

AD-A150 787 LIFETIME AND RELIABILITY OF RUBIDIUM DISCHARGE LAMPS
FOR USE IN ATOMIC FR. (U) AEROSPACE CORP EL SEGUNDO CA
CHEMISTRY AND PHYSICS LAB C H VOLK ET AL. 14 DEC 84
UNCLASSIFIED TR-0084A(5404-30)-1 5D-TR-84-55 F/G 13/1

LIFETIME AND RELIABILITY OF RUBIDIUM DISCHARGE LAMPS
FOR USE IN ATOMIC FR. (U) AEROSPACE CORP EL SEGUNDO CA
CHEMISTRY AND PHYSICS LAB C H VOLK ET AL. 14 DEC 84
TR-0084A(5404-30)-1 SD-TR-84-55 F/G 13/1

1/1

UNCLASSIFIED

TR-0084A(5404-30)-1 SD-TR-84-55

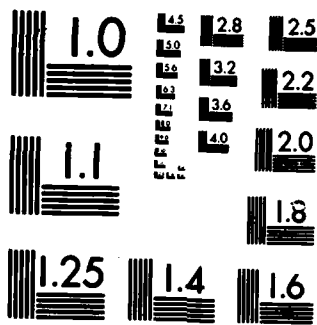
F/G 13/1

NL

END

FILMED

OFIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

REPORT SD-TR-84-55

(2)

Lifetime and Reliability of Rubidium Discharge Lamps for Use in Atomic Frequency Standards

C. H. VOLK and R. P. FRUEHOLZ
Chemistry and Physics Laboratory
Laboratory Operations
The Aerospace Corporation
El Segundo, CA 90245

T. C. ENGLISH
Efratom, A Division of Ball Corporation
Irvine, CA 92715

and

T. J. LYNCH and W. J. RILEY
Electronic Components Division
EG&G Inc.
Salem, MA 09170

14 December 1984

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

DTIC
ELECTE
MAR 4 1985
S B

Prepared for
SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, CA 90009-2960

85 02 19 057

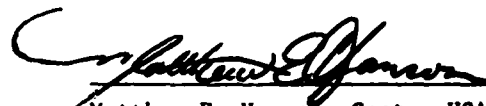
DTIC FILE COPY
AD-A150 787

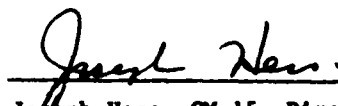
This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-83-C-0084 with the Space Division, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009-2960. It was reviewed and approved for The Aerospace Corporation by S. Feuerstein, Director, Chemistry and Physics Laboratory, and J. B. Bryson, Associate Principal Director for Communications. Captain D. Galanos, SD/YEZ, was the Air Force project officer.

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

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

for Capt. D. Galanos, SD/YEZ


Matthew E. Hanson, Capt., USAF
Chief, Satellite Development Branch


Joseph Hess, GM-15, Director,
West Coast Office, AF Space
Technology Center

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SD-TR-84-55	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) LIFETIME AND RELIABILITY OF RUBIDIUM DISCHARGE LAMPS FOR USE IN ATOMIC FREQUENCY STANDARDS		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER TR-0084A(5404-30)-1
7. AUTHOR(s) C. H. Volk, R. P. Frueholz, T. C. English, T. J. Lynch, and W. J. Riley		8. CONTRACT OR GRANT NUMBER(s) FO4701-83-C-0084
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, CA 90245		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Space Division Los Angeles Air Force Station Los Angeles, CA 90009-2960		12. REPORT DATE 14 December 1984
		13. NUMBER OF PAGES 53
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Alkali discharge lamps Atomic frequency standard Rubidium atomic clocks Rubidium lamps		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The results of various studies concerning the lifetime and reliability of the rubidium discharge lamp used in the rubidium atomic frequency standards are reported. The primary life-limiting process in these lamps involves diffusion of the rubidium atoms into the glass envelope of the lamp, making them unavailable to the discharge. The rate at which rubidium atoms diffuse into the glass is dependent on lamp conditions, including lamp size, type of		

DD FORM 1473
(FACSIMILE)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

glass, lamp temperature, and rf drive power. The calorimetric technique to measure the elemental rubidium content in a lamp and its use for quality control in the lamp manufacturing process are discussed.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

PREFACE

We acknowledge the various contributions of many people, including R. A. Angel, P. A. Bertrand, R. A. Brose, R. A. Cook, H. U. Eckert, S. A. Jackson, P. F. Jones, C. M. Kahla, C. M. Klimcak, W. A. McDermid, L. R. Martin, G. A. To, L. U. Tolentino, and M. Wun-Fogle, all of The Aerospace Corporation; W. Weidemann, H. Fruehauf, and J. Hayner of Efratom, a Division of Ball Corporation; E. Jechart, formerly of Efratom; and S. Goldberg and J. McDonald of EG&G, Electronic Components Division, and F. Chang formerly of EG&G.

This work was supported in part by the United States Air Force Space Division Contract No. F04701-83-C-0084, in part by internal funds at Efratom, a Division of Ball Corporation, and in part by EG&G, Electronic Components Division, under contract to Rockwell International Space Operations/Integration and Satellite Systems Division, Purchase Order No. MOJ3BGR-484107E.

DTIC
ELECTE
S MAR 4 1985 D
B

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



CONTENTS

PREFACE.....	1
I. INTRODUCTION.....	9
II. LAMP FAILURE MECHANISM IDENTIFICATION.....	11
A. Quenching of Excited Rb Atoms.....	11
B. Rb Reaction with Impurities.....	13
C. Interaction of Rb with Glass.....	13
1. Secondary Ion Mass Spectrometry (SIMS) Studies.....	14
2. Electron Spectroscopy for Chemical Analysis (ESCA) Experiments.....	16
III. CALORIMETRIC DETERMINATION OF Rb CONSUMPTION.....	21
IV. Rb LAMP LIFE INVESTIGATIONS.....	27
A. Corning 1720 Glass.....	27
1. Efratom Operating Conditions.....	27
2. EG&G Operating Conditions.....	33
B. Schott 8436 Glass.....	35
C. Schott 8437 Glass.....	35
1. Alkali Interdiffusion.....	39
2. Rubidium Diffusion.....	41
D. Summary of Empirically Derived Consumption Laws.....	45
V. ACCELERATED LAMP LIFE PROCEDURE/QUALITY CONTROL TESTING.....	47
VI. SUMMARY.....	57
REFERENCES.....	59

FIGURES

1.	Typical Rb discharge lamp.....	12
2.	Rb penetration into a Pyrex glass surface from SIMS analysis.....	15
3.	Experimental Rb penetration from SIMS analysis data and fit curve for Pyrex glass samples with discharge present and without discharge.....	17
4.	Rb-glass interaction.....	19
5.	Calorimetric measurement of the Rb content of a Rb lamp.....	24
6.	Photograph of EG&G lamp showing Rb metal driven to front face in preparation for calorimetric measurement.....	25
7.	Typical Rb consumption data for Efratom lamp operated under the Efratom normal conditions.....	29
8.	Results of the lamp life test conducted by Efratom for Corning 1720 glass lamps.....	32
9.	Composite plot of Rb consumption data for EG&G lamps measured at EG&G.....	34
10.	Composite plot of Rb consumption in Schott 8436 lamps of the Efratom design operated under Efratom normal conditions.....	36
11.	Rb life/consumption data for Schott 8437 glass lamps.....	40
12.	Schott 8437 glass lamp data with a fit, solid line, to the two-glass model of Rb consumption.....	42
13.	Schott 8437 glass lamp data fit to diffusion model.....	44
14.	Solution of Eq. (13) is shown as a function of the dimensionless parameter kt	50
15.	Extrapolated Rb lamp lifetime versus lamp temperature for lamps of the Efratom design constructed out of Corning 1720 glass.....	54

TABLES

I.	Comparison of Lamp Operating Conditions.....	28
II.	Lamp Measurement Results.....	38

I. INTRODUCTION

The discharge lamp is a critical component of the rubidium (Rb) gas cell atomic frequency standard (clock) and other optically pumped devices. The conventional lamp used in devices such as the gas cell atomic clock is of the type described by Bell, Bloom and Lynch¹ and Brewer² consisting of a glass envelope containing a charge of the appropriate metal, e.g., Rb, and a buffer gas under a pressure of a few Torr. The lamp is usually ignited by an rf coil that surrounds the glass envelope. The spectral emission properties of the lamp have long been recognized as extremely important in the operation of the optically pumped devices, and have been thoroughly studied.³⁻⁷ On the other hand, with one notable exception,⁵ almost no consideration appears to have been given to the life-limiting factors and hence the reliability of this type of lamp. This situation changed drastically in early 1979, however, because of lamp failures in some of the Rb clocks aboard the satellites⁸ of the NAVSTAR Global Positioning System (GPS). As a result of these lamp failures, an effort was begun to develop a long-lived sapphire Rb lamp.⁹ At about the same time, an extensive investigation¹⁰ of the failure mechanisms of glass lamps was initiated. This latter investigation identified the primary failure mechanism of the low-power, electrodeless Rb discharge lamp to be the diffusion of Rb atoms into the glass envelope of the lamp. The rate at which the atoms diffuse into the glass then controls the life of the lamp. We report studies that have been concerned with Rb consumption in discharge lamps, their objectives being to quantify various aspects of lamp life and lamp reliability. Based on these studies, estimates have been made of the dependence of lamp life on parameters such as initial Rb content, lamp size, lamp operating temperature, rf drive power, and the glass type used to construct the envelope. The parameterization of lamp life that we present can be used to estimate lamp and hence device reliability.

In Section II of this report we review the effort to identify the primary failure mechanism of the low-power Rb discharge lamp. The development of the calorimetric technique to measure the elemental Rb content in a lamp is discussed in Section III; the analyses of Rb consumption measurements and Rb lamp life tests are discussed in Section IV. The prospects for having an accelerated lamp life test or quality control test are presented in Section V. Although this report concerns only the Rb discharge lamp, it should be pointed out that the results presented here apply also, in varying degrees, to other electrodeless discharge lamps containing such elements as sodium (Na), potassium (K), cesium (Cs), and mercury (Hg).

II. LAMP FAILURE MECHANISM IDENTIFICATION

A typical electrodeless discharge lamp^{1,2} is displayed in Fig. 1.⁹ The lamp consists of a glass envelope whose front we designate as the lamp face and the opposite end as the tip-off region. Glasses that have been used for the lamp envelope include Corning 7740 (Pyrex), Corning 1720, Schott 8436, and Schott 8437. The glass envelope contains the metal charge along with a buffer gas. The buffer gas provides a source of electrons to sustain the rf-induced plasma and is required to limit the mean free path of the electrons. Typical buffers presently used are either krypton (Kr) or xenon (Xe) at a pressure of a few Torr. The excess metal charge is constrained by thermal gradients in the tip-off region. The tip-off is formed when the lamp is "pulled" off the vacuum manifold. The lamp envelope is mounted in a metal base with a thermal potting material. The thermal potting material facilitates the transfer of heat from the base, which is the point of temperature control, to the glass envelope. The metal atoms in the vapor are due to the saturated vapor pressure above the metal charge, which is determined by the temperature of the metal, and thus good temperature control is essential for stable lamp operation. A plasma is sustained in the lamp by means of an rf field. Typically the rf frequency is around 100 MHz and powers ranging from tenths to tens of watts.

Several possible lamp failure mechanisms were investigated in response to the failures of the Rb atomic clocks on board the GPS satellites.¹⁰ These mechanisms included quenching of the excited Rb atoms; Rb reaction with impurities; and the interaction of Rb with the glass. We briefly summarize the results of that investigation.

A. QUENCHING OF EXCITED Rb ATOMS

The possible role of quenching in the failure of discharge lamps was investigated by studying the spectral emission from both normal and failed lamps. In the failed lamps only emission lines present in normal lamps were observed. No emission lines from possibly outgassed materials that could quench excited Rb atoms, such as hydrogen (H_2), nitrogen (N_2), or oxygen (O_2), were detected. These results are consistent with the absence of quenching species.

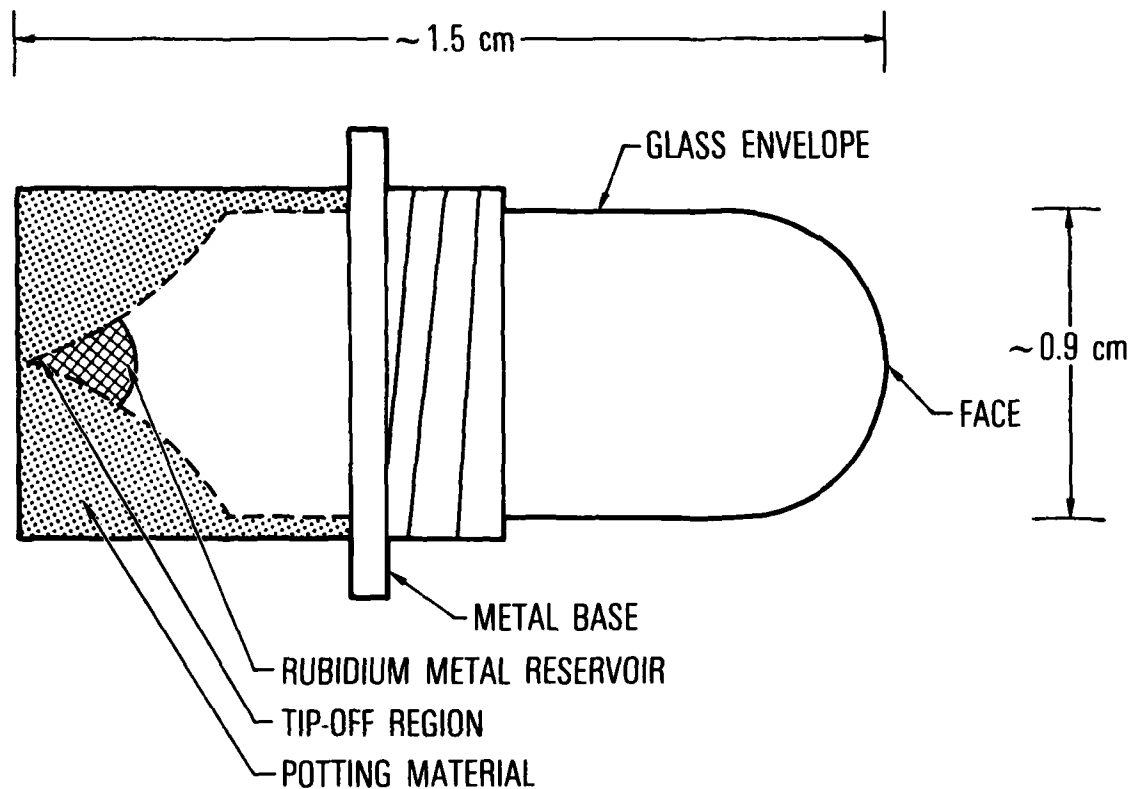


Figure 1. Typical Rb discharge lamp. Lamp consists of a glass envelope that contains excess Rb metal and a buffer gas. An rf coil, not shown, surrounds the exposed portion of the glass envelope and sustains a plasma in the lamp. Figure after Ref. (9).

B. Rb REACTION WITH IMPURITIES

Another postulated mechanism for the failure of the Rb lamp was the loss of Rb by reaction with species outgassed from the envelope to form nonvolatile rubidium oxide (Rb_2O). The most likely reactions are:



and



Experiments that tested for the presence of H_2 in failed lamps proved that reaction with H_2O is not significant. Rf-induced emission spectra from a series of standard lamps containing H_2 and Xe were analyzed to obtain a detection limit of H_2 in the presence of a Xe buffer. Comparisons of these spectra with those of failed lamps indicated that the pressure of H_2 in the failed lamps was less than 1 Torr. Removal of H_2 from the vapor by either the formation of RbH or through permeation through the glass was also ruled out. The loss of Rb through this mechanism was set at about 10 μg or less, which is small compared with the normal charge in a lamp of between a hundred and a few hundred micrograms. Based on the fact that reaction with H_2O was not significant, together with literature sources indicating that H_2O should evolve from the glass envelope much more readily than O_2 , it was argued that the second reaction was also not important in the failure of the Rb lamp. However, as will be discussed in Section III, there does seem to be a reaction of the Rb with some impurity in the lamp consuming between 10 and 20 μg . Although this amount of consumption is not significant in terms of the total charge of Rb, we show that it must be taken into account to properly predict the Rb consumption rate and hence the life of the lamp.

C. INTERACTION OF Rb WITH GLASS

To determine the disposition of Rb in lamps that had been in operation for some period of time, various surface analysis techniques were used. Previous studies that considered the reaction of Na with glass employed techniques such as absorption spectroscopy, magnified examination of the glass

cross section, or wet chemical etching. These techniques were suitable for studies concerned with Na-glass interactions because of the rate at which Na and glass react. In contrast, the reaction of Rb with glass under conditions similar to that found in discharge lamps is orders of magnitude slower than that of Na. To extract physical information concerning the Rb-glass interaction, it was necessary to study the functional form of the Rb penetration profile in the glass. Because of the extremely small amount of Rb that is consumed, simply studying the bulk penetration depth, as is typically done with Na, was found not to be adequate. To study the Rb penetration profile the following surface analysis techniques were used.

1. SECONDARY ION MASS SPECTROMETRY (SIMS) STUDIES

To obtain the highly accurate penetration profiles needed to analyze Rb permeation of glass the technique of SIMS was applied to cross-sectional pieces of Rb-exposed lamp walls. In the SIMS technique a 1.5- μ m-diameter beam of oxygen ions is aimed at the sample. Secondary ions sputtered from the surface are mass spectrometrically analyzed, allowing determination of elemental compositions. Lamp envelopes were broken and analysis performed along the fracture so that profiles of the Rb penetration into the glass could be obtained without the necessity of sputtering away large quantities of glass. Our tests were performed on Rb lamps with envelopes constructed of various glasses and operated under various conditions including heating with no lamp ignition. Varying the lamp conditions allowed the sensitivity of particular parameters of lamp life to be tested.

Figure 2 shows raw SIMS profiles of silicon (Si) and Rb for a lamp exposed to a plasma discharge. Zero micrometers is the inner surface of the lamp wall. The gradual increase of Si and Rb concentrations near zero is due to the finite width of the SIMS beam. Treating these data as simple one-dimensional diffusion allows fitting them to the form¹¹

$$\frac{C(X,t)}{C_0} = \text{erfc} \frac{X}{\sqrt{4Dt}} \quad (3)$$

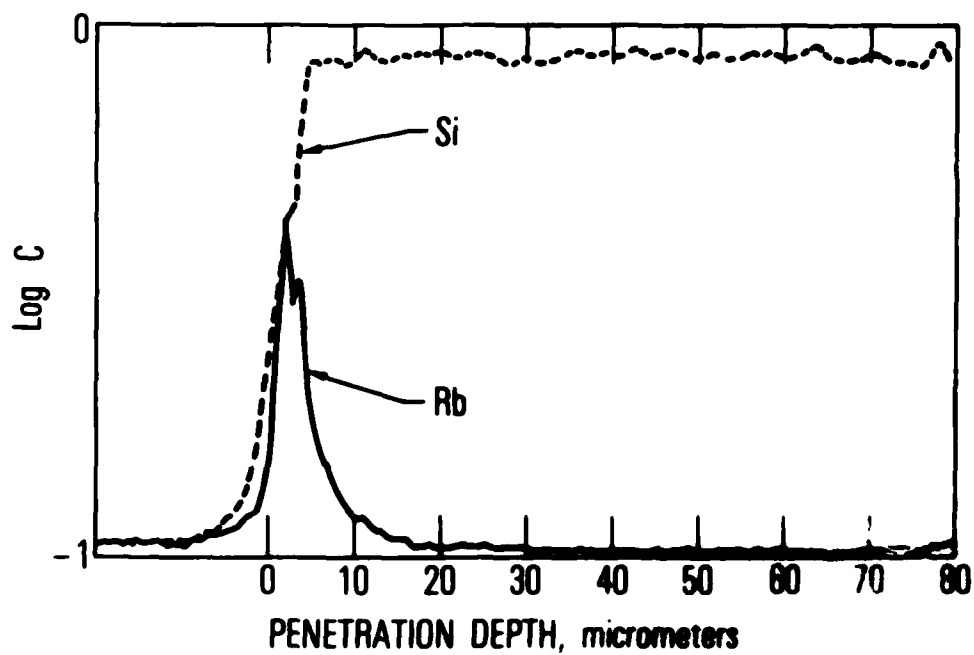


Figure 2. Rb penetration into a Pyrex glass surface from SIMS analysis. The surface occurs at 0 μm . The sharp decrease and increase in Rb concentration near 4 μm is believed to be due to inhomogeneities in the glass and not related to the penetration mechanism.

where X is the penetration depth, t is the exposure time, C_0 is the Rb concentration at the wall, and D is the diffusion coefficient.

Experimental Rb data along with fit curves for lamps made of Pyrex glass are shown in Fig. 3. The data displayed in Fig. 3a were obtained from a sample run under typical lamp conditions; the data in Fig. 3b were obtained from a sample run under similar conditions as that for Fig. 3a but in the absence of an rf plasma. In both cases displayed in Fig. 3 the diffusion coefficient is found to be approximately $3 \times 10^{-14} \text{ cm}^2/\text{s}$. This is in good agreement with high-temperature diffusion coefficient data¹² extrapolated into the low-temperature regime (about 140°C).

The SIMS Rb penetration profiles indicate that Rb has penetrated many micrometers into the glass. This is particularly clear in Fig. 3b, whose sample was exposed to Rb vapor for a longer period of time than that of Fig. 3a. The depth of Rb penetration cannot be attributed to a smearing of the true profile resulting from the finite width of the SIMS ion beam. This beam, which is only approximately 1.5 μm in diameter, would smear a surface layer to a depth of at most 2 μm . In fact, in Fig. 3b the amount of Rb that has diffused beyond 2 μm is greater than the amount found in the surface region.

2. ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA) EXPERIMENTS

The chemical form of the Rb within the glass was investigated using ESCA. In this method the surface of the sample is exposed to monochromatic X rays and the photoejected electrons are energy-analyzed. The resulting core electron binding (ionization) energies are characteristic of both a given element and its chemical form.

Rb-exposed lamp walls were analyzed along with pure samples of rubidium hydroxide (RbOH) and Rb_2O as reference standards. The glass samples typically had a yellow-brown discoloration as long as they were kept in dry atmospheres. However, upon exposure to moist air they became colorless in a matter of seconds. The rapidity of this change in discoloration indicates that Rb exists in a colored form on a thin surface layer, probably less than 0.1 μm thick. The results of our ESCA studies suggest that this colored form is Rb_2O . From

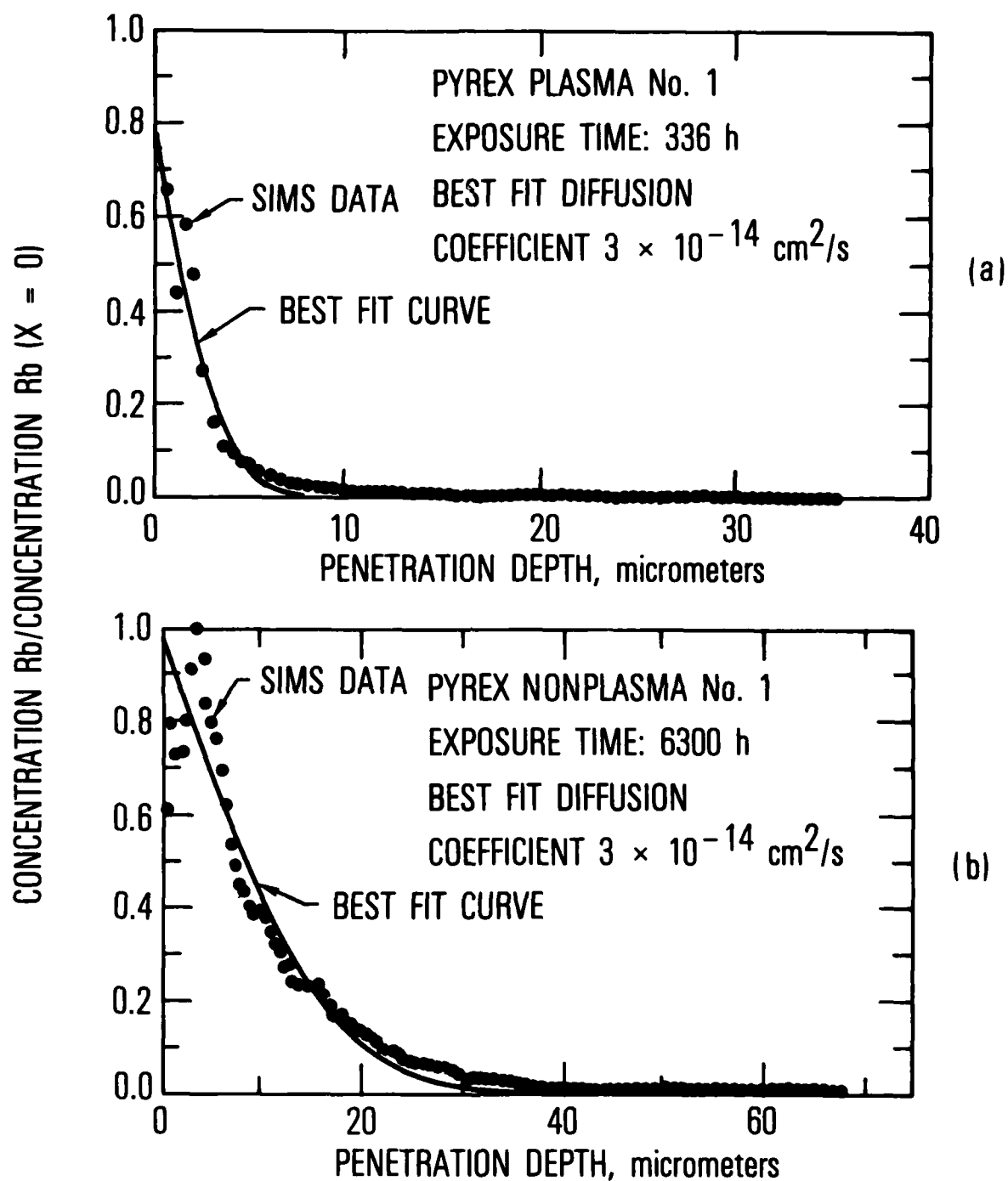


Figure 3. Experimental Rb penetration from SIMS analysis data (●) and fit curve (—) for Pyrex glass samples (a) with discharge present and (b) without discharge.

the SIMS data it was seen that most of the Rb had diffused many micrometers into the glass. While the surface layer is colored, our studies found that the majority of the Rb is in the bulk glass in a colorless form, most likely as Rb-silicate. The disappearance of the colored layer when the glass samples were exposed to the ambient environment is believed to be due to the conversion of Rb_2O to RbOH in the presence of water vapor.

Figure 4 is a diagram summarizing the results of our investigations into the Rb-glass interaction. Near the inside surface of the lamp, Rb is found in the form of Rb_2O , which gives the lamp its yellow-brown color after some period of use. The amount of Rb_2O is found to decrease with increasing distance into the glass. The total amount of Rb in this surface layer has been determined to be small in terms of the total Rb consumed in a lamp over many years of operation. In the bulk glass Rb is found in a colorless form, most likely as a Rb-silicate. The penetration profiles of the Rb in the bulk glass have been found to fit quite well to a diffusion form. Based on these results we have concluded that the primary failure mechanism for low-power Rb discharge lamps is a diffusion of Rb into the glass walls. The amount of Rb that is consumed over many years of operation is very small compared with the amount of glass in the lamp envelope, thus there is no saturation effect and the Rb consumption continues, for all practical considerations, forever.

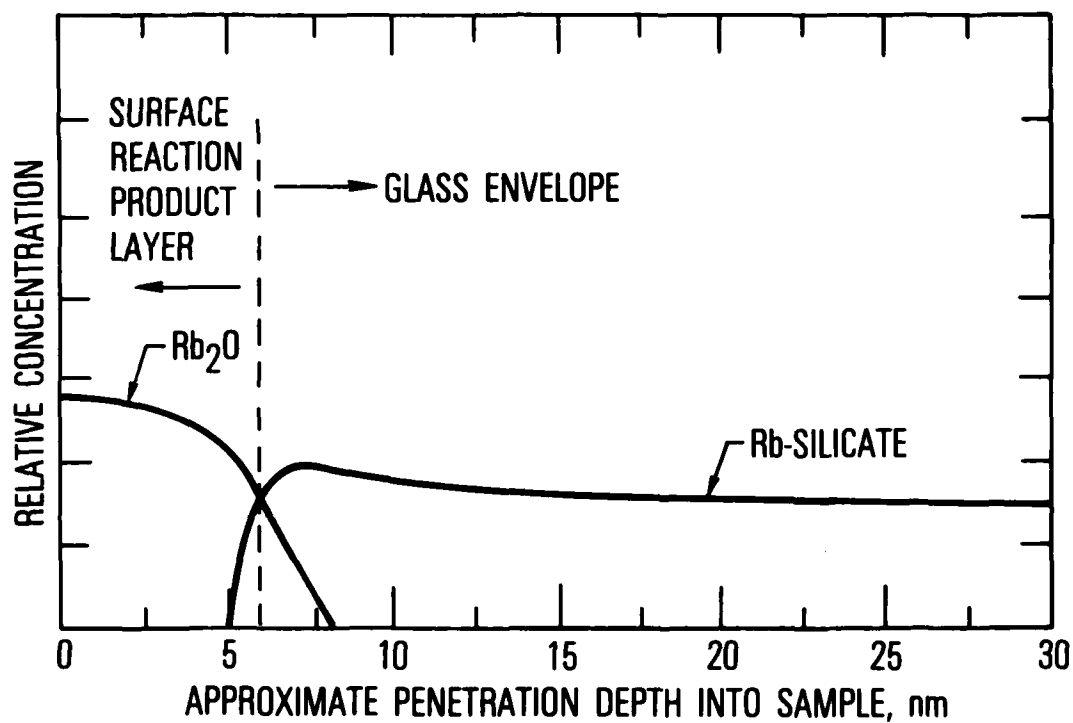


Figure 4. Rb-glass interaction. Rb atoms are found to react with oxygen atoms near the glass surface and then diffuse into the glass as Rb_2O . Unreacted Rb atoms also diffuse in the glass and react to form Rb-silicate.

III. CALORIMETRIC DETERMINATION OF Rb CONSUMPTION

Simple diffusion in glass has been extensively studied.¹³ In principle, one should be able to use the diffusion law to predict the amount of Rb consumed in a specified length of time or, conversely, to determine the lamp fill requirement for a desired lamp life. In simple diffusion the total mass of the material consumed, M , penetrating the glass as a function of time, is given by Eq. (4):

$$M = 2AC_0\sqrt{t\frac{\pi}{D}} \quad (4)$$

where A is the surface area, C_0 is the density of the penetrating species at the glass surface, and D is the diffusion coefficient of the penetrating species for the particular glass. The difficulty with Eq. (4) is in obtaining precise knowledge of both C_0 and D in the lamp application. The density of Rb at the glass surface certainly depends on the temperature of the Rb reservoir that controls the Rb vapor pressure in the lamp. However, based on a mathematical model of the discharge lamp¹⁴ the density of Rb at the lamp wall is predicted to also be a strong function of the rf drive power applied to the lamp. Unfortunately, at present it is not possible to model the exact functional dependence of Rb density on lamp drive power. Additionally, the diffusion coefficients for Rb in the glasses of interest are not well known. The SIMS analyses that we have performed on various lamps have not provided detailed enough information concerning the diffusion coefficients. The best way, to date, to determine the rate of Rb diffusion into the glass envelope of a lamp is by performing Rb consumption measurements under the lamp conditions of interest.

One way to evaluate the rate of Rb consumption in a discharge lamp is to operate numerous lamps to failure and then postanalyze, typically with either atomic absorption (AA) or neutron activation analysis (NAA), to determine the initial Rb fill in a lamp. In this manner a Rb consumption rate for a particular set of lamp operating conditions can be derived. There are many

disadvantages to this procedure, including the enormous amount of time that it takes to generate any information. During the course of work performed in support of the GPS program, it was suggested that a differential scanning calorimeter (DSC) could be used to measure the amount of Rb in a lamp.¹⁵ Because this technique has proven to be so successful and has significant implications for future lamp work, the following description is given.

In DSC, sample and reference objects are both heated such that their temperatures increase at the same rate. Heating rates are measured in degrees Celsius per minute. The instrument measures the heat flow, in calories per minute, required to maintain this heating rate for both sample and reference. The difference between these two heat flows is the instrument output, which is typically plotted versus time.

If the sample and reference are identical there will be no differential signal. Typically, though, the reference is an inert material (e.g., sand) and the sample is the material of interest. If the sample does not undergo a phase transition while being heated, the difference signal will be proportional to the difference in heat capacities of the sample and reference. This signal may be electronically nulled out. When the sample undergoes a phase transition, for example, melting as is the case for Rb, additional heat is required to maintain its heating rate due to the heat of the phase change. This increase in the differential signal will appear as a peak on the differential-signal-versus-time/temperature plot. The area under the peak will equal the additional calories required to melt the sample. After the phase transition the differential signal will return to a nearly constant value, again reflecting the difference in heat capacities of the sample and reference objects. This differential signal may be slightly different from the signal prior to the phase transition as a result of a change in the sample's heat capacity.

In the present Rb consumption studies DSC was used to measure the heat required to melt the Rb contained within a discharge lamp. This heat, when divided by Rb's heat of fusion, 6.14 cal/g, yields the amount of elemental

Rb. A typical DSC curve is shown in Fig. 5 for a lamp containing approximately 300 μg of usable, elemental Rb. Depending on the quality of the calorimeter, sensitivities in the microgram range can easily be realized.

The advantages of the DSC technique for lamp measurements are easily seen. The DSC measures only elemental Rb, i.e., usable Rb in the lamp. Once Rb has reacted with the glass or other material, it no longer melts at the same temperature as metallic Rb, and thus does not contribute to the DSC signal. DSC can thus be used to monitor the rate of disappearance of the elemental Rb from the lamp reservoir. The fact that a consumption rate can be determined for an individual lamp implies that the DSC techniques can potentially be used to monitor quality control in the lamp manufacturing process. The DSC technique is also nondestructive, unlike AA and can be accomplished in considerably less time than NAA; 3 to 5 DSC scans of a lamp can be accomplished in about an hour, whereas the turnaround time for a lamp on a single NAA measurement is about 3 to 5 months.

At EG&G, Rb lamp fill measurements are made using a standard Perkin-Elmer Model DSC-2C Differential Scanning Calorimeter and a Hewlett-Packard Model 3390A Reporting Integrator. The latter instrument gives a numerical reading of the amount of Rb in a lamp. After an initial calibration, the measurement process is very straightforward. The most critical aspect is "chasing" the Rb to a spot on the face of the lamp (see Fig. 6) so that it all makes good thermal contact to one calorimeter pan. A dummy (empty) lamp is placed on the other pan. A small amount of thermally conductive grease is used between the faces of the lamps and the pans. Typical repeatability between measurements is $\pm 0.5 \mu\text{g}$, both for the same "chase" and when the Rb is redistributed and rechased into a new spot. Absolute accuracy is dependent on the calibration procedure and is believed to be about $\pm 10\%$. It is the repeatability that is of most concern for the Rb consumption measurements.

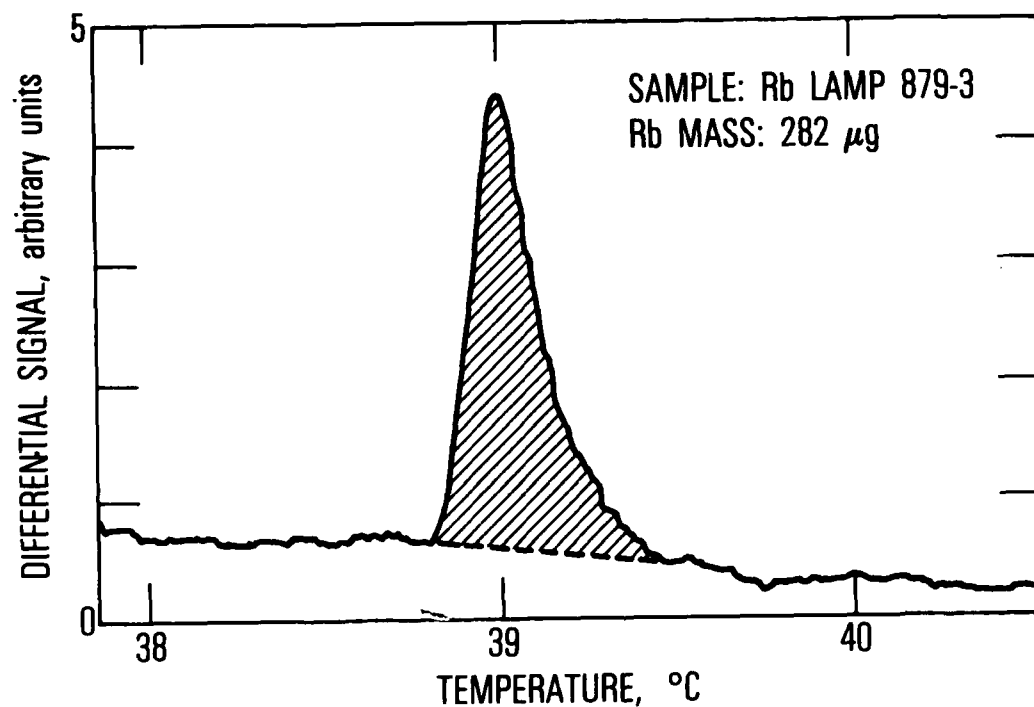


Figure 5. Calorimetric measurement of the Rb content of a Rb lamp. The differential heat pulse is displayed against temperature for a typical Rb lamp measurement. The area under the pulse can be integrated to determine the total energy that was required to melt the Rb sample and thus determine the elemental Rb content of the lamp.

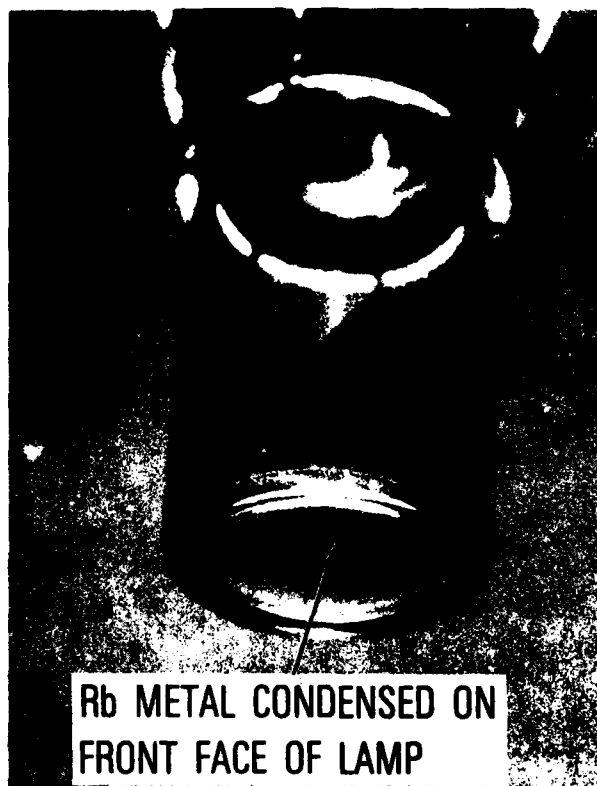


Figure 6. Photograph of EG&C lamp showing Rb metal driven to front face in preparation for calorimetric measurement. The Rb metal must form a tight, compact sample to achieve best measurement with calorimeter.

IV. Rb LAMP LIFE INVESTIGATIONS

Over the past several years a number of efforts have been undertaken to specify the requirements to ensure reliable operation of the Rb discharge lamp. These studies have included three types of glass: Corning 1720, Schott 8437, and Schott 8436. With the Corning 1720 glass lamps, two different lamp operating conditions have been studied, corresponding to those used in the Efratom and EG&G Rb frequency standards, respectively. These lamp conditions are shown in Table I. Circumstantial evidence^{1,16} indicates that it is possible to "overfill" a lamp, thereby generating excessive lamp noise. A possible physical mechanism for such a phenomenon is the displacement of excess Rb in a lamp by thermal and/or mechanical forces, which produces changes in light intensity with concomitant frequency instability when the lamp is used in a Rb clock. A quantitative understanding of Rb consumption allows the lamp fill to be chosen so as to minimize noise while providing adequate life for the intended application. The results of the various lamp studies follow.

A. CORNING 1720 GLASS

1. EFRATOM OPERATING CONDITIONS

An extensive effort was undertaken at The Aerospace Corporation to measure the Rb consumption rates in Efratom-type, Corning 1720 glass lamps using the calorimetric technique. Lamps of the Efratom design, manufactured both at Efratom and at Aerospace, were studied. All the lamps were operated in oscillators built by Efratom to ensure that each lamp was subjected to the same rf drive power. Figure 7 shows typical results of Rb consumption in this kind of lamp. In Fig. 7 the log of the Rb consumed is plotted versus the log of the lamp operating time. Rb consumption is measured in units of micrograms; the lamp operating time is given in hours. Fitting to a linear function on the log scale yields the power-law relation for Rb consumption in time. For this particular lamp, the fitting process yielded

$$M_{\text{Rb}}(t) = 10t^{0.26} \quad (5)$$

Table I. Comparison of Lamp Operating Conditions

User/Glass	Efratom/Corning 1720 ^a	EG&G/Corning 1720 ^b	Efratom/Schott ^a
outside diameter (cm)	0.9	0.8	1.0
length (cm)	~ 1.5	~ 0.7	1.5
interior surface area (cm ²)	~ 4	~ 2.3	5.1
operating temperature ^c (°C)	120	115	120
rf frequency (MHz)	~ 100	110	~ 100
rf drive power (W)	< 2	0.45	< 2

^aT. C. English and E. Jechart, "Development of A Sapphire Lamp for Use in Satellite-Borne Atomic Rubidium Clocks," Proceedings, 35th Annual Symposium on Frequency Control, US Army Electronics Command, Ft. Monmouth, NJ (1981), pp. 637-645. Copies available from Electronic Industries Association, 2001 Eye Street, NW, Washington, DC 20006.

^bW. J. Riley, "A Rubidium Clock for GPS," Proceedings of the 13th Annual Precise Time and Time Interval Applications and Planning Meeting, Naval Research Laboratory, Dec. 1-3, 1981, NASA Conference Publication No. 2220, pp. 609-630.

^cLamp operating temperature is controlled at the base of the lamp. The rest of the lamp envelope is hotter depending on the rf drive power and the particular thermal paths associated with the lamp structure. Thermal gradients along the glass envelope can typically be 30°C or more.

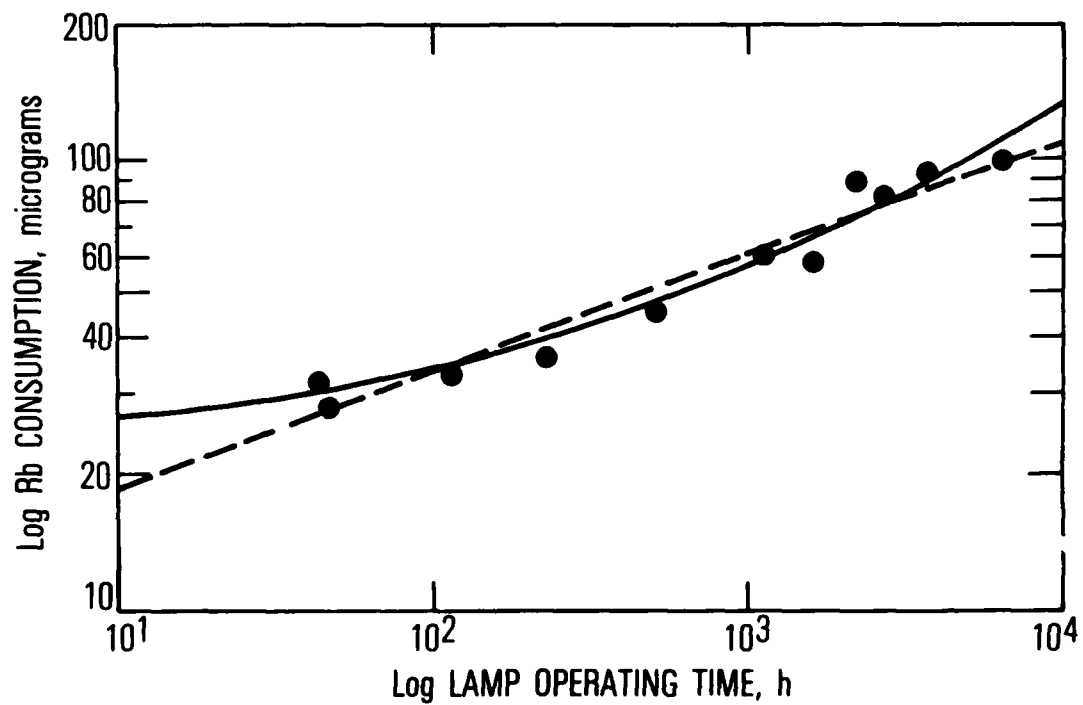


Figure 7. Typical Rb consumption data for Efratom lamp operated under the Efratom normal conditions. Measurements are denoted by the symbol "•". The solid line is a power-law fit to the data, and the dashed line represents a fit to the diffusion law [see Eq. (6) in the text].

with $M_{Rb}(t)$ the mass of Rb consumed in micrograms in a time t , in hours. This fit is shown as the dashed line in Fig. 7.

Equation (5) is clearly not of the diffusion form given by Eq. (4). Measurements on other lamps yielded other power-law relationships for the amount of Rb consumed in a specified lamp operating time. These results presented two difficulties: 1) the power laws that were derived did not have a simple physical explanation, and 2) each lamp seemed to exhibit its own consumption law. It was found, however, that all the Rb consumption data could be fit quite well and quite consistently if one assumed that in addition to simple diffusion of the Rb into the glass, there was also a mechanism by which a small amount of Rb was consumed almost instantaneously at the outset of lamp operation. In this model one predicts the Rb consumption to obey a law of the form

$$M_{Rb}(t) = R \sqrt{t} + B \quad (6)$$

The first term on the right-hand side of Eq. (6) corresponds to simple diffusion, see Eq. (4), and the second term represents some immediate consumption of Rb. Fitting the data shown in Fig. 7 to the form of Eq. (6) yields

$$M_{Rb}(t) = 1.09 \sqrt{t} + 24 \text{ } \mu\text{g} \quad (7)$$

which is represented by the solid line in Fig. 7. It is not unreasonable to consider that the Rb could getter some small amount of impurity in the lamp (see Section II). As long as the amount of the impurity is small and more impurity does not evolve from the lamp walls as a function of time, this initial clean-up process in the lamp could take place almost instantaneously. One feature of this model is that each lamp could have a different quantity of Rb consumed in the clean-up process. The amount of Rb consumed should depend on the impurity level in the particular lamp, which in turn should depend to some extent on the particular processing to which a lamp was subjected during its manufacture.

Averaging the results from ten lamps, where some individual lamps had operating times over 10,000 h, the following Rb consumption law for Corning 1720 glass lamps of the Efratom design operated under the normal Efratom conditions, see Table I, was obtained:

$$M_{\text{Rb}}(t) \approx (1.4 \pm 0.4) \sqrt{t} + (18 \pm 6) \mu\text{g} \quad (8)$$

The factor of approximately 18 μg reflects both the proposed instantaneous consumption of Rb and the error in the calorimetric measurement. The measurement errors should tend to cancel on the average over ten lamps. Thus the 18 μg is the quantity of Rb that one would expect to see consumed on the average upon the initial turn-on of this type of lamp.

Previously a life test of Rb lamps constructed out of Corning 1720 glass was conducted at Efratom. The test involved lamps that were operated to failure and then analyzed using NAA to determine the initial Rb fills. The results of that study are displayed in Fig. 8. A fit of the data shown in Fig. 8 to the form of Eq. (6) yields the relation

$$M_{\text{Rb}}(t) = (1.45 \pm 0.1) \sqrt{t} \quad (9)$$

which is shown in Fig. 8 as the solid line through the data points. Because in this test only one consumption point in time per lamp could be acquired, i.e., total lamp life and initial Rb fill, the second term in Eq. (6) could not be evaluated for the individual lamps. Since the amount of Rb that may be instantaneously consumed could be different for each lamp, fitting lamp data from life tests to the form of Eq. (6) cannot, a priori, be justified. However, if all the lamps had been processed in a sufficiently identical manner then one could claim that life test data would yield the same information as the consumption measurements. In this particular case, the instantaneous consumption factor seems to have been vanishingly small, implying that the processing of these lamps was quite good. The fit to this particular life test data then is sensitive only to the diffusion process. Comparing Eq. (8) with Eq. (9) shows that there is excellent agreement for the factor describing the rate of diffusion of the Rb into the glass.

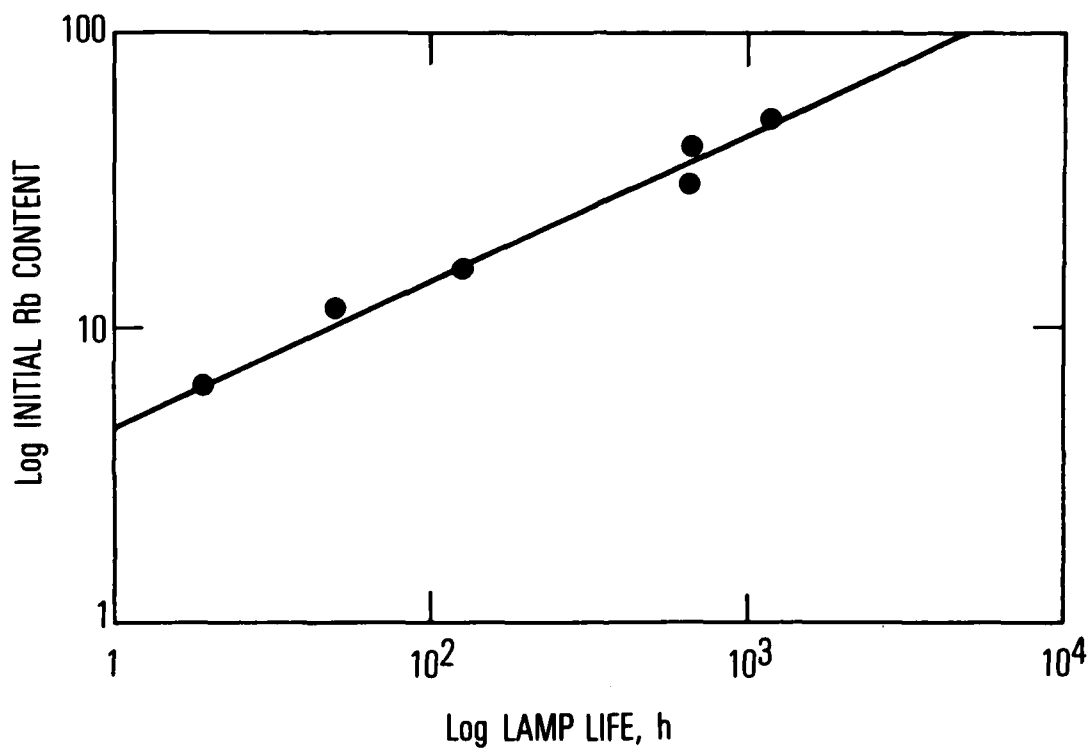


Figure 8. Results of the lamp life test conducted by Efratom for Corning 1720 glass lamps. Each symbol "•" represents a lamp that was operated to failure. Total operating life is plotted on the horizontal axis versus the initial Rb fill of the lamp on the vertical axis.

2. EG&G OPERATING CONDITIONS

Studies of Rb consumption, using DSC, in lamps of the EG&G design and operated under the EG&G normal conditions (see Table I) have been conducted at both EG&G and at Aerospace. The consumption data exhibited features similar to that found in the studies conducted with Efratom-type lamps in that power-law fits to the data yielded time dependences much slower than that of simple diffusion. Typical consumption data yielded $M_{Rb}(t) = 3.7t^{0.25}$. Assuming that the Rb consumption results from two processes, simple diffusion and rapid, initial clean-up, provides consistent fits to almost all the data for the EG&G lamps. The EG&G and Aerospace studies gave essentially the same results, with the uncertainties in the Aerospace data being somewhat larger due to the poorer quality of the DSC used for that work.¹⁷ Rb consumption in the EG&G lamp, operated under EG&G normal conditions, can be described by the relation

$$M_{Rb}(t) = (0.2 \pm 0.05) \sqrt{t} + (14 \pm 3) \mu g \quad (10)$$

In Fig. 9 we show a composite plot of all the Rb consumption data measured at EG&G. For the sake of clarity, the factor representing the instantaneous Rb consumption, the factor B in Eq. (6), was determined for each lamp represented in Fig. 9 and subtracted from the consumption data for each lamp before plotting. The data in Fig. 9 represent Rb consumption through diffusion only. Each symbol in the figure represents a different lamp. From Eq. (10) it is seen that the term representing the rapid consumption of Rb in the lamp appears to be about the same size as that found in the Efratom lamp. This fact seems to indicate that the phenomenon is inherent in the lamp manufacturing process. The fact that the term describing the diffusion of the Rb into the glass is smaller for the EG&G case compared to that of the Efratom case can be readily understood by referring to Eq. (4) and Table I. From Eq. (4) it is seen that the diffusion term depends on the inner surface area of the lamp, the density of the Rb at the walls, and the diffusion coefficient for the glass. Since both types of lamps were made of Corning 1720 glass we expect the diffusion coefficients to be nearly identical.¹⁸ The inner surface area for the EG&G lamp is seen from Table I to be about a factor of 2 less

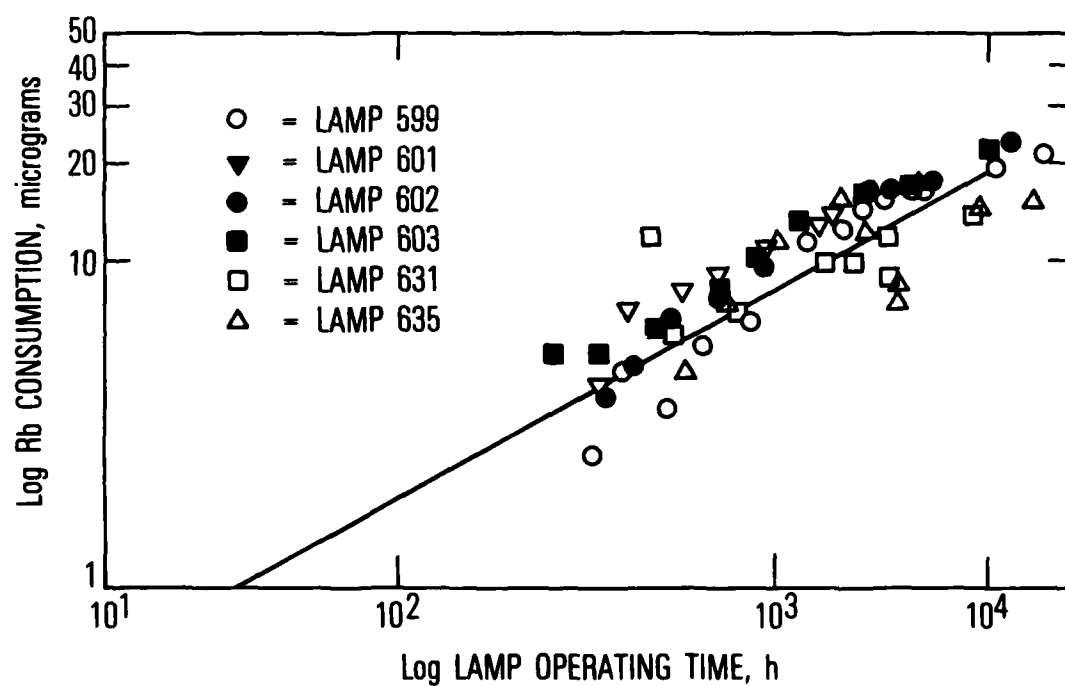


Figure 9. Composite plot of Rb consumption data for EG&G lamps measured at EG&G. Solid line represents a diffusion law fit to the data; see Eq. (6) in the text. The initial Rb consumption factor was subtracted from the data for each lamp before plotting.

than that for the Efratom lamp. Additionally, the rf drive power of the EG&G lamp is about a factor of 2 or 3 smaller than that for the Efratom lamp. Eckert's lamp model¹⁴ would predict the Rb concentration at the walls to be smaller for the EG&G lamp, because the rf drive power is smaller, than for the Efratom lamp. Thus both factors, the surface area and the rf power, are such that one would predict a slower Rb consumption rate from diffusion in the EG&G lamp than in the Efratom lamp. Unfortunately, Eckert's model¹⁴ is not sufficiently developed for a quantitative comparison to be made between the results of the consumption/life tests and the model predictions. We believe that it is clear, however, that the Rb consumption in Corning 1720 glass lamps is well described by an initial rapid consumption followed by long term simple diffusion.

B. SCHOTT 8436 GLASS

Rb consumption measurements have been performed for a small sample of Schott 8436 glass, Efratom-type lamps operated under the Efratom normal conditions. The consumption measurements to date are shown in Fig. 10. The solid line in Fig. 10 is a fit of the consumption data to the form of Eq. (6). The resulting Rb consumption law was found to be

$$M_{Rb}(t) = (0.9 \pm 0.15) \sqrt{t} \pm 7 \text{ } \mu\text{g} \quad (11)$$

The fit shown in Fig. 8 is noteworthy in that it indicates that the model used to describe Rb consumption in Corning 1720 glass lamps is valid also for the Schott 8436 glass lamps. The seemingly lower diffusion rate for the Schott 8436 glass lamps tends to indicate that this glass is slightly more alkali resistant in the lamp application than the Corning 1720 glass.

C. SCHOTT 8437 GLASS

Schott 8437 glass was used for the lamp envelopes of the early GPS Rb clocks. The failures of lamps on the early GPS satellites prompted a change from Schott 8437 glass to Corning 1720 glass for the lamp envelope. However, it was felt that it would still be important to understand the Rb consumption phenomenon in the Schott 8437 glass lamps to ensure that the optimal glass choice had been made.

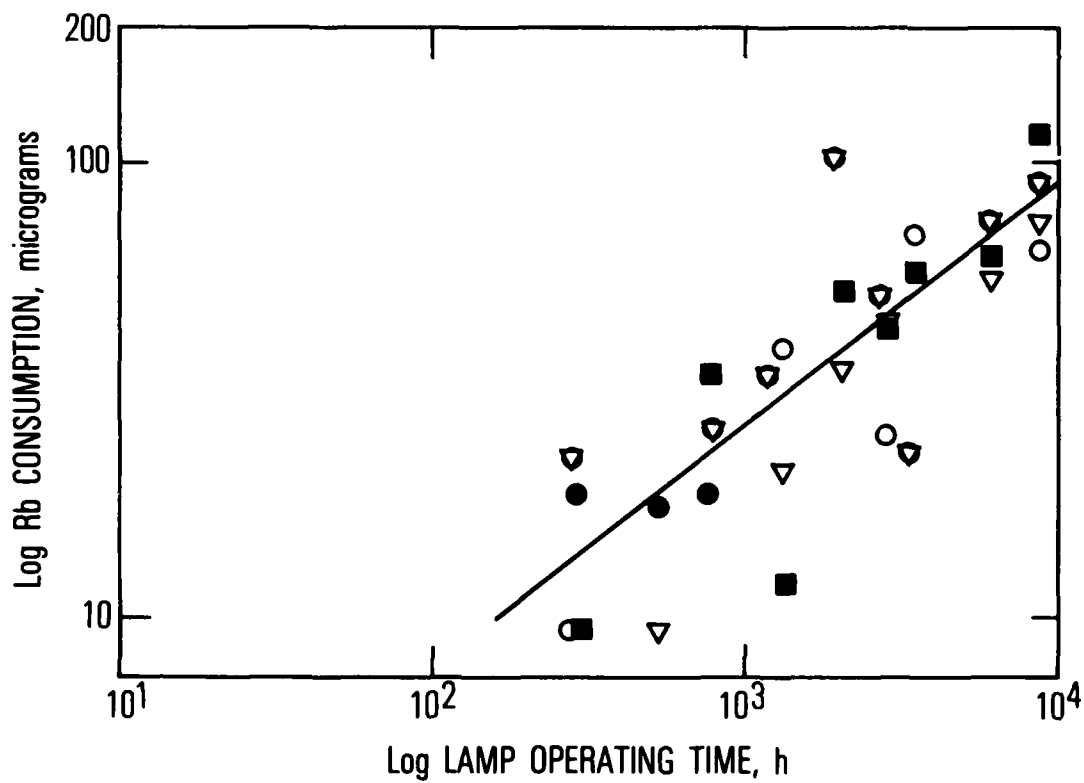


Figure 10. Composite plot of Rb consumption in Schott 8436 lamps of the Efratom design operated under Efratom normal conditions. Each symbol represents a different lamp. Solid line is a diffusion-law fit to the data; see Eq. (6) in the text.

All the envelopes for lamps involved in this particular study were manufactured by Efratom Elektronik GmbH in Munich, Germany. The low-filled, short-lived lamps were filled by Efratom California, Inc., for special-purpose testing at the time of the GPS failures; the other lamps exhibiting long life were filled in Munich as part of Efratom's regular lamp production and testing. These particular lamps were manufactured and put into tests before the technique of calorimetry had been developed to measure initial Rb lamp fill. Efratom California, Inc., had analyzed lamp life versus lamp fill for the sample of short-filled lamps by operating the lamps to failure and then using either NAA or AA to determine the initial Rb fill. Some of the normal production lamps, i.e., those filled in Munich, however, are still operating after eight years of almost continuous, nonaccelerated life-testing and thus it was necessary to determine the amount of Rb that had been consumed during the operating life to date. For these lamps both the total Rb, i.e., the initial Rb fill, and the amount of Rb remaining in the reservoir had to be determined. NAA was used to determine the initial Rb fill, and DSC was used to measure the Rb mass still in the reservoir.

Owing to the nature of the glass envelope, only the ^{85}Rb content in the lamp can be determined using NAA. Because a nonnatural isotopic fill is used in the Efratom lamps,¹⁹ a precise determination of the isotopic ratio had to be made before the total Rb could be determined from the NAA results. A laser excitation fluorescence technique²⁰ for this measurement was employed that provided an accuracy of about 4% on the $^{87}\text{Rb}/^{85}\text{Rb}$ ratio. This ratio then allowed computation of the total Rb fill from the NAA determination of the ^{85}Rb content. Error bars were assigned to the ^{85}Rb determination based on the results of a previous study of the accuracy of NAA.^{21,22} The errors quoted for the total Rb fill in Table II incorporate both the uncertainties in the isotopic ratio measurement and the assumed inaccuracies in the NAA evaluation. To ensure that there were no systematic effects in the NAA results, other lamps, not shown in Table II, were included as a check. The Rb fills in these lamps were known with high accuracies through previous NAA and DSC measurements. No evidence for any systematic errors in the NAA results was found.

Table II. Lamp Measurement Results

Lamp No.	Total Rubidium from NAA (μg)	Rubidium Reservoir from DSC (μg)	Rubidium Consumed (μg)	Operating Time ± 700 (h)
881-3	397 ± 40	300 ± 20	97 ± 45	25×10^3
604	184 ± 20	0	184 ± 20	50.6×10^3
613	220 ± 22	0	220 ± 22	57.8×10^3
397	221 ± 21	53 ± 5	169 ± 22	69.4×10^3
400	233 ± 23	30 ± 4	203 ± 23	69.4×10^3
633	229 ± 22	64 ± 5	165 ± 23	69.4×10^3
718	266 ± 26	28 ± 2	238 ± 26	69.4×10^3

The DSC results are affected by two major error sources: the uncertainty in the "glass correction" factor²³ and the repeatability of a lamp measurement. A glass correction factor is applied to the DSC measurement to account for perturbations in observed DSC signals due to the lamp's glass envelope. Lamps Nos. 604 and 613 had failed during their operation and thus we identically assigned zero to their Rb reservoir contents. For completeness we verified that the DSC yielded no detectable Rb signal.

We display in Fig. 11 a plot of lamp operating times versus Rb consumed for all Schott 8437 lamps involved in life testing. In Fig. 11 each point represents an individual lamp. Points represented by an "●" with no error bars are lamps that were life tested at Efratom. These lamps were operated until failure and then were analyzed by either NAA or AA to determine the initial Rb fill. No error bars are indicated because of insufficient information on their analyses. Points for which error bars are displayed represent those lamps that were analyzed for consumed Rb. There are five points in Fig. 11 that correspond to lamps that have not failed and thus those points represent Rb consumed over the operating time of the lamp. One of these lamps has operated for 25,000 h, and the remainder have operated for about 70,000 h each.

Rb consumption in lamps with Corning 1720 glass and Schott 8436 glass envelopes was found to be well understood in terms of diffusion of the Rb into the glass plus an initial rapid consumption. The life test data from lamps with Schott 8437 glass envelopes, however, does not definitely support that model. Although the Schott 8437 life test data do not allow a definite description based on a single model, they do provide us insight into the following Rb consumption models.

1. ALKALI INTERDIFFUSION

In some studies of the alkali attack on glass, in particular with Na, it has been shown that the process of alkali atoms or ions diffusing into the glass structure is accompanied by a reverse migration of the alkali atoms already present in the glass.²⁴ Schott 8437 glass has a Na content of about 2% by weight. Under this model, we would expect a one-for-one exchange of Rb

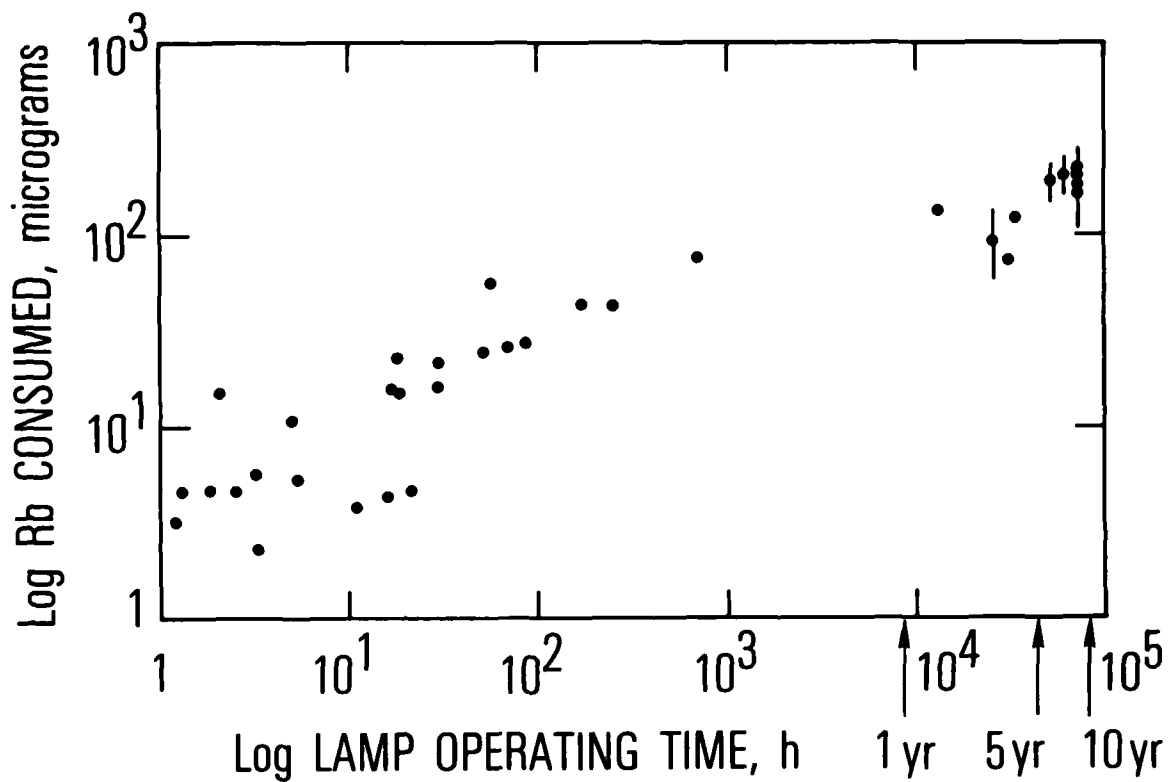


Figure 11. Rb life/consumption data for Schott 8437 glass lamps. Total operating times versus either total Rb fills, if lamp has failed, or consumed Rb, if lamp is still operating, are plotted for a number of lamps with Schott 8437 glass envelopes.

for Na during the operation of the lamp. As Na diffused out of the glass envelope, a Rb-Na amalgam would form. The amalgam would then affect the quality of the DSC scan since a pure Rb melt would no longer be seen. No effect like this was observed, which would have been quite pronounced in lamps Nos. 397, 400, 633, 718, and 881-3; consequently, we believe that this process does not significantly contribute to Rb consumption in these lamps.

2. RUBIDIUM DIFFUSION

Because the data presented in Fig. 11 do not definitely support the model that we used to describe Rb consumption in Corning 1720 glass and Schott 8436 glass lamps, we propose two alternative explanations to describe this data.

a. The "Two-Glass" Model

Assume that the Rb diffusion into the Schott 8437 glass is described by two different diffusion processes: one that controls the Rb diffusion through a thin surface layer, and a second process in the bulk of the glass. Under this model, the thin surface layer controls the rate of Rb consumption in the short term, and the bulk glass controls the consumption process in the long term, i.e., after the thin layer has been saturated. In Fig. 12 we re-plot the Schott 8437 lamp data together with a prediction of Rb consumption under this "two-glass" model, assuming a diffusion coefficient in the first layer, with thickness 2.5 μm , of $\sim 1 \times 10^{-14} \text{ cm}^2/\text{s}$ and for the bulk glass of $\sim 5 \times 10^{-16} \text{ cm}^2/\text{s}$. The model is seen to fit the data fairly well with diffusion coefficients that are of the correct order of magnitude. However, there are no data in the critical transition region, i.e., between 10^2 and 10^4 h, and thus the experimental support for this model is weak.

The origin of a two-glass condition in these lamps can be physically understood in a number of ways. A cleaning process in the manufacture of the lamp, e.g., an HF or some other rinse, might alter the characteristics of the glass in a narrow region at the inner surface. Additionally, the plasma could possibly change the glass properties to some depth. This may be similar to the brown surface layer that occurs during lamp operation. On the other hand, we have not seen an analogous phenomenon for the Corning 1720 or Schott 8436 glasses. It may be that a similar effect occurs for these lamps, but takes

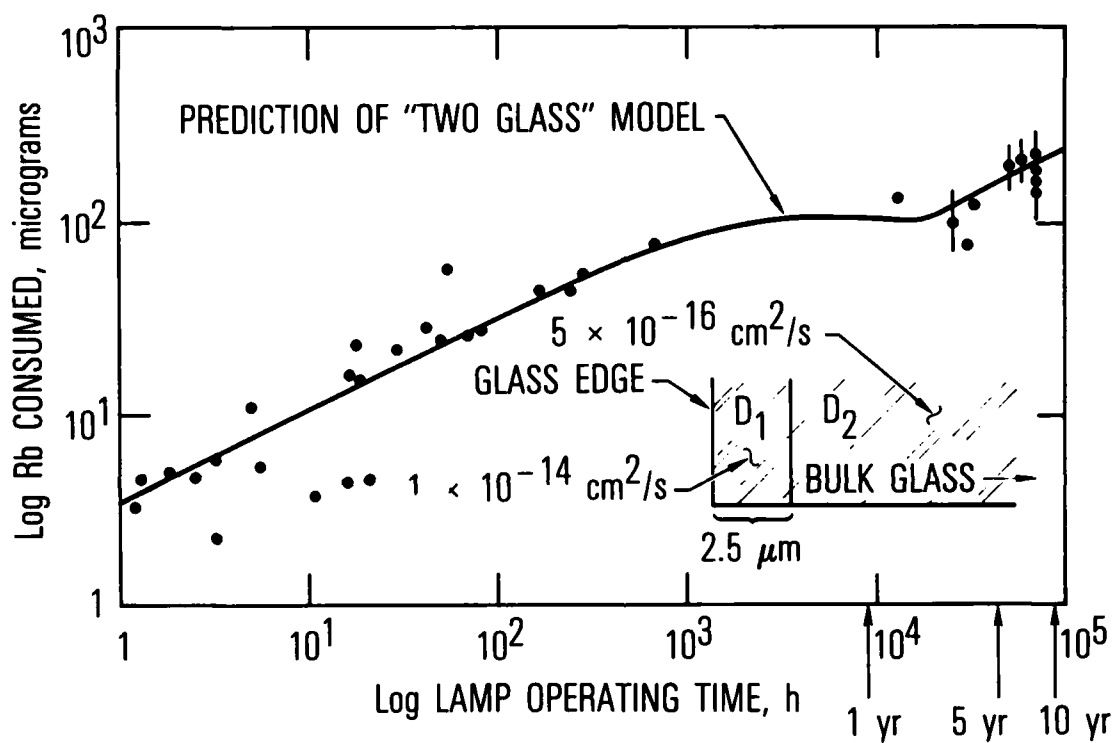


Figure 12. Schott 8437 glass lamp data with a fit, solid line, to the two-glass model of Rb consumption. Inset shows the two different diffusion regions in the glass: a narrow region characterized by a relatively large diffusion coefficient for the Rb, and the bulk glass, which has a lower diffusion coefficient.

place after a much longer time and thus simply has not been observed yet. Because we have no information concerning the manufacture of the Schott 8437 lamps, we must present the two-glass model as speculation.

b. Simple Diffusion

In Fig. 13 we display fits of the Schott 8437 lamp data to simple diffusion forms. Because the data naturally breaks into two groups—short-lived lamps, with operating times less than 10^3 h; and long-lived lamps, with operating times greater than 10^4 h—we show two diffusion fits. A possible explanation is that the data below 10^3 h result from subjecting the lamp to some anomalous procedure during manufacture that resulted in a high rate of Rb consumption. Fitting the long-term data to a simple diffusion form yields

$$M_{\text{Rb}}(t) \approx (0.8 \pm 0.2) \sqrt{t} \quad (12)$$

In this fit, the initial rapid consumption term given in Eq. (6) was found to be insignificant and hence was neglected.

The fact that the Rb consumption in both Corning 1720 glass lamps and Schott 8436 glass lamps is well described by essentially simple diffusion, makes the short-term lamp life data for the Schott 8437 glass lamps and hence the two-glass models somewhat suspect. Additionally, lamps for both Schott glasses exhibited about the same Rb consumption rate in the long term, which is what one would expect based on the presumed similarities between the two glasses. More experimental work would be needed to determine whether the Schott 8437 glass lamps are exhibiting either a different consumption process or simply a manufacturing anomaly. Finally, whether the two-glass model or simple diffusion is the correct picture is not critical to long-term lamp life prediction. In the long term, greater than 10^3 h, the lamp life predictions, derived from the consumption data fits to each model, are seen to converge.

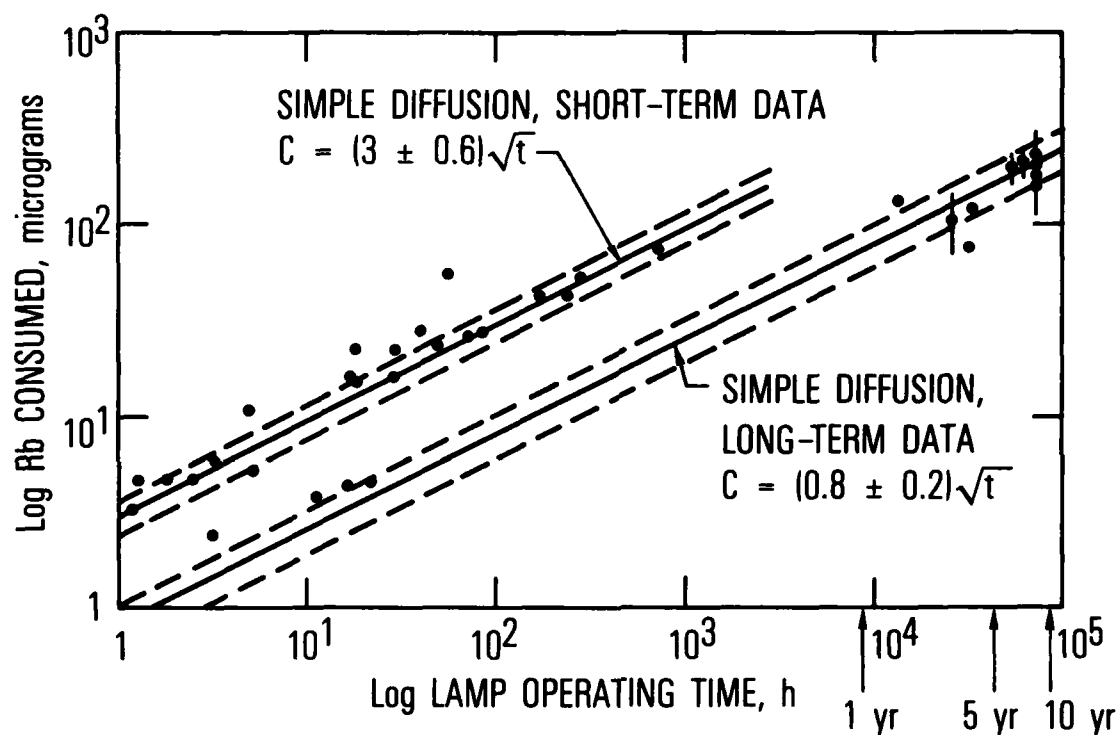


Figure 13. Schott 8437 glass lamp data fit to diffusion model. Because the data seemed to break up into two distinct groups, two fits were performed. Compared with the longer-lived lamps, the short-lived lamps show a much increased diffusion rate.

D. SUMMARY OF EMPIRICALLY DERIVED CONSUMPTION LAWS

Rb lamp tests have yielded the following consumption laws for various lamp conditions:

1. Efratom, Corning 1720 Glass Lamps:

$$M_{Rb}(t) \approx (1.4 \pm 0.4) \sqrt{t} + B$$

2. EG&G, Corning 1720 Glass Lamps:

$$M_{Rb}(t) \approx (0.2 \pm 0.05) \sqrt{t} + B$$

3. Efratom, Schott 8437 Glass Lamps (consumption law based on the long-lived lamps only):

$$M_{Rb}(t) \approx (0.8 \pm 0.2) \sqrt{t} + B$$

4. Efratom, Schott 8436 Glass Lamps:

$$M(t) \approx (0.9 \pm 0.15) \sqrt{t} + B$$

The factor B represents the small amount of initial Rb consumption that we believe occurs in these lamps. This initial Rb clean-up typically involves up to 20 μg of Rb. We have at the present time no way to predict, a priori, how much Rb will be initially consumed in a particular lamp; however, we think that any initial consumption much greater than 20 μg most likely indicates an anomaly in the lamp processing.

The various empirically derived consumption laws show the effects of the different parameters in Eq. (4). Comparing the Corning 1720 results from Efratom and EG&G lamps demonstrates the effects of both lamp size and rf drive power on Rb consumption. Efratom uses a larger lamp, with greater rf power than does EG&G. The consumption rate of Rb in the Efratom lamp is consequently higher. The results from the Efratom Schott glass lamps compared with those from the Corning 1720 glass lamps seem to indicate that both of the Schott glasses, at least in the long term, have lower diffusion coefficients for Rb than does Corning 1720 glass.

Although the empirically derived consumption laws give strong support for the validity of Eq. (4), it is not possible at the present time to use Eq. (4) to derive the Rb consumption rate for an arbitrary set of lamp conditions. The biggest single problem concerns the exact dependence of the Rb concentration at the lamp walls on the rf drive power. The analytical model of the rf discharge is not sufficiently developed to allow more than a qualitative description of the lamp. Additionally, there are no good measurements of the Rb diffusion coefficients for the glasses of interest. The consumption measurements thus provide us with the best characterization of lamp life and reliability.

V. ACCELERATED LAMP LIFE PROCEDURE/QUALITY CONTROL TESTING²⁵

Accelerated life testing is an extremely useful technique for determining device reliability. In an accelerated test, the operating life of a device is compressed by some means into a time much shorter than the normal lifetime. Performance characteristics can then be monitored for a statistical sampling of devices, and estimates for the normal reliability of the device can be made. Equally important is quality control testing to ensure that particular components have been manufactured properly and will perform according to the prediction of the statistical sampling. To investigate possible means of accelerating the life of a discharge lamp, Rb lamps, all of the Efratom design and constructed out of Corning 1720 glass, were operated under various temperature and rf drive power conditions. Rb consumption rates were determined using DSC. Lamp lifetimes for a given initial Rb fill—for this analysis we arbitrarily used an initial fill of 400 μg of Rb—were then extrapolated for the specific operating conditions.

The lifetime of Rb discharge lamps is limited by the reaction of Rb vapor with the glass envelope of the lamp. In this section we show that there is a good analogy between this type of reaction and the reaction of a gas with a quiescent liquid. The kinetic theory of the latter type of reaction has been well developed by Danckwerts, and the same mathematical description may be applied to the lamps. The theory has some adjustable parameters that may be used to fit lamp lifetime data, and, therefore, it may be used to predict the effect of temperature on lifetime and the time dependence of Rb consumption. While this description of the lamp behavior is simplified and incomplete, it provides a useful conceptual framework for the further understanding of lamp behavior and shows the limitations of accelerated lifetime testing.

The traditional picture of glass is that it is simply a liquid of very high viscosity. While this view is now regarded as oversimplified (and we shall show one way in which it fails), it is very useful as an analogy for reaction kinetics across a phase boundary. The theory of gas-liquid reactions has been well developed for certain simplified cases, and we shall apply the

version given by Danckwerts²⁶ to the reaction of Rb vapor with Corning 1720 glass. The theory gives a physical picture of the nature of the reaction, and permits the prediction of consumption-versus-time curves as a function of temperature from a limited set of data.

The theory incorporates just two phenomena: diffusion and reaction. In the version employed here, the diffusion problem is simplified to include only diffusion in the condensed phase. This is justified because both gas phase diffusion and the sticking probability of the gas on the surface are sufficiently rapid that the rate of the overall process is not limited by gas processes. Thus, in this theory, it is assumed that an arbitrarily thin surface layer of the condensed phase is in Henry's law equilibrium with the partial pressure of the gas phase reactant, and that the overall transfer of gas across the phase boundary is governed by diffusion into, and reaction with, the condensed phase. The diffusivity of the gas in the condensed phase, the solubility of the gas, and the reaction rate constant are the parameters required by the theory, although these parameters have different temperature dependences that must also be included.

The theory predicts that the consumption of gas will vary as the square root of time if diffusion is the dominant process in the condensed phase, and that the consumption will vary linearly with time when chemical reaction dominates. In the region where both processes are competing, the theory predicts an initial square-root-of-time behavior, followed at long times by a linear behavior. It must be pointed out that the validity of this theory rests on the assumption that there are no glass saturation effects. While this is a very good approximation for Rb, it would not be as good for more rapidly reacting species such as Na. Once the reaction between the Na and glass has saturated, consumption will change from linear to square root, implying a diffusion-limited process.

In the case of the Rb plus glass reaction, we have experimentally shown the consumption of Rb to have a square-root-of-time dependence at low temperatures and a linear time dependence at high temperatures. This implies that chemical reaction does not set in until high temperatures are reached, and

therefore, the chemical reaction has a low pre-exponential factor and a high activation energy. The pattern of diffusion at low temperatures and reaction at high temperatures has been seen for other alkali metal plus glass reactions.^{27,28}

We will follow the nomenclature used by Danckwerts²⁶ with some minor simplifications. The equation for diffusion and reaction in a condensed phase is

$$D \frac{d^2 a}{dx^2} = \frac{da}{dt} + ka \quad (13)$$

where D is the diffusivity of the gas in the condensed phase, a is the concentration of gas in the condensed phase, x is the distance from the surface, and k is the first-order chemical reaction rate constant. The boundary conditions are

$$a = A^*, \quad x = 0, \quad t < 0 \quad (14a)$$

$$a = 0, \quad x > 0, \quad t = 0 \quad (14b)$$

$$a = 0, \quad x = \infty, \quad t > 0 \quad (14c)$$

where A^* is the concentration of the gas right at the surface, given by Henry's law and assuming equilibrium with the partial pressure of gas present in the bulk gas phase. The solution to this equation with these boundary conditions is

$$Q = A^* \left(\frac{D}{k}\right)^{1/2} \left[\left(kt + \frac{1}{2}\right) \operatorname{erf} (kt)^{1/2} + \left(\frac{kt}{\pi}\right)^{1/2} e^{-kt} \right] \quad (15)$$

where Q is the integrated consumption of gas, in moles per square centimeter of surface, t is the time, and erf is the error function. The exact solution is plotted in dimensionless form in Fig. 14. For times shorter than those shown in the figure, the consumption is a function of the square root of time:

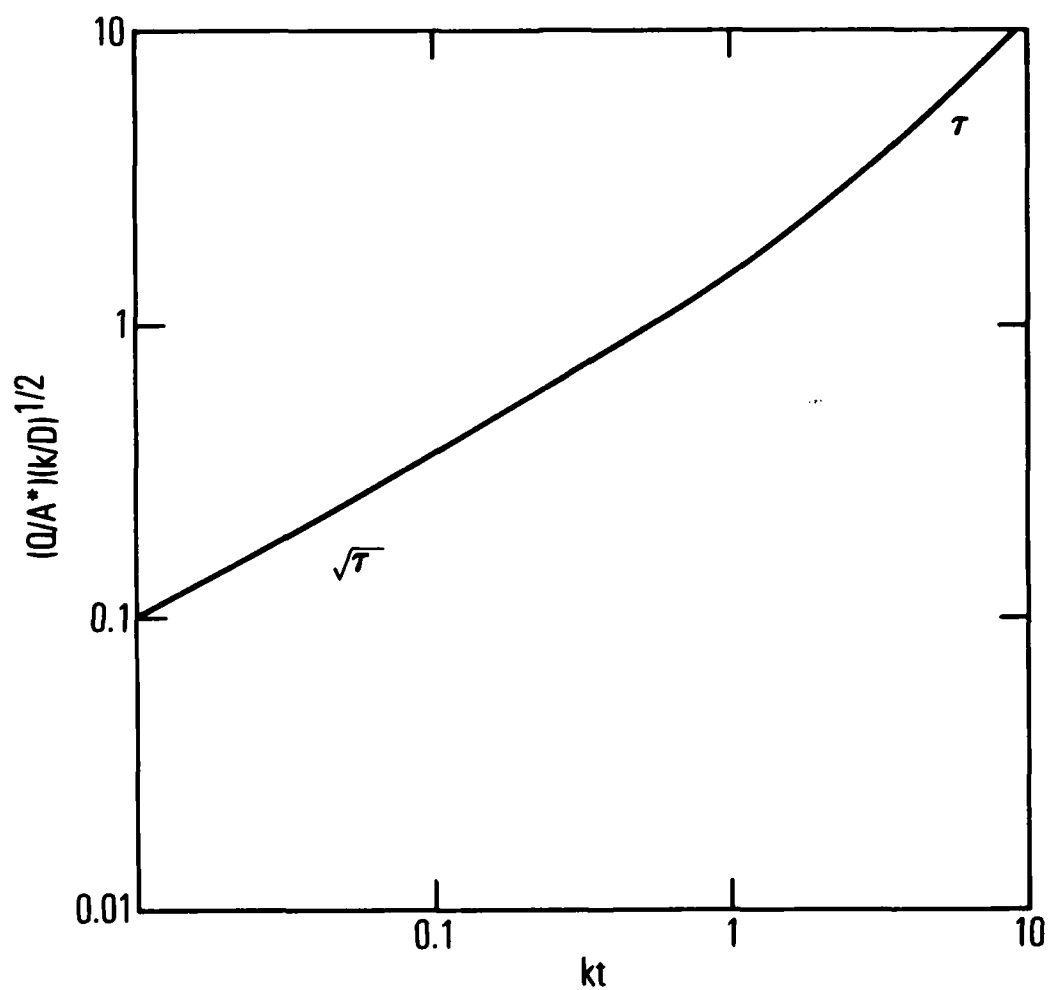


Figure 14. Solution of Eq. (13) is shown as a function of the dimensionless parameter kt . The time at which Rb consumption begins to be proportional to time depends on the strength of the reaction. This is not seen to occur for the Rb lamps studied under the normal operating conditions out to times approaching 10 yr.

$$Q = 2A^* \left(\frac{Dt}{\pi}\right)^{1/2}, \quad kt \ll 1 \quad (16)$$

For times longer than those shown in the figure, the consumption has a linear relation with time:

$$Q = A^* (Dk)^{1/2} t, \quad kt \gg 1 \quad (17)$$

All intermediate values must be read off the dimensionless figure. The two approximate solutions may be used for fitting experimental data, with the short time form approximating little chemical reaction and the long time form approximating rapid chemical reaction.

Three parameters are required by the theory: A^* , the concentration of dissolved gas at the surface; D , the diffusivity of gas in the condensed phase; and k , the first-order reaction rate constant.

For the value of A^* , we have found no direct measurements for Rb in the glass of interest, Corning 1720. In these experiments, the Rb vapor pressure is held more or less constant at 2×10^{-3} Torr, which is the equilibrium vapor pressure at 135°C. Our estimate for A^* is made by analogy with the solubility of Na vapor in glass, which is typically 2 wt% for glasses at 300 to 400°C in equilibrium with Na at that temperature.^{29,30} For a glass of density of 2.6 g/cm³, this corresponds to two moles (2 M) of Na metal per liter of glass. We have arbitrarily assigned the same molar concentration to Rb in our glass. Two moles per liter gives

$$A^* = 2 \times 10^{-3} \text{ M/cm}^3 \quad (18)$$

Clearly, the two systems are not the same. The only justification for this choice of A^* is that the 2 M figure seems to be constant for a wide range of conditions.

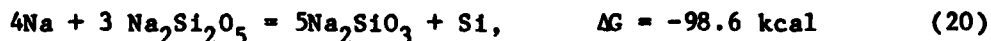
For the diffusivity, we use values obtained experimentally from the surface analyses, as described in Section II. For a liquid there is an inverse relationship between viscosity and diffusivity;²⁶ however, that relationship

was empirically found not to hold for this glass over the entire temperature range of interest. The failure of the empirically determined diffusivity to follow the viscosity shows that the glass-liquid analogy fails in at least this aspect, but this failure need not invalidate the model.

The chemical reaction rate is the most arbitrary of the three parameters. We have treated the rate constant and its temperature dependence as adjustable, and fit them to two points on the high-temperature end of the lamp lifetime data. High-temperature lamp lifetime data were obtained by operating lamps both at high temperature but with no rf discharge, and at high rf discharge powers. Lamps operated under high rf power were found to achieve high envelope temperatures as a result of rf heating effects. Lamp drive powers of 5 and 10 W resulted in lamp temperatures of 200 and 300°C, respectively. Because there was no way to separate rf and temperature effects in this model, we simply lumped all the data together, characterizing each lamp by some temperature. Although not entirely correct, it is not totally unreasonable to think that each lamp might have a characteristic temperature that would allow Rb consumption to be appropriately described by the combined effects on diffusion and reaction. The constant so obtained is

$$k = 1.6 \times 10^{13} \exp\left(\frac{-26,000}{T}\right) \text{ s}^{-1} \quad (19)$$

Alkali metals are not thermodynamically capable of reducing pure silica to give Si plus a metal oxide, but they are able to produce more alkaline glasses and Si:²⁸



Rb is very likely to exhibit this same kind of reaction, although the free energy change will probably be different. This kind of reaction may continue until 2.0 wt% metal has been absorbed. Thus, the reactivity exceeds the solubility—a feature required by the solutions to the theory. The exact nature of the reaction and its thermodynamics are not required by the theory, however.

In Fig. 15 the actual lamp lifetimes as a function of temperature are given. The solid curve is the exact solution to the theory when employing the parameters chosen in the previous section. A lamp lifetime is defined for this analysis as the time required for a lamp to consume 400 μg of Rb, and in many cases, this was determined by extrapolation. Using the internal surface area of an Efratom lamp we find that this lifetime corresponds to

$$Q = 1.18 \times 10^{-16} \text{ M/cm}^2 \quad (21)$$

Although the data shown in Fig. 15 have a good deal of scatter about the fit line, we believe that the qualitative agreement between the data and the model is quite good. The scatter is due at least in part to the uncertainties in the temperature measurements and a possible inhomogeneity of the lamp envelope temperature. Figure 15 indicates that the reaction process between the Rb and the glass starts to become important above 200°C. To properly accelerate the life of the discharge lamp, i.e., increase the rate of Rb consumption without changing the primary consumption mechanism, lamps' temperatures must remain below 200°C. Referring to Fig. 15 one can see that the model predicts a maximum lamp life compression of about a factor of 2 for a temperature limit of 200°C. A factor of 2 is certainly not adequate, especially when lamp lifetimes of many years are desired. It is doubtful that even with an improved model the conclusion that lamp life acceleration is severely restricted would be altered.

Despite the fact that a lamp life acceleration technique does not appear to be feasible, it should be possible using the DSC technique to verify the quality of a lamp and ensure its reliability. In all cases, with the possible exception of the Schott 8437 glass lamps, Rb consumption was found to obey relation (6):

$$M_{\text{Rb}}(t) = R\sqrt{t} + B$$

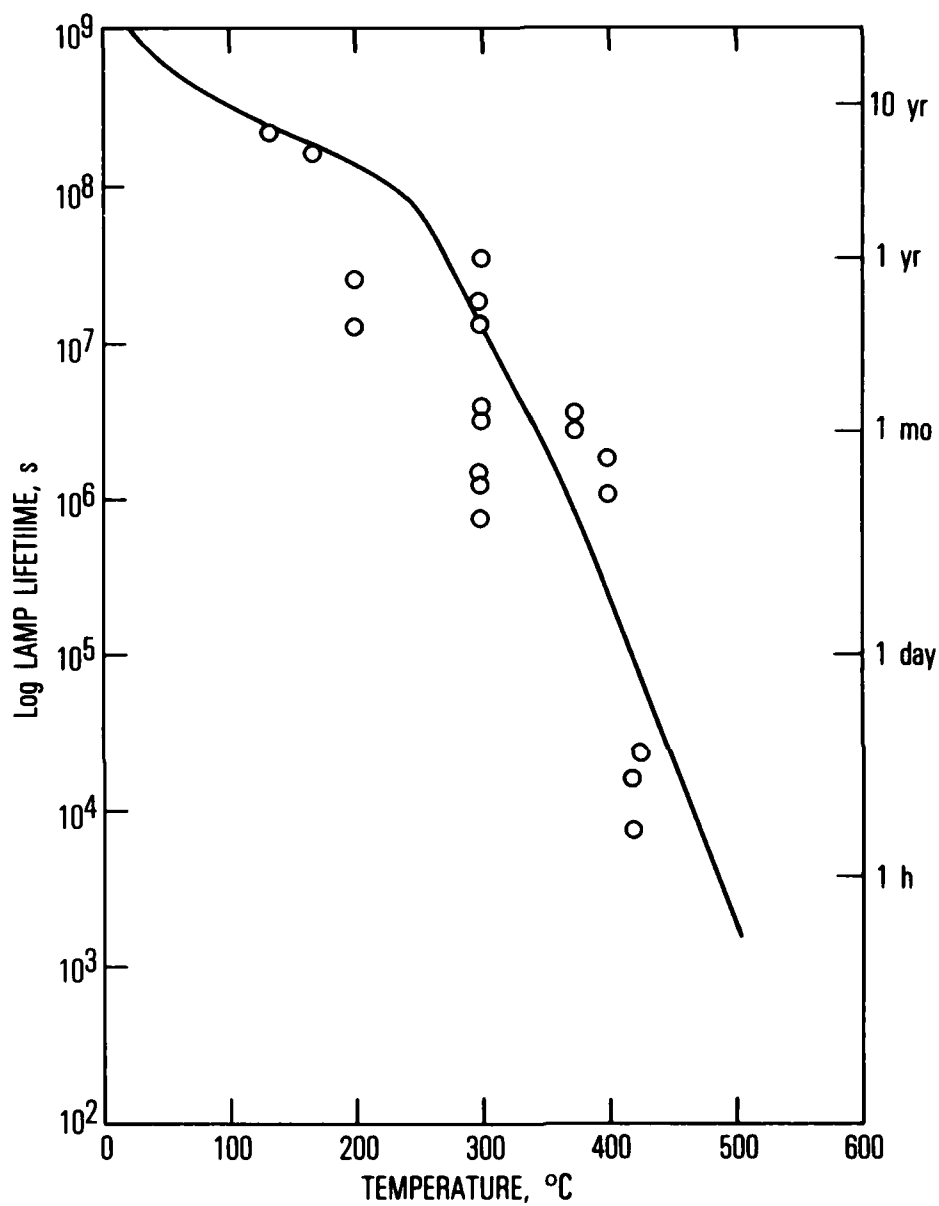


Figure 15. Extrapolated Rb lamp lifetime versus lamp temperature for lamps of the Efratom design constructed out of Corning 1720 glass. Rb lamp lifetime here is arbitrarily defined to be the time it takes a lamp to consume 400 μ g. Solid line is model prediction based on some adjustable parameters. Above 200°C the Rb consumption process is seen to change from diffusion to reaction. This change severely limits the degree to which lamp failure may be accelerated.

The factor R is dependent on the particular lamp conditions. Once this factor is established it can be used as a guide to judge the quality of all subsequently manufactured lamps. Specifically, one can measure Rb consumption in a lamp over its first 1000 h (~ one month) and uniquely determine its consumption law, i.e., the factors R and B can be found for a particular lamp. Comparing the consumption law obtained for a specific lamp with the general consumption law obtained in a more extensive study of lamps under the particular operating conditions will allow one to determine whether that particular lamp is behaving normally or had been subject to any processing anomalies. Because lamp failure is due primarily to the deterministic, predictable phenomenon of diffusion of Rb into the glass walls of the lamp and is not statistical in nature, it is sufficient to know that a particular lamp has been properly manufactured to predict its lifetime, once the general law for Rb consumption for that type of lamp has been determined. The screening of a rubidium lamp therefore involves (1) visual inspection for dimensional tolerances and processing defects, (2) measurement of Rb fill for compliance with limits set with regard to life and noise, and (3) burn-in with calorimetric determination of Rb consumption. Experience has shown that defective lamps have either (1) obvious defects, (2) improper fill, or (3) rapid Rb consumption (not necessarily obeying the $\sqrt{t}$ law). An accelerated life test would be useful to establish lamp consumption laws under different conditions in a minimum amount of time, but an accelerated test is not required to ensure reliable lamp operation under previously tested conditions.

VI. SUMMARY

Extensive studies have been conducted on the reliability of the Rb discharge lamp under a limited set of different operating conditions. Under conditions in which this lamp is typically used, the primary life-limiting process was identified to be the diffusion of the Rb atoms into the glass envelope. Because the diffusion of Rb into the glass is completely deterministic, the lamp lifetime can be specified in principle by knowing the initial Rb content and the lamp operating conditions. The reliability of a particular lamp can be ensured by using the DSC technique to identify the presence of any anomalies in the rate of Rb consumption for a particular lamp. With adequate manufacturing procedure and careful initial lamp testing, lamp lifetimes in excess of ten years can easily be guaranteed. This type of reliability makes these lamps well suited for use in Rb atomic frequency standards designed for use in satellite applications.

REFERENCES

1. W. E. Bell, A. L. Bloom and J. Lynch, "Alkali Metal Discharge Lamps," *Rev. Sci. Instrum.* 32, 688 (1961).
2. R. G. Brewer, "High Intensity Low Noise Rubidium Light Source," *Rev. Sci. Instrum.* 32, 1356 (1961).
3. H. Fukuyo, K. Iga, N. Kuramochi and H. Tanigawa, "Temperature Dependence of Hyperfine Spectrum of Rb D₁ Line," *Jpn. J. Appl. Phys.* 9, 729 (1970).
4. H. Fukuyo, K. Iga and N. Kuramochi, "Spectral Characteristics of Rb⁸⁷ Lamps Containing Different Carrier Gases," *Bull. Tokyo Inst. Technol.* 113, 67 (1972).
5. H. Oyamada, K. Takahashi, Y. Sato and H. Uchida, "A Consideration of Rubidium Lamp Stability for Rubidium Frequency Standard," *Proceedings, 28th Annual Symposium on Frequency Control, US Army Electronics Command, Fort Monmouth, NJ*, pp. 340-343 (1974). Copies available from Electronic Industries Association, 2001 Eye Street, NW, Washington, DC 20006.
6. T. Tako, Y. Koga and I. Hirano, "Spectral Profiles of Rb-D Lines," *Jpn. J. Appl. Phys.* 14, 591 (1975).
7. N. Kuramochi, H. Fukuyo, I. Matsuda and N. Shiomi, "Spectral Profiles of the Rb Light Source," *Jpn. J. Appl. Phys.* 15, 949 (1976).
8. D. M. Tennant, "NAVSTAR Global Positioning System (GPS) Clock Program: Present and Future," *Proceeding of the 12th Annual Precise Time and Time Interval (PTTI) Applications and Planning Meeting, Dec. 2-4, 1980, Greenbelt, MD, NASA Conference Publication 2175*, pp. 703-718.
9. T. C. English and E. Jechart, "Development of A Sapphire Lamp for Use in Satellite-Borne Atomic Rubidium Clocks," *Proceedings, 35th Annual Symposium on Frequency Control, US Army Electronics Command, Ft. Monmouth, NJ*, pp. 637-645 (1981). Copies available from Electronic Industries Association, 2001 Eye Street, NW, Washington, DC 20006.
10. R. P. Frueholz, M. Wun-Fogle, H. U. Eckert, C. H. Volk and P. F. Jones, "Lamp Reliability Studies for Improved Satellite Rubidium Frequency Standard," *Proceedings of the 13th Annual Precise Time and Time Interval (PTTI) Applications and Planning Meeting, Dec. 1-3, 1981, Washington, DC, NASA Conference Publication 2220*, pp. 767-788.
11. J. Crank, The Mathematics of Diffusion, Oxford University Press, London (1957), Chapter 8.

12. Kirk-Othmer Encyclopedia of Chemical Technology, V. 11, M. Grayson, ed., John Wiley and Sons, Inc., New York (1980), p. 826.
13. R. H. Doremus, "Diffusion in Non-Crystalline Silicates," in Modern Aspects of the Vitreous States, J. D. MacKenzie, ed., Butterworth Inc., Washington, DC (1962), Vol. 2, pp. 1-77.
14. H. U. Eckert, An Analytical Model for RF Inductive Glow Discharge Columns in Metal-Gas Mixtures and Application to the Rb-Xe System, TR-0082(2472-06)-1, The Aerospace Corporation, El Segundo, CA (12 July 1982).
15. T. Lynch of EG&G, Electronic Components Division conceived the original idea that calorimetry might be applied to measuring Rb in discharge lamps and made the first such measurements.
16. T. J. Lynch and W. J. Riley, "Test Results for Prototype GPS Rubidium Clock," Proceedings of the 15th Annual Precise Time and Time Interval (PTTI) Applications and Planning Meeting, Dec. 6-8, 1983, Washington, DC (1984).
17. The consumption measurements at Aerospace were performed with a Perkin-Elmer DSC-1b; those at EG&G were done with a Perkin-Elmer DSC-2c.
18. It is possible that a change in the diffusion coefficient of a glass could occur during the lamp processing. We think that this is unlikely, but must be considered since it cannot be disproven at the present time.
19. E. Jechart, Gas Cell Atomic Frequency Standard Having Selected Alkali Vapor Isotopes, U. S. Patent No. 3903481, September 2, 1975.
20. P. J. Elving, J. D. Winefordner and I. M. Kolthoff, ed., Analytical Laser Spectroscopy, John Wiley and Sons, New York (1979), pp. 518-520.
21. Private communication from R. P. Frueholz, M. Wun-Fogle and C. H. Volk, The Aerospace Corporation, 1982.
22. Private communication from L. E. Kovar, Technical Director, General Activation Analysis, Inc. to R. P. Frueholz, 1982.
23. Private communication from M. Wun-Fogle and R. A. Cook, The Aerospace Corporation, 1982.
24. G. H. Frischat, U. Eichlorn, R. Kirchmeyer and H. Salge, "Alkaliionenaustausch an Silicatglasern," Glastech. Ber. 47, 107 (1974).
25. This section is based primarily on the work of Dr. L. R. Martin of The Aerospace Corporation.
26. P. V. Danckwerts, Gas-Liquid Reactions, McGraw-Hill, New York (1970).

27. J. Lau and P. W. McMillan, "Interaction of sodium with simple glasses," J. Mater. Sci. 17, 2715 (1982).
28. C. A. Elyard and H. Rawson, "The resistance of glasses of simple composition to attack by sodium vapor at elevated temperatures," Advances in Glass Technology, Plenum Press, New York (1962), pp. 270-286.
29. C. J. Brinker and L. C. Klein, "Behavior of silicate and borosilicate glasses in contact with metallic sodium. Part 1. Sodium silicate glasses," Phys. Chem. Glasses 21, 141 (1980).
30. C. J. Brinker and L. C. Klein, "Behavior of silicate and borosilicate glasses in contact with metallic sodium. Part 2. Borosilicate glasses," Phys. Chem. Glasses 22, 23 (1981).

LABORATORY OPERATIONS

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military space systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

Aerophysics Laboratory: Launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion, propellant chemistry, environmental hazards, trace detection; spacecraft structural mechanics, contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; cw and pulsed laser development including chemical kinetics, spectroscopy, optical resonators, beam control, atmospheric propagation, laser effects and countermeasures.

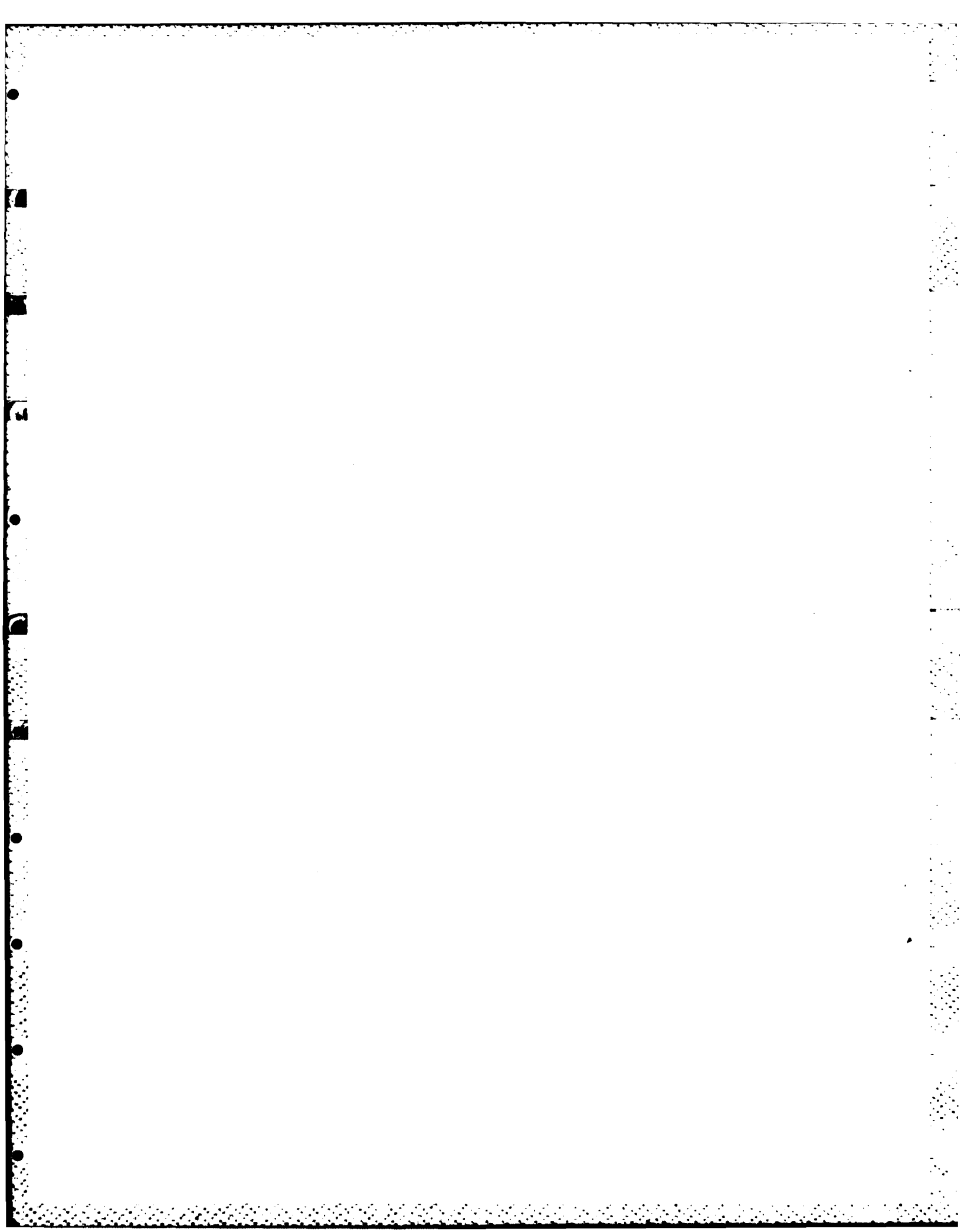
Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiation transport in rocket plumes, applied laser spectroscopy, laser chemistry, laser optoelectronics, solar cell physics, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photosensitive materials and detectors, atomic frequency standards, and environmental chemistry.

Electronics Research Laboratory: Microelectronics, GaAs low noise and power devices, semiconductor lasers, electromagnetic and optical propagation phenomena, quantum electronics, laser communications, lidar, and electro-optics; communication sciences, applied electronics, semiconductor crystal and device physics, radiometric imaging; millimeter wave, microwave technology, and RF systems research.

Information Sciences Research Office: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence and microelectronics applications.

Materials Sciences Laboratory: Development of new materials: metal matrix composites, polymers, and new forms of carbon; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures as well as in space and enemy-induced environments.

Space Sciences Laboratory: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation.



END

FILMED

4-85

DTIC