AD-762 430

# URANIUM-OXYGEN RADIATION STUDIES

Walter H. Wurster

Calspan Corporation

Prepared for:

Defense Nuclear Agency
Advanced Research Projects Agency

April 1973

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

AD 762430

DNA 3046Z
Calspan No. WB-5117-A-2
April 1973

# URANIUM-OXYGEN RADIATION STUDIES
# INTERIM REPORT

WALTER H. WURSTER

Sponsored by:
DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
ARLINGTON, VA. 22209

Monitored by:
DEFENSE NUCLEAR AGENCY
WASHINGTON, D.C. 20305

CALSPAN CORPORATION
BUFFALO, N.Y. 14221
CONTRACT NO. DNA001-72-C-0098
ARPA ORDER NO. 1433
TASK NO. ZL 433
WORK UNIT NO. 09

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

DDC
RECEIVED
JUN 28 1973
D

APPROVED FOR PUBLIC
RELEASE; DISTRIBUTION UNLIMITED

22

UNCLASSIFIED
Security Classification

## DOCUMENT CONTROL DATA – R & D

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

1. ORIGINATING ACTIVITY *(Corporate author)*
Calspan Corporation
P. O. Box 235
Buffalo, New York 14221

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE
URANIUM-OXYGEN RADIATION STUDIES

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Interim Report

5. AUTHOR(S) *(First name, middle initial, last name)*
Walter H. Wurster

6. REPORT DATE
April 1973

7a. TOTAL NO. OF PAGES
15

7b. NO. OF REFS
6

8a. CONTRACT OR GRANT NO.
DNA 001-72-C-0098

b. PROJECT NO.
ARPA Order 1433
c. Task No. E50

d. Work Unit No. 09

9a. ORIGINATOR'S REPORT NUMBER(S)
WB-5117-A-2

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
DNA 3046Z

10. DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES
*

12. SPONSORING MILITARY ACTIVITY
Defense Advanced Research Projects Agency, monitored by Defense Nuclear Agency

13. ABSTRACT

This report is the second Semi-Annual Technical Report on a research program whose objectives are to measure absolute spectral radiances from uranium-oxygen mixtures. The measurements are made under controlled conditions of temperature and species concentrations, and include infrared data between 8 and 14 μm. The final objective of the program is to provide a sufficiently broad data base to permit the specification of equilibrium radiation from uranium oxides for the conditions of interest to ARPA objectives. To date, the first task of the research effort has been addressed, namely, an assessment of the applicability of the exploding-wire-aerosol shock tube technique to the problem. Aerosol distribution and vaporization times have been measured. Successful IR measurements (12-14 μm) of a $U-O_2$ test mixture have been made. The use of $UF_6$ as a means to calibrate uranium concentrations in the shock tube was extensively tested and found inapplicable. A shock tube modification for more uniform aerosol distribution has been incorporated and will be tested shortly. In addition, the IWIR radiometer has been upgraded for increased sensitivity. Further testing involves measurements with varying wavelengths and bandpasses over a range of temperatures and $U/O_2$ ratios.

DD FORM 1 NOV 65 1473

*Items 9a, 10, 11 to be completed by sponsor

UNCLASSIFIED
Security Classification

Security Classification

| 14 KEY WORDS | LINK A ROLE | LINK A WT | LINK B ROLE | LINK B WT | LINK C ROLE | LINK C WT |
|---|---|---|---|---|---|---|
| Metal Oxides | | | | | | |
| uranium | | | | | | |
| infrared | | | | | | |
| quantitative spectra | | | | | | |
| equilibrium radiation | | | | | | |
| high temperature | | | | | | |

Security Classification

DNA 3046Z
Calspan No. WB-5117-A-2
April 1973

**Calspan**

On November 17, 1972 Cornell Aeronautical Laboratory (CAL) changed its name to Calspan Corporation and converted to for-profit operations. Calspan is dedicated to carrying on CAL's long-standing tradition of advanced research and development from an independent viewpoint. All of CAL's diverse scientific and engineering programs for government and industry are being continued in the aerosciences, electronics and avionics, computer sciences, transportation and vehicle research, and the environmental sciences. Calspan is composed of the same staff, management, and facilities as CAL, which operated since 1946 under federal income tax exemption.

# *URANIUM-OXYGEN RADIATION STUDIES*
# *INTERIM REPORT*

This work was supported by the Defense
Nuclear Agency under subtask ARPA ZL433-09

Walter H. Wurster

Calspan Report No. WB-5117-A-2

Sponsored by:
DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
ARPA ORDER NO. 1433
TASK NO. ZL 433
WORK UNIT NO. 09
Monitored by:
DEFENSE NUCLEAR AGENCY

April 1973
CONTRACT NO. DNA001-72-C-0098

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

Calspan Corporation
Buffalo, New York 14221

## ABSTRACT

This report is the second Semi-Annual Technical Report on a research program whose objectives are to measure absolute spectral radiances from uranium-oxygen mixtures. The measurements are made under controlled conditions of temperature and species concentrations, and include infrared data between 8 and 14 $\mu$m. The final objective of the program is to provide a sufficiently broad data base to permit the specification of equilibrium radiation from uranium oxides for the conditions of interest to ARPA objectives. To date, the first task of the research effort has been addressed, namely, an assessment of the applicability of the exploding-wire-aerosol shock tube technique to the problem. Aerosol distribution and vaporization times have been measured. Successful IR measurements (12-14$\mu$m) of a U-$O_2$ test mixture have been made. The use of $UF_6$ as a means to calibrate uranium concentrations in the shock tube was extensively tested and found inapplicable. A shock tube modification for more uniform aerosol distribution has been incorporated and will be tested shortly. In addition, the LWIR radiometer has been upgraded for increased sensitivity. Further testing involves measurements with varying wavelengths and bandpasses over a range of temperatures and U/$O_2$ ratios.

## FOREWORD

This is the second Semi-Annual Technical Report on Contract DNA-001-72-C-0098 and covers the period 16 July 1972 through 15 January 1973. The work is sponsored by the Advanced Research Projects Agency and monitored by The Defense Nuclear Agency. Dr. Charles Blank is the Contract Officer.

Principal contributors to the effort reported herein were Dr. C. E. Treanor and W. H. Wurster of the Aerodynamic Research Department at Calspan.

TABLE OF CONTENTS


| | Page |
|---|---|
| TECHNICAL SUMMARY . . . . . | 1 |
| DISCUSSION OF THE EXPERIMENTAL METHOD . . . . | 4 |
| RESULTS AND DISCUSSION . . . . . | 8 |
| REFERENCES CITED . . . . . | 11 |
| FIGURES . . . . . | 12 |

## TECHNICAL SUMMARY

This report is the second Semi-Annual Technical Report on a research program whose objectives are to measure absolute spectral radiances from uranium-oxygen mixtures. The measurements are made under controlled conditions of temperature and species concentrations, and include infrared data between 8 and 14 μm.

The initial program was undertaken to assess and demonstrate the applicability of the Calspan exploding-wire-aerosol shock tube facility toward obtaining the required data. Recently the contract was amended to extend the period of performance to April 1973, to complete these radiation studies. This Semi-Annual Technical Report is presented from the overall point of view of the contract as it is presently structured. As such, this technical summary very briefly reviews the overall problem, the method of attack, and the present status. Details are contained in the subsequent body of this report.

The general problem of metal oxide radiation under various environmental conditions depends upon two items: the gasdynamic and thermodynamic conditions that prevail, which, coupled to the kinetics, determines the various oxide concentrations and degree of excitation; secondly, given the aforementioned information, additional data are needed to specify the absorptive and radiative behavior of these oxide molecules. It is the latter question to which the present studies are addressed.

The experimental plan is to produce an aerosol of uranium in a controlled mixture of oxygen and inert gas such as argon. This aerosol is shock heated, thereby vaporizing the metal particles, and providing a gaseous mixture of U, $O_2$ and argon at high, equilibrium temperatures. The final data comprise absolutely measured spectral radiances over wavelength regions of interest. The parameters of the experiment are the temperature, relative $U/O_2$ ratios and wavelength range and resolution. Details of the

technique are given later in the report, as well as evidence for the very clean spectra that result. This is an important feature of the technique, because quantitative radiometric measurements only have meaning if it has been separately shown that the radiating species have been identified.

To date, most of the effort has been directed toward the initial phase of work - assessment and validation of aerosol-shock tube technique. The vaporization time has been measured, and found to be satisfactorily short, compared to total test time duration. This will permit quantitative spectral data to be taken on purely gaseous $U/O_2$ systems.

In addition, I R radiation has been successfully recorded. A radiometer with a 12 - 14 μm bandpass filter was used to obtain radiance data from the shock-heated test gas. It was shown that the radiance required the presence of $O_2$ in the test gas, providing an initial corroboration that the molecular oxide is radiating in that I R wavelength window.

Finally, the distribution of the aerosol in the shock tube was measured, and found to be non-uniform. Although this feature is not critical in the experiment, a uniform distribution is desirable. Present effort is being addressed to this problem, which was successfully treated in early work with aluminum aerosols.

A supporting theoretical effort has also been underway during this reporting period. This effort involves the use of best available data to provide thermodynamic functions of uranium atoms and oxide molecules. These functions are used to calculate the relevant species concentrations for the thermodynamic conditions generated in the shock tube. They are especially useful in providing scaling parameter checks for proper identification of radiating species in the test gas.

The major portion of the effort during this reporting period was directed toward:

a) the problem of quantitative measurement of the uranium concentration in the shock tube,

b) the production and measurement of uniform aerosol concentrations in the shock tube,

c) the continued experiments to determine optional operating parameters of temperature, and relative concentrations of uranium and oxygen and

d) upgrading the sensitivity of the radiometer used for the LWIR (8-14 $\mu$ m) measurements.

For reference and completeness, a discussion of the experimental method and a brief description of the apparatus is presented. The balance of the report discusses the results of the past reporting period and the present status. A no-cost time extension through April 1973 has been obtained to complete the research, with the draft of the final report due 15 May 1973.

## DISCUSSION OF THE EXPERIMENTAL METHOD

Several methods have been reported[2] which address the problem of obtaining metals and metal oxides in gaseous mixtures for spectroscopic studies. They include ground metal slurrys on substrates, the use of metal-organic compounds, and particulate dust injection. For spectroscopic studies, it can be appreciated that the use of any substances other than the pure metal of interest results in overlapping, contaminated spectra which can seriously compromise the subsequent analyses. This is especially true for IR measurements, where the use of photographed spectra is precluded, and the identification and ssubtraction of radiating species in contaminated spectra is rendered prohibitively difficult.

The method developed at Calspan, which is described in the following section, has been shown to produce very clean spectra[3]. In aluminum, as will be shown later, the spectra contain only atomic Al resonance lines and the blue-green band system of AlO. No hydrocarbon species were present, the usual Na and Ca lines were the only background radiators. This early work with Al was initially performed for ARPA under Project Defender. Subsequent studies to complete the development of the technique were carried out under Calspan Internal Research funding. As discussed in the following section, these studies have put the technique on a sound basis, and it can be applied directly to the present research problem.

The overall experimental method takes advantage of the use of shock tubes to produce sources of gas at high equilibrium temperatures. Essentially, the method consists of exploding a wire of suitable material in a controlled atmosphere, thereby producing a metallic smoke, or aerosol, containing the particular species under study. The resultant aerosol is permitted to expand into the vacuum of the driven section of a shock tube, and is subsequently subjected to shock heating. The end result is the complete vaporization of the aerosol particles, and the formation of the molecular species of interest in the thermodynamic equilibrium.

The range of temperatures attainable in these experiments is a

significant feature of the technique, because the temperature dependence of the species concentrations and their excited state populations serve as a valuable diagnostic for identification. Beginning with an aerosol containing U, O and Ar, at very high equilibrium temperatures (~6,000°K), one would expect predominantly neutral and ionized atomic species. As the temperature is decreased in similar tests using weaker shock waves, the molecular oxide concentrations would increase. Thus the metal oxide band radiation will go through a maximum, limited on the low temperature side by the Boltzmann factor in excited state population, and on the high side by molecular dissociation.

For normal gases the concentration of radiating particles is known, and the emitted intensity per particle, or the optical transition probability, can be obtained from quantitative spectral measurements. In the extension of such studies to gases containing normally solid materials, it will be seen that emitter concentrations become a critical parameter. While the partial pressures of gases introduced into the shock tube test section can be accurately determined, there is no a priori way of assessing the quantity of metallic aerosol. Thus, the resultant molecular oxide emitter concentrations must be obtained by separate but simultaneous measurements on the same gas sample. This can be accomplished by quantitative spectroscopic analysis on lines of the parent atom, for which the transition probabilities are known. Thus, by knowing the temperature of the mixture and the atomic concentrations of the metal, the oxide concentration is obtained by calculation, using the equilibrium constant. The final result for the metal oxide transition probability therefore depends on the atomic line f-numbers and the appropriate thermochemical constants for the metal-oxygen system.

In aluminum oxide studies this concentration measurement technique is quite straightforward. Published f-numbers for the resonance doublets of Al are available together with several determinations of the transition probabilities for the AlO ($B^2\Sigma - X^2\Sigma$) bands. However, the relevant data for the U-$O_2$ system is much sparser and more poorly known. This applies both to thermochemical data, as well as the radiative behavior of the uranium oxides.

Indeed, evidence for the identification and existence of UO bands in the IR is currently the subject of research by two groups of workers.[4,5] The point to be made here is that the analysis of the spectroscopic data of these experiments will need to rely upon best available data, which are still in a state of flux. This point is addressed further in a later section in this report.

Apparatus

The experimental apparatus developed at Calspan has been described in detail in Reference 3. A typical experiment is shown diagrammatically in Figure 1. The essential features are a fully instrumented, stainless-steel shock tube and the aerosol generator. The latter is a small chamber in which test gases can be mixed. It also contains electrodes between which suitable wires are exploded by capacitance discharge, thereby forming the aerosol test gas. The shock tube test section is equipped with a number of sapphire observation windows for coupling to a wide variety of spectral instrumentation. To date, photographic and radiometric data have been taken. Typical spectra from earlier studies can be seen in Figure 2. Laser absorption techniques have been used as diagnostics for aerosol size and distribution measurements, and separate measurements of aerosol vaporization times have been made. Band reversal techniques have also been employed in a program to study population inversions in metal oxide energy levels.

For the U-$O_2$ experiments reported herein, the following details apply. The depleted uranium was obtained in the form of .006 inch sheets, and was sheared to .040 inch strips. The electrode spacing is approximately 0.75 inch. It was found that considerably more energy was required to explode this foil strip than for the Al wire used in earlier experiments. Presently, 3200 joules are used at 10KV. According to Reference 6, this produces an aerosol of sub-micron size, which permits rapid vaporization in the shock tube. The foil strip is exploded in a pre-mixed atmosphere of argon with controlled amounts of oxygen, after which it is expanded into the vacuum of the shock tube test section. Typical initial pressures in the tube range from 25 to 100 torr. Figure 3 shows some early results in U-$O_2$ mixtures. These results have been discussed in Reference 1.

In addition to the spectrograph and the monitoring photodiode ($0.8 < \lambda < 1.1 \mu m$) shown in Figure 1, specific instrumentation was added for these studies. A radiometer for far IR measurements was used to record radiation between 8-14 μm. The radiometer comprised a Hg-Cd-Te detector operated at 80°K, together with a 12-14 μm bandpass filter. It was coupled to the shock tube by means of an Irtran II window. Provision was made for absolute calibration with a standard blackbody source, although to date most measurements have been exploratory and qualitative.

For measuring the aerosol distribution in the shock tube, four windows were installed along the length of the tube. This was conveniently done by replacing every other wave speed detector shown in Figure 1 with a window mount. This arrangement provided two foot spacing of speed detectors and windows along the 12 foot test section of the tube. By using a single photomultiplier tube detector about 10 feet from the shock tube, the test gas radiance behind the incident shock tube could be recorded as the shock wave (and the test gas volume) moved past each window along the shock tube.

Results of measurements made with these diagnostic instruments have been presented in Reference 1 and are continued in the next section of this report.

## RESULTS AND DISCUSSION

It has already been shown[1] that the exploding-wire aerosol shock-tube technique was adaptable to the spectroscopic study of radiation from $U/O_2$ mixtures. The vaporization time as measured by LWIR (12-14 m) radiation was shown to be less than 50 μS, well within the equilibrium test time in the shock tube. Further it was shown that the presence of $O_2$ produced a steady radiance in this wavelength region, demonstrating that the emitting species is likely a uranium oxide.

Before continuing the balance of the measurements, it was decided to address two components of the experiments, namely, the use of gaseous $UF_6$ as a uranium concentration calibration technique, and secondly, the production and measurement of more uniform aerosol distribution in the shock tube. The former task was more rigorously pursued; it is necessary to the final data analysis. The second item is not critical, but would be experimentally and analytically convenient.

It was planned to use shock-heated $UF_6$ to produce U and/or $U^+$ lines over a range of concentrations and temperatures. Curves of growth of suitable lines from a heated, completely equilibrated sample of $UF_6$ would permit the quantitative assessment of U in the subsequent experiments with the aerosol. Use of $UF_6$ directly to obtain LWIR radiance is precluded because of the complications and contamination of the spectra. For spectra in the visible, any interference could be photographed and avoided. This does not apply to the inherently lower-resolution and non-photographable LWIR. Indeed, as has been demonstrated, the chief advantage of the pure-metal aerosol technique lies in the purity of the resultant spectra (Figure 2).

The experience with $UF_6$ proved unsuccessful on several counts. Primarily, no atomic lines were ever obtained in any of the spectra. The extensive number of shock tube experiments were conducted over a range of temperatures from 4500 to 9500°K, and with $UF_6/A$ concentrations of 1 and 2%. The wavelengths of the photographed spectra extended from 2400-8000A. Only a smooth continuum was recorded. It begins at 2500-2700A and extends into the infrared. Further tests or attempts at the identifications

of the continuum were abandoned, since the objectives of the $UF_6$ tests were not to be met.

Use of this fluorine compound proved to be quite injurious to the overall apparatus. Some of the tubing in the aerosol loading system had to be replaced; the heat transfer gauges, used successfully for shock wave velocity measurements for years without replacement, were chemically attacked and rendered inoperative; in addition, the shock tube windows were discolored and required repolishing.

During the process of refurbishing the system, a modification was also incorporated to produce a more uniform aerosol distribution in the shock tube. It consists primarily of an added volume at the end of the shock tube, into which the aerosol-laden gas can expand during the charging of the tube. After this expansion, a gate valve closes off this volume. The gate then actually constitutes the end of the shock tube where the shock wave reflects. Based on past experience, this technique should produce a more uniform aerosol distribution.

Testing with this system will be performed during the next quarter, using the method described earlier in this report. For convenience, Al aerosols will be used initially, and then the work with U will be pursued.

A study has been underway to evaluate alternate methods for U concentrations to be measured, so that the $U/O_2$ mixture radiances can be quantified. It is most desirable to measure these parameters simultaneously in the shock-heated, equilibrium gas-phase mixture. Thus, methods involving separate experiments with aerosol settling and subsequent counting (radioactivity) or weighing are presently considered least desirable. The use of available U or U+ lines in the shock-heated mixtures seems presently the most attractive technique. The latest transition probability data on known lines are being sought from NBS. This method was not originally chosen, since the overall shock-tube operating regime in concentration, temperature and pressure becomes more restricted when compatible atomic line and molecular band radiances are simultaneously to be measured. The technique of using the

cooler incident shock to produce the molecular band radiation, and the hotter reflected shock (on the same test) to produce the corresponding atomic lines requires a known or measured aerosol distribution along the tube. The forthcoming distribution tests discussed earlier will be useful in determining the feasibility of this approach.

Finally, the LWIR radiometer was upgraded for increased sensitivity during the past quarter. The instrument now utilizes a 1.5-inch diameter germanium lens to permit imaging the Hg:Cd:Te detector directly into the Irtran shock tube window. Various filters will be used between 8-14 $\mu$m to measure the radiance from the uranium-oxygen mixtures when testing is resumed.

## REFERENCES CITED


1. W. H. Wurster, Semi-Annual Technical Report: "Uranium-Oxygen Radiation Studies," CAL Report No. WB-5117-A-1, 1972.

2. R. W. Nicholls, W. H. Parkinson, and E. M. Reeves, Appl. Optics, 2, 919 (1963)

   R. Watson, A. L. Morsell, and W. J. Hooker, Rev. Sci. Instr., 38, 1052 (1967)

3. T. J. Falk, J. Chem, Phys., 48, 3305 (1968)

4. S. Ambromowitz, N. Acquista, and K. R. Thompson, J. Phys, Chem. 75, 2283 (1971)

5. S. D. Gabelnick, G. T. Reedy and M. G. Chasanov (Private Communication)

6. F. G. Karioris, B. R. Fish and G. W. Royster, Jr., Aerosols from Exploding Wires, pg. 299 in Exploding Wires, Vol, 2, edited by W. Chase and H. Moore, Plenum Press, New York, 1962.

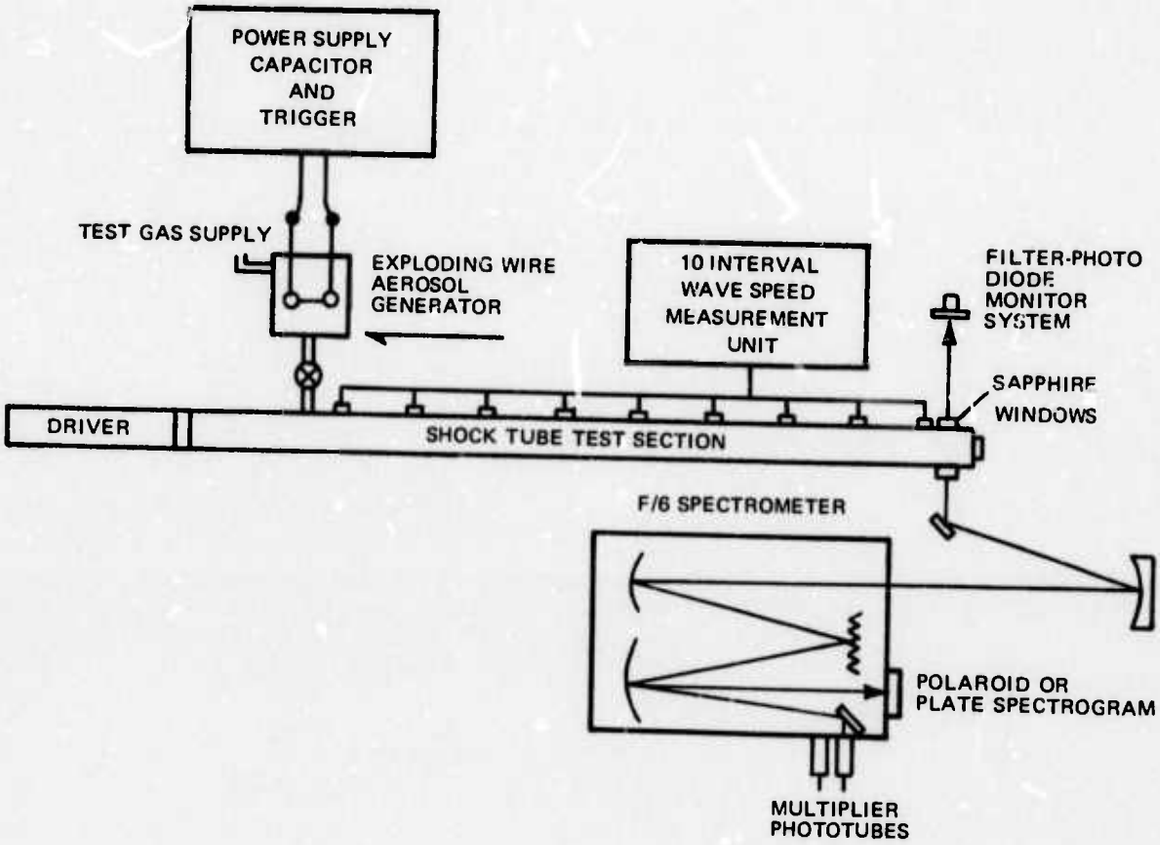
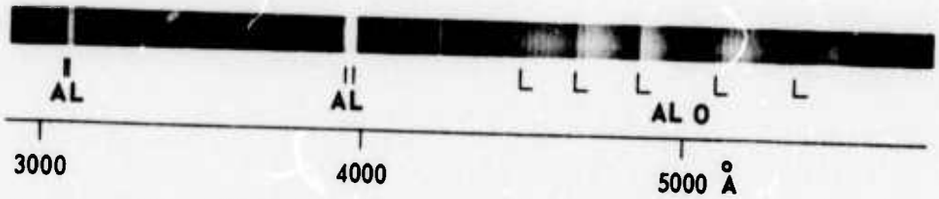



Figure 1 SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS FOR THE MEASUREMENT OF METAL OXIDE SPECTRA. (INSTRUMENTATION SPECIFIC TO THE URANIUM-OXYGEN STUDIES IS DESCRIBED IN THE TEXT.)




AEROSOL CHAMBER – P = 11 PSIA, 5% $O_2$ - 95% ARGON

AL WIRE, 0.125 MM DIAM, 2.54 CM LENGTH

C = 1$\mu$ F, V = 6000 VOLTS

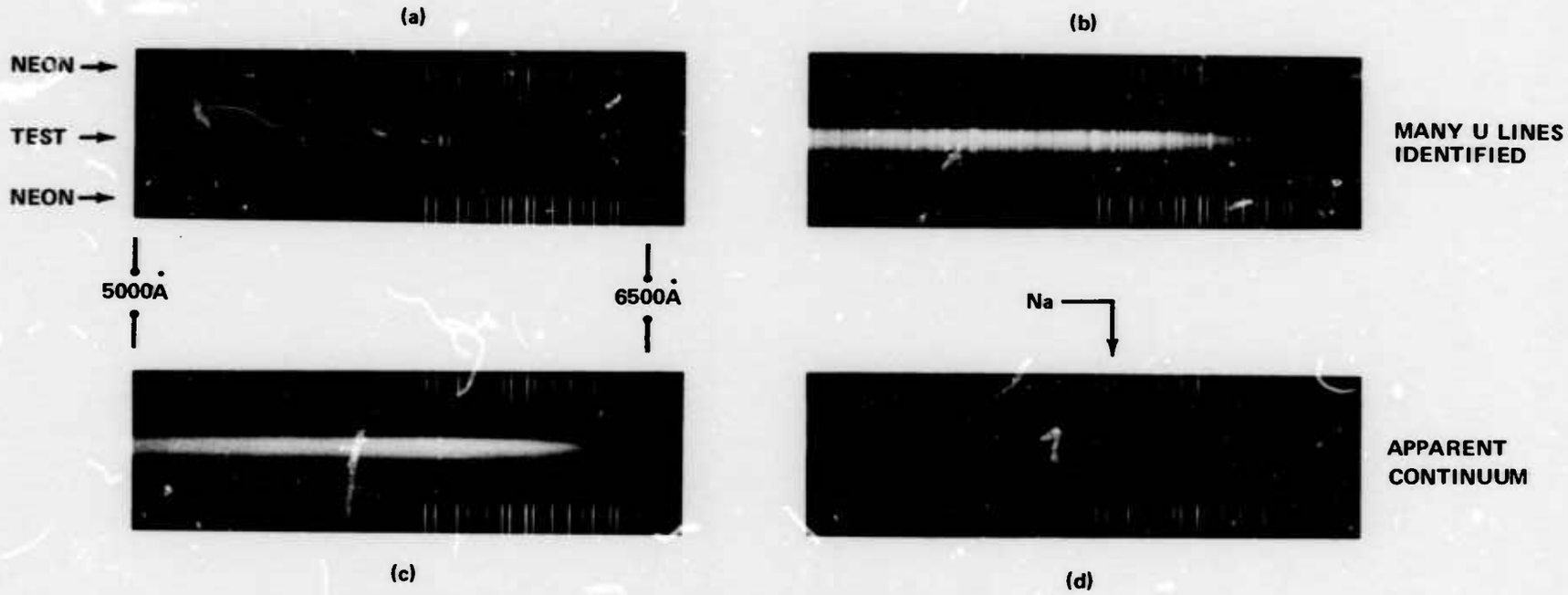
SHOCK TUBE – $P_1$ = 50 TORR, $V_S$ = 5000 FT/SEC

$T_{REFL.}$ = 4000°K

TYPICAL SPECTRUM FROM THE CAL AEROSOL SHOCK TUBE USING AL WIRE

BeO SPECTRA AT TWO TEMPERATURES

Figure 2




(a), (b): U AEROSOL IN ARGON, T ~ 5000°K, P ~ 10 ATM; AEROSOL DENSITY CHANGED

(c): U AEROSOL IN 5% $O_2$ - ARGON, T ~ 4000°K, P ~ 10 ATM; SLIT ~ 100 $\mu$

(d): REPEAT OF (c), SLIT ~ 50 $\mu$

AEROSOL PRODUCED BY EXPLODING PURE U FOIL STRIP (.006 x .040 x 5/8 IN)

Figure 3 URANIUM AEROSOL SHOCK TUBE SPECTRA