration can be achieved and therefore a relatively more homogeneous Kryptonate results. This high-temperature bombardment process had been conducted with wires. Considerable modification of the ion-bombardment system was necessary in order to heat the osmium powder during bombardment.

The standard ion-bombardment system was modified to accommodate a heater, osmium powder container and water jacket. The final system developed is shown in Figure 4. This system enabled the osmium powder to be heated to temperatures approaching 600°C during actual bombardment.

Over 25 runs were conducted with this system using various pressures, bombardment voltages, currents, time and osmium powder temperatures. In general, the specific activity of the resulting osmium Kryptonate increases with increasing powder temperature, as well as with increasing bombardment current. The highest specific activity attained by ion-bombardment was 0.16 microcuries/milligram. This activity level was attained at a bombardment voltage of 3 kilowatts, bombardment current of 0.4 milliamps, a pressure of 1.5 microns and a source temperature of 600°C.

Approximately 100 milligrams of osmium Kryptonate could be prepared in a single ion-bombardment run. This amount of material was sufficient for evaluation.

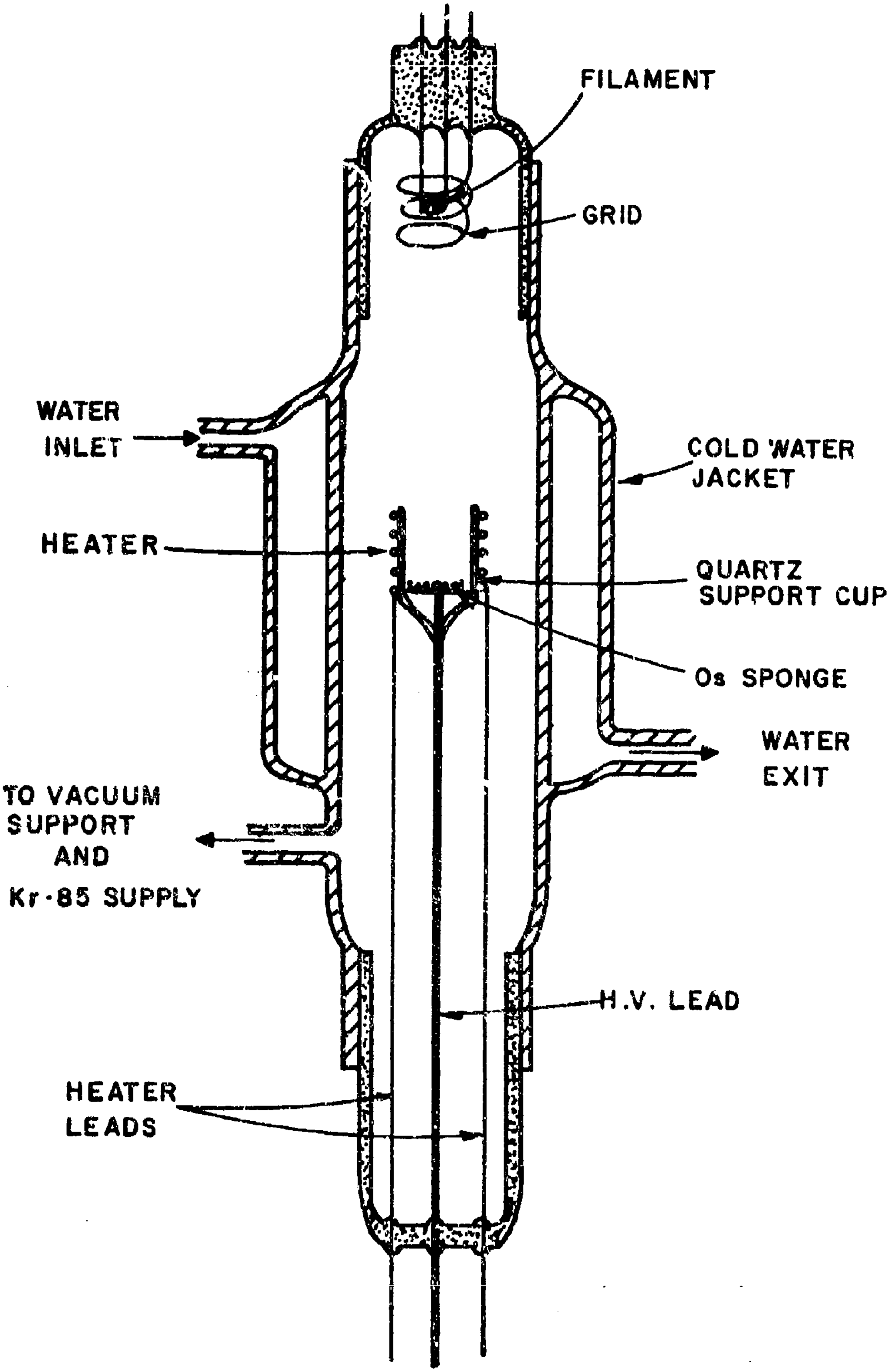

Figure 4. Ion Bombardment Apparatus

The ion-bombarded prepared Kryptonate was evaluated using a typical gas flow test system capable of providing concentrations from 0-40% O_2. The sensor material (Os-Kr^{85}) was placed in a quartz tube which could be heated to temperatures up to 1000°F. Kryptonates prepared at the higher specific activity levels (0.1-.16μc/mg) showed excellent initial response and sensitivity (5 sec and 1200 counts per minute per % O_2); however, the signal rapidly decayed with time indicating that homogeneity had not been achieved. Despite numerous attempts at attaining deeper penetration levels of Kr^{85} within the osmium particles, osmium Kryptonate prepared by ion-bombardment consistently proved to be unsatisfactory. Even though specific activities ultimately attained were of the same order of magnitude as those Kryptonates prepared by the diffusion technique (see below), the degree of homogeneity achieved (as measured by the life of the source) was considerably poorer. As a result, detailed evaluation as to temperature dependency, concentration dependency, etc., was not conducted with osmium Kryptonate prepared by ion-bombardment.

2. Diffusion

Kryptonates can be prepared by a high-pressure, high-temperature technique. The sample is placed in an autoclave which is then pressurized with 5% Kr^{85} in krypton gas. The autoclave is then heated to temperatures up to 500°C. Under these conditions, and given sufficient time, krypton-85 gas will diffuse into the sample forming a Kryptonate.

In general, the amount of krypton-85 retained by the sample will be an exponential function of temperature, linear with pressure and will depend on the square root of time.

For a high-melting material such as osmium, the temperature is limited to a maximum of 500°C which is the structural limit of the available autoclaves. The pressure is limited by the amount of krypton-85 available (1 liter-atm) and the packing volume. Thus the only parameter that can be increased without limit is the time. Unfortunately this is a half-order dependency; thus in order to double the specific activity, one must quadruple the time.

A number of diffusion preparations were conducted. The early preparations were conducted with krypton-85 gas supply which had been in use for several years. A number of long runs at maximum preparation conditions (500°C, 3000 psi, 3-4 weeks) resulted in specific activities of

0.001 μc/mg to 0.003 μc/mg. These levels were not sufficient to detect oxygen. It was known that the total activity of the krypton-85 gas supply had been reduced over the past years. This gas had been and indeed is still sufficient for the preparation of many various Kryptonates. However, if this gas supply had been contaminated, particularly with oxygen, then this contamination coupled with the decreased specific activity of the gas would account for the inadequate osmium Kryptonates which had been prepared.

A new krypton-85 gas supply was obtained and was utilized for all subsequent preparation of osmium Kryptonates. The specific activities of the Kryptonates attained and the preparation conditions are shown in the table below.

Table VII

Osmium Kryptonate Preparation by Diffusion

Run	Temperature °C	Pressure (psi)	Time (hrs)	Specific Activity (μc/mg)
1	400°C	2000	122	0.019
2	400°C	2000	355	0.035
3	500°C	2200	353	0.140
4	500°C	2200	670	0.201

From the above, it can be seen that under the same conditions of temperature and pressure, the specific activity varies as the square root of the duration of the run (the time).

Although the resulting specific activity was of the same order of magnitude as that obtained via ion-bombardment (0.16 μc/mg) the degree of homogeneity (as will be discussed below) was considerably improved.

B. Results

The results discussed below were obtained using the test system shown in Figure 5. Glass tubing and brass fittings were used throughout the system. The essential element of this system is the sensor cell. This cell is a quartz tube containing the osmium Kryptonate. Glass wool packing was used to prevent loss of the sensor powder. A wire wound

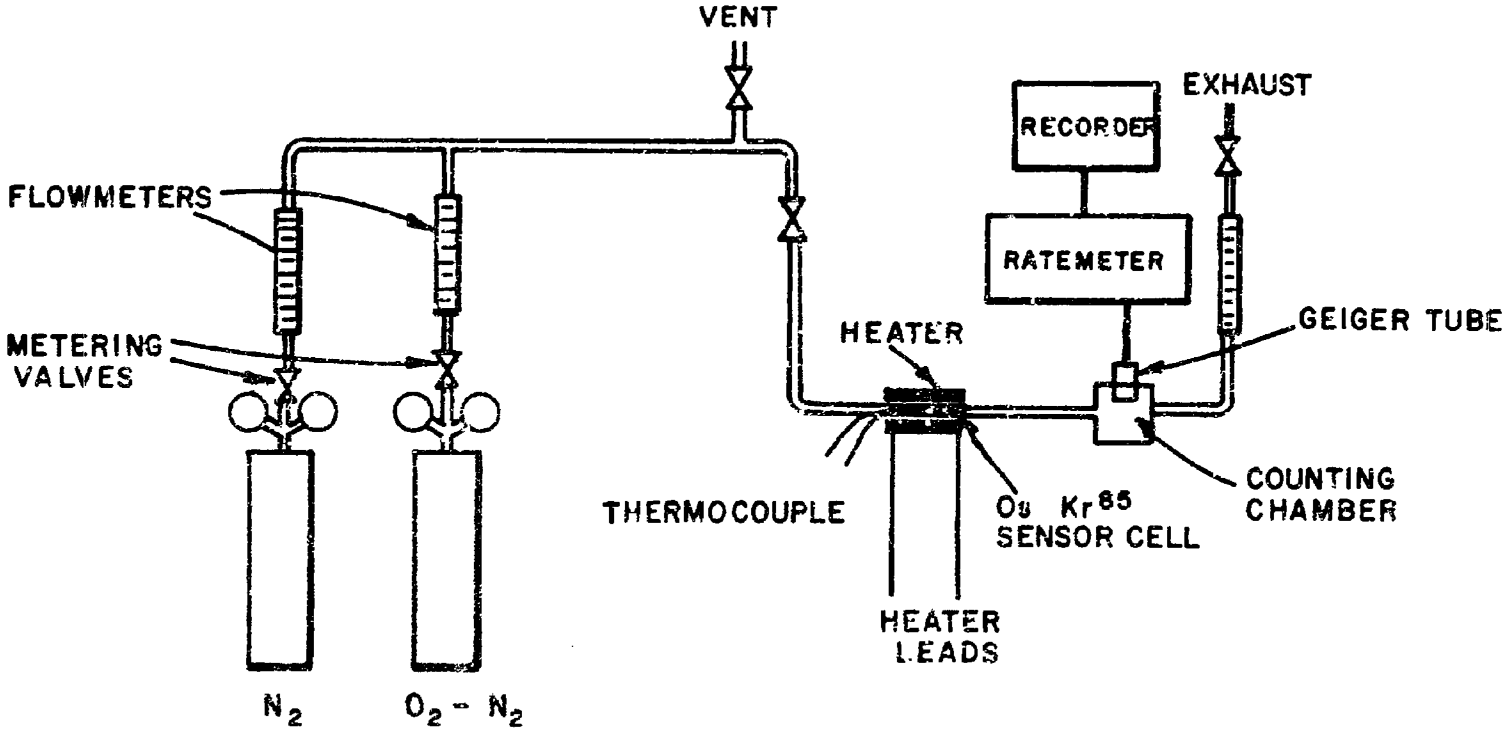

Figure 5. Oxygen Detection System

heater was used to heat the sensor to the desired operating temperature. The temperature of the sensor was constantly monitored by means of a thermocouple. Flow rates and mixing ratios were determined using calibrated flowmeters and controlled by fine metering valves. An Amperex Geiger counter (Type 18505) mounted in a 60 cc chamber was used to monitor the effluent activity. The readout mechanisms consisted of a Nuclear of Chicago, Model 1620, ratemeter and a Bausch and Lomb V.O.M. - 5 recorder.

1. Sensitivity

A relatively simple Kryptonate detection system was used to evaluate the osmium Kryptonate. The effluent activity released from the quartz sensor cell containing the Kryptonate was detected using an end window Geiger tube mounted in a 60 cc volume chamber. Even with this relatively low efficiency counting chamber (approximately 4% efficient), sensitivities adequate to cover the desired range of oxygen concentrations (0 to 40%) were attained.

Figure 6 presents the results attained with a Kryptonate of specific activity 0.140 µc/mg operating at a temperature of 750°F. The sensitivity of the Kryptonate at this temperature and with the counting apparatus employed is 1000 cpm/1% O_2. Since the response is linear, at a concentration of 40% O_2, 40,000 cpm would be attained. If it were necessary, this sensitivity could be easily increased by increasing the counter efficiency (20% efficiency can be obtained with pancake G.M. tubes) or by increasing the specific activity of the sensor, (with the osmium Kryptonate of 0.20[illegible] µc/mg a sensitivity of 1500 cpm/1% O_2 was attained). Thus the sensitivity of the osmium Kryptonate is more than adequate to cover the oxygen concentration range of interest. With the relatively simple laboratory apparatus used in these experiments, this sensor can detect 0.1% oxygen. This lower limit can be increased without difficulty by at least a factor of ten.

Using the laboratory test system depicted in Figure 5, response times attained were of the order of 5 seconds. The response time appeared to be limited only by the gas flow rate and counting chamber volume. Thus, with small distances between the sensor cell and the counting chamber, a small volume counting chamber (20cc), and with faster flow rates (3 ℓ/min) response times of the order of 1 second should be realized.

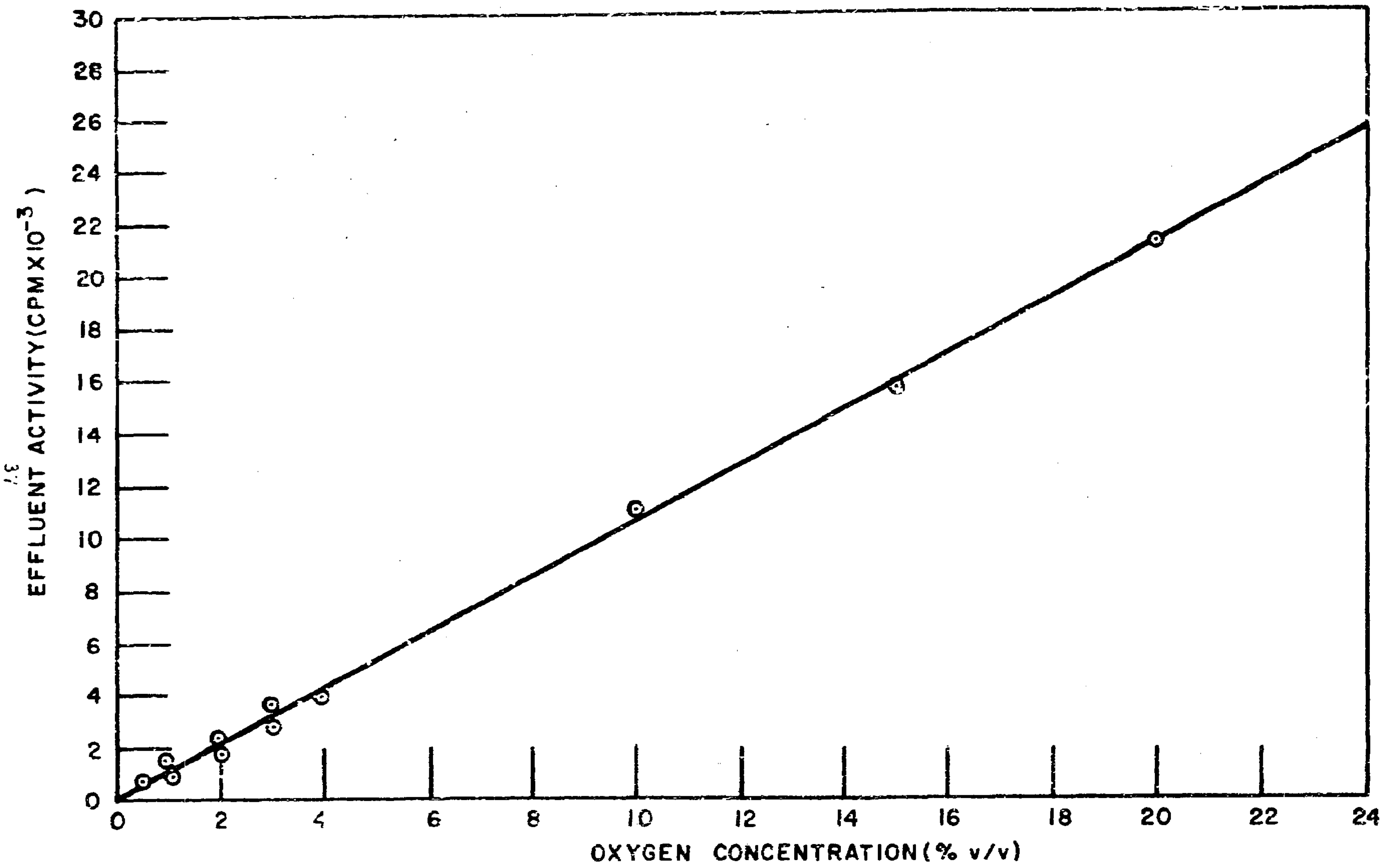

Figure 6. Response of Os$\cdot$Kr^{85} to O_2 at 750°F

2. Temperature Dependency

The response of the osmium Kryptonate shows an Arrhenius temperature dependency. The variation of effluent activity released with temperature at a constant oxygen concentration of 1% is shown in Figure 7. The response of the osmium Kryptonate can then be completely described by the equation

$$\mathrm{KCPM} = 7.3 \times 10^{6}\ O_2\ e^{\frac{-10.6 \times 10^{3}}{T}} \qquad (1)$$

where KCPM is the effluent activity released in thousands of CPM

O_2 is the oxygen concentration in %

T is the temperature in degrees Kelvin.

The activation energy for this system is thus 21 Kcal/mole ($10.6 \times 10^3 \times R$, where R is the molar gas constant).

From Eq. (1) the temperature coefficient of the response signal can be approximated by

$$\frac{\Delta \mathrm{KCPM}}{\mathrm{KCPM}} = -10.6 \times 10^{3}\ \frac{\Delta T}{T^{2}} \qquad (2)$$

or, at an assumed operating temperature of 672°K (750°F),

$$\frac{\Delta \mathrm{KCPM}}{\mathrm{KCPM}} = .0235\ \Delta T. \qquad (3)$$

Thus the count rate will increase by as much as 10% with a temperature increase of only 4°K. It is apparent that temperature control of the sensor is extremely important.

3. Sensor Lifetime

The sensor lifetime is dependent on a number of factors such as temperature, reaction efficiency, flow rate, etc. One of the most important of these factors is the degree of homogeneity of the Kryptonate. If the depth of penetration achieved during the Kryptonate preparation is very shallow, then the effluent activity released on reaction with a constant gas concentration will not be constant, but rather will decrease with time.

A measure of the degree of homogeneity is the time for which the effluent activity released is constant during reaction with a constant gas concentration. This parameter can be expressed in terms of concentration-time units (ct). Thus, for example, a particular sensor life can be expressed as 10% O_2-min. This would indicate that the sensor would operate continuously for 10 min at a 1% oxygen concentration, for 5 min at a 2% oxygen concentration, etc. In actuality, the signal continues for a longer period of time than indicated by the ct value; however, for time periods greater than the value determined by the ct value, the sensitivity decreases as a function of time. The ct values presented in this report were obtained only when the effluent activity released at a constant oxygen concentration was constant with time.

In the table below are presented the concentration-time values attained for various osmium Kryptonates. These results were attained using the apparatus previously described with a total flow rate through the sensor cell of 0.5 liters/minute. The sensor cell was loaded with 1.0 grams of osmium Kryptonate.

Table VIII

Concentration-Time Values

Specific Activity (μc/mg)	Operating Temperature °F	Concentration-Time (% O_2-min)	Kryptonate Preparation Run
.035	750	5.0	2
.140	750	26.0	3
.201	750	31.1	4
.201	600	140.	4

The depth of penetration and hence the degree of homogeneity is expected to be dependent on the square root of the time of Kryptonate preparation. That this is true can be seen from the results attained with Kryptonate sensors 3 and 4. These sensors were prepared under the same conditions of temperature and pressure; however, the preparation time for run 4 was 1.9 times as long as run 3 (see Table VII). Hence it would be expected that the degree of homogeneity (the ct value at the same operating temperature) for Kryptonate 4 would be 1.38 higher than for run 3. The actual value is 1.30, which is in excellent agreement.

In addition, the degree of homogeneity should be an exponential function of the temperature of preparation. Kryptonate run 2 was conducted at 400°C while Kryptonate run 3 was conducted at 500°C. Both runs were conducted at approximately the same pressure and for the same length of time. The ct values should then be in the same ratio as their specific activities. The actual ratios obtained differ by only 20% (4.0 for specific activity vs 4.8 for ct values). This difference can be attributed in part to decreased counting efficiency for Kr^{85} betas lying at greater depths into the surface of the Os particle as a result of attenuation of the betas by the covering Os layer.

At a sensor operating temperature of 750°F, the life of the cell was approximately 30% O_2-minute. Thus, the cell would last for 30 minutes if the average concentration was 1% O_2 during this time period, or the cell would last for 3 minutes if the average O_2 concentration was 10%. By reducing the operating temperature to 600°F the life of the cell is increased to 140% O_2-min. Since the reaction rate decreases by a factor of ten over this temperature interval (see Figure 7), it would be expected that the lifetime at 600°F would approach 300% O_2-min. This discrepancy is believed to be due to experimental errors, particularly in the actual temperature values.

It is apparent that the lifetime of the sensor can be increased by increasing its homogeneity. Considering the long preparation times required, this is best accomplished by increasing the Kryptonate preparation temperature. Higher preparation temperatures can be achieved by utilizing special autoclaves such as cold-wall autoclaves with internal heaters. Such an approach would require a considerable modification of the present Kryptonate apparatus, but such apparatus is well within the present state-of-the-art. An increase in preparation temperature of only 100°C above the present maximum of 500°C, would result in a theoretical increase in the depth of penetration by a factor of 5.

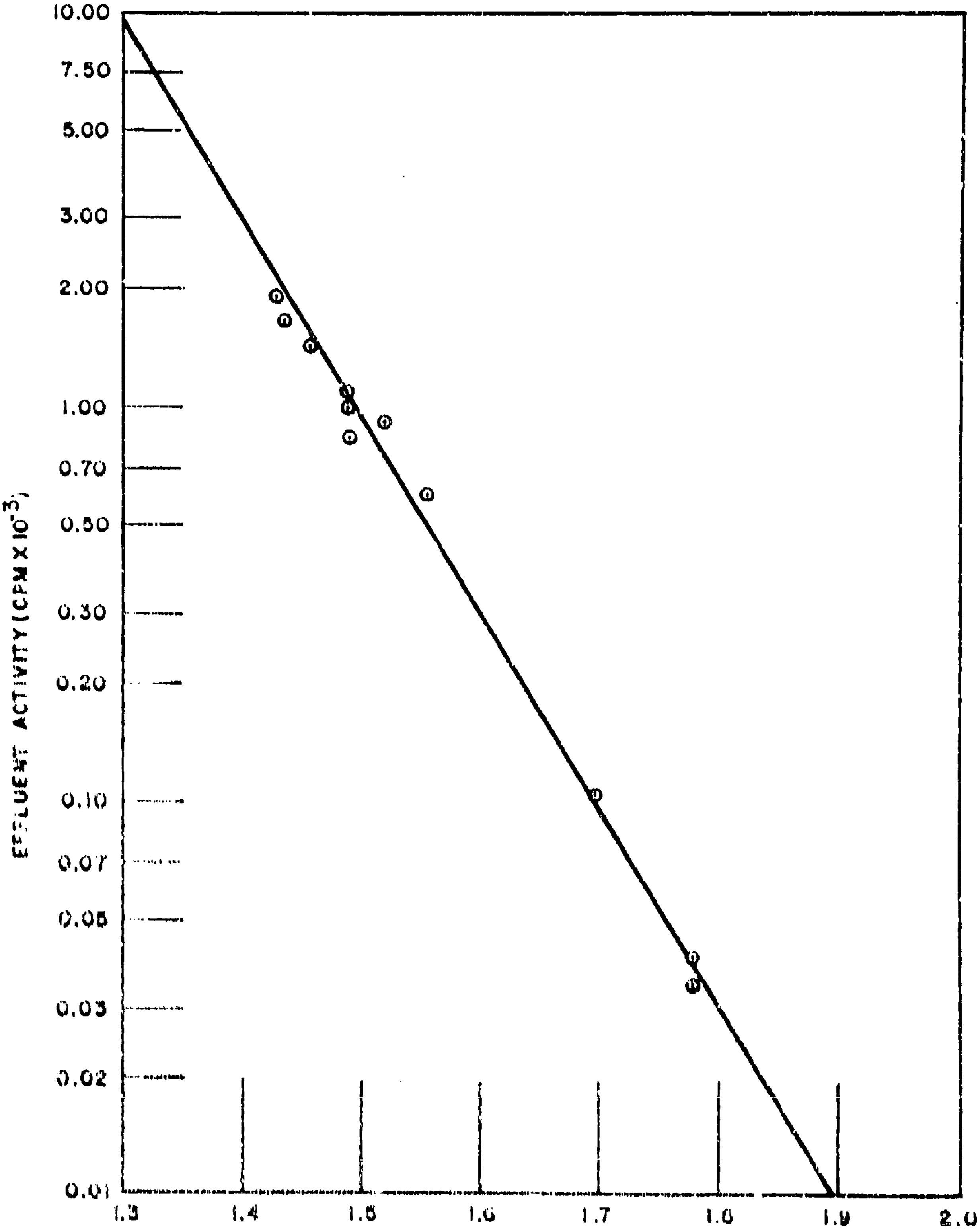

Figure 7. Arrhenius Temperature Dependency

Assuming that the present degree of homogeneity achieved is quite low, (less than 20%), then a 100°C higher preparation temperature would produce a considerably more homogeneous source. It would be expected that one gram of such a source operated at a temperature of 600°F would have a lifetime of the order of 1000% O_2-minutes.

This lifetime could be further increased by increasing the amount of osmium Kryptonate in the sensor cell. Economic (high cost of osmium) as well as technical factors (pressure drops) would limit the quantity that can be used. However, it would appear that an increase in sensor material to at least 5 grams would be practical. This should result in approximately an additional factor of 5 increase in the lifetime. Thus ultimate lifetimes of the order of 5000% O_2-min should be possible.

4. Detection of Oxygen in the Presence of JP-6

By passing the oxygen containing test stream through a column of liquid JP-6 fuel, a saturated vapor concentration of JP-6 (0.6% by weight) could be attained simultaneously with various oxygen concentrations. The effect of hydrocarbon vapors on the osmium-oxygen reaction could then be ascertained. Repeated tests conducted in this manner indicated no change in response of the osmium Kryptonate to oxygen, i.e., the simultaneous presence of JP-6 fuel at 0.6% by weight and oxygen did not detectably affect the response of the osmium Kryptonate to oxygen in the concentration range of interest.

SECTION III

SUMMARY AND RECOMMENDATIONS

An investigation to determine the applicability of the radiochemical exchange technique using osmium Kryptonate for detecting oxygen in the ullage space of fuel tanks aboard aerospace flight vehicles was conducted.

Osmium Kryptonate prepared by the diffusion technique showed excellent response and sensitivity to oxygen. The effluent activity released from the Kryptonate sensor was found to be directly proportional to the oxygen concentration, and at a constant oxygen concentration, was found to be an exponential function of temperature. Sensitivities adequate to cover the oxygen concentration range of interest (0.5%-40.0% O_2 v/v) were attained at a sensor operating temperature of 600°F. The simultaneous presence of JP-6 fuel at 0.6% by weight and oxygen did not detectably affect the response of the osmium Kryptonate to oxygen in the concentration range of interest.

The lifetime of the sensor is dependent mainly on the degree of homogeneity of the source. Lifetimes attained during this investigation were of the order of 140% O_2- min to 300% O_2-min. This lifetime is believed inadequate for the intended application. However, at least a factor of 25 increase in lifetime is projected by increasing the homogeneity of the source and by increasing the amount of osmium used in the sensor cell. The homogeneity of the source is best increased by employing higher temperatures in the Kryptonate preparation process. This would require considerable modification of the present preparation apparatus.

Based on the above results, it is recommended that:

1. Osmium Kryptonate be prepared at temperatures of the order of 700°C and for preparation times of the order of 700 hours. This would greatly increase the degree of homogeneity and hence increase the operating life. Such an effort would require the use of special autoclaves that would be capable of withstanding the higher temperatures at the normal preparation pressures (~2000 psi).

2. The effect on the overall detection system as a function of increasing amount of osmium Kryptonate be ascertained. Larger amounts of osmium Kryptonate in the sensor cell will also increase the lifetime. However, this will result in increased pressure drops and subsequent difficulties in the gas flow system. The importance of this effect and the actual increase in lifetime with increasing amount of osmium Kryptonate should be ascertained.

3. If the pressure within the ullage space of the fuel is expected to be other than 1 atm, then the total pressure dependence of the Kryptonate sensor should be determined. It would be expected that the sensitivity of the sensor would vary directly as the oxygen partial pressure only and be independent of the total pressure; however, this should be verified.

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13. ABSTRACT

This report covers two separate and distinct efforts associated with the evaluation of hazardous vapors aboard advanced aircraft. Part I is concerned with an experimental evaluation of prototype instruments based on a catalytic oxidation technique for the detection of hydrocarbon vapors aboard advanced aircraft. Two hydrocarbon vapor probes were placed in the engine compartments of a JT-12 engine housed in a wind tunnel. The response of the probes to controlled leakages of JP-4 fuel under varying engine operating conditions was ascertained. The prototype instruments operated completely satisfactorily. Reproducible results under identical engine operating conditions were attained. Response times were of the order of two seconds and the lower limit of detection was approximately 0.3% of the lower inflammability limit for JP-4. Part II is concerned with the evaluation of osmium Kryptonate®* for the detection of oxygen in the ullage space of fuel tanks aboard advanced aircraft. Sensitivities adequate to cover the oxygen concentration range of interest (0.5% - 40.0% O_2v/v) were attained at a sensor operating temperature of 600°F. The response of the sensor to oxygen was independent of JP-6 vapor concentration. Lifetimes attained during this investigation were of the order of 140% O_2 - min. to 300% O_2-min. Methods for increasing this lifetime are indicated and are within the present state-of-the-art.

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