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IIT Research Institute

Report No. IITRI-U6002-69
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

National Aeronautics & Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama

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March 1, 1968 through August 31, 1968

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Huntsville, Alabama

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FOREWORD

This is Report No. IITRI-U6002-69 (Triannual Report) of IITRI Project U6002, Contract No. NAS8-5379, entitled "investigation of Environmental Effects on Coatings for Thermal Control of Large Space Vehicles." This report covers the period from March 1, 1968 through August 31, 1968. Previous Triannual Reports were issued on October 25, 1963; March 5, 1964; July 20, 1964; December 21, 1964; February 23, 1965; July 20, 1965; November 9, 1965; February 28, 1967; September 22, 1967; January 15, 1968 and April 15, 1968.

Major contributors to the program during this period include Gene A. Zerlaut, Project Leader; Robert Boutin, coating and specimen formulations; George Kimura, vacuum technology and space simulation tests; Michael Marcour, pigment synthesis investigations; Dr. Gorgon Noble, solid-state studies on zinc orthotitanate; Frederick O. Rogers, general paint technology and zinc orthotitanate studies; and Henry DeYoung, reflectance measurements and space simulation tests. The work reported herein was performed under the technical direction of the Research Projects Laboratory of the George C. Marshall Space Flight Center; Mr. Daniel W. Gates acted as the Project Manager.

Prior to March 15, 1966, this contract was funded under Codes 124-09-05-26-04, 124-09-05-00-14, 933-50-01-00-00 and 908-20-02-01-47.

Respectfully submitted,
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DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

I. INTRODUCTION

The general requirement under this contract is the development of thermal-control surface coatings that possess very low but stable ratios of solar absorptance (α_s) to infrared emmittance (ϵ_h). Historically, this program has been divided into three major phases: (1) inorganic pigment technology, (2) silicone-photolysis and silicone-paint investigations, and (3) general coatings investigations.

The relative emphasis on each major task has varied during the course of the program according to the urgency of the various problems elucidated by our investigations as well as the availability of both funds and personnel.

The work reported in the last Triannual Report (IITRI-U6002-63) consisted principally of zinc orthotitanate studies. Both reactive encapsulation and solid-state studies were reported. The use of reactive encapsulation was shown to be effective in stabilizing zinc orthotitanate against ultraviolet irradiation-induced damage in vacuum. Both potassium silicate and sodium acid phosphate were observed to reduce degradation. Of the two, pigmentation in potassium silicate was the most effective in preventing the creation of the broad, bleachable absorption band centered at about 800-nm that is characteristic of untreated zinc orthotitanates. It was also shown that heat treatment and reaction with sodium acid phosphate are important in affecting stability of zinc orthotitanate that is used to pigment the Owens-Illinois "650" Glass resin system.

The review of the solid state behavior of zinc oxide and rutile titanium dioxide (the precursor oxides to zinc orthotitanate) that was undertaken during the past year, combined with experimental studies on the nature of the photoinduced, "bleachable" infrared degradation of zinc oxide, have led directly to the initial electron spin resonance studies of zinc orthotitanate that are presented herein.

This report is devoted to: (1) a continuation of the solid-state studies of zinc orthotitanate; (2) a review of the literature pertaining to the synthesis of new, potentially stable, white pigments; (3) a discussion of the experimental synthesis of new pigment candidates and an examination of their stability to ultraviolet irradiation in vacuum; and (4) a resume of the design, construction and assembly of a combined-environment-irradiation facility that employs the IRIF-II and a new, low-flux, low-energy proton gun.

II. ZINC ORTHOTITANATE STUDIES

A. Introduction

Six zinc orthotitanate pigments, all extracted with 10% acetic acid, were prepared under the different conditions shown in Table 1. Samples of each of the pigments listed were furnished to Dr. William Campbell at the University of Ohio Research Foundation for dynamic differential thermal analysis, to Dr. R.W. Bartlett of Stanford Research Institute for plasma annealing (performed separately under Contract NAS8-2127 0, and Dr. Gordon A. Noble of IITRI for electron spin resonance analysis or irradiated specimens.

The objective of the plasma annealing is to firmly establish the necessity for lowering the surface free energy of "stable" pigment candidates, as well as to produce a stable zinc orthotitanate pigment. Reaction at high temperatures in a plasma environment is expected to preclude aggregation and agglomeration, and should thereby eliminate the need for subsequent dry and wet grinding operations. We have observed that a stable zinc orthotitanate can be prepared by reacting the precursor oxides at 1050°C; unfortunately, the resultant pigment is too large and too hard to utilize effectively as a candidate pigment (IITRI Report U6002-55).

B. EPR Studies

A high-temperature, solid state reaction presents much more difficulty in producing a stoichiometric product than other types of reactions involving fluids. Physical and chemical mixing of

Table 1

ZINC ORTHOTITANATES* PREPARED AT DIFFERENT TEMPERATURES

1. Reacted at 925°C for 18 hr (sieved to less than 80 mesh).
2. Reacted at 925°C for 18 hr (dry ground in ball mill).
3. Reacted at 1050°C for 18 hr (sieved to less than 50 mesh).
4. Reacted at 1050°C for 18 hr (dry ground in ball mill).
5. Reacted for 18 hr at 925°C, dry ground in ball mill, and reacted at 1050°C for 5 hr (sifted to less than 150 mesh).
6. Reacted for 18 hr at 925°C, dry ground in ball mill, and reacted at 1050°C for 5 hr (dry ground in ball mill).

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*All zinc orthotitanates were wet ground in 5% acetic acid to remove excess zinc oxide, washed and dried.

unreacted components may occur even after washing and calcining. These can often be detected by chemical or x-ray examination. However, when the excess zinc or titanium (as in this case) is present at a low concentration, it may be distributed as defects in the solid. Even if a separate phase is present, a strained region or a crystalline boundary may also exist. All these regions are susceptible to the decoration techniques of gamma and ultraviolet radiation. There are also two aspects to the application of electron paramagnetic resonance methods to these samples of (irradiated) zinc orthotitanate: The identification of the molecular species responsible for the resonance and the relationship of the resonance to the preparation of the material. Although it would be esthetically satisfying to have a model for the various resonances, we find it is better to proceed to the application of the resonance information first.

1. The sample treatment

Correlation of sample preparation and plasma treatment with thermal behavior and optical properties, as determined by ultraviolet spectroscopy and electron spin resonance, is the objective of these studies. The six specimens listed in Table 1 were both -irradiated and stored at 77°K. Sample 5 was irradiated at room temperature with ultraviolet light in the apparatus shown in Figure 1, and stored at 77°K.

2. The EPR data

A typical resonance derivative spectrum of gamma-irradiated material is presented in Figure 2. The resonance signal is similar in all six samples. The spectrum appears to be resolvable into seven component lines. The g factors lie in the range greater than two. This indicates a spectrum due to a species with a closed shell, which trapped a hole. However, an electron-pair-deficient molecule gaining one electron would also show such a shift. The g shift mechanism is analogous to many free radicals.

The resonance signals are rather complicated and separation into components would seem to be arbitrary. However, since six samples were available, it was possible to conclude that differences in the ratios of the signal amplitudes indicate that the resonances were caused by different species.

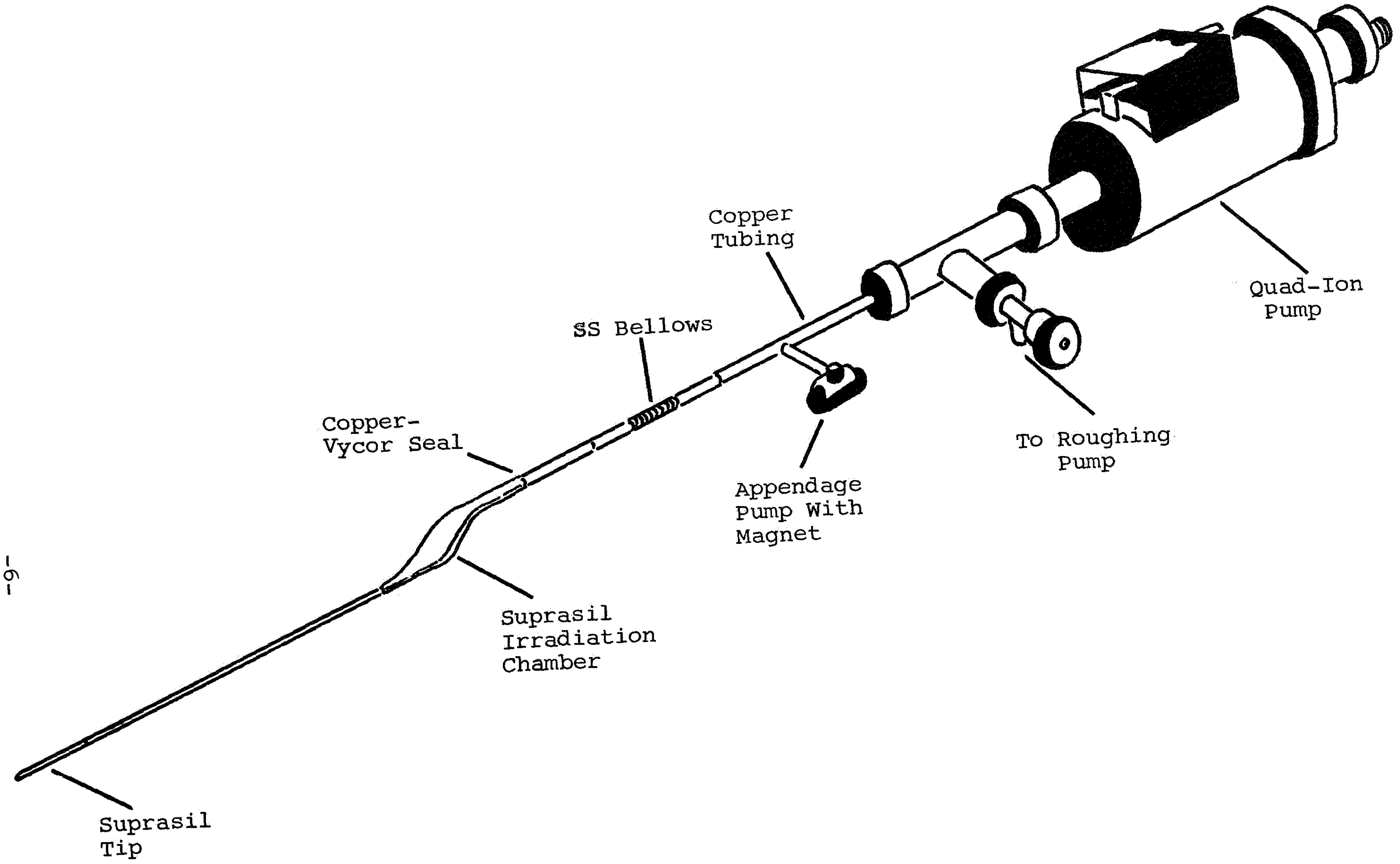

Figure 1 - ULTRAVIOLET IRRADIATION APPARATUS (EPR)

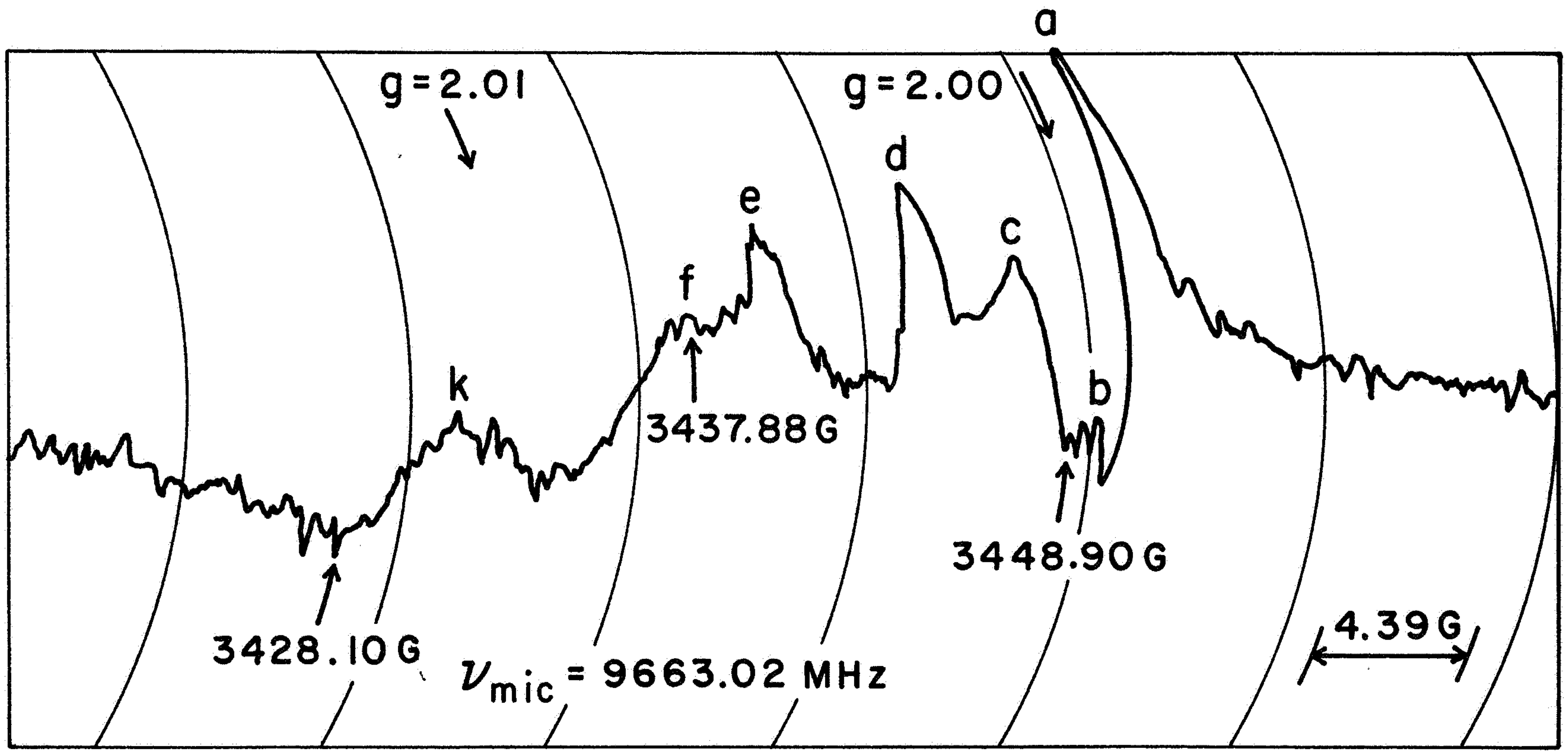

Figure 2 - EPR AT ~77°K IN Zn_2TiO_4, (SAMPLE 5), GAMMA IRRADIATED AT ~77°K

The problems of intrepreting the spectra of powders are especially apparent in this work. In particular, correlation with treatment differences might indicate that certain portions of the derivative spectra are associated with particular treatments. However, no portion of the signal will integrate to give a reasonable line shape. This is probably due to the fact that the spectra of the different species overlap. Variations in observation parameters have not been successful in removing this difficulty. The nature of the resonance signals is such that it is not advisable to attempt to integrate to obtain line shapes and moments because the results would not be meaningful. A general observation of the line shapes seems to indicate that the g-factor is given by the peak derivative position in most cases; i.e., the homogeneous broadening of the spectral lines is small. There are many more positive peak components than negative derivative peak components. The sign is not significant, but this indicates that all resonance lines are asymmetrical and sharply rising on the same side. Some experimental difficulty arose because the resonances show some signs of saturation; i.e., the spectrum depends on the amount of microwave power applied to the sample. Measurements were standardized at a fixed input power, but conditions at the sample could cause the amount of saturation to vary because it was impossible to operate at a power so low that no components saturated. This effect was not investigated further to correlate components. All measurements were made at 77°K.

Since the line shapes are not interpretable it is not possible to say which point indicates the true g value. If the seven components of the spectrum are labeled in increasing g-values or decreasing fields the components b, c, d, e are always in the range from 2.00 to 2.01. The component a is very close to 2.00 and may be slightly below this value in some samples. The component f is very close to 2.01 and the component k is always between 2.01 and 2.02 (letters g, h, i, j are ommitted to avoid confusion). The line k is well resolved and seems to have a line shape corresponding to homogeneous broadening. This g-factor is taken at the zero cross over points.

It is remarkable that the lines are so narrow. Increased modulation seems to obscure information rather than to bring out new lines. A standard modulation amplitude of 0.21 gauss was used. The width between peaks is greater than this in general and the widths of components are about this magnitude. A very simple symmetrical bell shaped absorption curve should have a derivative signal containing one positive and one negative peak. Similarly, a powder resonance signal of convenient proportions should have two peaks at the ends of the spectrum. Therefore, differences between peaks were compared among samples. Two such components should change in amplitude in a constant ratio. No association of pairs is presented as significant.

3. Attempted correlations

The identification of resonances is disappointing because they do not seem to correspond to those in ZnO, TiO_2 or an earlier preparation of Zn_2TiO_4. The resonances overlap and it is difficult to judge the relative intensities. The negative slope of one line cancels the positive slope of the other so that two strong lines may give little signal. Fortunately the other side of the resonance may not be obscured so that it can be used as a measure of the line intensity. By comparing Table 1 and Table 2, only one correlation can definitely be established. Resonance C, a relatively weak line, seems to correlate with the temperature of reaction. This defect apparently is more easily decorated if the material is reacted at a higher temperature. It must be admitted that there is a significant probability of this occuring by chance.

4. Ultraviolet irradiation

Sample 1 (Tables 1 and 2) of zinc orthotitanate was placed in the apparatus shown in Figure 1, evacuated to 1×10^{-7} torr, and then outgassed at 500°C under high vacuum for 72 hr. The sample was then irradiated at 1 solar equivalent for 48 hr (using an AH6 source). The epr tube was then sealed off while the vacuum was maintained at 1×10^{-7} with an appendage ion pump; it was immediately cooled to 77°K. The sample was examined for resonance within 1 hr of irradiation; the CAT was used.

The sample showed a single distinct resonance (the resonance is shown in Figure 3). It was a powder spectrum with a g value at cross over very near 2.00. The curve was non-symmetrical and the slope on the high field side was about twice that on the low. It probably could be characterized by two g-values. However no

Table 2

APPROXIMATE RELATIVE INTENSITIES

Sample Res.	1	2	3	4	5	6
a	W	M	S	S	M	S
b	---	---	W	?	?	W
c	W	W	M	M	W	W
d	S	S	M	S	S	S
e	W	M	M	M	M	W
f	?	W	W	W	W	?
k	S	W	W	M	M	W

W = weak, M = medium, S = strong

definite correlation can be made with the gamma irradiated samples. After about 20 hr at liquid nitrogen temperature the signal had deteriorated.

5. Discussion and conclusions

In the space environment the optical properties of the paint must be considered from a dynamic viewpoint. Dynamic is used here to indicate that time is an important variable in the description of the system. In particular, the time influences the reaction through the lifetime of metastable species formed by the radiation and present only during the radiation and for a short time thereafter. The optical absorption during irradiation and the kinetics of the reaction depend on the concentration of the intermediates. This in turn depends on intensity and the distribution of the light. The effect might be viewed as only a restatement of the concept of synergistic phenomena but it

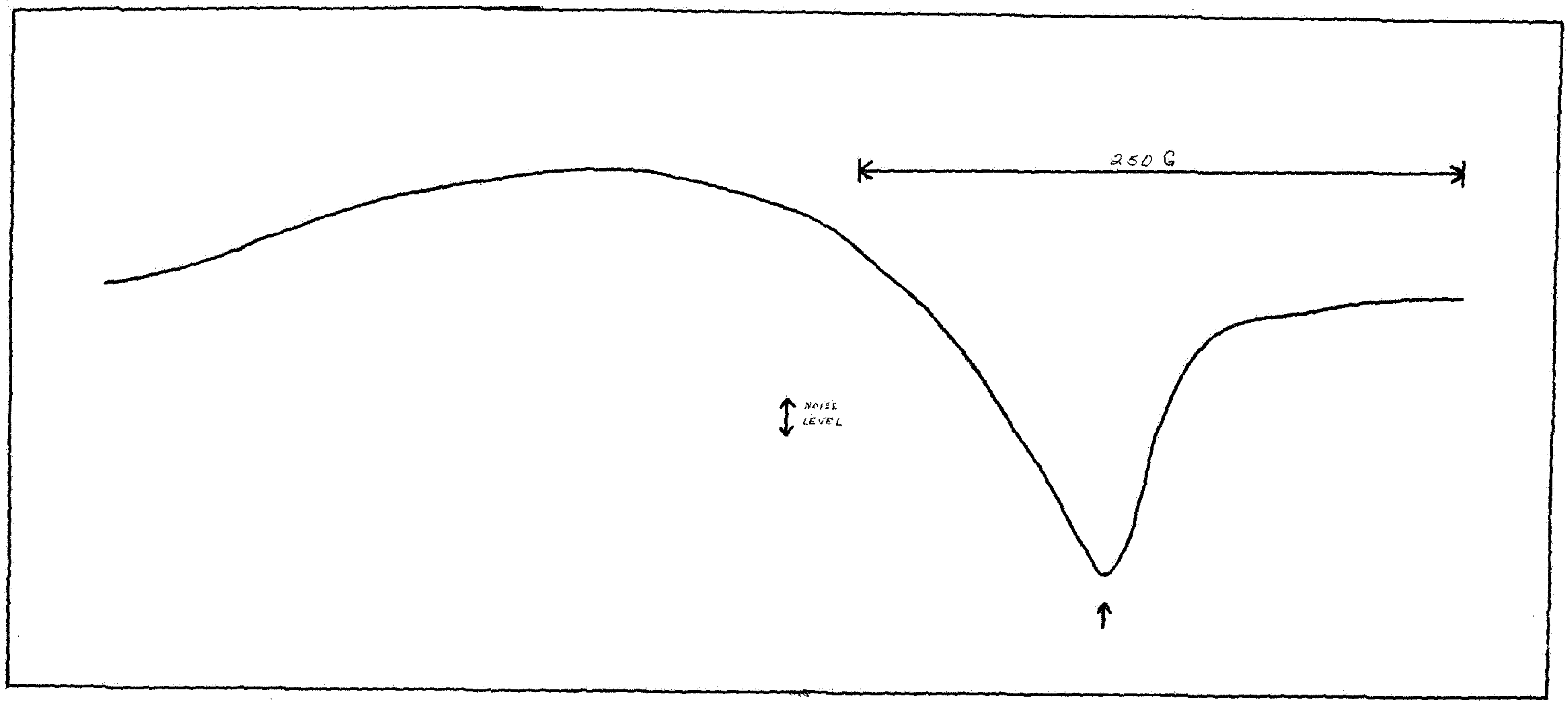

Figure 3 - EPR AT~77°K IN Zn_2TiO_4, (SAMPLE 1) UV IRRADIATED AT ~300°K

should be noted that it can produce a dependence of rate constant on intensity when only one radiation source is present.

In order to discuss this quantitatively we must know the lifetime of the metastable species. This viewpoint indicates that low temperature stable defects under gamma irradiation may play a role at high temperature. Certainly, if the metastable nature of the ultraviolet center is confirmed, the mechanisms involving metastable species must be investigated.

The most convenient method of defect decoration of high molecular weight materials is gamma irradiation. The use of low temperatures (77°K) prevents agglomeration or annihilation of centers by back reactions. The presence of many resonance signals would seem to indicate that there are many defects in the solid. However visual examination indicates that after irradiation the samples are white at low temperatures and EPR examination after warming to room temperature shows no resonance. We must still consider Zn_2TiO_4 a relatively stable material. It seems that these samples are probably more completely stoichiometric and homogeneous than earlier preparations where initially evidence was found for two phases by x-ray methods. A more recent preparation showed resonances due to preparation process alone. Magnetic resonance measurements after high energy irradiation is one of the most sensitive checks on the perfection of fundamentally stable materials such as the double oxides. The relative strength of the signals indicate a concentration less than 0.01%. It should be noted that resonances due to O_2-related species have been seen in ZnO. If these are not observed in the titanate, O_2^- may still be present but in such an environment that it cannot be recognized. Table 3 is a list of g-factors associated with O_2^- resonances in a variety of solids by many authors. The resonances as reported would show little superficial resemblence because of the environmental effects.

Table 3

G-FACTORS ASSOCIATED WITH O_2^- RESONANCES

O_2^- in	g_1	g_2	g_3	$\bar{g}$
KCl	1.9512	1.9551	2.4359	2.12
MgO	2.0011	2.0073	2.077	2.03
NaO_2	2.000	2.000	2.175	2.06
H_2O_2	2.0023	2.0144	2.0302	2.01
Bi Zeolite	2.0090	2.046	2.057	2.04
Na Zeolite	2.0066	2.016	2.113	2.05
ZnO (Fugita)	2.010	2.0133	2.043	2.02
ZnO (L + J)	2.002	2.0082	2.051	2.02
TiO_2	2.002	2.0106	2.0216	2.03
ZnO (Noble)	2.003	2.009	2.011	2.01

C. DDTA and Plasma-Calcining Experiments

Dynamic differential thermal analysis spectra were determined on the zinc orthotitanate specimens listed in Table 1. Specimens 3 and 5 exhibited thermograms with the least character; the largest endotherms were exhibited by specimens 1 and 2. These data, as well as the results of plasma calcination at Standford Research Institute, will be discussed in the next Trannual Report. It is planned to relate these data to EPR and optical spectra at that time.

III. POTENTIALLY-STABLE, NEW, WHITE PIGMENTS

A. Introduction

Theoretical considerations have led us to believe that certain binary and ternary systems containing complex anions should be excellent candidates as highly-reflective, space-stable, white pigments. Not only do such materials offer the strong possibility of possessing high refractive indices, but the very structure that assures high refractivity, namely high (electron) density, is also believed to be important to stability. That is, these less symmetrical structures should have stabilities that are related to the reduction of vacancy formation and ionic mobility. Although these factors may not be very important to "gaseous-sorption" bleaching, such as the ultraviolet-induced "bleachable" damage exhibited by rutile titanium dioxide and certain zinc orthotitanates, the surface state nature of this type of degradation is believed to be limited to materials having semiconductor character, and should be amenable therefore to encapsulation. We have not attempted at this time to ascertain the semiconducting properties of the pigments studied.

On the basis of ionic refractivities after Fajans and Joos, the double titanates, tungstates and stannates can be expected to possess high refractive indexes (ref. 1). In general, high refractive indices can be obtained by utilizing the following concepts:

1. a cation of high atomic weight and low charge
2. an anion of high charge and high atomic weight or
3. complex ions.

Also, "if a compound of element A has a high refractive index, then a compound of B, in the same group but of a greater atomic weight, may be expected to have a higher one" (ref. 2).

It was decided to investigate the optical and physical properties, first through a thorough literature search, and second in the laboratory, of the following groups of compounds: titanates, tungstates, stannates and double zirconium silicates (double zircons). We will first discuss our findings in the literature, later review the concept of the single crystal as it applies to stability in the space environment and finally give a resume of our findings in the laboratory.

B. Literature Search

1. Titanates

A thorough literature search on the properties and methods of preparation of the zinc titanates was reported in IITRI Report No. U6002-47 and will not be discussed here. We will confine our report to properties and methods of synthesis for lithium, lanthanum, gaddinium and tin titanates.

a. Lithium titanates: - Six lithium titanates are discussed in the literature:

$LiTiO_2$ (or $Li_2OTi_2O_3$)

Li_2TiO_3 (or Li_2OTiO_2)

$Li_2Ti_2O_5$ (or Li_2O2TiO_2)

$Li_2Ti_3O_7$ (or Li_2O3TiO_2)

$Li_4Ti_5O_{12}$ (or $2Li_2O5TiO_2$)

$Li_4Ti_7O_{16}$ (or $2Li_2O7TiO_2$)

Lundberg and Anderson (ref. 3) mention the existence of a series of compounds with the general formula of $Li_xTi_{4-x/4}O_8$. They explain that this series of compounds has a ramsdellite structure with "tunnels" that can accommodate a varying number of lithium atoms. No other reference could be found in the literature which substantiates Lundberg and Anderson's thesis. $LiTiO_2$ is described by Reuter and Weber (ref. 4) and by Lecerf (ref. 5). The latter author gives the color of $LiTiO_2$ as black.

Li_2TiO_3 is repeatedly mentioned in the literature, notably by Kutolin and Vulikh in Russia (ref. 6) and Lecerf in France (ref. 5), who implies, although he does not definitively state it, that Li_2TiO_3 crystals are white. Jonker (ref. 7), Yamaguchi (ref. 8) and Barblau (ref. 9) have all synthesized Li_2TiO_3, although each author used different methods and reacted the products of synthesis at widely varying temperatures ranging from 650 to 1250°C in environments such as vacuum, CO_2 or atmospheric conditions. $Li_2Ti_2O_5$ is only mentioned by Barblau and his coworkers (ref. 10), where $Li_2Ti_3O_7$ is discussed by two separate investigators - the previously cited Lundberg and Anderson (ref. 3) and Jonker (ref. 7). There is some doubt as to the very existance of $Li_4Ti_7O_{16}$, which was reported by Bertant and Durif (ref. 11), since Jonker claims that the x-ray pattern of $Li_4Ti_5O_{12}$ agrees with the pattern previously attributed to $Li_4Ti_7O_{16}$.

b. Lanthanum titanates: - Five different titanates are reported in the literature:

La_2TiO_5 (or $La_2O_3TiO_2$)
$La_2Ti_2O_7$ (or $La_2O_32TiO_2$)
$La_2Ti_3O_9$ (or $La_2O_33TiO_2$)
$La_4Ti_9O_{24}$ (or $2La_2O_39TiO_2$)
$LaTiO_3$

$La_2Ti_2O_7$ is of special interest to us because of its outstanding transmission properties, which were reported by Merker and Herrington (ref. 12). Transmission data were not available for the other titanates, but at least one of them must be ruled out as totally unsuitable: It is $LaTiO_3$, which is reported to be black by Kestigian and Ward (ref. 13). $LaTiO_3$ and compounds in the solid solution series between $La_{0.69}TiO_3$ and $LaTiO_3$ are reported to have a cubic perovskite structure by Kestigian and Ward, but this is contested by Johnston and Sestrich (ref. 14), who claim that the crystals are orthorombic. They relate this orthorombic structure to the previously reported cubic perovskite structure by doubling the cubic unit cell in the c direction and using face diagonals for a and b.

The various authors agree on the structure of $La_2Ti_2O_7$: It has a distorted pyrochlore structure. This is reported by Merker and Herrington who synthesized this compound by flame fusion and by Collongues and his coworkers (ref. 15), who prepared it by coprecipitation of $LaCl_3$ and $TiCl_3$. The colors of $LaTiO_3$ and $La_2Ti_2O_7$ are complete opposites in spite of the rather small difference in oxygen content. This should not deter us from selecting $La_2Ti_2O_7$ as a potential space stable pigment. $La_2Ti_2O_7$ and $LaTiO_3$ are made from different initial components - namely Ti_2O_3 for the former and TiO_2 for the latter. Furthermore, no author reports significant problems in synthesizing either compound. In fact, MacChesney and Sauer (ref. 16) do not show the presence of $LaTiO_3$ in their phase diagram of the La_2O_3-TiO_2 system.

The other three titanates are described by MacChesney and Sauer. They personally discovered the existence of La_2TiO_5 and $La_4Ti_9O_{24}$, and received a personal communication from Jonker who identified $La_2Ti_3O_9$. The existence of this latter compound was later confirmed by Kestigian and Ward (ref. 17) and Repp (ref. 18). The optical properties of these compounds are unfortunately not discussed in these papers; the emphasis was placed on methods of preparation and the measurement of dielectric properties.

c. Gadolinium titanates: - Two forms of gadolinium titanates are reported in the literature:

Gd_2TiO_5 (or $Gd_2O_3TiO_2$)
$Gd_2Ti_2O_7$ (or $Gd_2O_32TiO_2$)

We will discuss our findings since they have a definite academic interest. However, it should be noted that the cost of gadolinium oxide, which is quoted by American Potash and Chemical Corporation to be $300/lb, will probably prove to be a deterrent to the use of $Gd_2Ti_2O_7$ as a pigment. This is especially true if one considers that the equivalent lanthanum titanate can be made from La_2O_3, which costs $7/lb. $Gd_2Ti_2O_7$ has excellent transmission properties which are very similar to those of $La_2Ti_2O_7$. Both are reported by Merker and Herrington (ref. 12). They believe that the weak absorption at 0.9 micron in the gadolinium titanate-transmission curve is due to contamination by ytterbium. Roth (ref. 19) indicates that $Gd_2Ti_2O_7$ has a pyrochlore structure with cubic symmetry. Both Queyroux (ref. 20) and Collongues and his coworkers (ref. 15) describe Gd_2TiO_5 as being monoclinic derived from the fluorite type and the cell dimensions reported by these two authors are in good agreement. Queyroux (ref. 20, 21) makes an interesting observation concerning gadolinium oxide: It has a cubic cell structure at ordinary temperatures which becomes monoclinic when heated to 1000°C according to Perez y Jorba (ref. 22), where Queyroux notes that this transformation occurs at 1250°C. They both agree that the reaction is reversible and Perez y Jorba states that the cubic structure can be restored by grinding the monoclinic oxide, followed by prolonged heating at 900°C.

d. Tin titanates: - A thorough search in Chemical Abstracts did not provide any information on crystal types, cell dimensions or transmission properties of tin titanates. A British patent (ref. 23) was granted to Siemens and Halske A.G. for the production of titanate mixtures of tin, but no mention is made of the synthesis of pure tin titanate. The existence of preparation procedures is implied in the abstracts of two Russian publications (ref. 24, 25) on the dielectric properties of tin titanate. Khodakov and Kromakov studied the small dielectric losses of solid solutions of $SnTiO_3$ and $BaTiO_3$, whereas Kaczmarek discussed variations in dielectric constants of solid solutions of $BaTiO_3$ and $SnTiO_3$ in a pulsed electric field. A phase diagram of the SnO_2-TiO_2 was developed by Padurow (ref. 26).

2. Tungstates

A publication by Cockayne and Ridley (ref. 27) indicated that not only calcium tungstate, but varium and strontium tungstates as well, have outstanding transmission properties. This opens the possibility of preparing solid solutions of two or three of these tungstates that hopefully will have transmission properties and stability superior to that of the individual components. Calcium, barium and strontium ions have different sizes and it is believed that a judicious apportionment of these cations could relieve some of the stresses now present in the calcium tungstate lattice.

a. Calcium tungstate: - The most commonly prepared form of calcium tungstate is $CaWo_4$. Nassau and Broyer (ref. 28) report the existence of Ca_6WO_9.

Cell dimensions of $CaWO_4$ are reported in two different publications and are in good agreement. A very careful study of interatomic distances in $CaWO_4$ was carried out by Kay, Frazer and Almodovar (ref. 29). They report that the slightly distorted WO_4 tetrahedron contains a W-O distance of 1.788 A° and O_1-W-O_2 angles of 113°27' and 107°56'. Nassau and Broyer (ref. 28) state that the distorted $(WO_4)^{2-}$ ions are held apart by Ca^{2+} ions which are surrounded by eight oxygens at the corners of a distorted cube. The structure, a scheelite structure, is described as "very compact." The melting point of $CaWO_4$ has been reported to be 1535°C, 1566°C or 1576 ± 5°C by three different investigators.

Fairly good agreement exists between the transmission spectra given by Nassau and Broyer and the data of Cockayne and Ridley (ref. 27). The former report that their data does not entirely agree with data presented by Gillette (ref. 30) and they attribute the structure in the 500- to 3000-mm region shown by Gillette to the presence of either impurities or excess WO_3.

Various investigators report preparing $CaWo_4$ by precipitation from Na_2WO_4 and $CaCl_2$ solution.

Reduction of W^{6+} to W^{5+} by heating $CaWO_4$ in hydrogen at 1000°C produces a black compound that can be reoxydized to white $CaWO_4$ by heating in oxygen.

b. <u>Barium tungstates:</u> - No less than six different barium tungstates have been reported in the literature; $BaO.WO_3$ and $3BaO.WO_3$ have been repeatedly discussed and used whereas $BaO.2WO_3$, $BaO.3WO_3$ $BaO.4WO_3$ and $5BaO.12WO_3$ are described only by Shivahare (ref. 31). He formed these compounds by titrating a solution of Na_2WO_4 with $BaCl_2$ in the presence of nitric acid. He observed that upon aging the following reaction took place:

$$5BaO.12WO_3 \longrightarrow 4(BaO.3WO_3) + Ba(OH)_2,$$

whereas the normal $(BaO.WO_3)$ and the $(BaO.2WO_3)$ tungstates were quite stable.

Normal barium tungstate appears to be a promising candidate as a pigment for space vehicles; it exhibits good optical properties, which are described by Cockayne and Ridley (ref. 27), and has a rather high heat of formation, which is discussed by Rezukhina and his coworkers (ref. 32).

The preparation of $BaO.WO_3$ can be performed by the method employed by Shivahare (ref. 31). This precipitation technique was also utilized by Kislyakov and his coworkers (ref. 33). An entirely different approach to synthesis was used by Zmud and Ostapchenko (ref. 34), who heated to 1600°C (usually to 1200°C) mixtures of WO_3 and $BaCO_3$. A third technique used in the synthesis of $BaWO_4$ is described by Van Uitert and Soden (ref. 52). $BaWO_4$ crystals were grown by crystallization from a Na_2WO_4 melt.

This technique was used to grow single crystals and it gave a yield superior to the method previously employed to grow single crystals in a NaCl melt.

c. Strontium tungstates: - A considerable number of strontium tungstates are reported in the literature.

$SrO.WO_3$

$3SrO.WO_3$

$3SrO.8WO_3$

$5SrO.12WO_3.28H_2O$

$SrO.2WO_3$

$SrO.3WO_3$

$SrO.4WO_3$

$3SrO.7WO_3.16H_2O$

$4SrO.10WO_3.26H_2O$

Two general methods of preparation hsve been employed. The first one consists of precipitating various strontium tungstates by adding strontium chlorides to the corresponding sodium tungstates. This method yielded five different strontium tungstates and is discussed by Shivahe (ref. 35). The other method used to prepare the strontium tungstates consists of reacting $SrCO_3$ and WO_3 at temperatures ranging from 800 to 1200°. This is discussed by Fesenko (ref. 36) and Belyaev (ref. 37) and their coworkers.

3. Stannates

A quite complete discussion of the properties of the meta and orthostannates by Dupuis (ref. 38) indicated that the zinc, magnesium and calcium stannates might yield adequate space-stable coatings. We must rule out iron, copper, nickel, cobalt and manganese metastannates as they are not white.

a. Calcium stannates: - Two forms of calcium stannate are reported in the literature: The metastannate ($CaSnO_3$) and the orthostannate (Ca_2SnO_4). The crystalline structure of the metastannate is the object of much controversy. Goldschmidt (ref. 39) and Nagay-Szabo (ref. 40) indicate that $CaSnO_3$ has a cubic cell but disagree on the size of the unit cell, with Nagay-Szabo doubling the edge dimension. Megaw (ref. 41) believes the structure of $CaSnO_3$ is monoclinic whereas Tanaka (ref. 42), Smith and Welch (ref. 43), Couganour (ref. 44) and Rooksby (ref. 45) all believe that $CaSnO_3$ has an orthorombic structure although they give it extremely different cell dimensions.

The structure of calcium orthostannate is reported to be orthorombic by Troemel (ref. 46).

b. Barium stannates: - Barium metastannate has a cubic structure which is described by four different authors. Nagay-Szabo (ref. 40), Megaw (ref. 41), and Smith and Welch (ref. 43) show very good agreement on the cell dimensions (a=4.12Å) whereas Wagner and Binder (ref. 47) attribute a larger dimension to

$CaSnO_3$ (a=4.28Å). Barium orthostannate has been synthesized and described by Weiss and Faivre (ref. 48). It has a tetragonal structure.

c. Zinc stannates: - We could find only one reference on zinc metastannate: Dupuis (ref. 38) claims that, upon heating, the metastannate is stable up to 500°C and is completely transformed to the orthostannate when the temperature reaches 900°C.

Zinc orthostannate (Zn_2SnO_4) has a spinel structure. Very good agreement is found between Colin (ref. 39) and Natta and Passerini (ref. 49) on cell dimension.

C. Experimental Investigations

We have divided the experimental work into three parts: First, we describe our efforts to define optimum experimental techniques; second, we report our results on the reflectance of various tungstates that were purchased from Sylvania Electric Products Inc.; and third, we describe the preparation of new pigments at IITRI and their reflectances as measured on a Beckman DK-2 Spectrophotometer equipped with an Edwards-type integrating sphere.

1. Experimental Techniques

a. Water mull and PS-7 binder: - A technique has been developed at IITRI and described in numerous previous communications whereby a water suspension of pigment is sprayed on a preheated substrate, usually aluminum: Reflectance is then measured. This technique has proved to be entirely satisfactory when "soft" pigments are tested. Among those pigments we find New Jersey

Zinc Company's SP500 zinc oxide, duPont's FF anatase titanium dioxide and orthotitanates that we have prepared at reaction temperatures not exceeding 1000°C. Where higher temperatures are used to prepare the meta and orthotitanates, and meta and orthostannates, the resulting clinkers are extremely hard to grind and even prolonged jar milling does not produce sufficient size reduction. It becomes very difficult to suspend and spray these hard, jewel-like particles and their adhesion to the aluminum substrate is insufficient. The use of a binder is necessitated for many of these materials.

We have made comparisons between reflectance data obtained with water suspension and potassium silicate-bound (PS-7) pigments. The accompanying table (Table 4) clearly indicates that the potassium silicate binder reduces reflectance, especially in the infrared region. This is ascribed principally to chemically-bound water in the silicate matrix. Furthermore, the differences in reflectance are not consistent from batch to batch, even for the same zinc orthotitanate pigment. This suggests the effect of a pigment-binder interaction, which further complicates data interpretation. The possibility of interaction between zinc orthotitanate and potassium silicate is supported by the evidence presented in the last Triannual Report (IITRI-U6002-63) pertaining to the effectiveness of potassium silicate in precluding the intense, bleachable absorption band that develops in zinc orthotitanate at about 850-nm wavelength. It should be noted that the identical pigment and grinding procedure was used in both

Table 4

COMPARISON BETWEEN REFLECTANCE OF PIGMENTS WET-MILLED IN WATER AND IN PS-7 BINDER

				Milled		% Reflectance at Wavelength, Microns					
Pigment	Reacted at T	Ground by	Batch	H_2O	PS-7	0.4	0.6	1.1	1.6	2.0	2.6
Zn_2TiO_4	1200°C	Hand	A-859	X		71	91	92	91	88	86
			A-856		X	68	81	82	77	56	41
Zn_2TiO_4	1100°C	Hand	A-810-1	X		57	88	91	90	87	84
			A-810-2		X	51	80	82	71	46	34
Zn_2TiO_4	1100°C	Machine	A-812-2	X		67	84	85	85	83	82
			A-812-3		X	58	70	72	62	36	24
Zn_2TiO_4	1000°C	Hand	A-857	X		75	94	93	92	89	85
					X	44	79	81	70	46	27

the water mull and silicate paint in order to minimize differences in particle size. A PBR of 4.5 was used in all paints and the thicknesses were approximately 2 mils in all cases. Pigment volume is the largest constant factor that could account for the differences in reflectance between powder and paint specimens. It cannot account for the "spectral" changes observed.

b. <u>Slurried mixes versus dry mixes:</u> - An exploratory program aimed at defining those compounds of the titanates, stannates, tungstates or double zicronium silicates which have high initial degrees of whitness, or reflectance, can be most successful if a large number of formulations are prepared and tested. This necessitated the use of more rapid albeit less precise techniques.

The mixing of various components prior to their reaction through solid solution can be best accomplished by suspending the individual components and then slurring them together, filtering and eventually drying. This, however is a rather time consuming series of operations and dry mixing of the individual components would be preferable providing the loss of accuracy is not excessive.

In general there does not appear to be a significant difference in reflectance between the slurried and dry mixed compounds except along the absorption edge where the slurried materials are more reflective than their dry mixed equivalents (see Table 5). This is probably caused by the presence of unreacted components. Dry mixing appears to be satisfactory for the initial screening of new compounds. However, the most promising of these compounds

Table 5

COMPARISON BETWEEN REFLECTANCE OF PIGMENTS PREPARED FROM DRY MIXED COMPONENTS AND FROM WET MIXED (SLURRIED) COMPONENTS

Pigment	Reacted at T	Ground by	Pelletized	Batch	Components Mixed		% Reflectance at Wavelength, Microns					
					Dry	Slurried	0.4	0.6	1.1	1.6	2.0	2.6
Zn_2TiO_4	1100°C	Hand	Yes	A-811	X		59	85	86	85	84	81
				A-813		X	60	78	81	81	80	79
Zn_2TiO_4	1000°C	Hand	No	A-853	X		47	91	92	90	88	86
				A-857		X	75	94	94	92	89	85
Zn_2TiO_4	1100°C	Hand	No	A-810-1	X		57	88	91	90	87	84
				A-812-1		X	78	91	93	93	91	90
Zn_2TiO_4	1100°C	Machine	No	A-810-3	X		37	84	87	86	84	81
				A-812-2		X	67	84	85	85	85	82
Zn_2TiO_4	1200°C	Hand	No	A-858	X		56	85	86	84	81	76
				A-859		X	71	91	92	91	88	86
Zn_2TiO_4	1100°C	Hand	No	A-855	X		76	90	90	84	69	63
				A-856		X	68	81	82	77	56	41

Note: Batches A-855 and A-856 were wet milled in PS-7 binders. All others were wet milled in water.

should be prepared by slurring to determine their ultimate performance prior to subsequent modification such as chemical surface treatment or recalcination.

c. Pelleted versus loosely-packed powders: - Many of the authors cited in the literature search discussed in the preceding paragraphs apply very high pressure to the mixed components prior to fusion or solid solution reactions. This operation is not only time consuming, but necessitates the purchase of expensive equipment to exactly duplicate the procedure used in some laboratories (e.g., 20,000 to 40,000 psi used by Brixner, ref. 48). We have compared the reflectance data obtained on compounds prepared with and without compaction (pelletizing at 5000 psi) prior to high-temperature treatment and find little evidence that any increase in reflectance is gained by pelletizing (see Table 6).

d. Hand-ground versus machine-ground pigments: - Samples prepared at temperatures over 1100°C (stannates and titanates) have proven to be extremely difficult to hand grind which casts severe doubt on their usefulness as paint pigments in the conventional sense. New binders and new grinding techniques might have to be developed to successfully utilize exceptionally "hard" pigments. For the present we have assumed that such binders and grinding techniques can be developed to suit the requirements of the pigment. (While hand grinding a clinker prepared at high temperatures, we visually observed that the portion that could be ground more easily generally was whiter than the portion that required a greater grinding effort.) We made comparisons, which

Table 6

COMPARISON BETWEEN REFLECTANCE OF PIGMENTS MADE FROM PELLETIZED MIXED COMPONENTS AND NOT PELLETIZED MIXED COMPONENTS

Pigment	Reacted at T	Batch	Components Pelletized	% Reflectance at Wavelength, Microns					
				0.4	0.6	1.1	1.6	2.0	2.6
$ZnTiO_3$	1090°C	A-789	Yes	24	83	89	90	87	88
		A-790	No	34	89	93	94	93	92
$ZnTiO_3$	1200°C	A-795	Yes	33	81	87	88	87	85
		A-796	No	34	83	90	91	90	89
$ZnTiO_3$	1300°C	A-791	Yes	40	84	86	85	84	83
		A-792	No	46	83	85	85	85	84
Zn_2TiO_4	1300°C	A-793	Yes	57	79	84	85	84	82
		A-794	No	50	83	85	83	81	76

admitedly are not entirely valid, between the reflectance of that portion of the clinker that could easily be hand ground to pass through a 40-mesh screen and the larger fraction that required mechanical grinding (see Table 7). On the basis of the limited evidence, it appears that the portion of a clinker that easily can be ground is superior in initial reflectance. Previous experience indicates that severe grinding will cause surface defects and increase radiation damage thereby lowering performance in space environment. It is quite possible that the utilization of pigments prepared at high temperatures will require the discarding of that portion of the clinker that cannot be ground easily. Indeed, it is this consideration that prompted the "plasma" calcining at Stanford Research Institute discussed in Section IIC.

2. Pigment analysis

We purchased five tungstates from Sylvania Electric Products, Inc. and determined the reflectances of the pigments using the water-mull technique described earlier. The data which is summarized in Figs. 4 through 8 is in substantial agreement with the data shown by Cockayne and Ridley (ref. 25) for the three tungstates (calcium, barium, and strontium). We performed reflectance measurements further into the ultraviolet region than Cockayne and Ridley and it is interesting to notice that calcium tungstate has a definite absorption band at approximately 280-nm wavelength.

Strontium tungstate has the highest reflection in the 325 to 255-nm region and barium tungstate appears to be the least

Table 7

COMPARISON BETWEEN REFLECTANCE OF PIGMENTS WHICH HAVE BEEN HAND GROUND ONLY AND PIGMENTS WHICH HAVE HAND AND MACHINE GROUND

Pigment	Reacted at T	Components	Batch	Pigment Hand Ground -40 Mesh	Pigment Hand Ground +40 Mesh Then Machine Ground	% Reflectance at Wavelength, Microns					
						0.4	0.6	1.1	1.6	2.0	2.6
Zn_2TiO_4	1100°C	Slurried	A-812-1	X		78	91	93	93	91	90
			A-812-2		X	67	84	85	85	83	82
Zn_2TiO_4	1100°C	Dry Mixed	A-810-1	X		57	88	91	90	87	84
			A-810-3		X	37	84	87	86	84	81

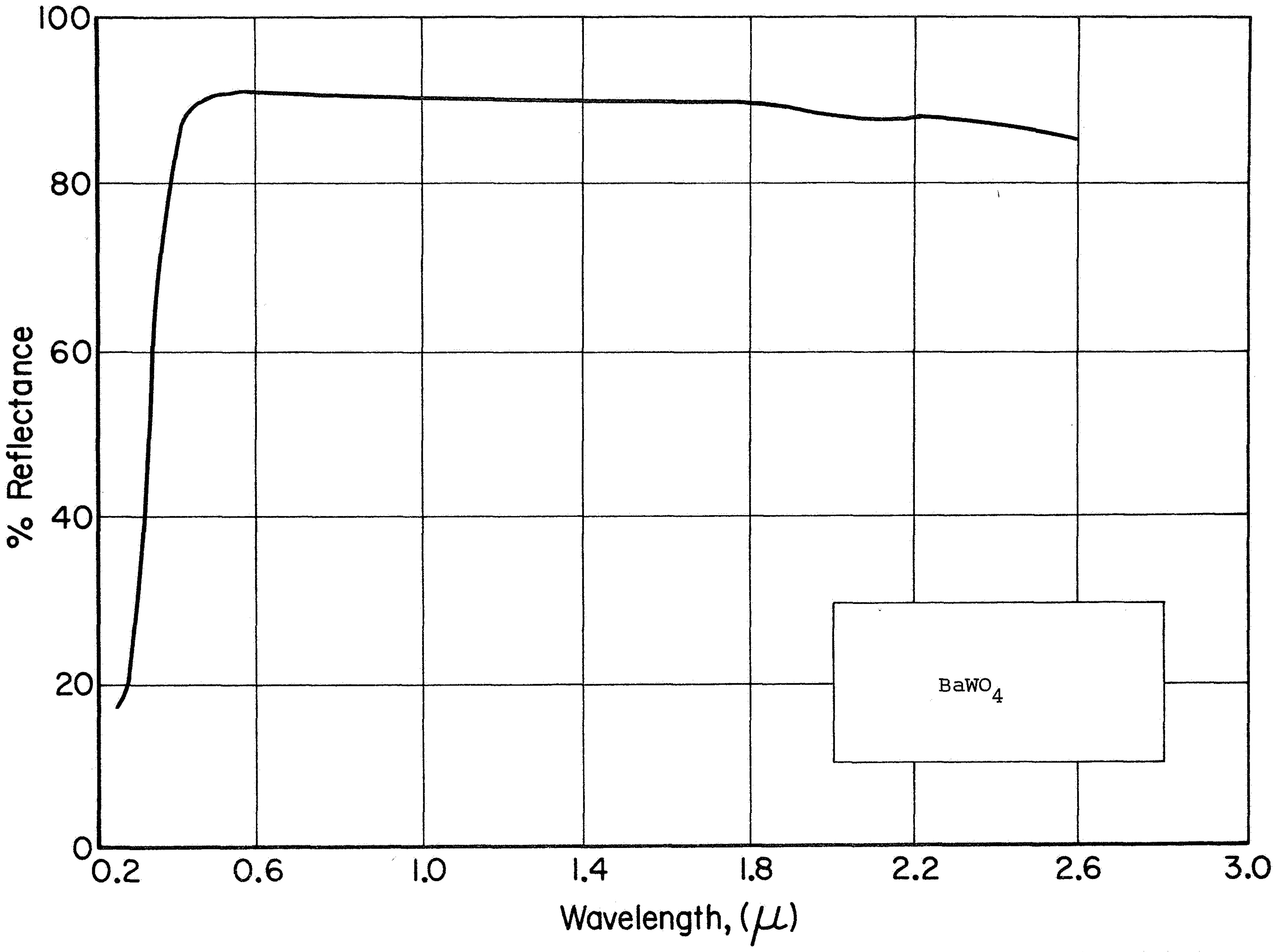

Figure 4 - ABSOLUTE HEMISPHERICAL REFLECTANCE OF WET-POWDER SPRAYED BARIUM TUNGSTATE

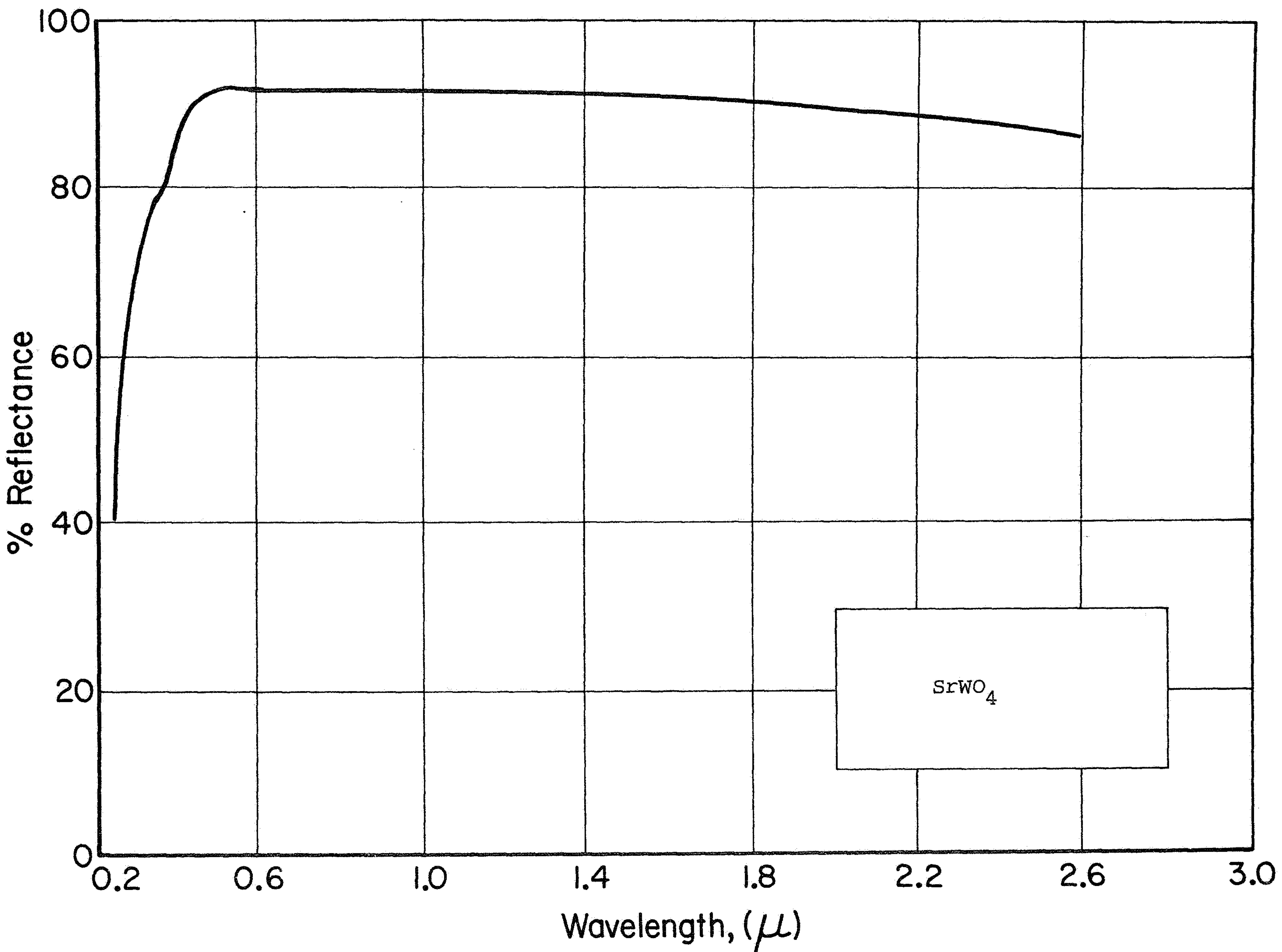

Figure 5 - ABSOLUTE HEMISPHERICAL REFLECTANCE OF WET-POWDER SPRAYED STRONTIUM TUNGSTATE

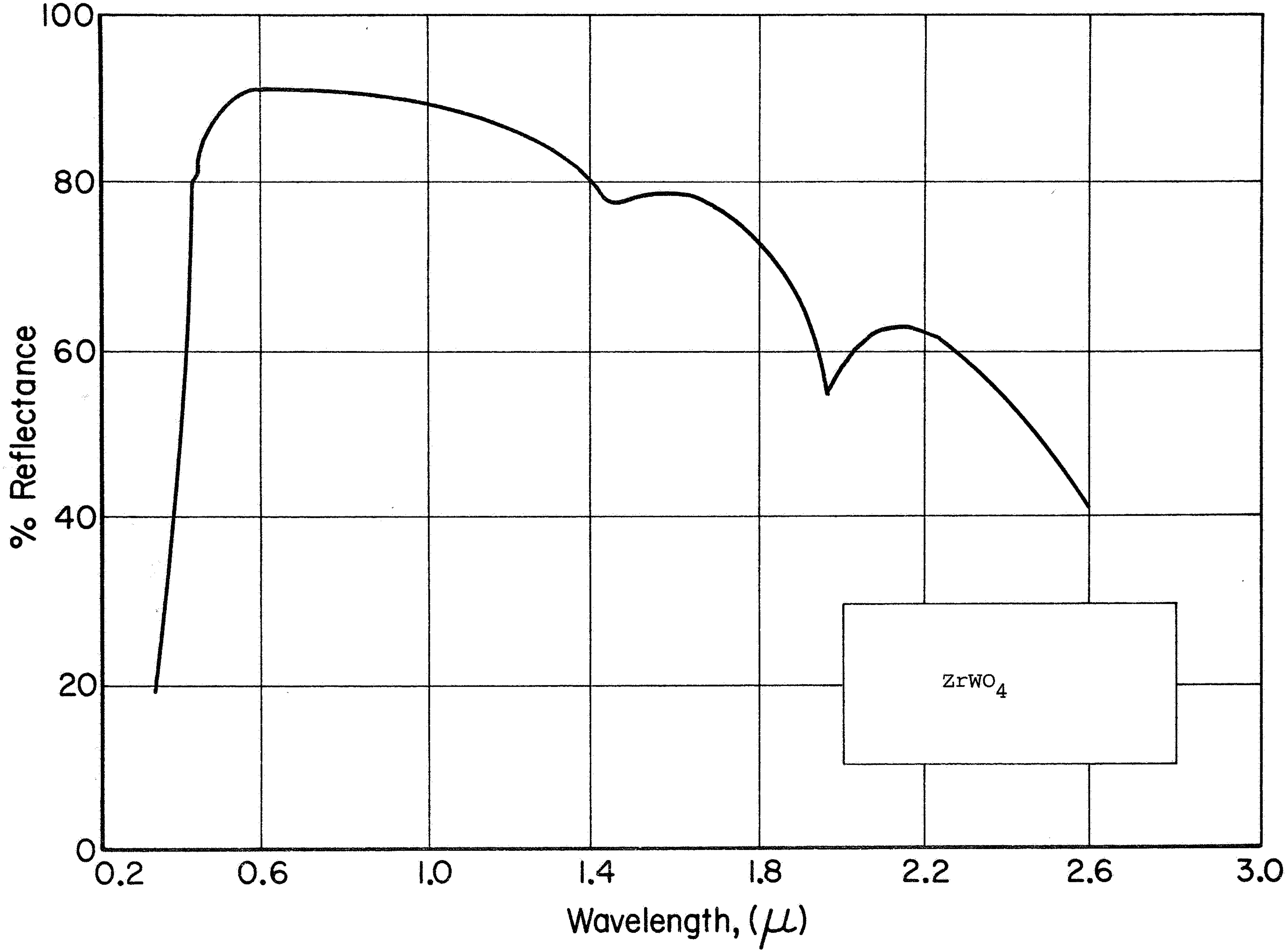

Figure 6 - ABSOLUTE HEMISPHERICAL REFLECTANCE OF WET-POWDER SPRAYED ZIRCONIUM TUNGSTATE

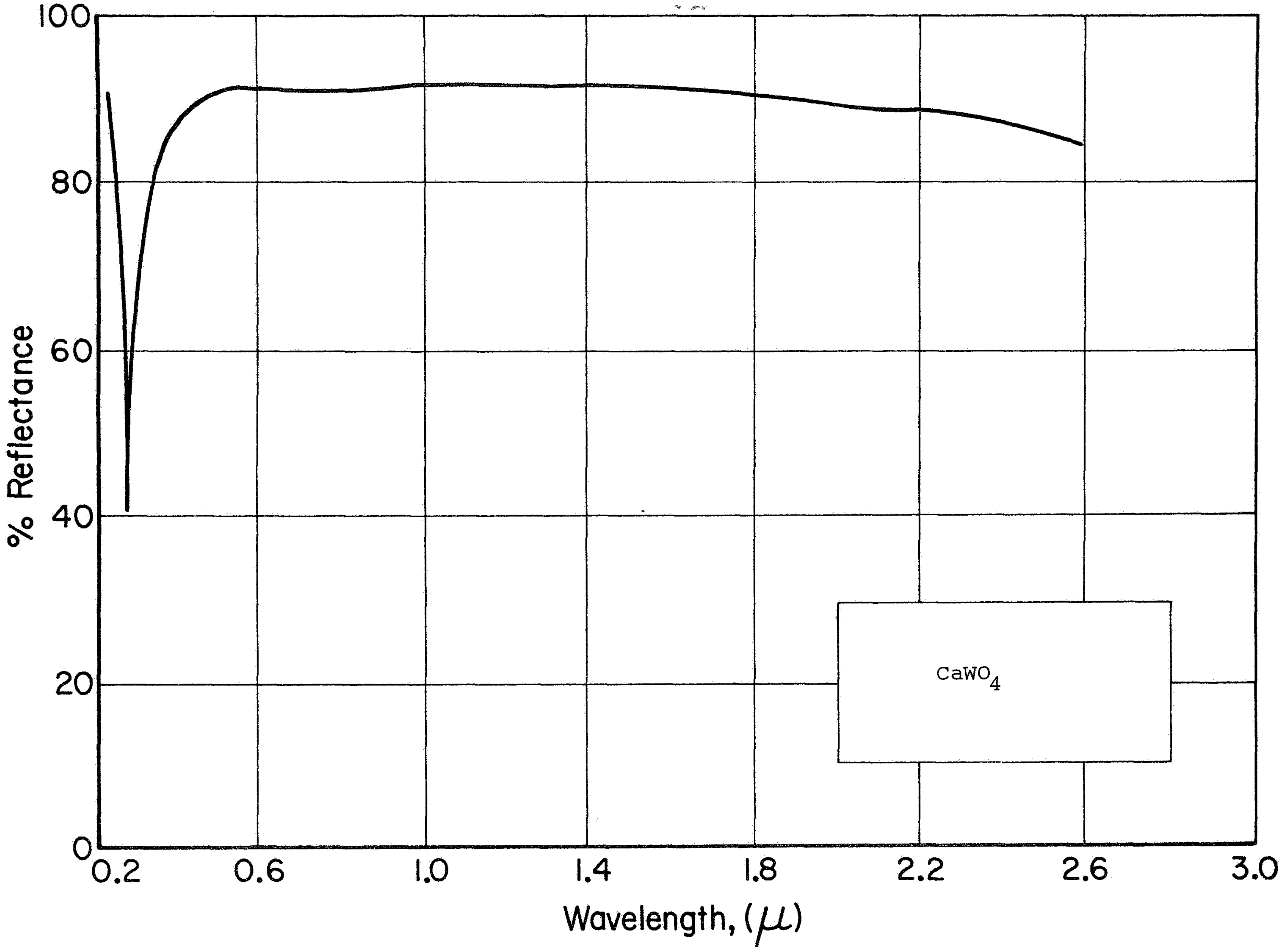

Figure 7 - ABSOLUTE HEMISPHERICAL REFLECTANCE OF WET-POWDER SPRAYED CALCIUM TUNGSTATE

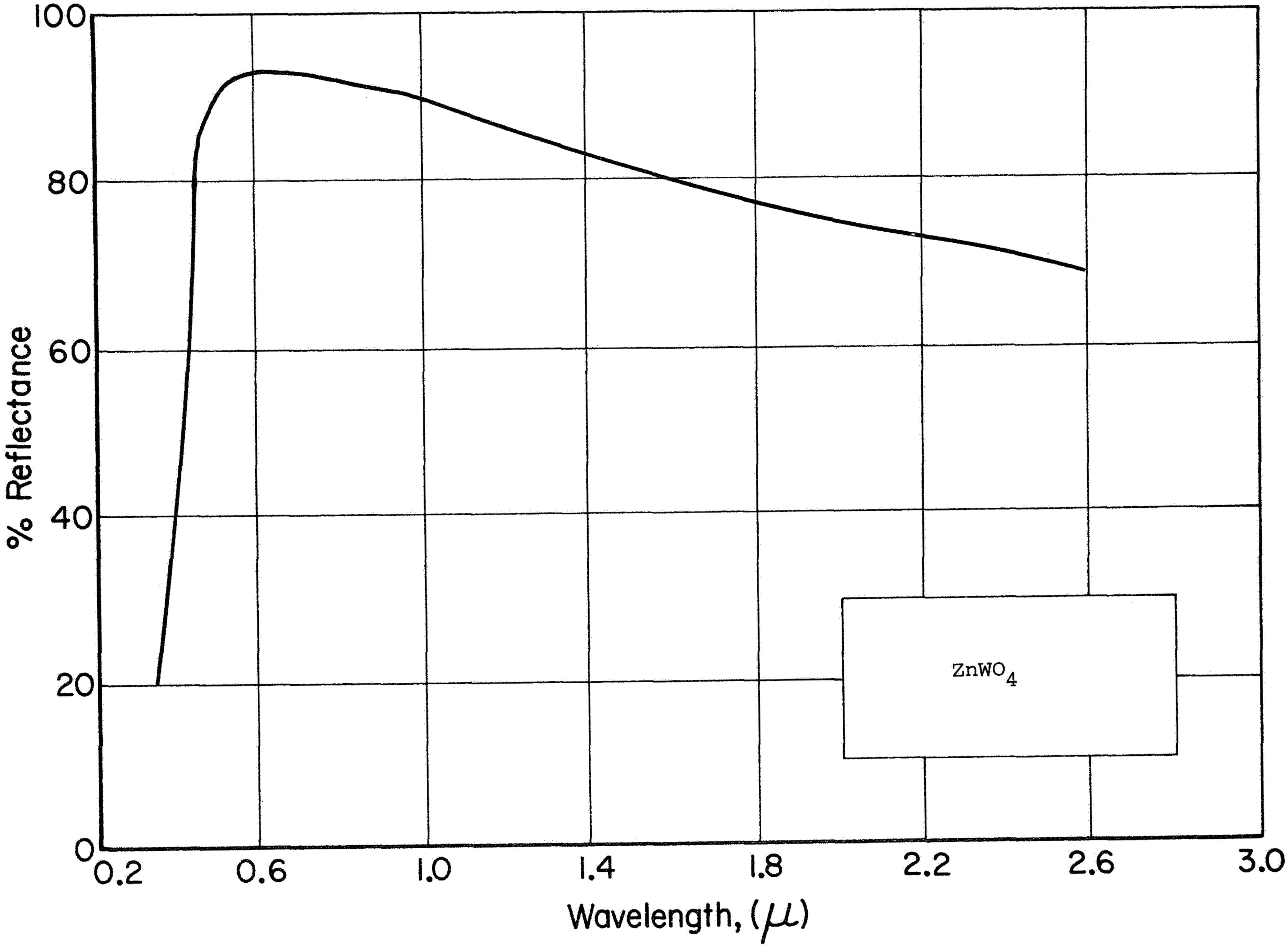

Figure 8 - ABSOLUTE HEMISPHERICAL REFLECTANCE OF WET-POWDER SPRAYED ZINC TUNGSTATE

promising of the three compounds. Zinc tungstate has a definite absorption edge at 375-nm wavelength. As shown by Figure 8, $ZnWO_4$ exhibits a gradual loss of reflectance between 460 and 380 nm. Zirconium tungstate exhibits a lower reflectance in the infrared region than the other tungstates that were tested; it also has a gradual loss of reflectance from 470 to 320-nm wavelength. The less promising reflectance data exhibited by zinc and zirconium tungstates should not preclude us from using them in solid solutions with either calcium, barium or strontium tungstate as a complex tungstate, which might well offer greater stability in space environment than a single tungstate.

3. Pigment preparation

We have attempted the formation of the compounds listed in Table 8 through solid-solution-type reactions at various temperatures and reaction times.

It is not our intent to discuss the reflectance data yielded by all the compounds listed above, or by simple mixtures that are not described in this report, since many of them only served in the preliminary definition of experimental techniques. However, we will briefly indicate the most promising combinations on which more exacting techniques of synthesis and analysis will be used to determine their ultimate performance in the space environment (and, perchance, terrestrial environments as well).

a. <u>Calcium metastannate:</u> - The most promising calcium stannate that we have prepared is $CaSnO_3$ (Batch A-773) reacted for 19.5 hours at 1000°C (Figure 9). When higher reaction

Table 8

EXPERIMENTAL PIGMENT SYNTHESES

Pigment Compound	Temperature Degree Centigrade	Time, Hours	Batch No.
$CaSnO_3$	1100	3	A-743
$SrSnO_3$	1100	3	A-745
$CaSnO_3$	500	5.75	A-747
$CaSnO_3$	500 + 1200	5.75 2.5	A-751
$CaSnO_3$	500 + 1200 + 1200	5.75 2.5 2.33	A-752
$ZnSnO_3$	1200	2.5	
$ZnSnO_3$	800	20	A-765
Ca_2SnO_4	800	20	A-766
$CaSnO_3$	800	20	A-767
Zn_2SnO_4	800	20	A-764
Zn_2SnO_4	1000	19.5	A-770
$ZnSnO_3$	1000	19.5	A-771
Ca_2SnO_4	1000	19.5	A-772
$CaSnO_3$	1000	19.5	A-773
Ca_2SnO_4	1200	17	A-780
Sr_2SnO_3	1200	17	A-781
Zn_2SnO_4	1200	17	A-782
Ca_2SnO_4	1300 + 1400	12 2	A-778
$CaSnO_3$	1300 + 1400	12 2	A-777

Table 8

EXPERIMENTAL PIGMENT SYNTHESES (Cont'd)

Pigment Compound	Temperature Degree Centigrade	Hours	Batch No.
Zn_2SnO_4	1300 + 1400	12 2	A-775
$ZnTiO_3$	1090	12	A-789, A-790
$ZnTiO_3$	1200	13.5	A-796, A-795
$ZnTiO_3$	1300	9	A-791, A-792
Zn_2TiO_4	1200	13.5	A-798
Zn_2TiO_4	1300	9	A-793, A-794
Zn_2TiO_4	1100	15	A-810, A-811, A-812, A-813
$ZnTiO_3$	1100	15	A-802
Zn_2TiO_4	1000	15.5	A-853, A-854, A-857
Zn_2TiO_4	1200	15	A-855, A-856, A-858, A-859

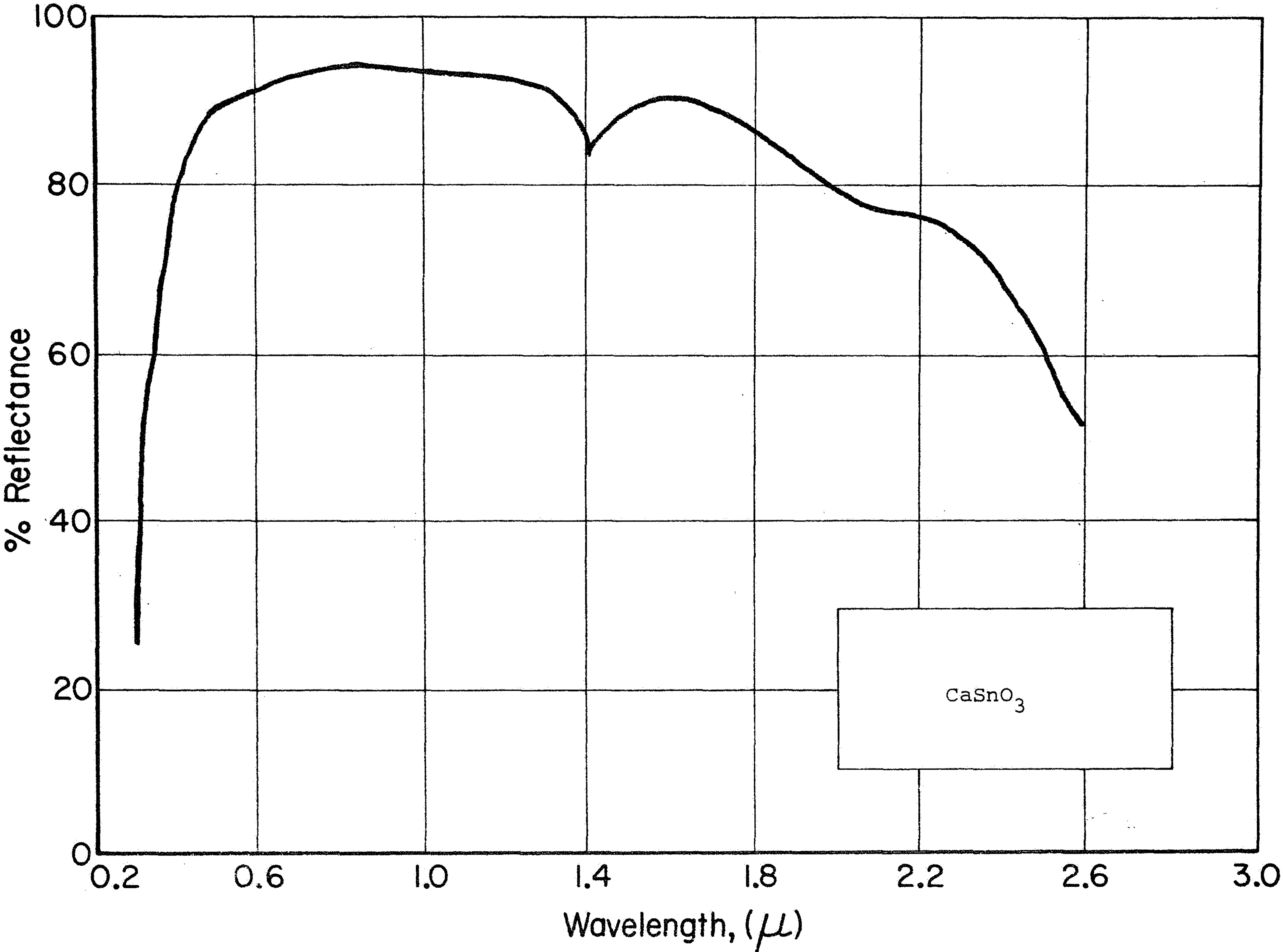

Figure 9 - ABSOLUTE HEMISPHERICAL REFLECTANCE OF A WET-POWDER SPECIMEN OF CALCIUM METASTANNATE (Batch A-770; 1000°C)

temperatures are used, the reflectance of the resulting compound progressively decreases, probably because of the decomposition of stannic oxide.

b. Zinc orthostannate: - Zinc orthostannate reacted for 19.5 hours at 1000°C (batch A-770) is more reflective than all the other zinc stannates that we have prepared (see Figures 10 and 11). Zinc stannates prepared at higher temperatures are less reflective and it is believed that this also is due to the decomposition of stannic oxide. Examination of Figures 10 and 11 show that, while the product prepared at 1300°C (Fig. 8) is less reflective in the visible portion of the spectrum, it exhibits greater reflectance in the 1500-nm-wavelength region. This is attributed primarily to the greater particle size of the high temperature product.

We wish to emphasize that prior to calcination (i.e., reaction) ZnO and SnO_2 were dry mixed and that no attempt was made to extract unreacted elementary oxides from the final product. There can be little question that slurrying and extraction of unreacted oxides would improve the initial reflectance of zinc orthostannate.

c. Zinc orthotitanate: - Our experiments largely confirm those discussed in a previous Triannual Report (IITRI-U6002-47). The higher the reaction temperature, the higher the total reflectance (Figures 12 and 13). Unfortunately, extremely "hard" crystals are formed if the reaction temperature is 1100°C (2010°F) or higher and we have had considerable difficulty in even painting our small test specimens with water "mulls" of these jewel-like

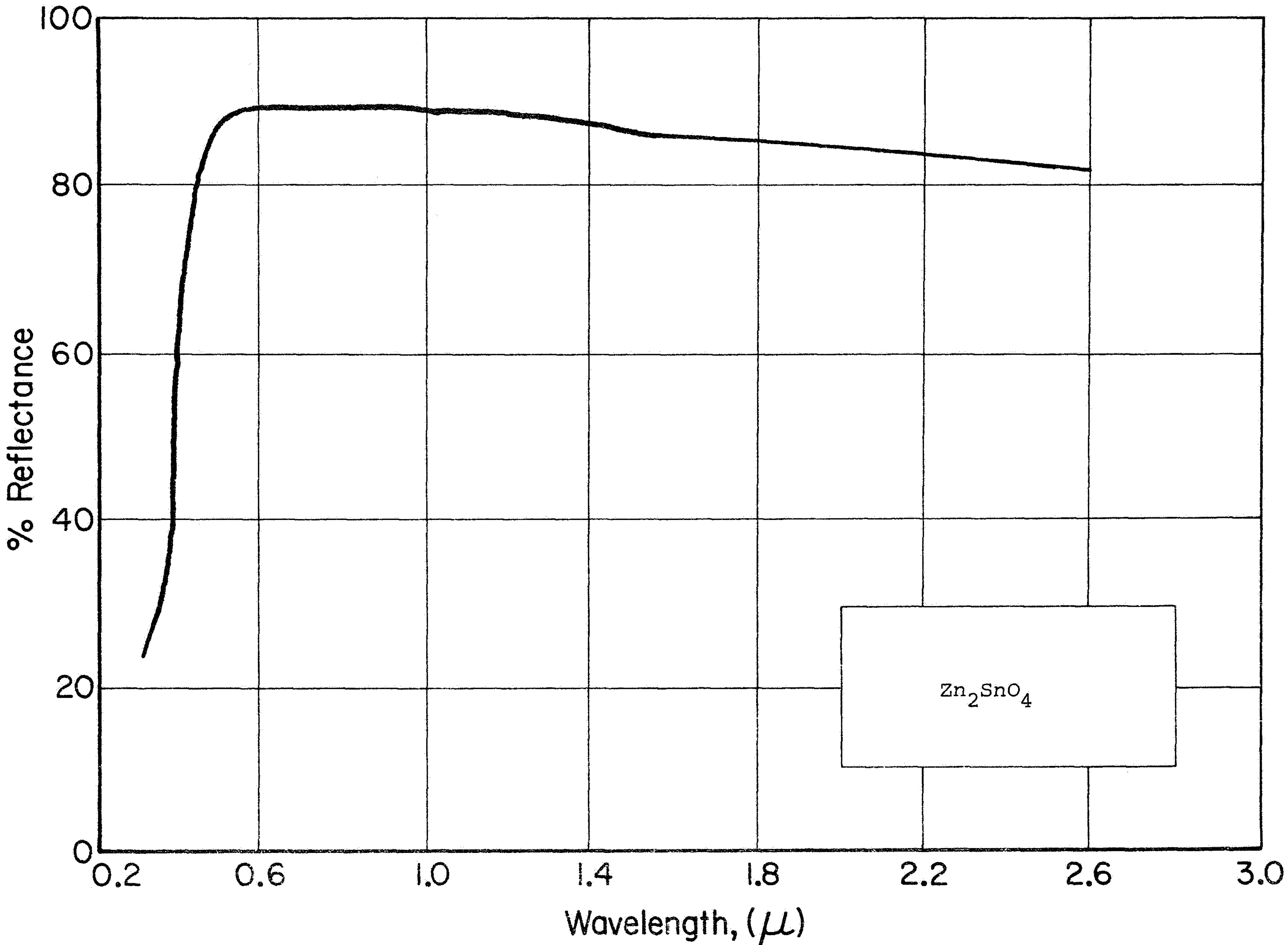

Figure 10 - ABSOLUTE HEMISPHERICAL REFLECTANCE OF A WET-POWDER SPECIMEN OF ZINC ORTHOSTANNATE (Batch A-773; 1300°C)

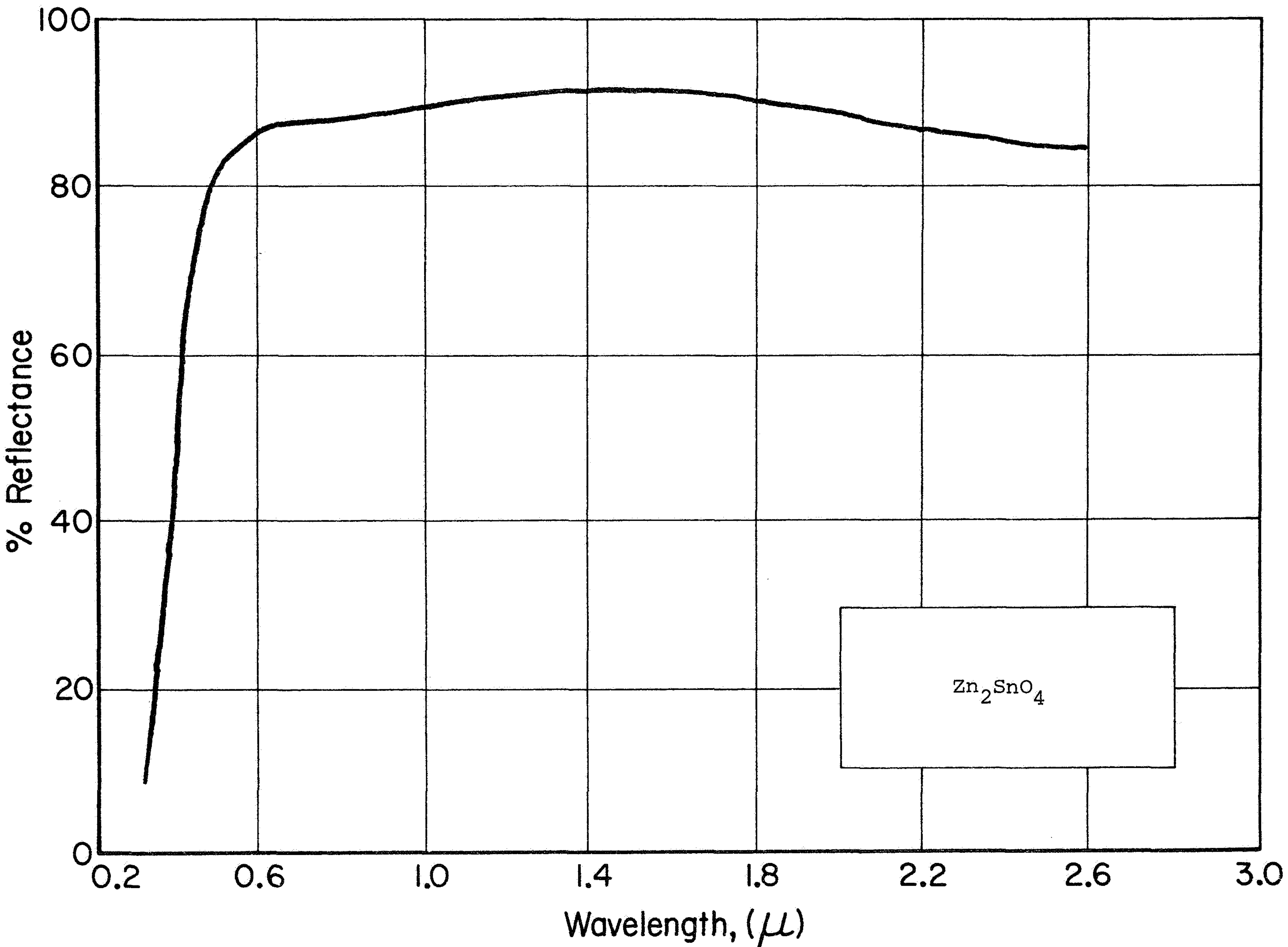

Figure 11 - ABSOLUTE HEMISPHERICAL REFLECTANCE OF A WET-POWDER SPECIMEN OF ZINC ORTHOSTANNATE (Batch A-775; 1300°C)

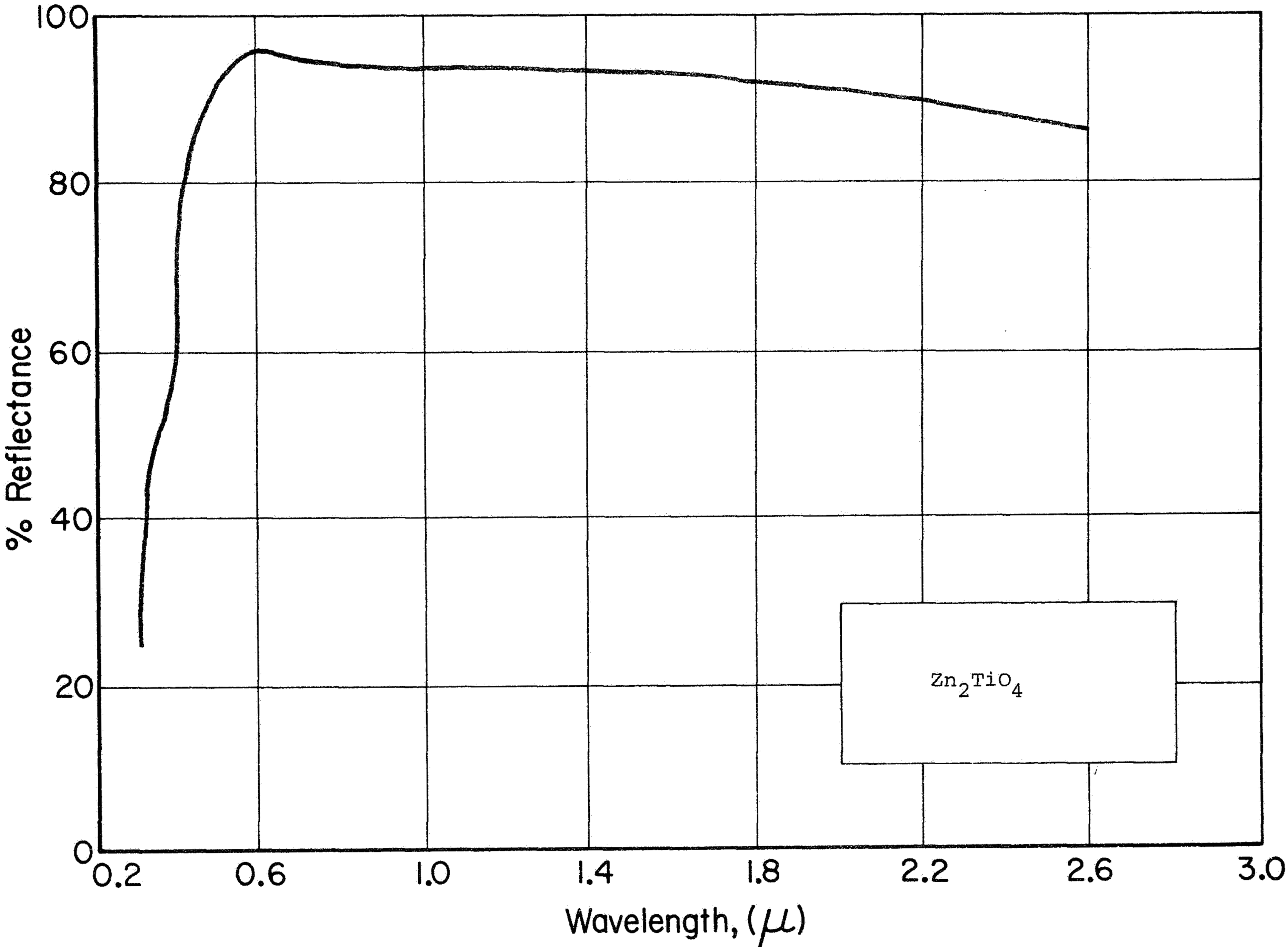

Figure 12 - ABSOLUTE HEMISPHERICAL REFLECTANCE OF A WET-POWDER SPECIMEN OF ZINC ORTHOTITANATE (Batch A-857; 1000°C)

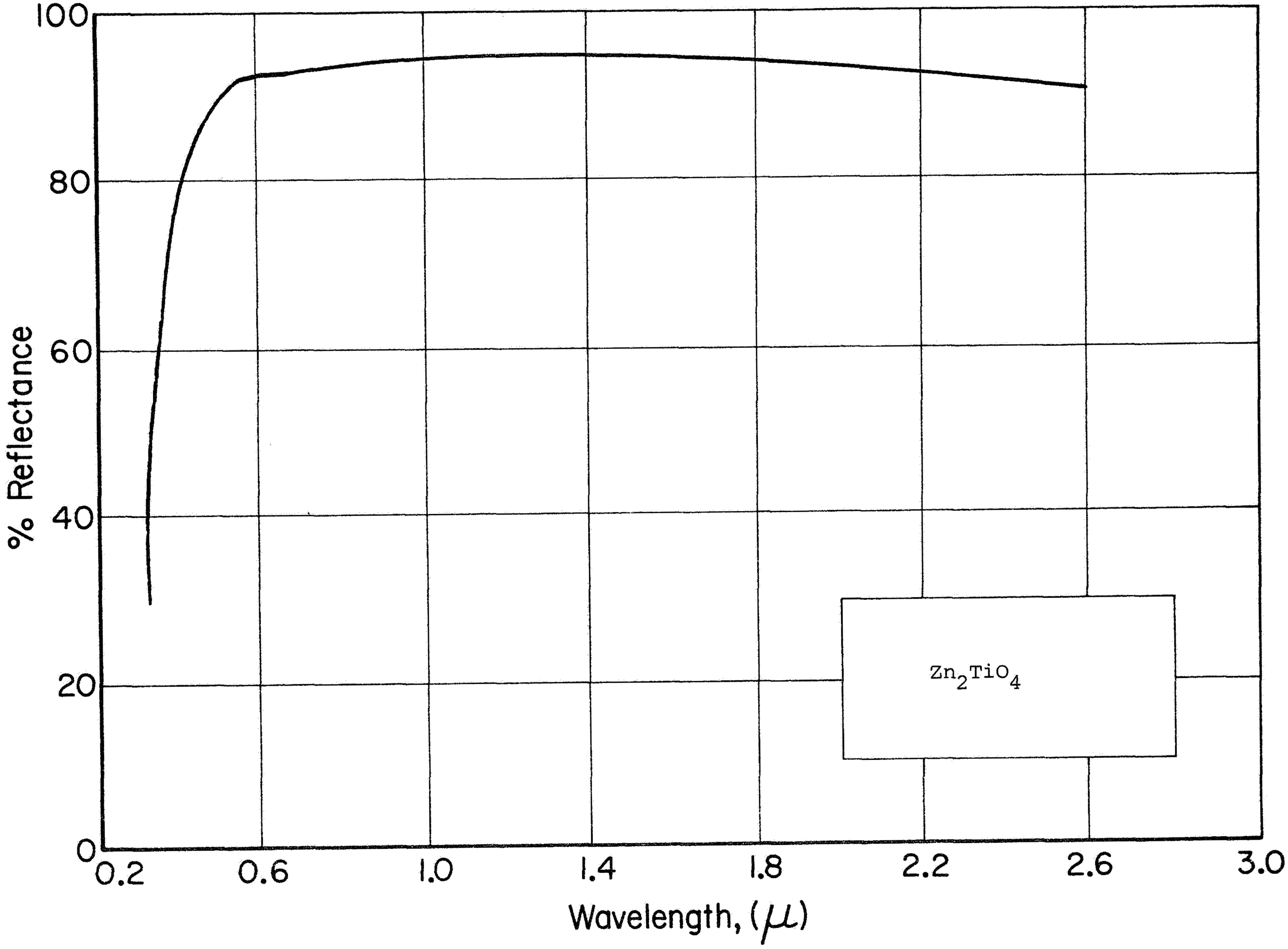

Figure 13 - ABSOLUTE HEMISPHERICAL REFLECTANCE OF A WET-POWDER SPECIMEN OF ZINC ORTHOTITANATE (Batch A-812; 1100°C)

crystals. It is planned to use different grinding techniques and different grinding media to resolve this problem. Hopefully, more energetic size reduction will not result in excessive surface damage in all pigments.

Examination of Figures 12 and 13 show that the product reacted at 1000°C exhibits the residual-ZnO reflectance shelf. The product reacted at 1100°C for 15 hr (Figure 12) does not exhibit strong ZnO-related absorption (no extraction with acetic acid was performed). This is the only batch ever observed to not have a strong residual-ZnO band at 375-nm wavelength.

D. Stability to Ultraviolet Radiation in Vacuum

Four calcium tungstate- and two double zirconium silicate-pigmented Owens-Illinois 650-resin paints were irradiated in the IRIF-II space simulation facility described in Figure 20. Ultraviolet irradiation was performed at nominal solar intensities of 4X employing a 5-kw Hanovia mercury-xenon radiation source, which was operated at 80% of capacity to maximize its lifetime.

Two "pure" and two "activated" calcium tungstates and calcium and zinc zirconium silicate paints were irradiated in three separate simulation tests. The data accumulated are presented in Table 9 and Figures 14 through 19. The spectra are presented as equal (solar)-energy increments to emphasize damage. The excellent stability of the calcium tungstate paints is particularly noteworthy, especially insofar as Z93 is observed to degrade slightly in the tests employing mercury-xenon radiation. (The Z93 specimen exhibited a solar absorptance

Table 9

EFFECT OF 600 ESH UV IRRADIATION IN IRIF-II ON THE SOLAR ABSORPTANCE OF SEVERAL THERMAL-CONTROL COATINGS

(Solar Intensity 4X)

Figure	Description	Exposure (ESH)	Solar Absorptance α_1	α_2	α_s	$\Delta\alpha_s$
14	$CaWO_4$/O-I 650	0	.116	.089	.205	---
		70	.119	.089	.208	.003
		600	.122	.083	.205	.000
15	Ca*WO_4/O-I 650	0	.128	.103	.231	---
		70	.132	.105	.237	.006
		600	.139	.108	.247	.016
16	$CaZrSiO_5$/O-I 650	0	.157	.129	.286	---
		70	.159	.133	.292	.006
		600	.164	.133	.297	.011
17	$ZnZrSiO_5$/O-I 650	0	.154	.113	.267	---
		600	.161	.109	.270	.003
	Z93	0	.129	.036	.165	---
		600	.148	.032	.180	.015

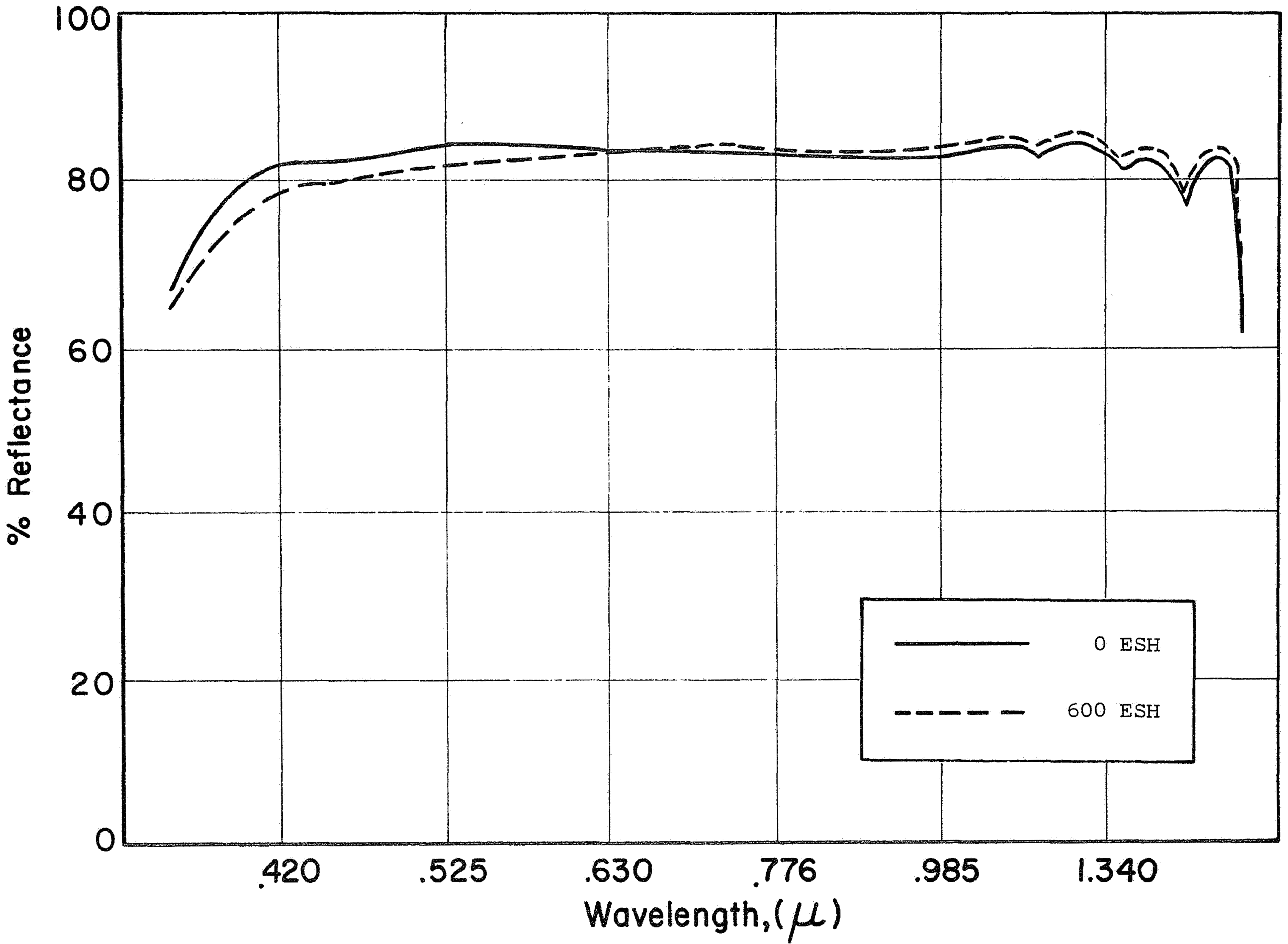

Figure 14 - SPECTRAL REFLECTANCE OF $CaWO_4$/O-I 650 PAINT AS A FUNCTION OF EXPOSURE TO 600 ESH OF UV IN IRIF-II

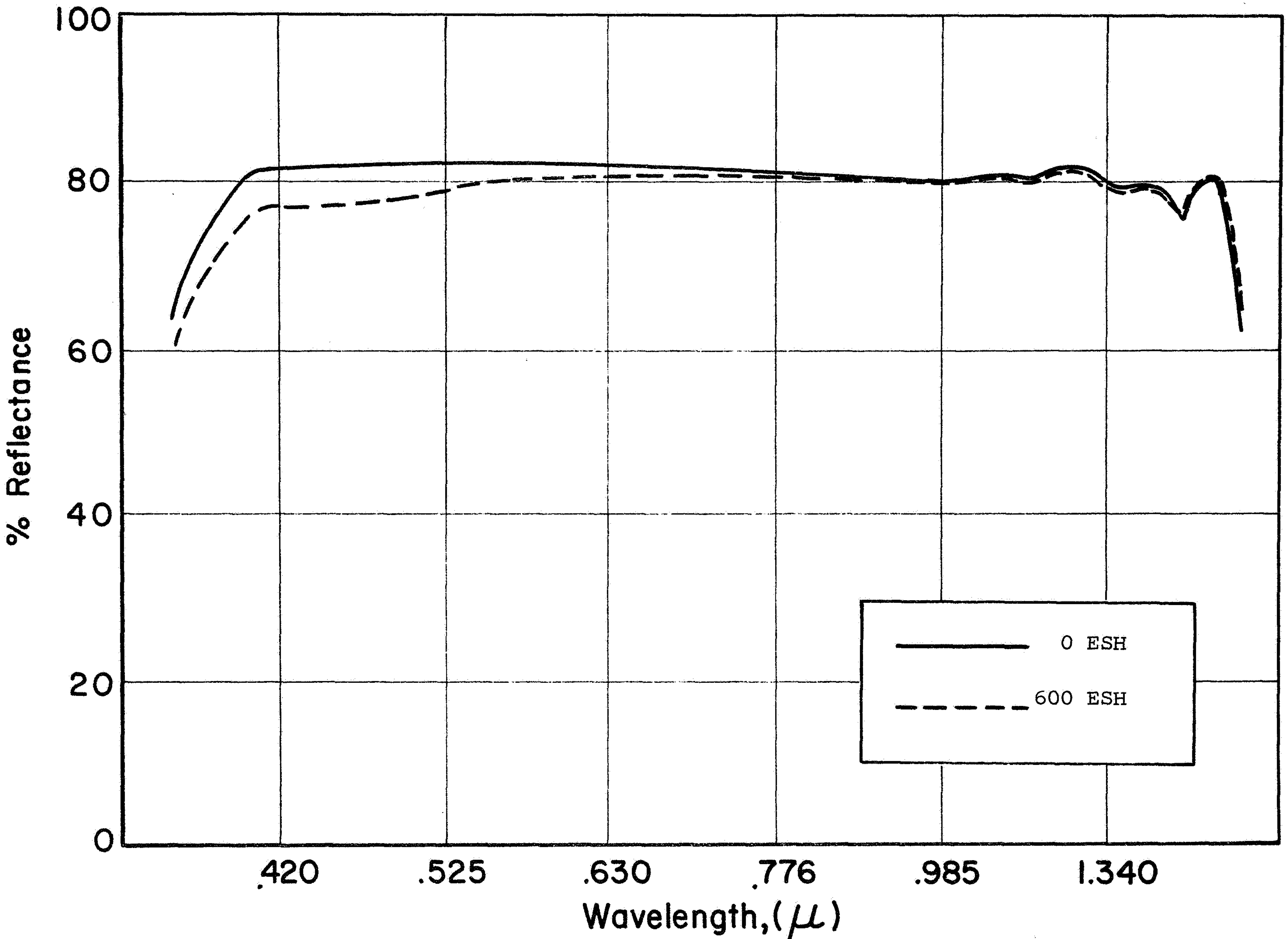

Figure 15 - SPECTRAL REFLECTANCE OF Ca*WO$_4$/O-I 650 PAINT AS A FUNCTION OF EXPOSURE TO 600 E OF UV IN IRIF-II

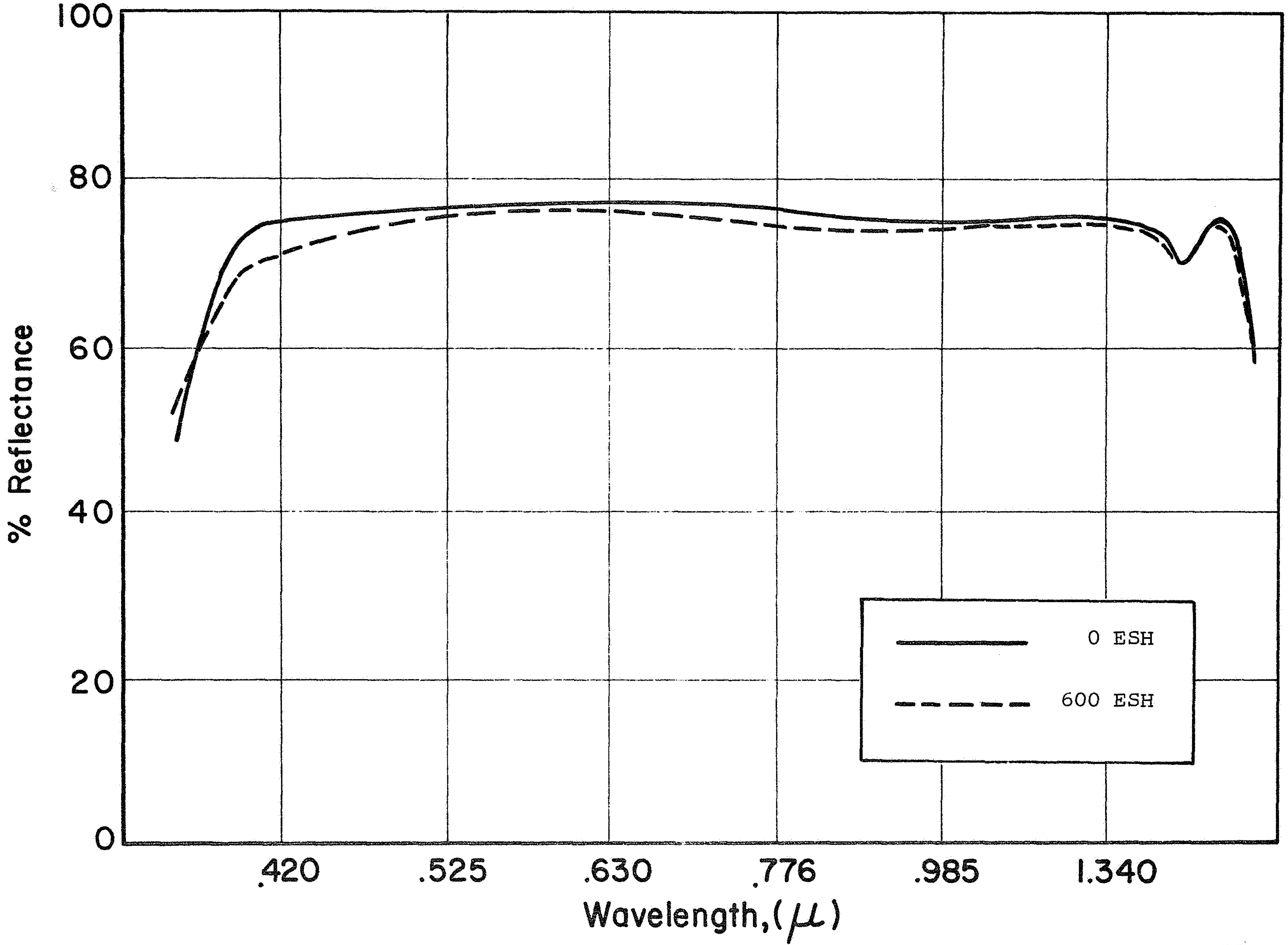

Figure 16 - SPECTRAL REFLECTANCE OF $CaZrSiO_5$/O-I 650 PAINT AS A FUNCTION OF EXPOSURE TO 600 ESH OF UV IN IRIF-II

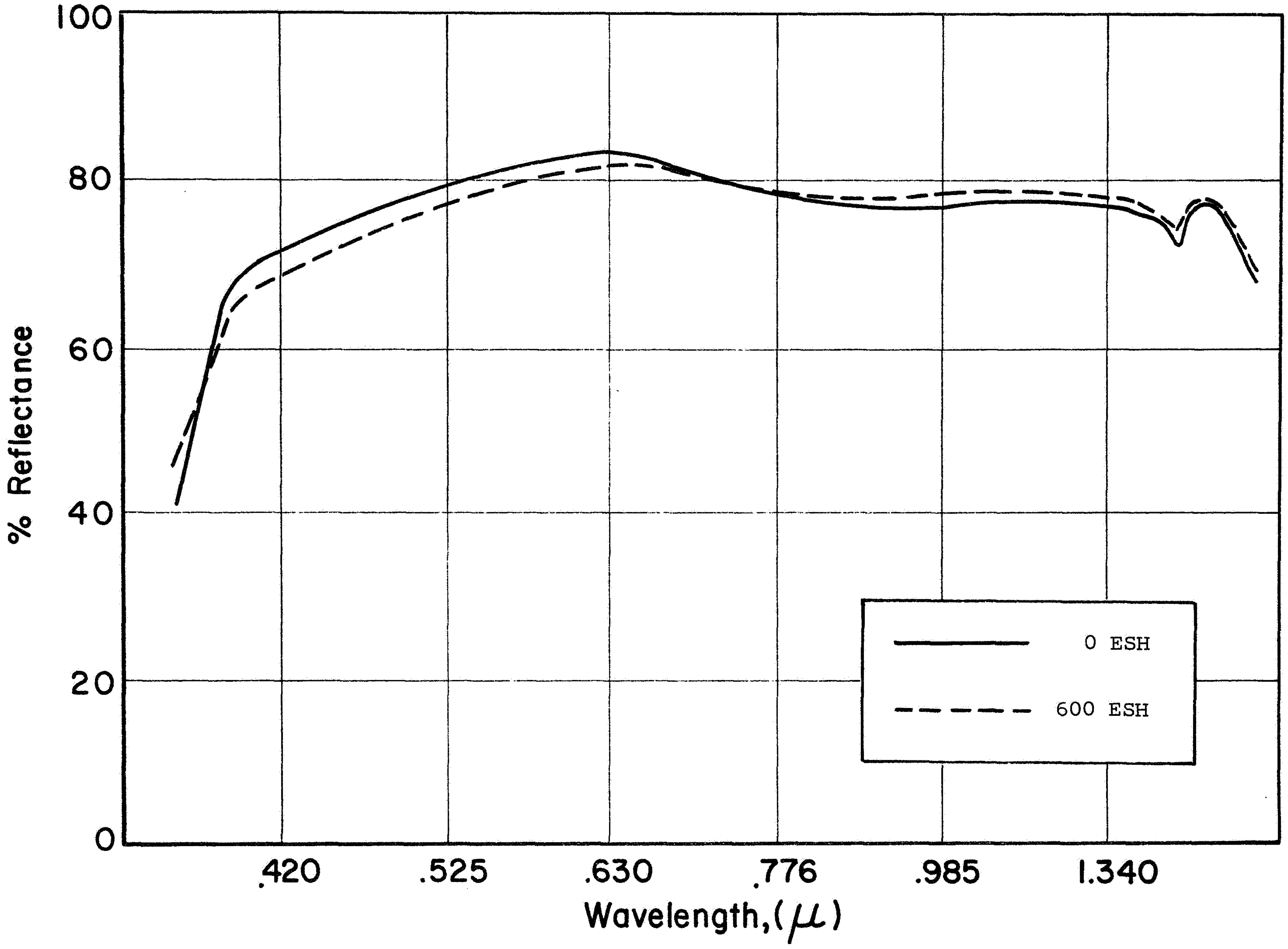

Figure 17 - SPECTRAL REFLECTANCE OF $ZnZrSiO_5$/O-I 650 PAINT AS A FUNCTION OF EXPOSURE TO 600 ESH OF UV IN IRIF-II

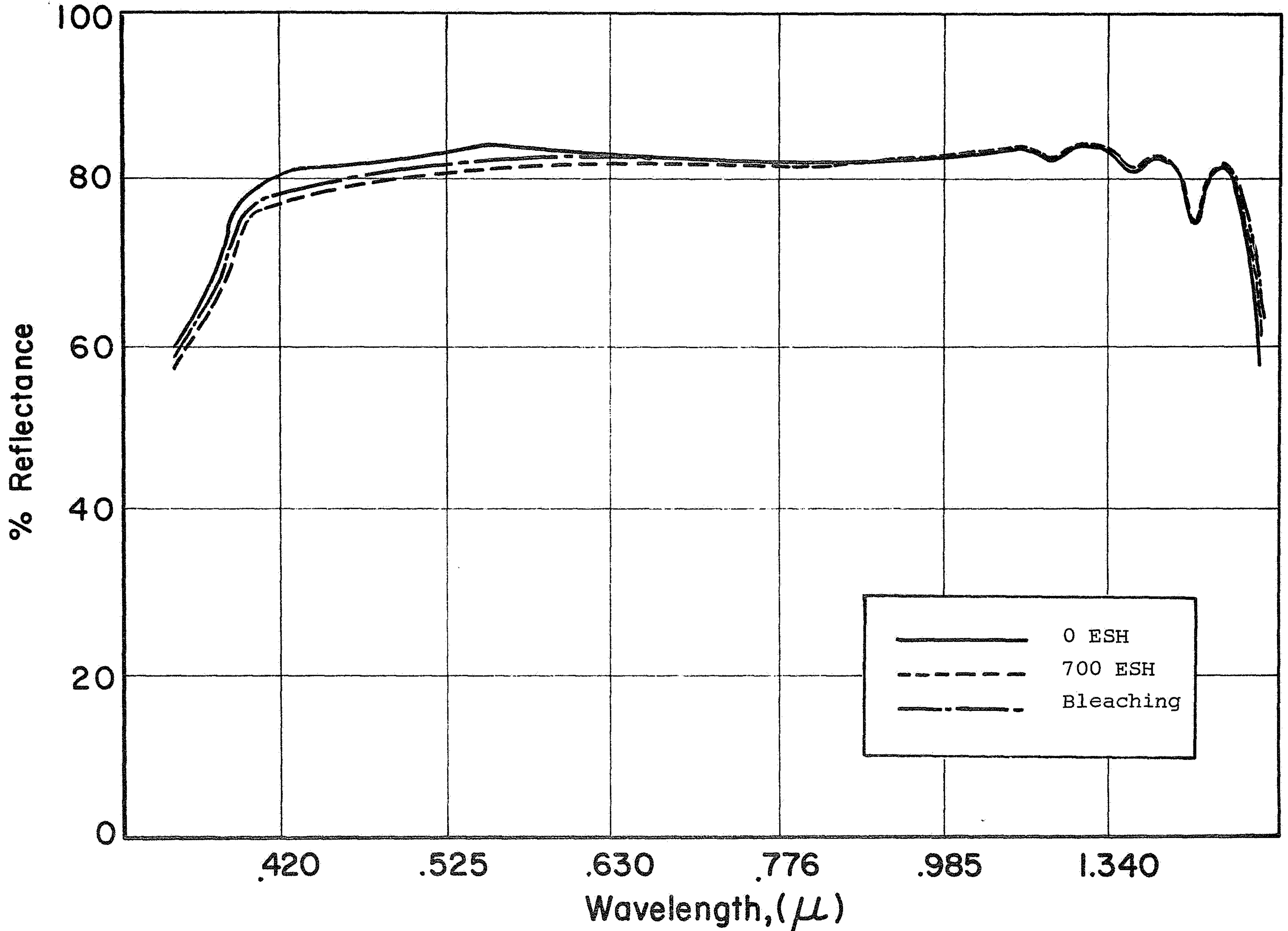

Figure 18 - SPECTRAL REFLECTANCE OF $CaWO_4$/O-I PAINT AS A FUNCTION OF EXPOSURE TO 700 ESH OF UV IN IRIF-II

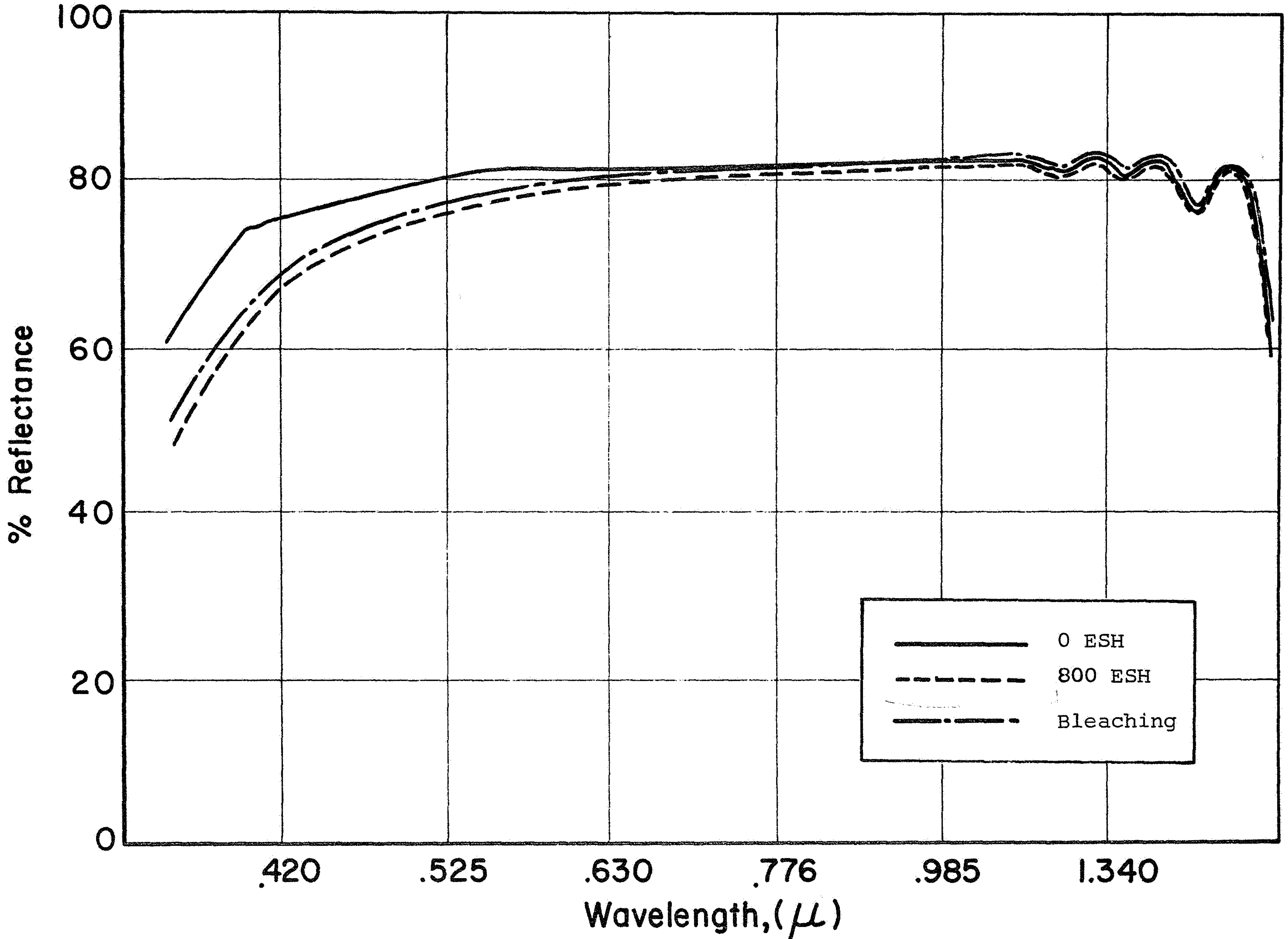

Figure 19 - SPECTRAL REFLECTANCE OF $Ca*WO_4/O-I$ 650 PAINT AS A FUNCTION OF EXPOSURE TO 800 ESH OF UV IN IRIF-II

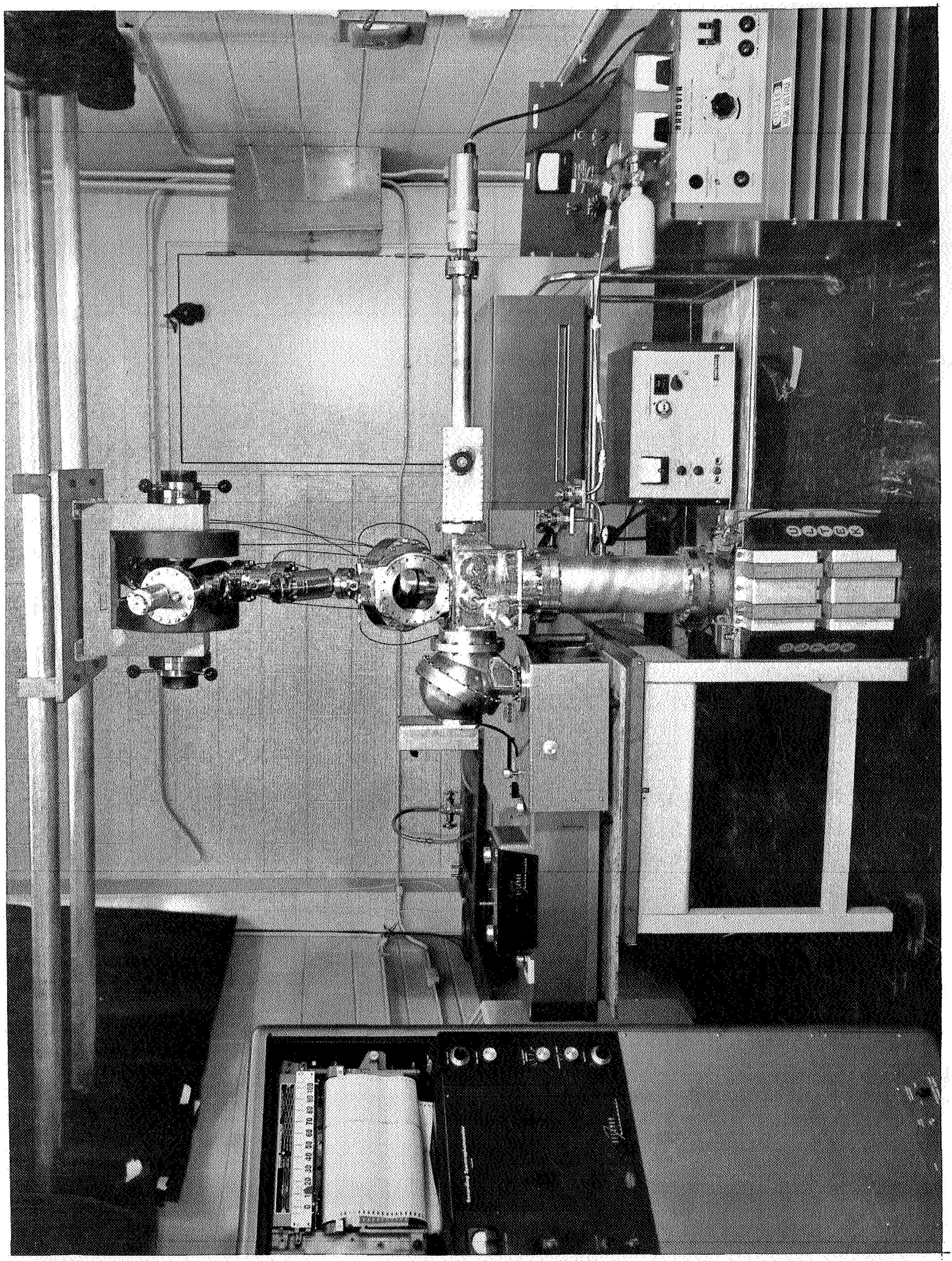

Figure 20 - THE COMBINED-RADIATION-ENVIRONMENT FACILITY (CREF)

increase of 0.015 in 600 ESH of mercury-xenon irradiation.) Paints pigmented with both "pure" and "activated" calcium tungstate were also irradiated in two additional ultraviolet-space-simulation tests (Figures 18 and 19). These data exhibit excellent agreement with the data presented in Figures 14 and 15. Both the activated and pure calcium tungstate paints exhibited slight bleaching in the visible region of the spectrum on admission of air to the space-simulation chamber.

The good stability of the double zirconium silicates (obtained from TAM) vindicates our earlier interest in these materials--interest that was subjugated by the discovery that the zinc orthotitanates appeared promising. With the development of sophisticated in situ testing facilities, the reexamination of calcium and zinc zirconium silicates becomes increasingly attractive. We plan to synthesize "pure" double zircons when additional heating elements are installed in our high-temperature furnace.

IV. COMBINED-RADIATION-ENVIRONMENT FACILITY (CREF)

A. Facility Description

A low-energy proton-irradiation gun has been designed and constructed for adaptation to the IRIF-II in situ Reflectometer (ref. 51). The facility is shown in Figure 20. The proton gun is composed of an rf (magnetically-confined) glow-discharge source (High Voltage Engineering Corporation, Model B-AH-TU-64) that is attached to an extractor lens used to attenuate the beam from the 40-microamp ion current at the source to the level required to deposit $\sim 10^9$ protons/cm^2-sec. The source and extractor lens are shown in Figure 21. The rf plates are removed to show the glow-discharge tube. The extractor lens, shown separately in Figure 22, aligns the emergent beam prior to entering the first Einzel lens (shown assembled in Figure 21 and unassembled in Figure 23). The proton beam is accelerated to approximately 5000 ev in the first Einzel lens and enters the magnetic field of the analyzer as a parallel beam.

A Varian low-impedance, 4-inch electromagnet (model V-4005), shown in Figure 21, equipped with a Model V-2900 power supply and a Fieldial Magnetic Field Regulator (to select and maintain the field and provide visual indications of the strength in guass), is mounted around a 45° elbow. The elbow assembly is shown in Figure 24. It is also shown in Figure 25, which is a photograph of the lower assembly. The beam, now approximately 100% H^+, enters a detection (Faraday-cup) element and then passes into the second Einzel lens, where it is accelerated to its final energy.

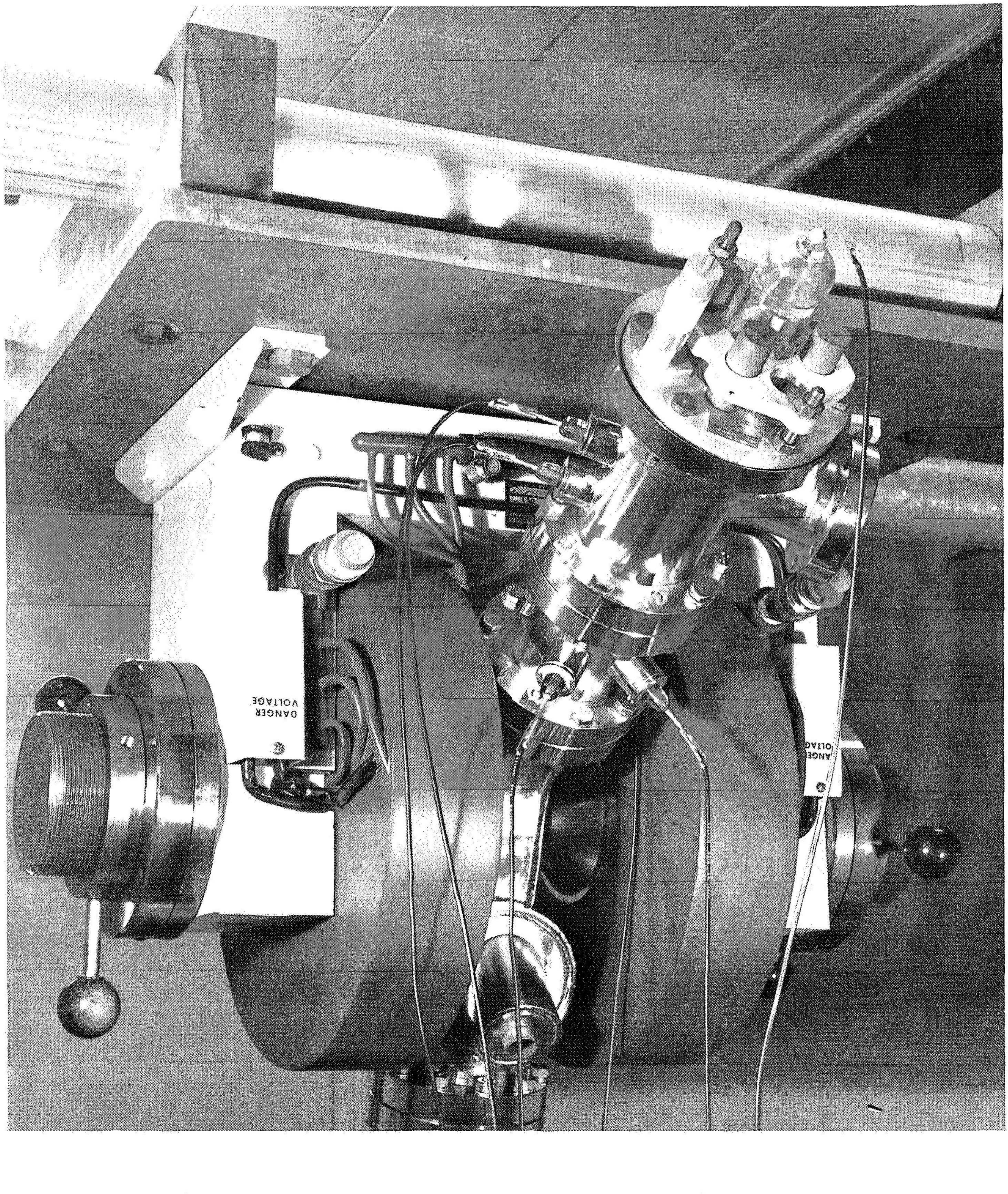

Figure 21 - PROTON SOURCE, EXTRACTOR LENS AND 1st EINZEL LENS

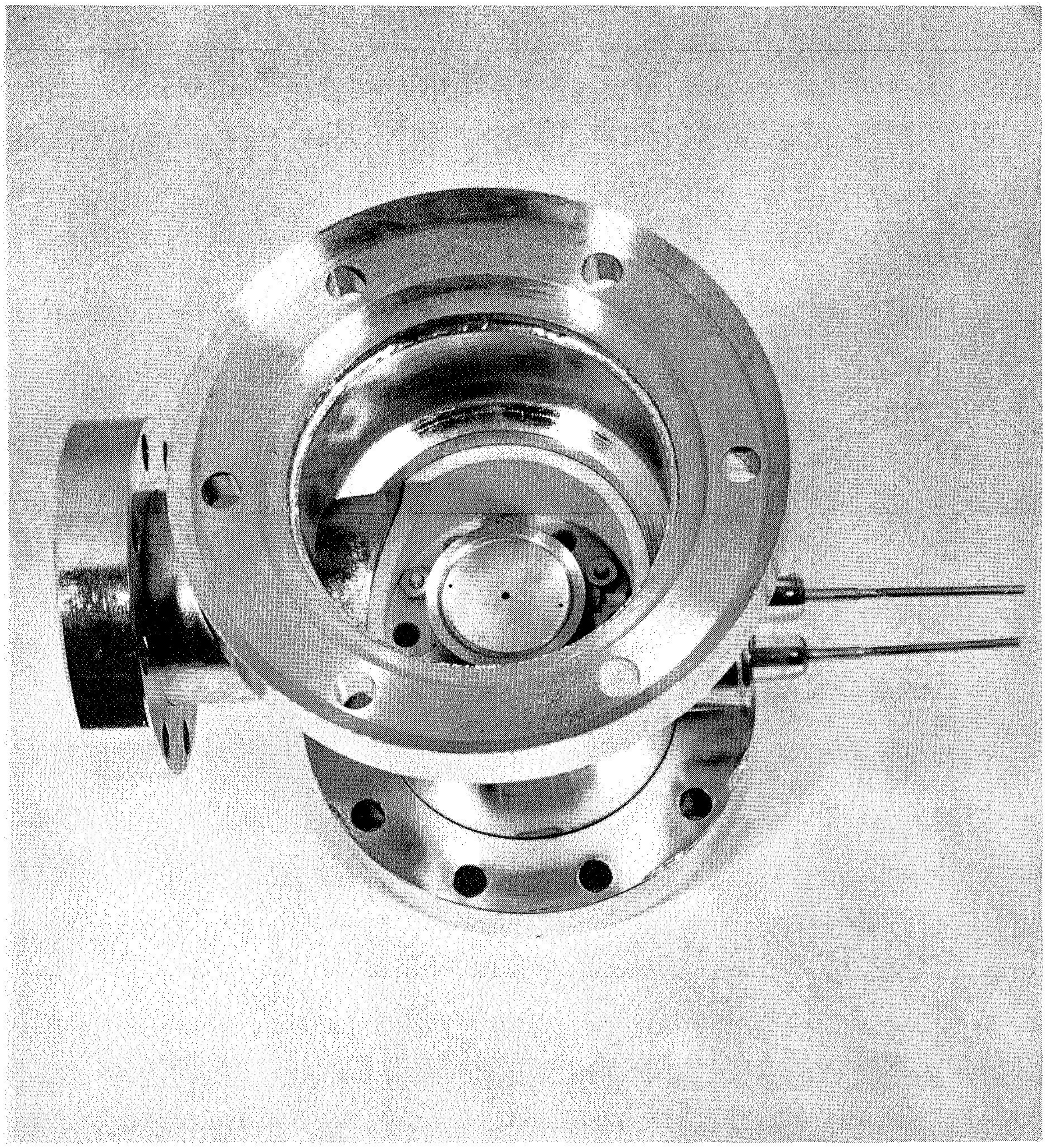

Figure 22 - EXTRACTION LENS TO REDUCE FLUX FROM RF SOURCE

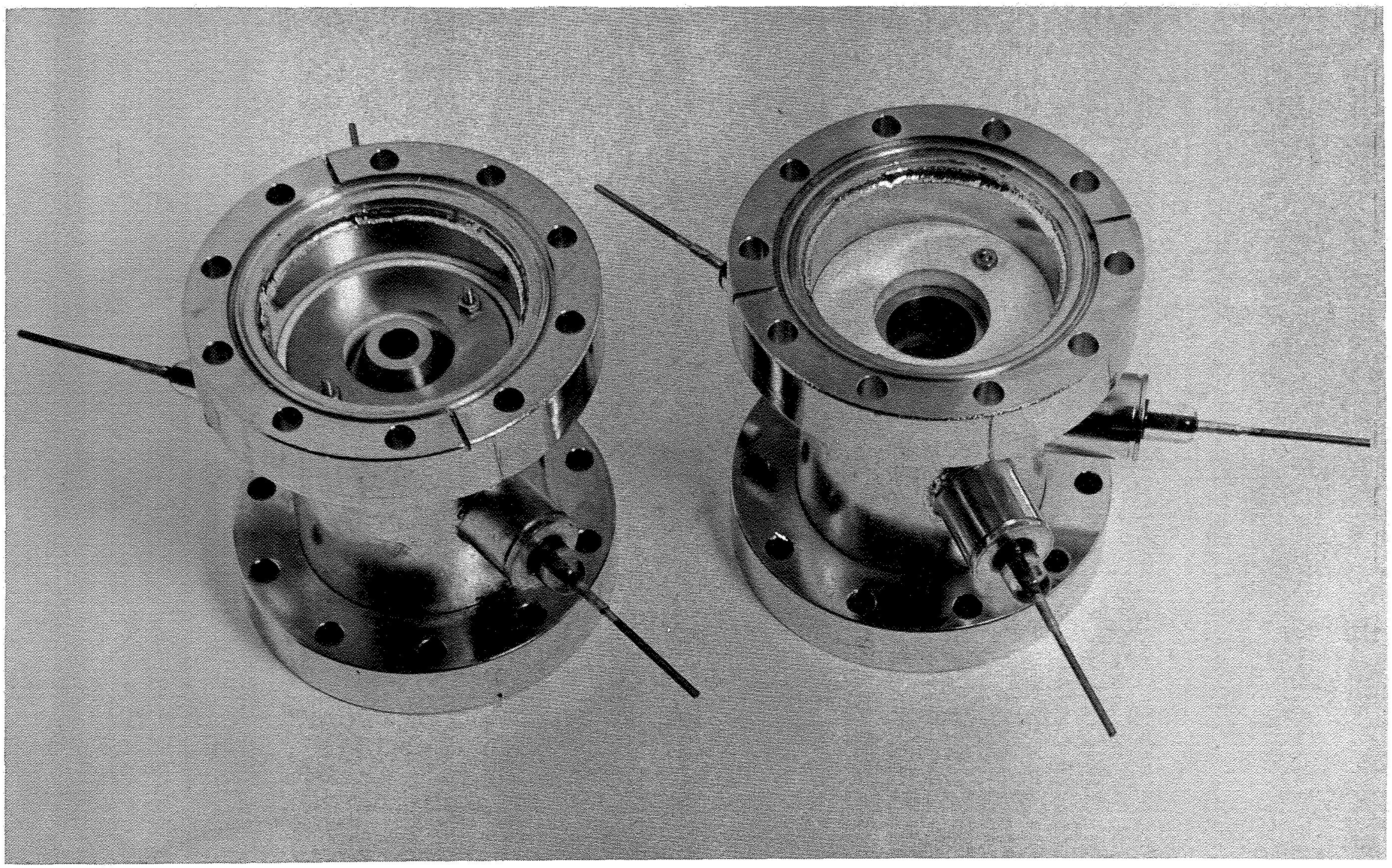

Figure 23 - TWO VIEWS (OF TWO) EINZEL LENS

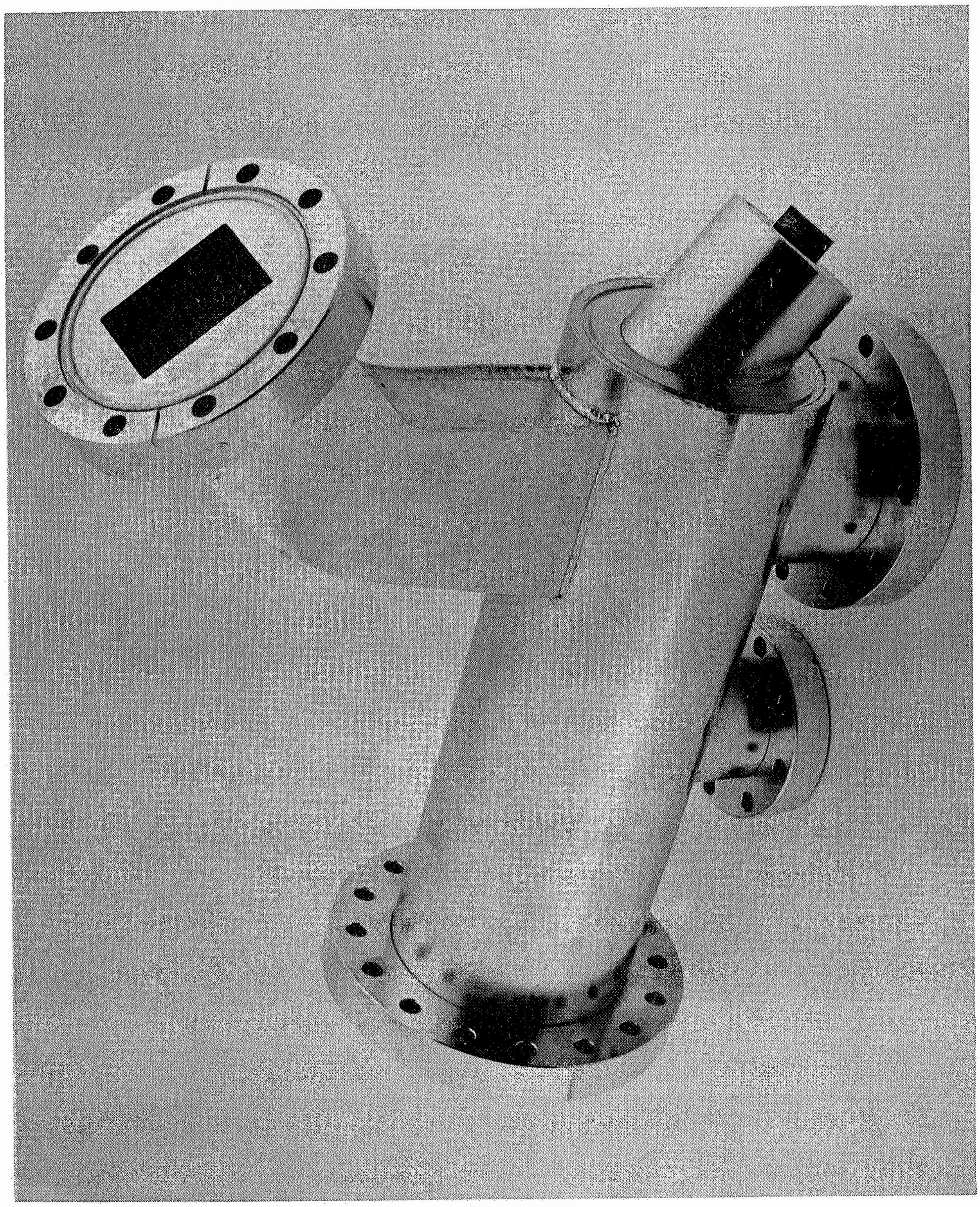

Figure 24 - 45° BEND (FOR MAGNET) AND FARADAY-CUP HOUSING

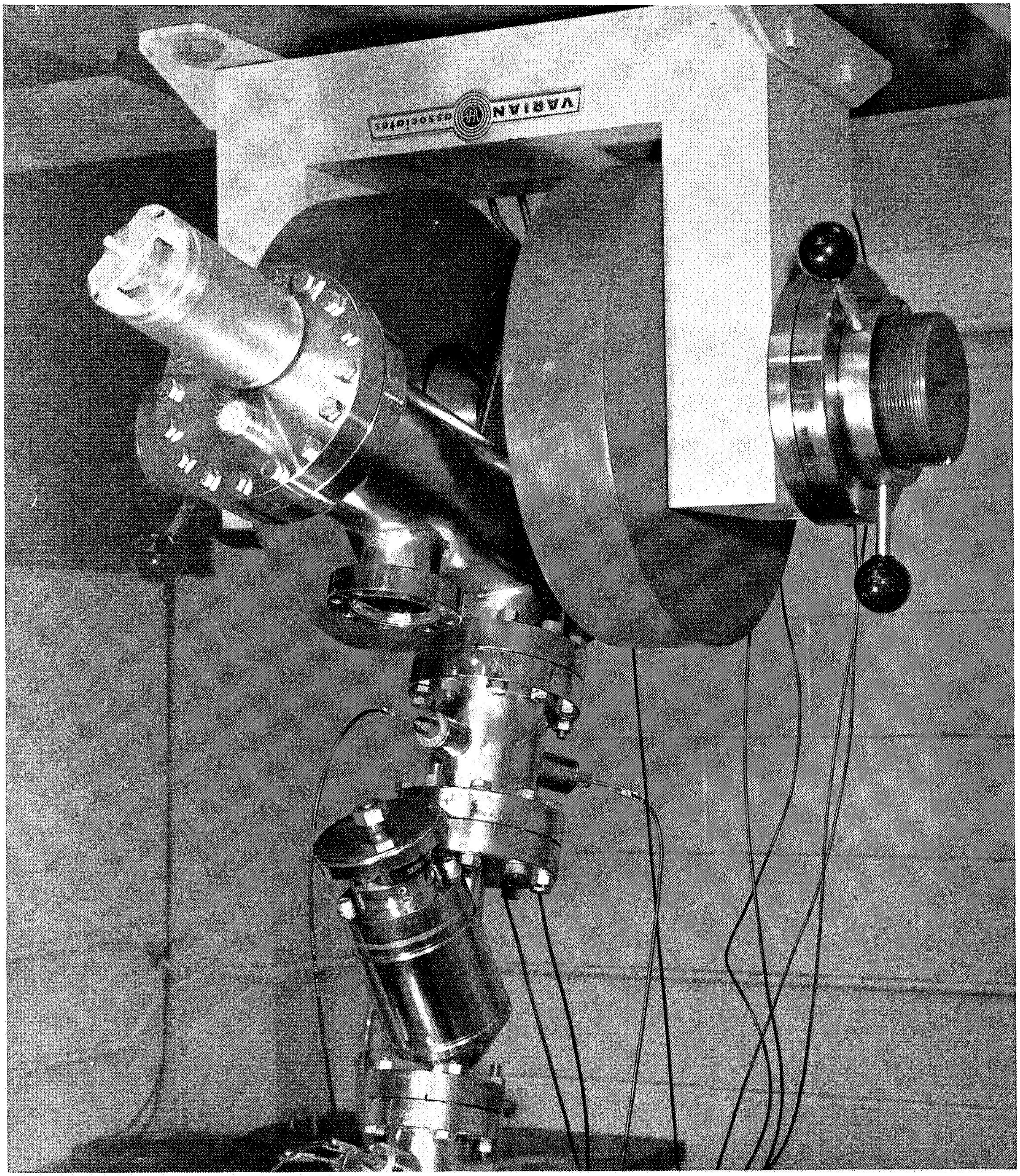

Figure 25 - MASS SEPARATOR AND MASS ANALYZER (SHOWING SECOND EINZEL LENS)

The Faraday cup housing is shown in Figures 24 and 25 and the Faraday cup in Figure 26. The Faraday cup is positioned with a magnetic chuck (Figure 27) actuated screw. The beam then passes through a valve element and then an element with two pair of deflection plates for sweeping the proton beam from position to position. The valve element is shown in Figure 28 and the sweep/ejection lens is shown in Figure 29. The beam then emerges into a housing (attached to IRIF-II) containing a 45° front surface mirror for ultraviolet irradiation. The housing, IRIF-II and the ultraviolet-source housing are shown in Figure 30.

The beam, which next passes through the mirror, is neutralized with electrons from a low-energy electron gun (whose energy can be controlled to provide either simple neutralization or an environmental factor). (The electron gun has yet to be installed.) A tungsten filament and a small suppression voltage are also employed to supply the electrons necessary to dissipate the space charge on dielectric samples.

B. Beam Calibration

Preliminary beam analysis and calibration have been performed by determining the characteristics of the unseparated beam. Figures 31 and 32 show the energy distribution of ions from the ion source. These distributions already indicate that the source emits a fairly mono-energitic beam of ions.

It has been determined that the beam spreads to a diameter of approximately 1.5 cm at a distance of 3-1/4 cm from the canal

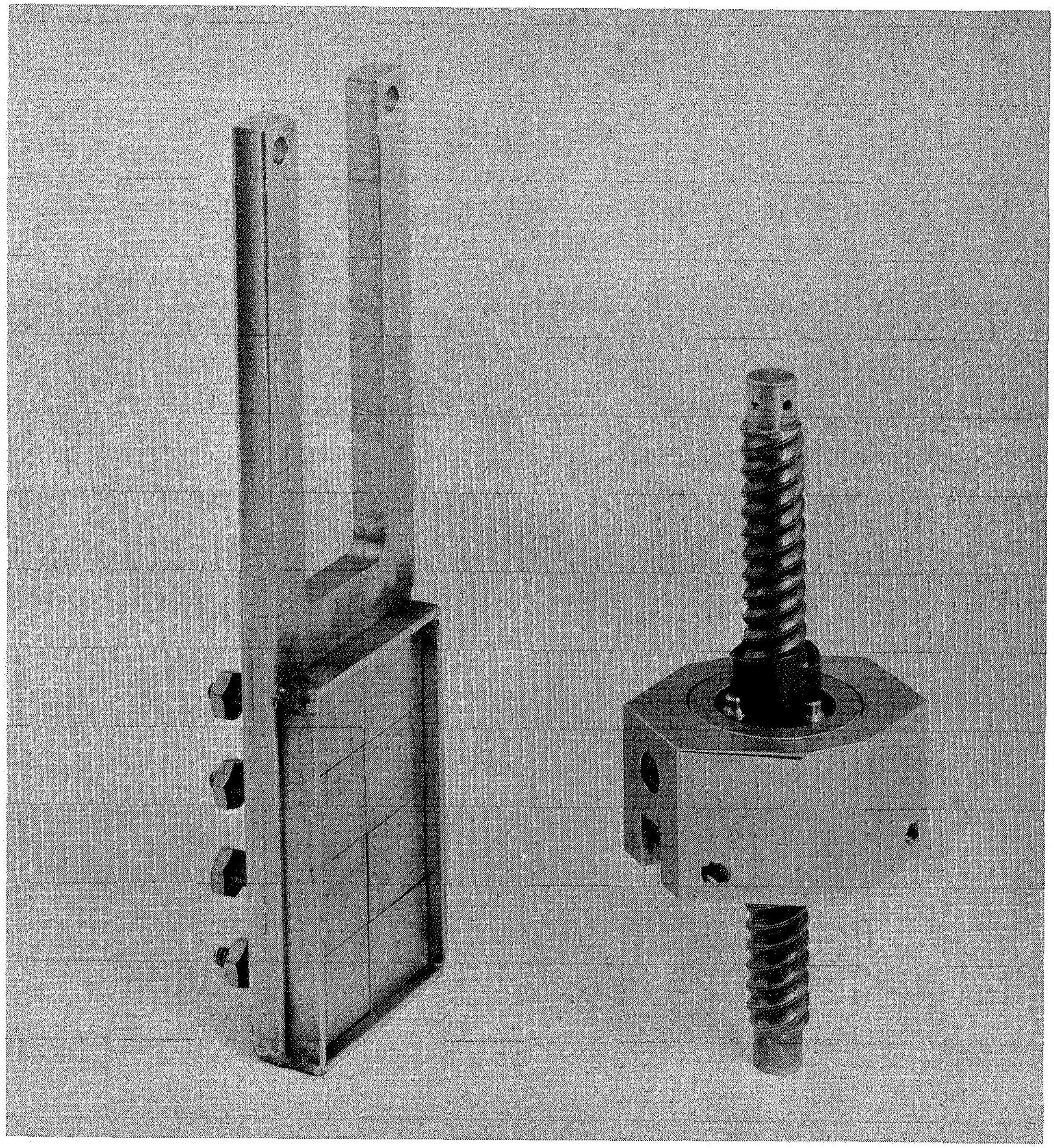

Figure 26 - FARADAY CUP FLUX MAPPER

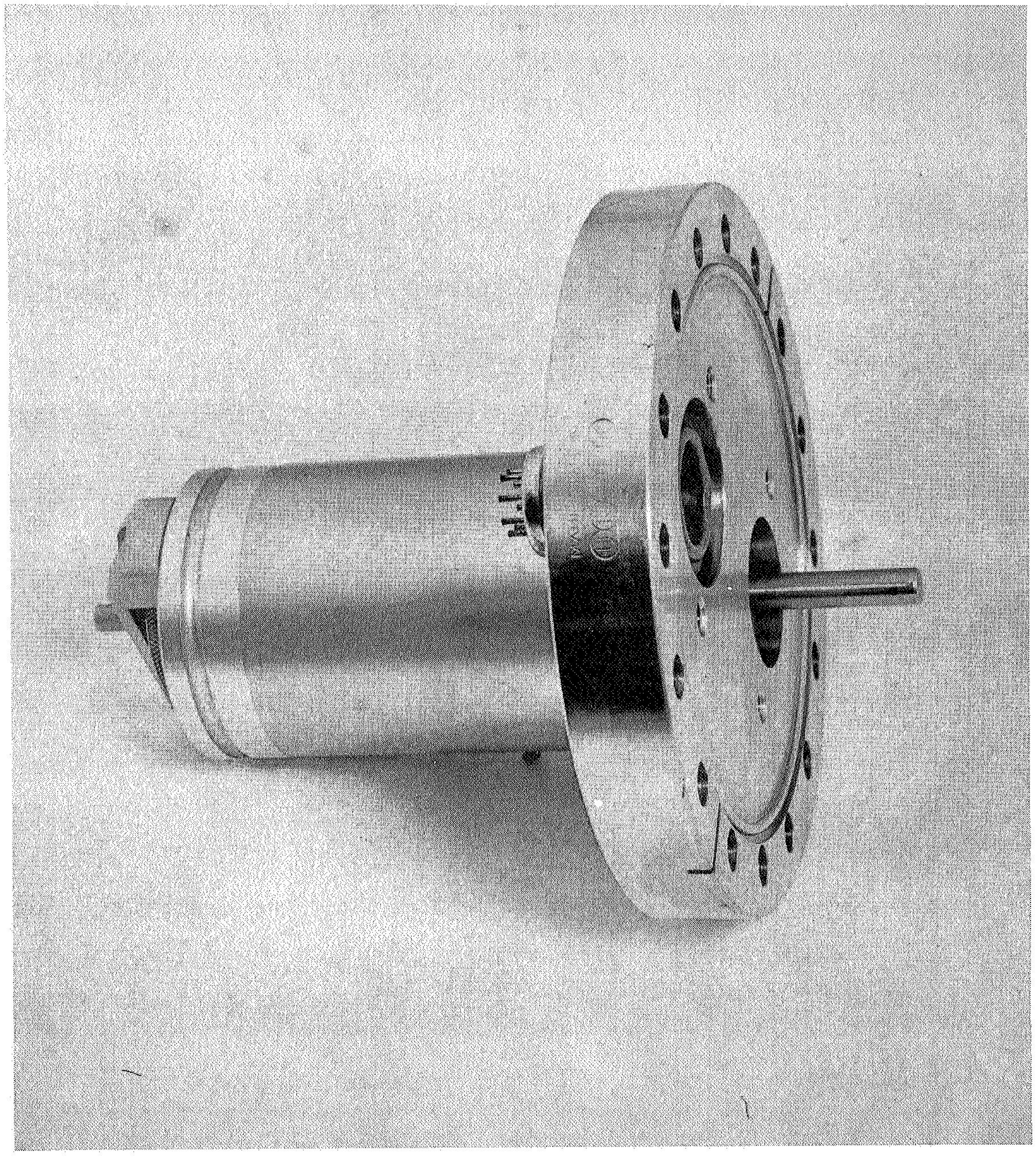

Figure 27 - MAGNETIC CHUCK

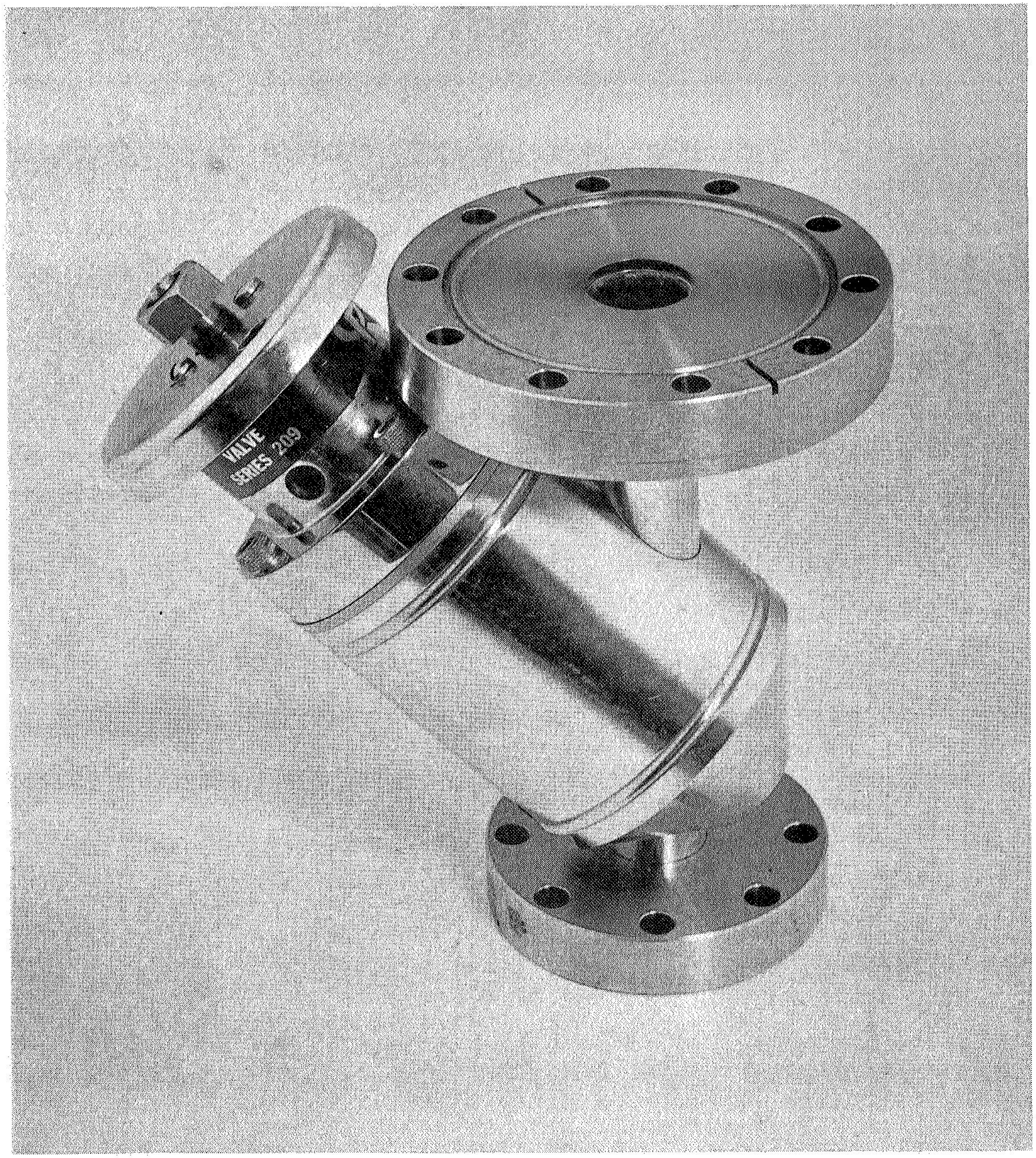

Figure 28 - VALVE ELEMENT

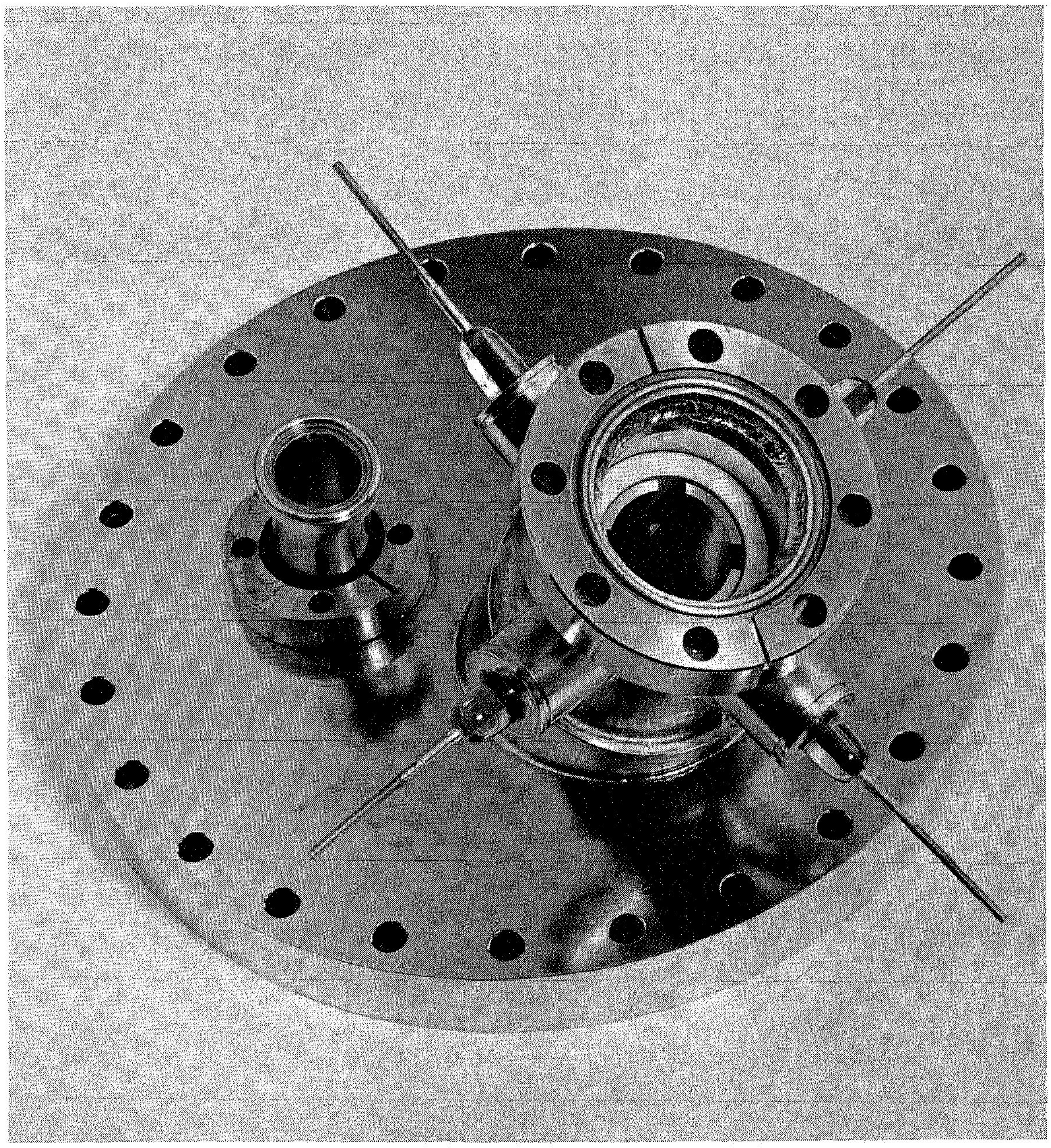

Figure 29 - EJECTION LENS (SWEEP/COLLIMATOR)

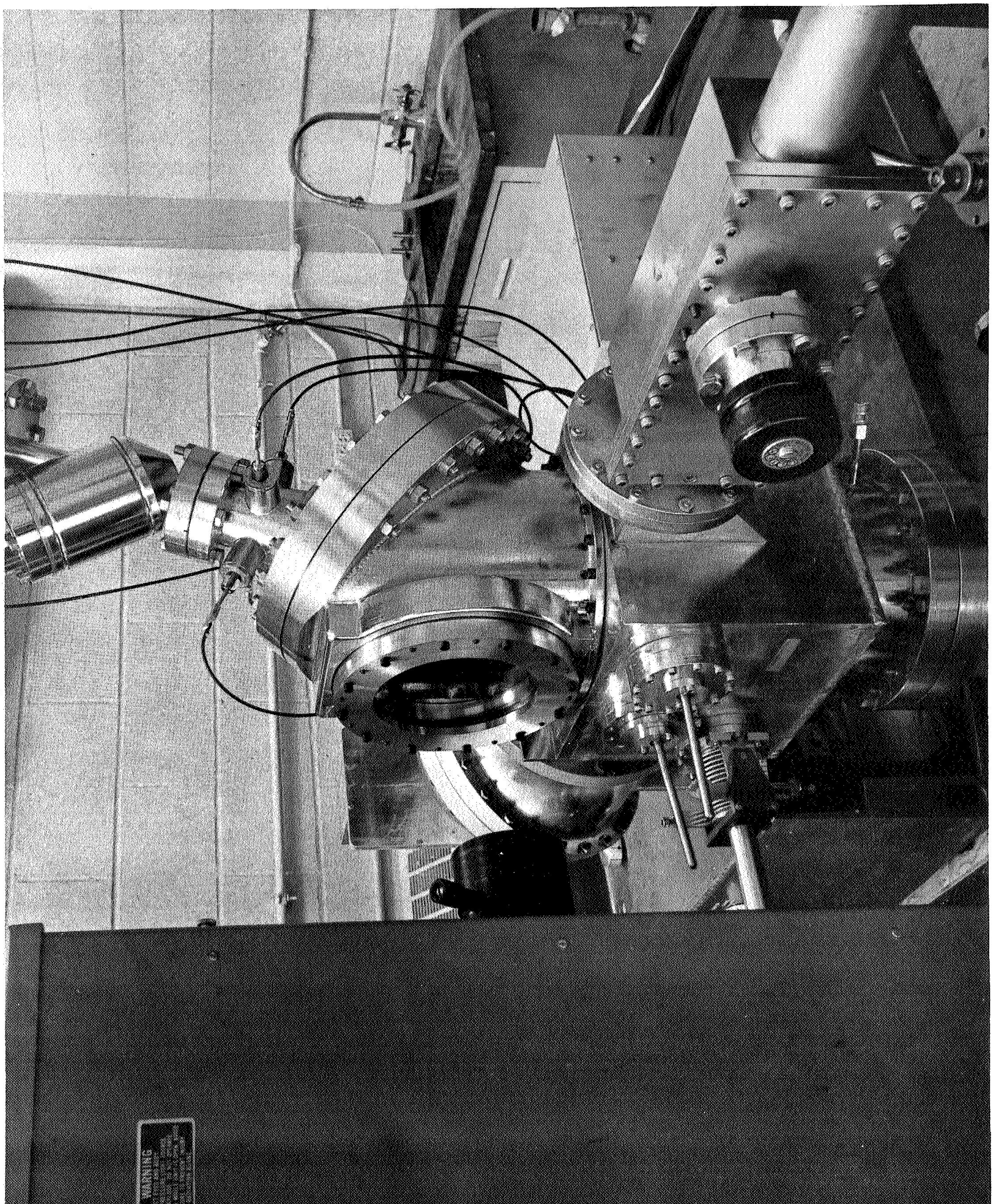

Figure 30 - MULTIPLE-SOURCE-ADAPTOR HOUSING (SHOWING SWEEP/COLLIMATOR LENS)

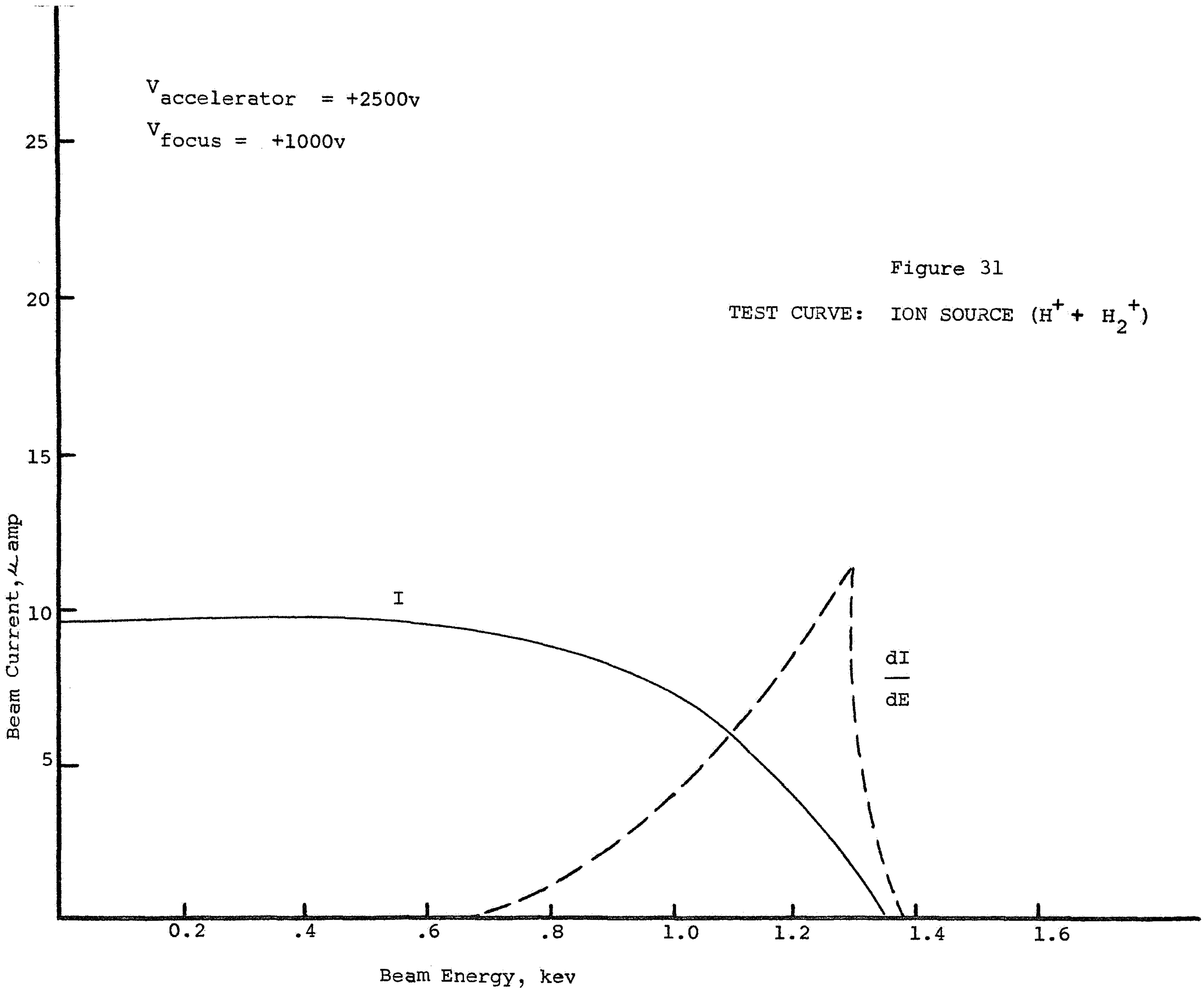

Figure 31

TEST CURVE: ION SOURCE ($H^+ + H_2^+$)

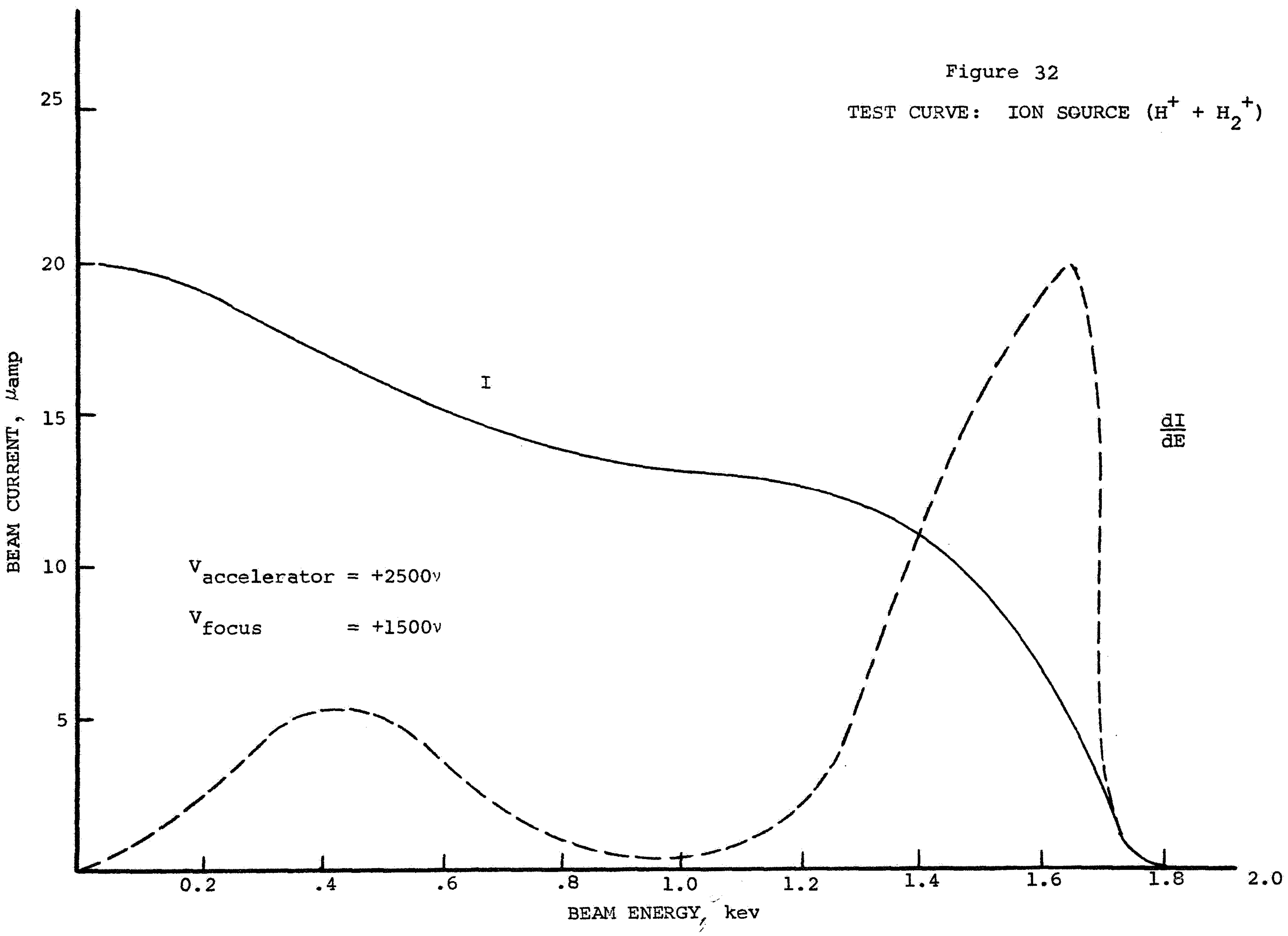

Figure 32

TEST CURVE: ION SOURCE ($H^+ + H_2^+$)

exit in the ion source. With two similar apertures spaced 5 cm from the canal exit, as is the case with the extractor lens shown in Figure 22, the beam intensity will be reduced by 10^{-6}. The hole diameter in the apertures is 2 mm in each case.

V. SUMMARY AND CONCLUSION

Even though Zn_2TiO_4 exhibits many resonance signals when its ground-state defects are decorated with gamma radiation, the relative strengths of the signals are small and are an indication of the general stability of this pigment. In addition, the signal generated by ultraviolet irradiation in vacuum completely decays within 20 hr, even at liquid nitrogen temperatures. Current and planned studies on zinc orthotitanate centers around (1) the problem of obtaining the desired particle-size distribution of the stable, high-temperature-reaction product, and (2) further defining the utility of reactive encapsulation in stabilizing the bleachable degradation that the low-temperature-reaction product exhibits. Plasma calcination of a preground product of a "lower"-temperature reaction is being evaluated along with an investigation into the available size-reduction techniques for application to the stable, "jewel-like" product of high-temperature reactions. Reactive encapsulants being considered include sodium acid phosphate and potassium silicate.

Theoretical considerations and recent experimental results indicate that Group II and IIIB binary and ternary cation systems, such as the titanates, tungstates, stannates and double zirconium silicates, offer considerable potential for new pigments stable to the combined-radiation environment of deep space. The Group IIA alkaline-earth metals calcium, strontium and barium and the Group IIB metal, zinc, are the most promising. Indeed, zinc orthotitanate (Zn_2TiO_4), zinc zirconium silicate ($ZnZrSiO_5$)

and calcium tungstate ($CaWO_4$) have all exhibited excellent stability to ultraviolet radiation in vacuum. Of the three, the most promising in terms of stability only is calcium tungstate. However, certain Group IIIB cations offer interesting possibilities; among them are scandium, yttrium and the lanthanide elements lanthanum and gadolinium.

The proton-irradiation facility is currently being placed in operation and will be employed in the coming months to determine the nature of the synergism exhibited by the binary-cation-oxide pigments of interest when irradiated by both low-energy proton and ultraviolet radiation in vacuum.

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