

NATIONAL BUREAU OF STANDARDS REPORT

9052

Technical Report
July, 1965 to August, 1966

Infrared Optical Measurements
Progress and Status as of August 13, 1966

Edited by

Harry J. Keegan

Metrology Division
Institute for Basic Standards
National Bureau of Standards
Washington, D. C. 20234

Supported in part by the
Advanced Research Projects Agency

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U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Harry J. Keegan*
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NBS-ARPA Infrared Optical Measurements Program

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PREFACE

This is the fiftieth month of the NBS-ARPA Infrared Optical Measurements Program which began June 28, 1962. It is financed in part by the Advanced Research Projects Agency, Department of Defense. It is coordinated with the Infrared Information Analyses (IRIA) infrared optical materials group under the Chairmanship of Mr. William Wolfe, University of Michigan.* It is also coordinated with the Committee of Target Finding and Anti-camouflage, the Institute for Defense Analyses; with the Infrared Information Symposium (IPIS); and other committees interested in infrared measurements and standards, such as, the committee on aerial survey of crops and animals, National Research Council - National Academy of Sciences.

*

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Infrared Optical Measurements

1. Objectives

The Advanced Research Projects Agency, Department of Defense, requested the Metrology Division, Institute for Basic Standards, National Bureau of Standards, to implement a program of development of standard measurement procedures and measurement of infrared optical materials. The program has as its objectives:

(a) The determination of optical scattering values of infrared materials.

(b) The determination of the emissivity of optical materials.

(c) The determination of refractive index of materials as a function of temperature from -180° to $+1000^{\circ}\text{C}$ and from 0.19 to 50 microns.

(d) The establishment of a refractive index testing and calibration service covering the portion of the spectrum from 0.19 to 50 microns.

(e) The determination of optical homogeneity of infrared materials.

(f) The development of wavelength standards for use in the calibration of spectrophotometers.

2. Introduction

This report describes the work of the National Bureau of Standards Metrology Division as related to the NBS-ARPA Infrared Optical Measurements Program carried out during the period July, 1965 through August, 1966.

During this period, the laboratories of the Metrology Division were relocated in the new NBS facility at Gaithersburg, Maryland. The relocation took place during the month of March, 1966. As a result, most of the laboratories concerned with this program were inactive for measurement purposes from mid-January to approximately the end of April, 1966. All of the laboratories are now operating as before the relocation with minor exceptions due primarily to the new facilities and these difficulties are being overcome as quickly as possible.

During the reporting period, the program suffered the loss of a number of personnel assigned to the program. Messrs. Munis and Massie left the staff of the NBS in March, 1966, and Mr. Finkel in May, 1966. Mr. Keegan retired from the staff of the NBS after more than 40 years of service in August, 1966. Since Mr. Keegan served as coordinator of this program, and editor of this report, the reporting period for this progress report covers the work on the program to the date of his retirement.

There are included as appendices to this report copies of a published Letter to the Editor of the Journal of the Optical Society of America and the manuscript of a paper presented before the American Astronautical Association's Third Goddard Memorial Symposium, held in March, 1965. Both of these papers have been reported in previous progress reports. The former as a paper presented before the October, 1965 meeting of the Optical Society of America, and the latter as being "in press" to be included in the Proceedings of the Third Goddard Memorial Symposium. Since these Proceedings have not as yet been published, the manuscript is appended here.

3. Total Scattering

B. P. Caldwell

The NBS infrared hazemeter has been reassembled and realigned at the new NBS site in Gaithersburg, Maryland. Several samples of Irtran-1, Irtran-6, and germanium were measured on the hazemeter at several wavelengths between 0.4 and 3.0 microns. The total transmittance, T_t , and the diffuse transmittance (forward scattering), T_d , of specimens are measured directly. These measurements are corrected for

instrument drift, zero point, and instrument scatter. The straight-through transmittance, $T_s = T_d - T_t$, is obtained by computation. All measurements were made at room temperature. The precision of the instrument at 0.6 through 2.5 microns is established to be 0.5 while above or below these wavelengths the precision will be lower because of low detector sensitivity.

Irtran-1

The transmittances for three thicknesses of Irtran-1 were measured at nine wavelengths. These samples were cut from the same piece of material. The results are shown in table I and figure 1. The transmittances of these same samples were reported in NBS Report 8626, ARPA Semiannual Technical Report for July 1, 1964 to December 31, 1964. Because the new values differ considerably from those values previously reported, the samples were remeasured for several different sphere geometries, including three sizes of exit apertures from 13 mm diameter to 30 mm diameter, a 13 mm spacer between the detector and the sphere, and incident beams of 10 mm diameter and 20 mm diameter. The transmittances obtained with the different sphere geometries all agree with the new values within the precision of the instrument. A more thorough investigation of Irtran-1 will be made to determine if the difference is due to instrument changes or specimen changes.

Table I

Percent Transmittance of Irtran-1 Specimens

Wavelength, λ (μ)		.4	.5	.6	.7	1.0	1.5	2.0	2.5	3.0
Thickness (mm)										
2	T _t	77	78	79	81	84	87	88	90	85
	T _d	73	76	72	68	49	25	14	8	7
	T _s	4	2	6	13	34	62	75	82	78
4	T _t	56	57	60	64	72	78	83	85	83
	T _d	53	58	60	62	59	38	24	16	8
	T _s	2	0	0	2	13	40	59	70	75
8	T _t	26	28	32	36	49	63	71	76	71
	T _d	25	29	32	36	48	54	48	37	23
	T _s	1	0	0	0	1	9	23	39	48

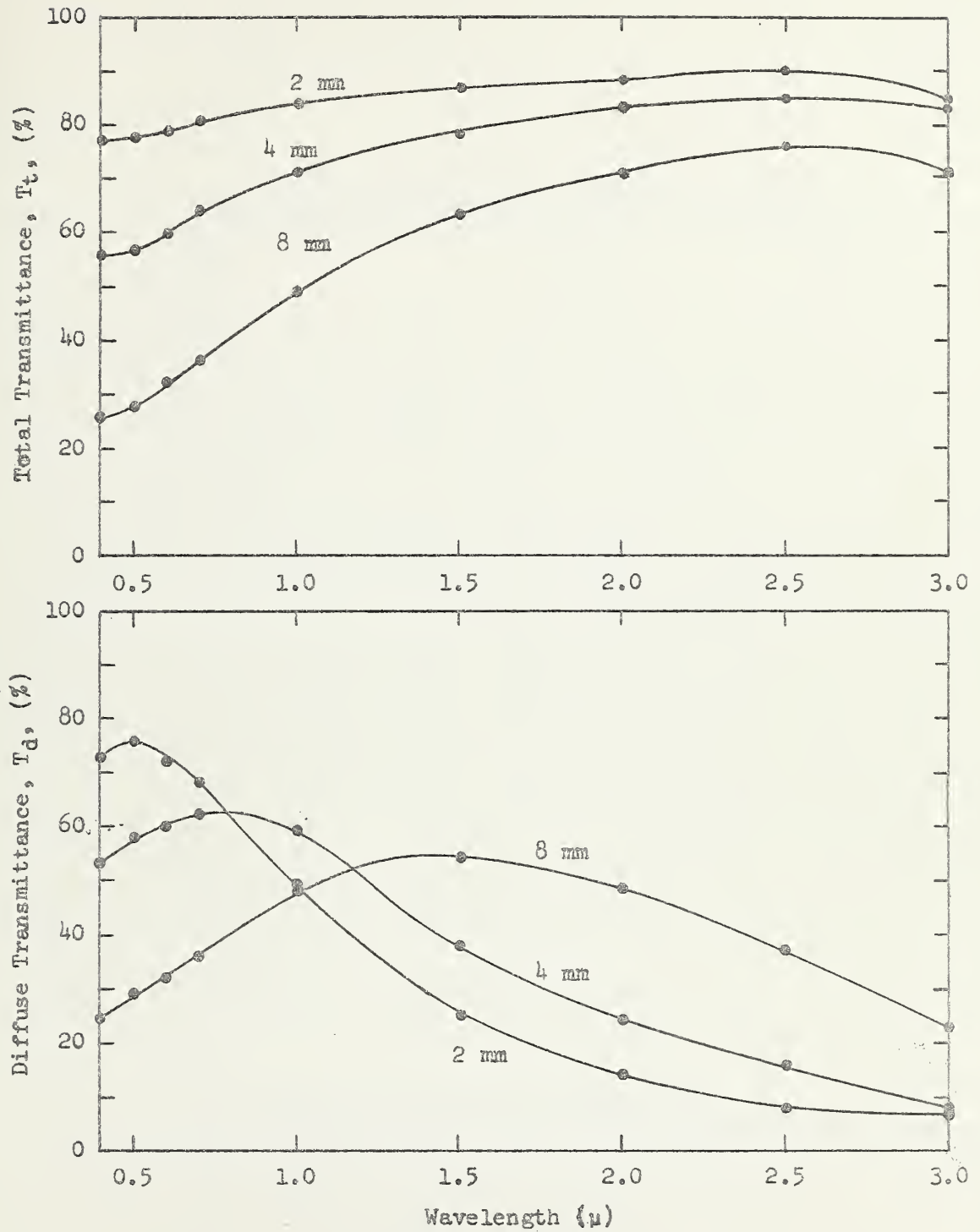


Figure 1. Transmittances of three thicknesses of Irtan-1 as a function of wavelength

Table II

Percent Transmittance of Irtran-6 Specimens

Wavelength, λ (μ)		.4	.5	.6	.7	1.0	1.5	2.0	2.5	3.0
Thickness (mm)										
1	T_t	3	0.8	0.5	0.9	61	66	66	66	66
	T_d	1	0.3	0.0	0.1	6	5	5	4	4
	T_s	2	0.4	0.4	0.8	55	61	61	62	62
2	T_t	3	0.8	0.6	0.9	58	64	64	64	64
	T_d	1	0.2	0.1	0.2	9	8	7	6	6
	T_s	2	0.6	0.4	0.6	49	56	58	58	58
6.4	T_t	3	0.7	0.6	0.7	55	62	62	62	58
	T_d	1	0.2	0.2	0.1	9	8	7	6	4
	T_s	2	0.5	0.4	0.6	47	54	55	56	54

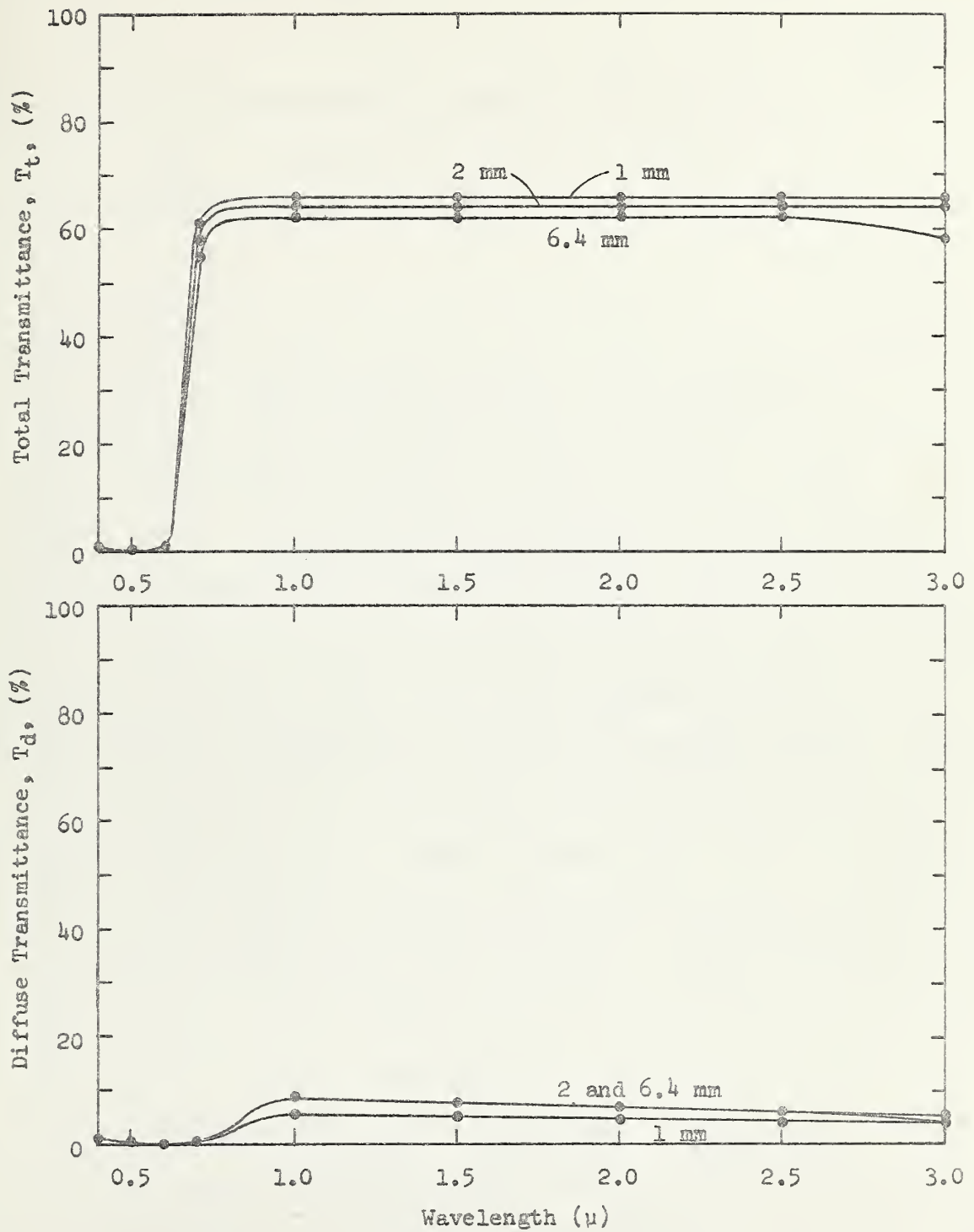


Figure 2. Transmittances of three thicknesses of Irtran-6 as a function of wavelength

Irtran-6

The transmittances for three thicknesses of samples of Irtran-6 were measured at nine wavelengths. The results shown in table II and figure 2 are the averages of three measurements.

Germanium

The transmittances for three thicknesses of four samples of pure germanium were measured at five wavelengths. These samples were cut from the same single crystal. The results are shown in table III and figure 3. The values obtained for two different samples both about 4 mm thick were the same within the precision of the instrument.

The samples measured were 1 1/4 inch diameter disks of good optical quality, with flat-parallel polished sides. The incident radiation was a collimated beam about 10 mm in diameter. All the samples show a decrease in forward scattering relative to straight-through transmittance as the wavelength increases. Irtran-1 has a considerable amount of forward scattering and is a much higher scattering material than either Irtran-6 or germanium. Irtran-1 has a high total transmittance throughout the wavelength region investigated, 80% to 90% for the 2 mm thick sample; Irtran-6 has less than 1% total transmittance in the visible region

Table III

Percent Transmittance of Germanium Specimens

Wavelength, λ (μ)	.5	1.0	1.5	2.0	2.5
Thickness (mm)					
2					
T_t	0.2	0.4	0.9	46	45
T_d	0.0	0.0	0.0	4	3
T_s	0.2	0.4	0.9	43	42
4					
T_t	0.1	0.3	0.4	45	44
T_d	0.0	0.1	0.1	3	3
T_s	0.1	0.2	0.3	42	41
8					
T_t	0.3	0.4	0.4	44	42
T_d	0.0	0.2	0.1	3	3
T_s	0.3	0.2	0.3	41	39

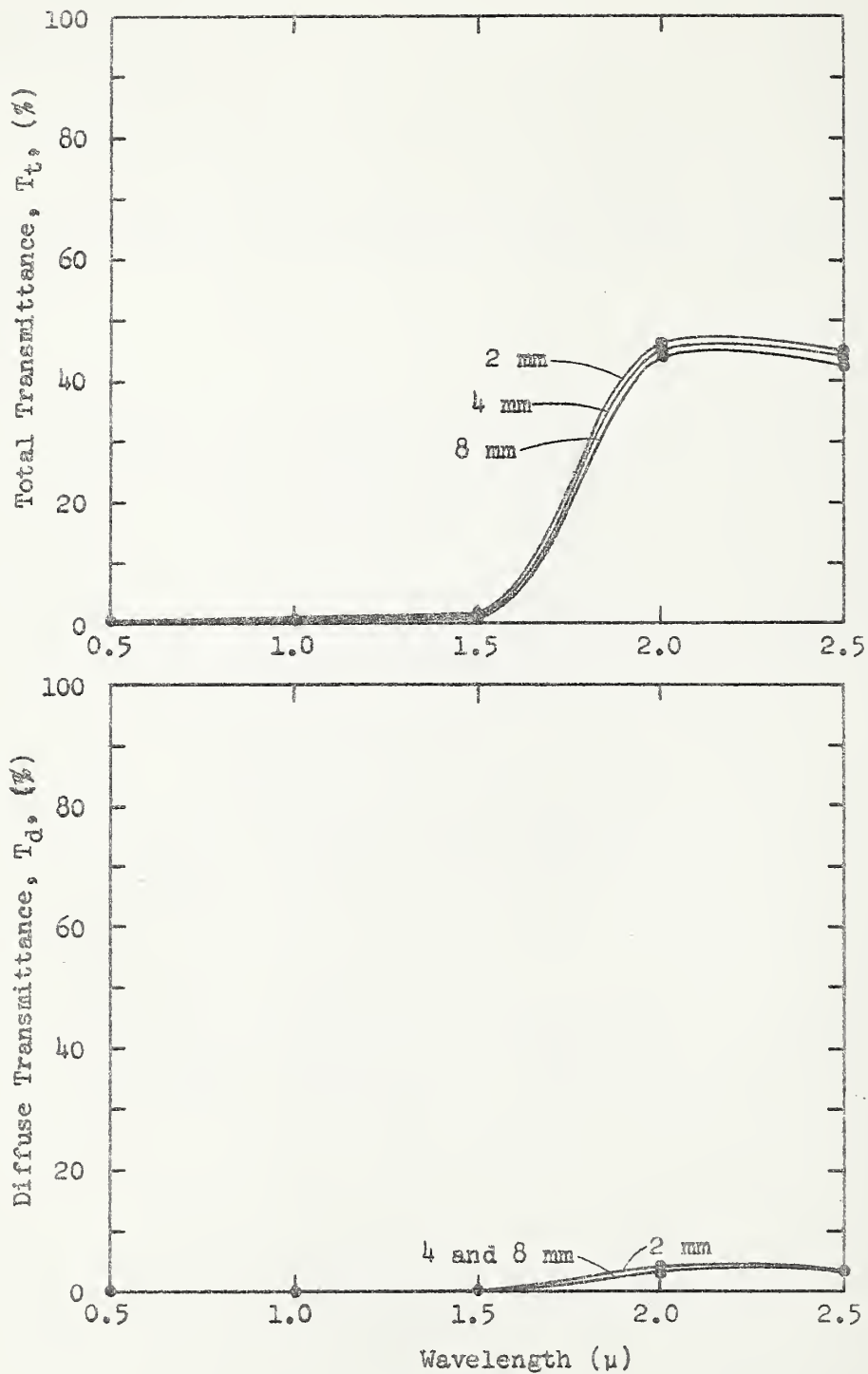


Figure 3. Transmittances of three thicknesses of germanium as a function of wavelength

but transmits about 65% for the 2 mm thick sample beyond 1.0 micron; the 2 mm thick sample of germanium has less than 1% total transmittance from the visible to 1.5 microns and about 45% beyond 2.0 microns. This type of data from several thicknesses of the same material will be useful in determining scattering and absorption coefficients of these materials as a function of wavelength.

4. Thermal Change in Refractive Index For Some Oxide Glasses

G. W. Cleek

The thermal change in refractive index has been measured for some oxide glasses from room temperature to 700°C, or to near the deformation point of the glasses. This work was done on an NBS project, but is reported here since the data are of interest to the program on the optical properties of materials.

The measurements were made by an interferometric technique with which interference fringes were recorded as a function of temperature for an expansion sample and for an index sample of the same glass. From this information the refractive index as a function of temperature was calculated along with the linear thermal expansion. All measurements were made with the 0.5876 micron line of He.

Table IV

Composition of Glasses

Oxide (Mol%)	SiO ₂ Silica	F-998 Germanate	F-75 Calcium Aluminate	F-1329 Phosphate	E-17 Bari Bora
SiO ₂	100		5.6		
GeO ₂		45			
BaO		18			36
La ₂ O ₃		7			
Ta ₂ O ₅		1			
TiO ₂		10			
ZnO		10			
ZrO ₂		5			
CaO			58.5		
MgO			8.4	27.7	
Al ₂ O ₃			27.5	12.9	
P ₂ O ₅				59.4	
B ₂ O ₃					64

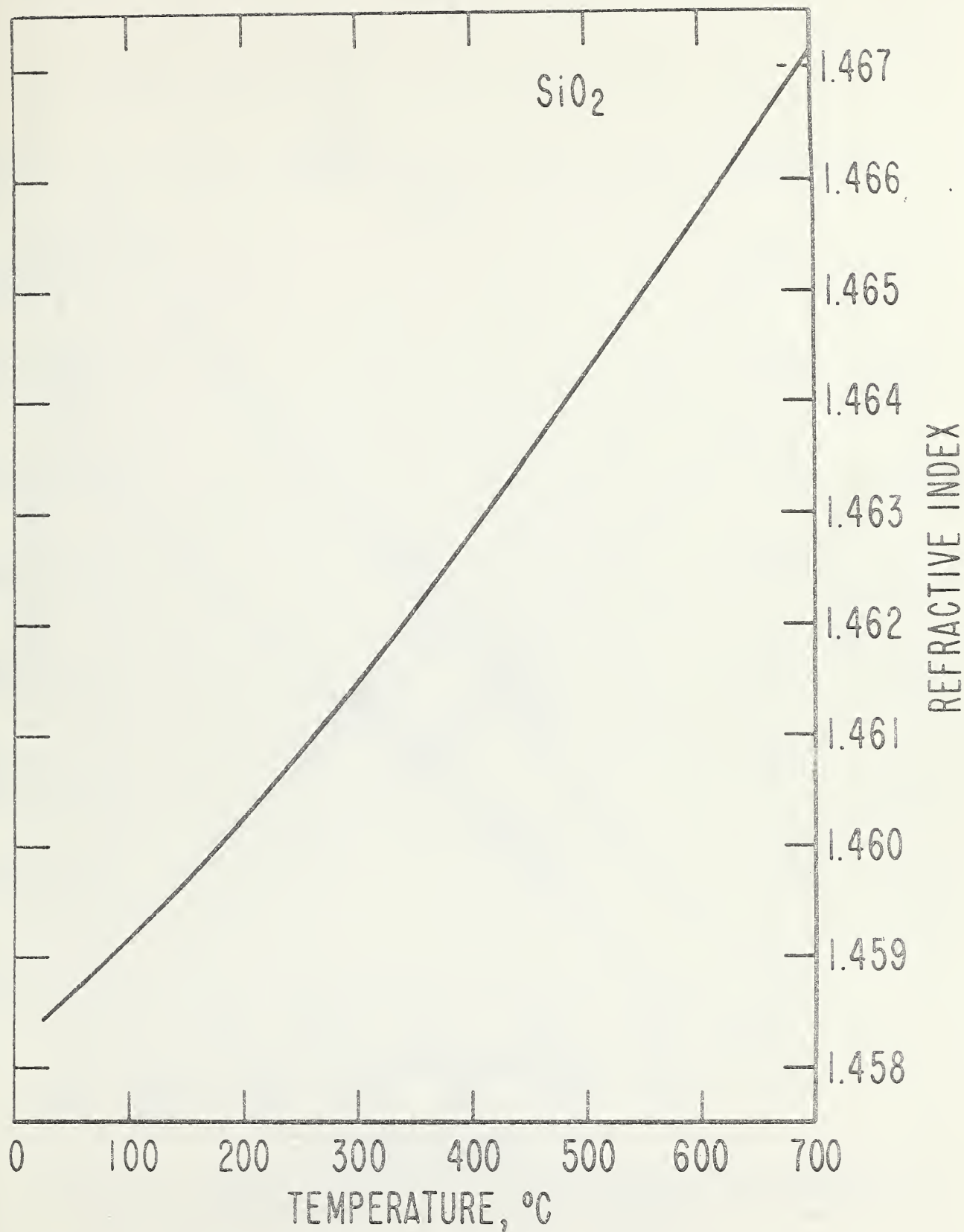


Figure 4. Thermal change in refractive index for fused SiO_2

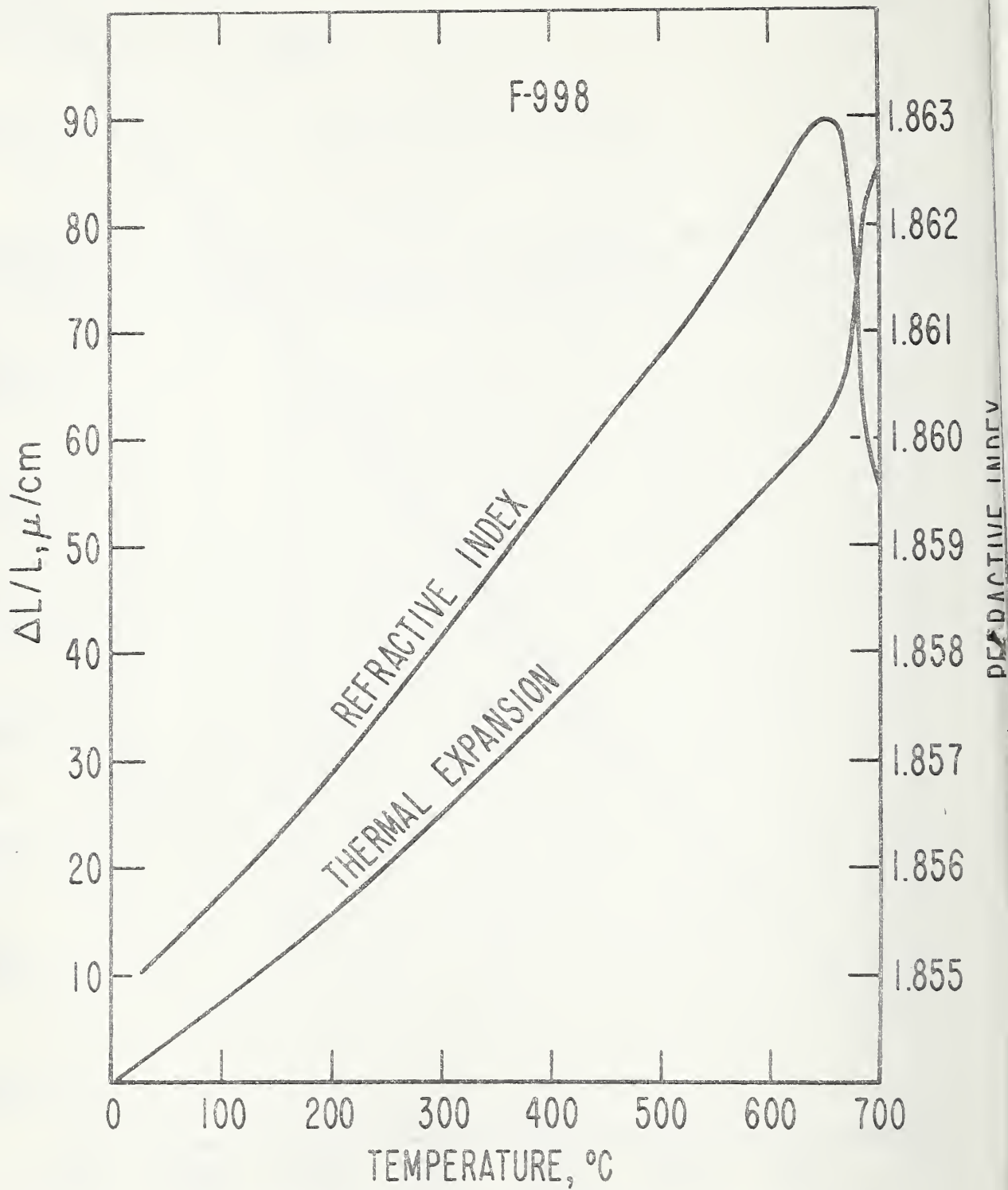


Figure 5. Thermal change in refractive index and linear thermal expansion for germante glass F-998

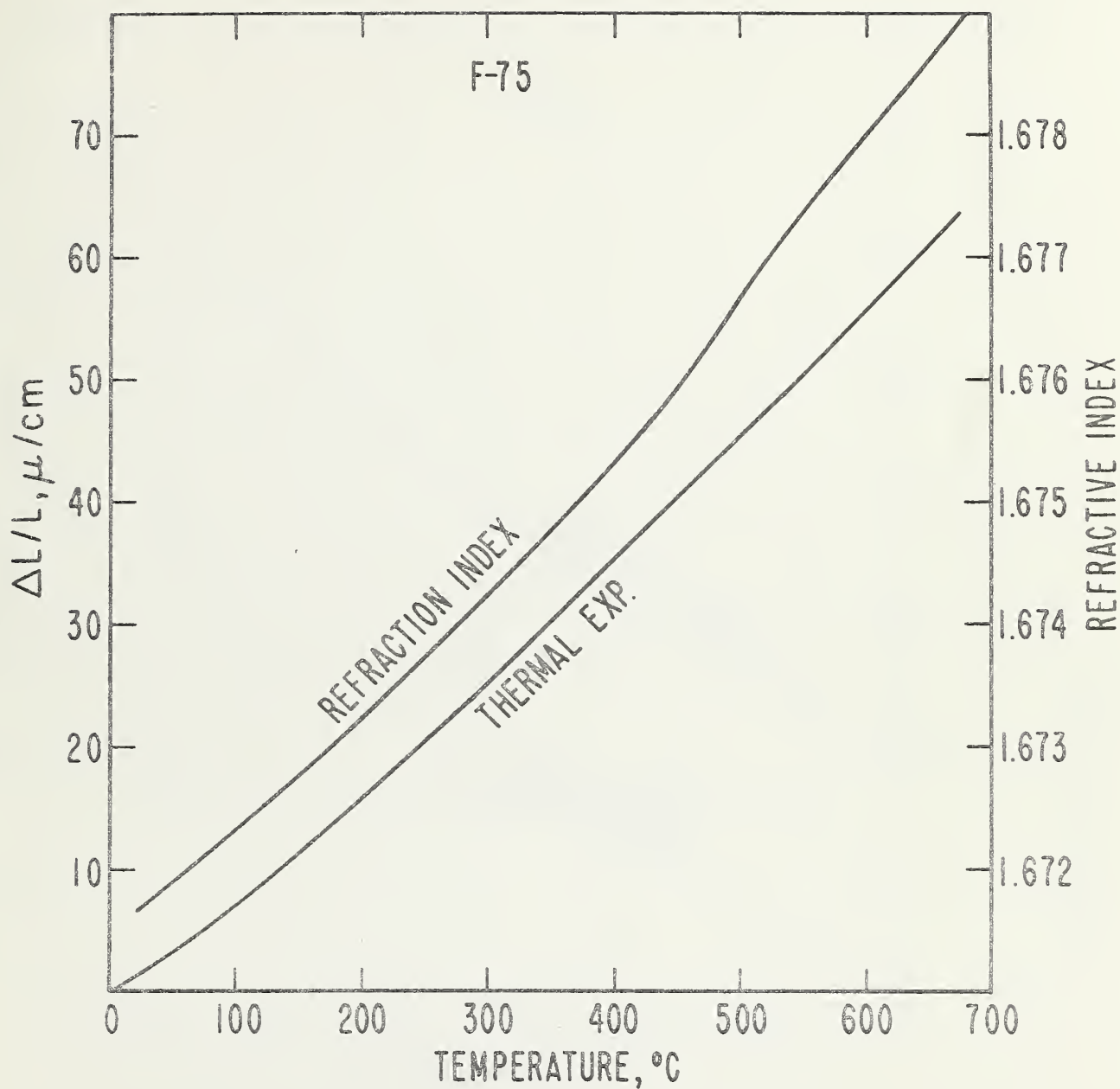


Figure 6. Thermal change in refractive index and linear thermal expansion for calcium aluminate glass F-75

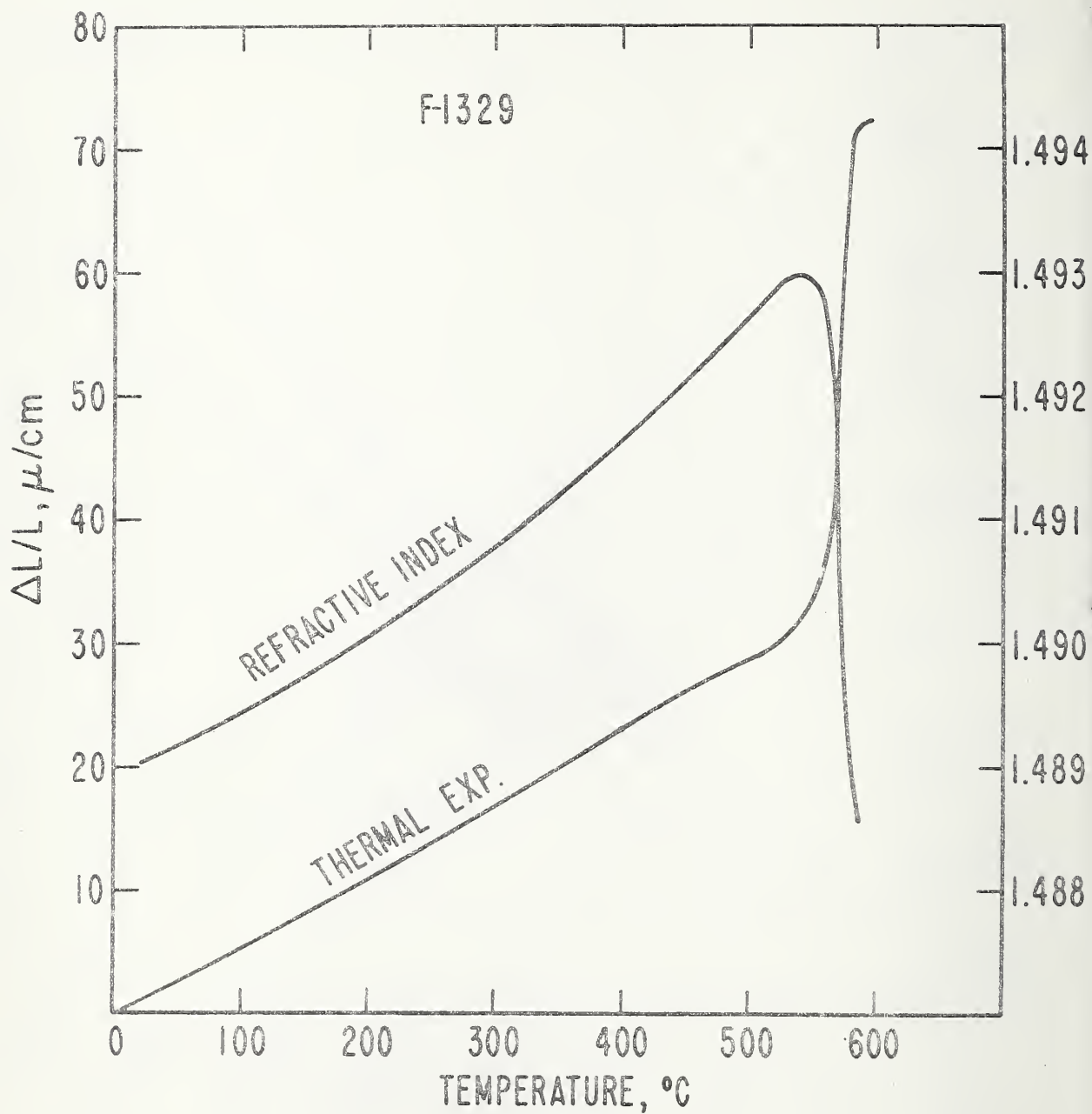


Figure 7. Thermal change in refractive index and linear thermal expansion for phosphate glass F-1329

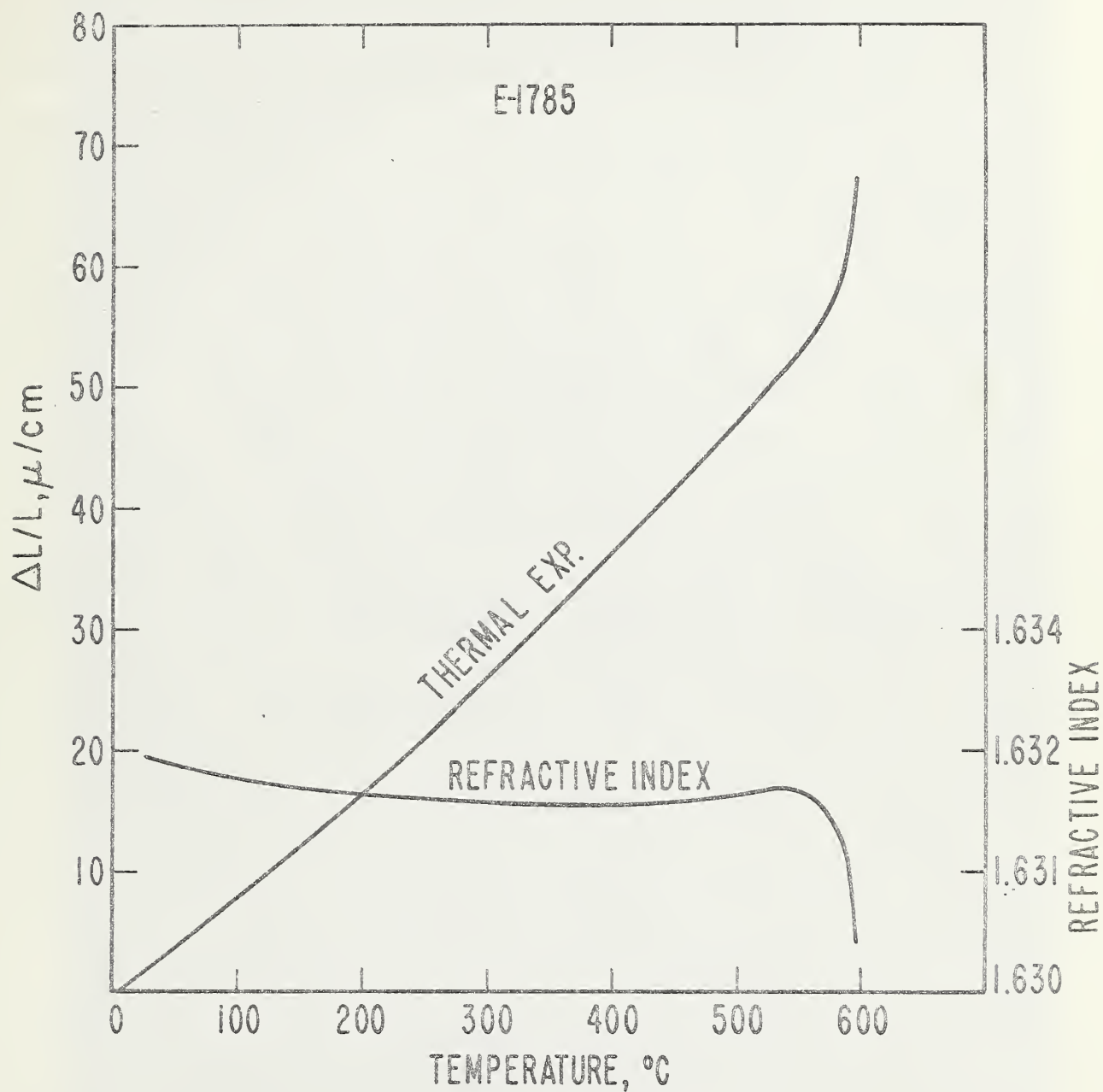


Figure 8. Thermal change in refractive index and linear thermal expansion for barium borate glass E-1785

The results for five different glasses, fused SiO_2 , F-998, F-75, F-1329 and E-1785 are shown in figures 4 to 8. The thermal expansion curves are plotted in each figure except for SiO_2 . In this case the thermal expansion was so small that only 4 fringes were counted over the temperature range to 700°C . A value of $5 \times 10^{-7}/^\circ\text{C}$ was used in the calculations of refractive index. As may be seen from the figures, all of the glasses had positive coefficients of refractive index as a function of temperature except glass E-1785. The index of this glass decreased slightly up to about 360°C , then increased slowly to 530°C which is about the beginning of the rapid expansion region. From this point on the refractive index decreased rapidly as far as measurements were possible.

The compositions of the glasses are shown in Table IV.

5. Homogeneity

F. W. Rosberry

Several samples of infrared transmitting materials were examined for surface flatness. These samples were also shadowgraphed and either observed visually with an image converter or photographed. Figure 9 shows a shadowgraph of a non-oxide chalcogenide glass containing Si Ge As Te and of about 1 cm thickness. Figure 10 is another shadowgraph of



Figure 9. Shadowgraph of a non-oxide chalcogenide glass, Si-Ge-As-Te, 1 cm thick

the same type of material but containing Ge Sb Se. This sample was of 8 mm thickness. Figure 11 shows a sample of the same material as in Figure 10 but of 4mm thickness. These samples have well prepared surfaces but have not been examined on the interferometer. It is doubtful if a recognizable interferogram can be obtained from this material. The wavelength range used in these photographs was determined on the low end by the threshold of transmission of the material and the longest wavelengths were about 1.2 microns.

The major portion of time in this period was spent on preparing for publication a paper entitled "The Measurements of Homogeneity of Optical Materials in the Visible and Near Infrared", which has been submitted to Applied Optics for publication.

6. Maintenance of Operation of the Cary-White 90

J. C. Schleter and J. M. Massie

The switching delay circuit in the reflectance attachment of the instrument failed. The circuit, as originally designed, required that a small synchronous clock motor with a slip clutch hold a micro-switch closed after

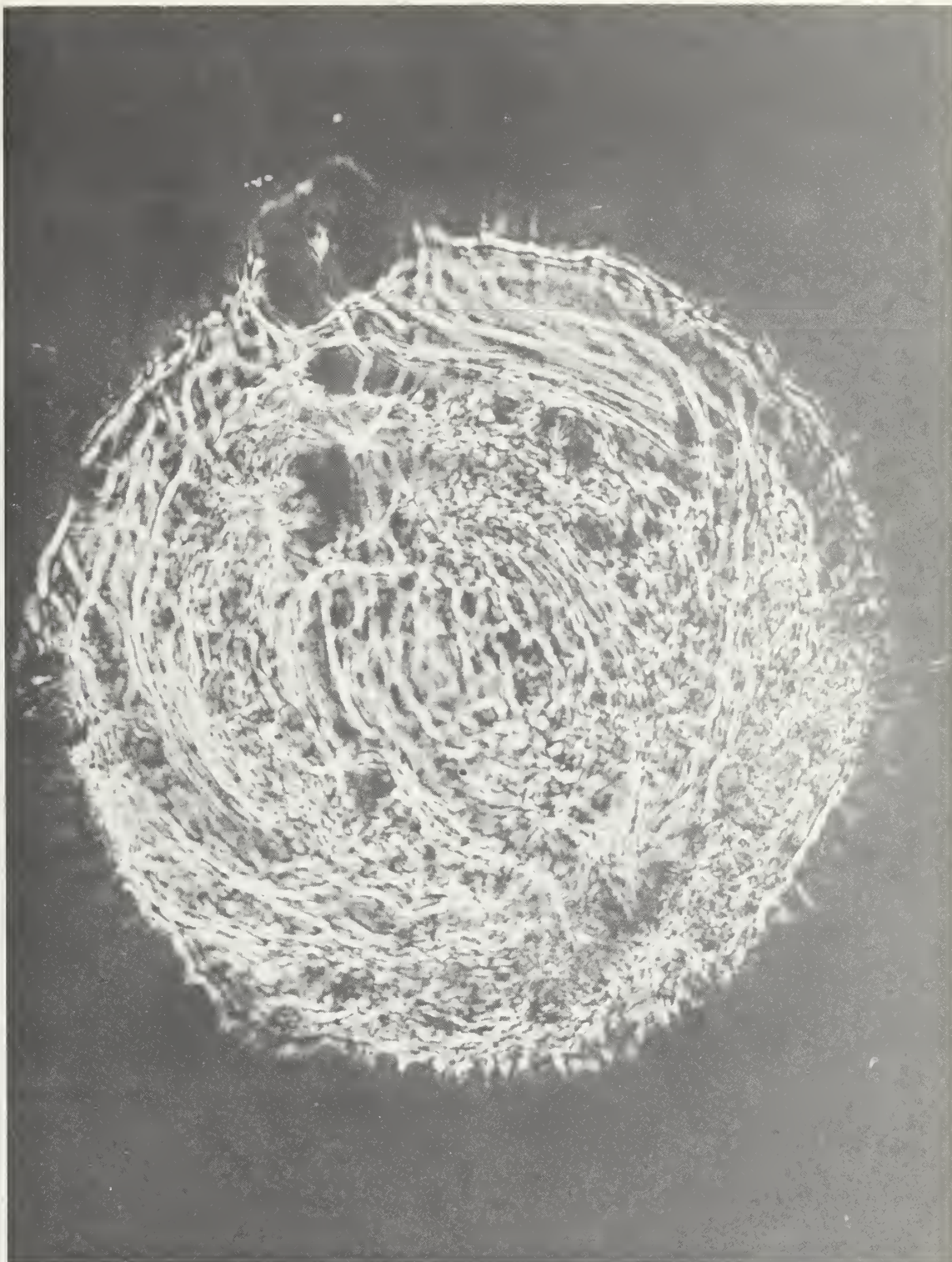


Figure 10. Shadowgraph of Ge-Sb-Se non-oxide chalcogenide glass, 8 mm thick

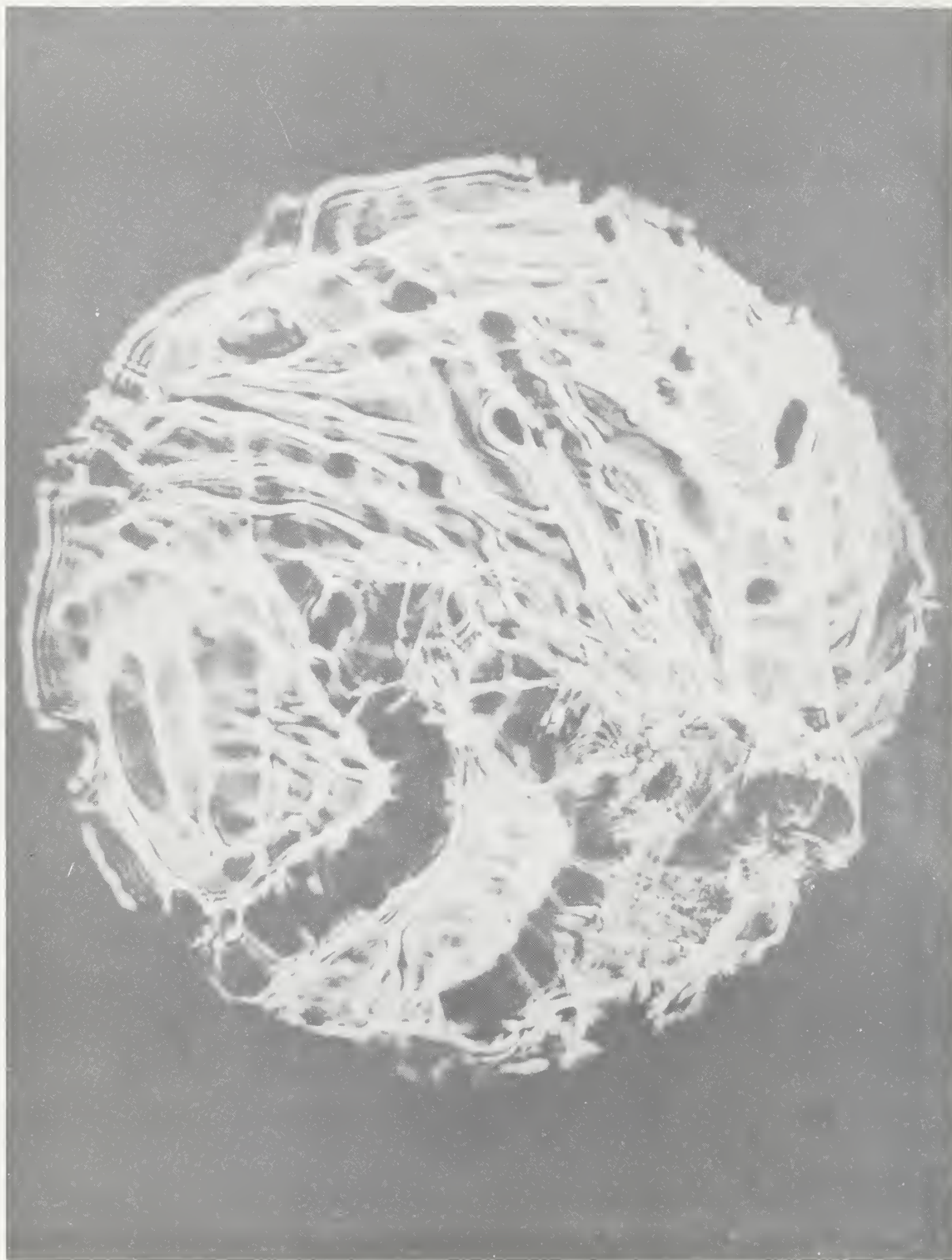


Figure 11. Shadowgraph of same material as figure 10 but for a sample thickness of 4 mm

the first 30 seconds of warmup time following the turning on of the reflectance attachment power supply. After about one year of use, the slip clutch operated in an intermittent fashion and did not always keep the micro-switch closed. The circuit was re-designed using a latching relay and a new micro-switch requiring less force to close it. With the re-design, when the switch is closed by the timing motor, the relay is latched, the necessary switching is accomplished, and the motor is cut out of the circuit so that it is no longer required to hold the micro-switch closed throughout the entire operation of the instrument. Previous to turning on the power supply the latching relay is released by means of a push-button.

7. Digital Read-Out Equipment

J. C. Schleter and J. D. Kuder

Mounting hardware for the encoders and trigger commutators were fabricated in the NBS main shop or Section 212.11 shop and have been mounted on the Cary 14, G. E., and Cary-White 90 recording spectrophotometers. The encoders and electronic packages were delivered October 19, 1965 by personnel of the Perkin-Elmer Corporation. The encoders and trigger commutators have been attached to the mounting

hardware on the three spectrophotometers. Special carts have been made to accomodate the paper tape punches, and noise suppressing boxes have been constructed to enclose the tape punches. The digital read-out equipment is currently being checked out.

8. Angular Scattering

R. H. Munis

A paper entitled "Development of an Angular Infrared Scattering Instrument" by R. H. Munis and M. W. Finkel is in the process of being reviewed at NBS. In this paper the design of the scattering instrument is discussed. The angular measurements of one IRTAN material at 3 wavelengths are shown. A radiative balance equation that involves the transmission, absorption, scattering, and reflection is written. From this equation the angular scattering function, $S(d, \theta)$, is defined as the ratio of the scattered intensity to the attenuated intensity. The attenuated intensity is defined as the sum of the scattered, absorbed, and reflected intensities. The scattering function is then integrated over all solid angles, $d\omega$, to obtain a total scattering function, $s(d)$. From this value the fractional part of the incident intensity, I_0 , that is scattered by the

specimen is calculated. Two values have been calculated for a specimen of IFTRAN 1 having a 3.8 mm thickness. A total scattering value of 0.489 has been calculated at 1 micron and a forward scattering value of 0.17 has been calculated at 2 microns.

These scattering values have been compared with the total scattering values obtained by the independent investigation of M. W. Finkel. It is very interesting to note that after applying the boundary conditions to the angular data the agreement with Finkel's data is within a few percent. The significance of this lies in the fact that the only boundary condition involved is n^2 which is the value of the refractive index of the medium. Thus, the relationship between the total scattering value computed from the angular data and the total scattering value measured by Finkel is given by

$$I_{\text{measured}} = n^2 I_{\text{computed}}$$

If this reasoning is correct, then when we take the ratio of the two sets of independent scattering data we should recover the value of the index of refraction of the medium. Two forward scattering measurements and one back scattering measurement at each of two wavelengths have been selected.

The ratio of

$$\frac{I_{\text{measured}}}{I_{\text{computed}}}$$

does in fact yield the index of refraction of the medium to within a few percent of the value measured by an independent method. Thus, we must come to the conclusion that if we can make two independent scattering measurements of a medium, then we can calculate any process that depends upon the index of refraction of the medium. This idea will be explored more fully in another paper to be published.

9. Temperature Control of Reflectance Samples on a Cary-White 90 Infrared Spectrophotometer over the Temperature Range 50 C to 85 C

V. R. Weidner

This study was undertaken to determine:

1. The temperature range of reflectance samples that could be obtained with the variable infrared source and sample holders of the Cary-White 90 spectrophotometer; and
2. The calibration of power input settings for the source and sample holders that will enable the operator to make spectral reflectance measurements at any desired temperature within this range.

Requests for measurements of infrared spectral reflectance measurements as a function of temperature, such as the one reported in NBS Test 212.11P-38/66, dated November 9, 1965, led to a need for procedures for controlling and measuring sample temperatures. In this test it was requested that a paint sample be measured at a number of temperature intervals between 25°C and 400°C to determine the effect of temperature on the infrared spectral reflectance. As a result of this request an extensive study was undertaken to calibrate the power input controls for the source and sample holders, and thermocouple equipment was procured for monitoring and controlling the reflectance sample temperature. The data shown in tables V and VI were derived from this study and enable the operator to approximately set the reflectance sample temperature over the temperature range 50°C to 850°C by means of the controls for the power input to the source and sample holders. Further adjustments are necessary to set the exact temperature desired. The acquisition of a Leeds & Northrop temperature potentiometer equipped with a chromel-alumel thermocouple for the temperature range 0°C to 1200°C, will now enable the operator to monitor the sample temperature and make any adjustments in the power input to the sample holder necessary in obtaining the desired sample temperature.

Table V
Cary-White 90 Spectrophotometer

Guide for controlling reflectance sample temperature between 50°C and 325°C when using the 2" x 2" sample holder with 20-volt 5-ampere line.

Desired temperature (approximate)	Power input settings to source and sample holder for:								
	Samples having a high reflectance (near 100%)			Samples having a medium reflectance (near 50%)			Samples having a low reflectance (near 0%)		
	Source	Sample holder		Source	Sample holder		Source	Sample holder	
50°C	50 watts	8 watts		47 watts	7 watts		45 watts	6 watts	
75	73	15		70	14		65	13	
100	97	25		87	21		75	18	
125	114	36		100	29		88	23	
150	133	48		119	39		103	31	
175	154	59		136	49		123	41	
200	176	70		155	60		139	51	
225	200	82		177	70		159	62	
250	225	95		197	80		179	71	
275	254	113		219	92		196	80	
300	278	130		245	107		215	90	
325	300	145		272	125		238	102	

Cary-White 90 Spectrophotometer

Guide for controlling reflectance sample temperature between 200°C and 850°C when using the 1/4" x 1" platinum ribbon sample holder with 2-volt 100-amp line.

Power input settings to sample holder for:

Desired temperature (approximate)	Power input settings to sample holder for:		
	100°C source image (97 watts)	200°C source image (178 watts)	300°C source image (274 watts)
200°C	12 watts	--	--
250	18	10 watts	--
300	23	16	--
350	29	22	12 watts
400	35	29	18
450	41	35	25
500	47	41	32
550	53	48	39
600	60	54	46
650	67	61	54
700	76	69	61
750	85	79	70
800	97	90	81
850	109	105	97

As a result of this calibration and the acquisition of the temperature potentiometer, the usefulness of the Cary-White 90 spectrophotometer has been extended to include the measurement of infrared spectral reflectance as a function of temperature over the temperature range of approximately 50°C to 850°C. The method is further discussed in the report of NBS Test 212.11P-50/66, dated December 6, 1965.

10. Useful Available Energy from a Variable Power Reflectance Attachment Source of a Cary-White 90 Spectrophotometer

V. R. Weidner

This study was undertaken to determine:

1. The useful range of slit-widths or spectral band pass settings of the instrument in the reflectance mode; and
2. The sensitivity of the instrument over a wide range of power settings on the reflectance attachment source for various slit-widths.

This information is important to the operator in selecting the proper power input to the source and the proper slit-width when confronted with various measurement problems. For instance, it may be desired to measure an organic material, easily damaged by heating. In this case, a low temperature source is required. The slit-width which

will give sufficient sensitivity with a low temperature source or the maximum resolution which can be expected with a source operating at this low temperature can be determined. Figures 12 to 15 summarize these investigations which are reported in NBS Test 212.11P-19/66. They show the relationship of slit-width and power input to the infrared source, to instrument sensitivity as a function of wavelength over a spectral range 2.5 to 20 microns. Referring to these graphs the operator can select the optimum settings for a particular measurement problem.

11. Emissivity

William B. Fussell

I. Theoretical Progress:

A. An iteration method has been developed for solving the two simultaneous, non-linear McMahon equations in the normal surface reflectance and internal transmittance generated by the measurement of the normal emissivity of two homogeneous samples of different thicknesses. The method is as follows:

(i) Let T_1 and T_2 be the normal internal transmittances of two samples whose corresponding normal emissivities are E_1 and E_2 .

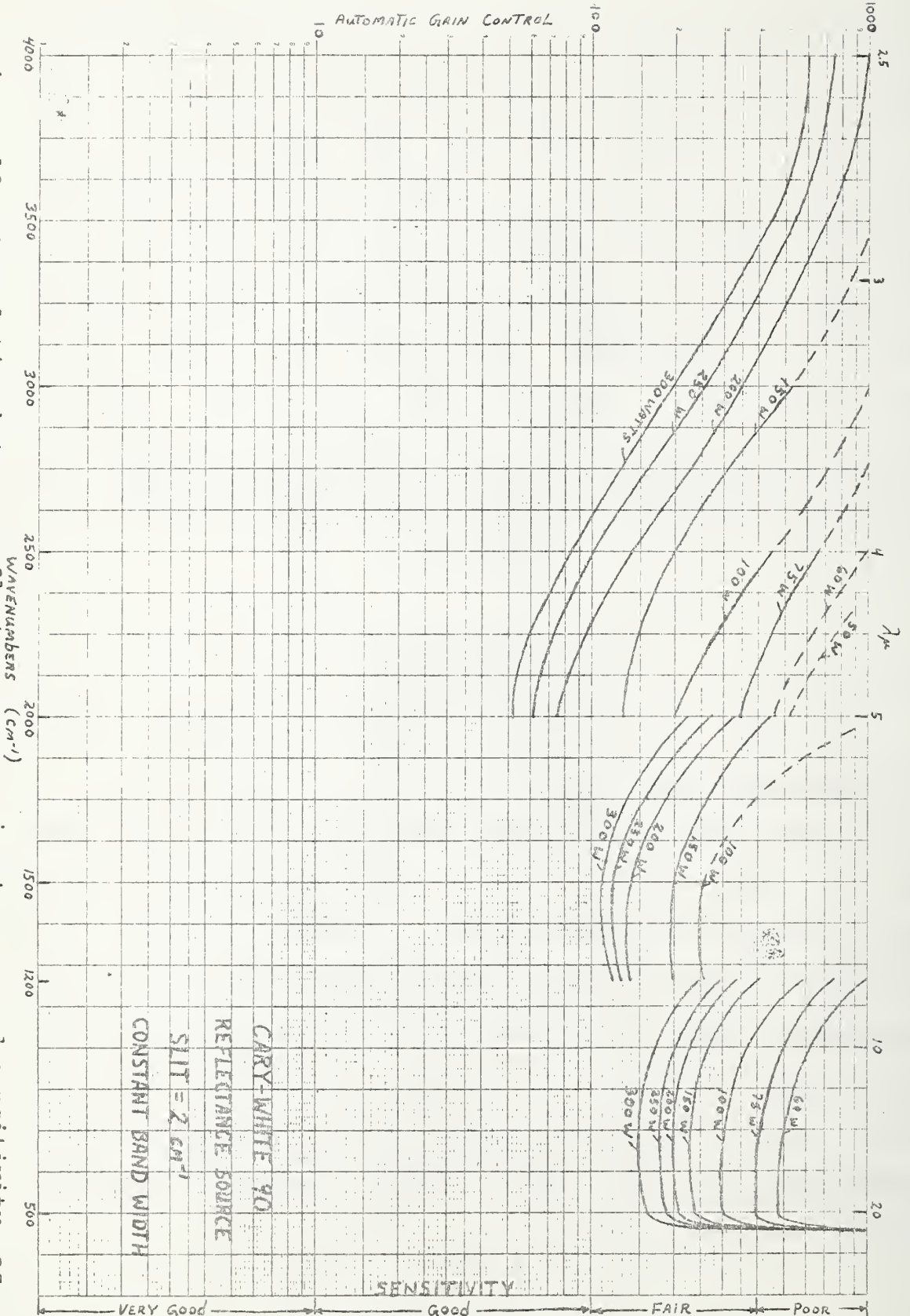


Figure 12. Correlation between reflectance source input power and sensitivity, as indicated by the automatic gain control meter, for a constant slitwidth of 2 cm^{-1} wavenumbers

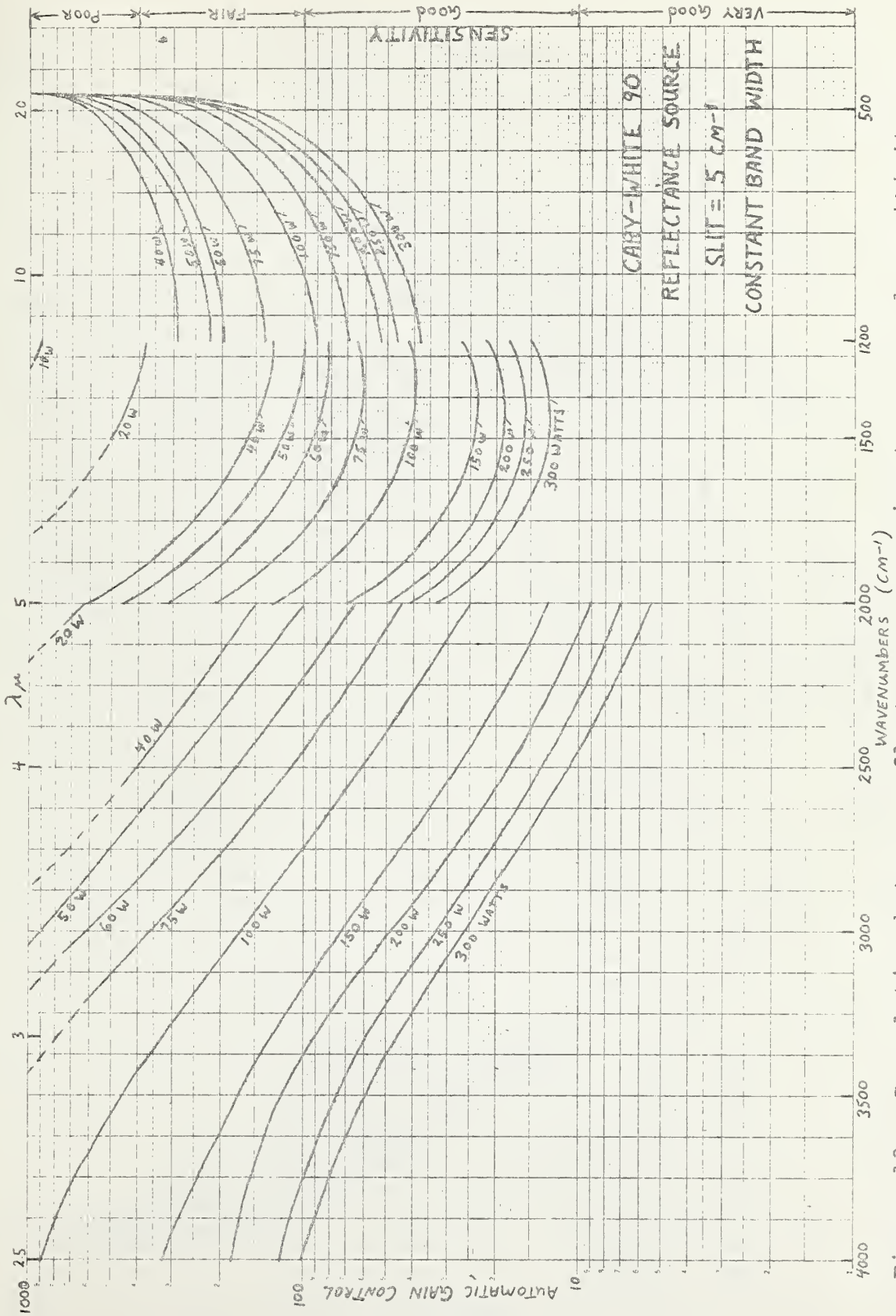


Figure 13. Correlation between reflectance source input power and sensitivity, as indicated by the automatic gain control meter, for a constant slitwidth of 5 cm⁻¹ wavenumbers

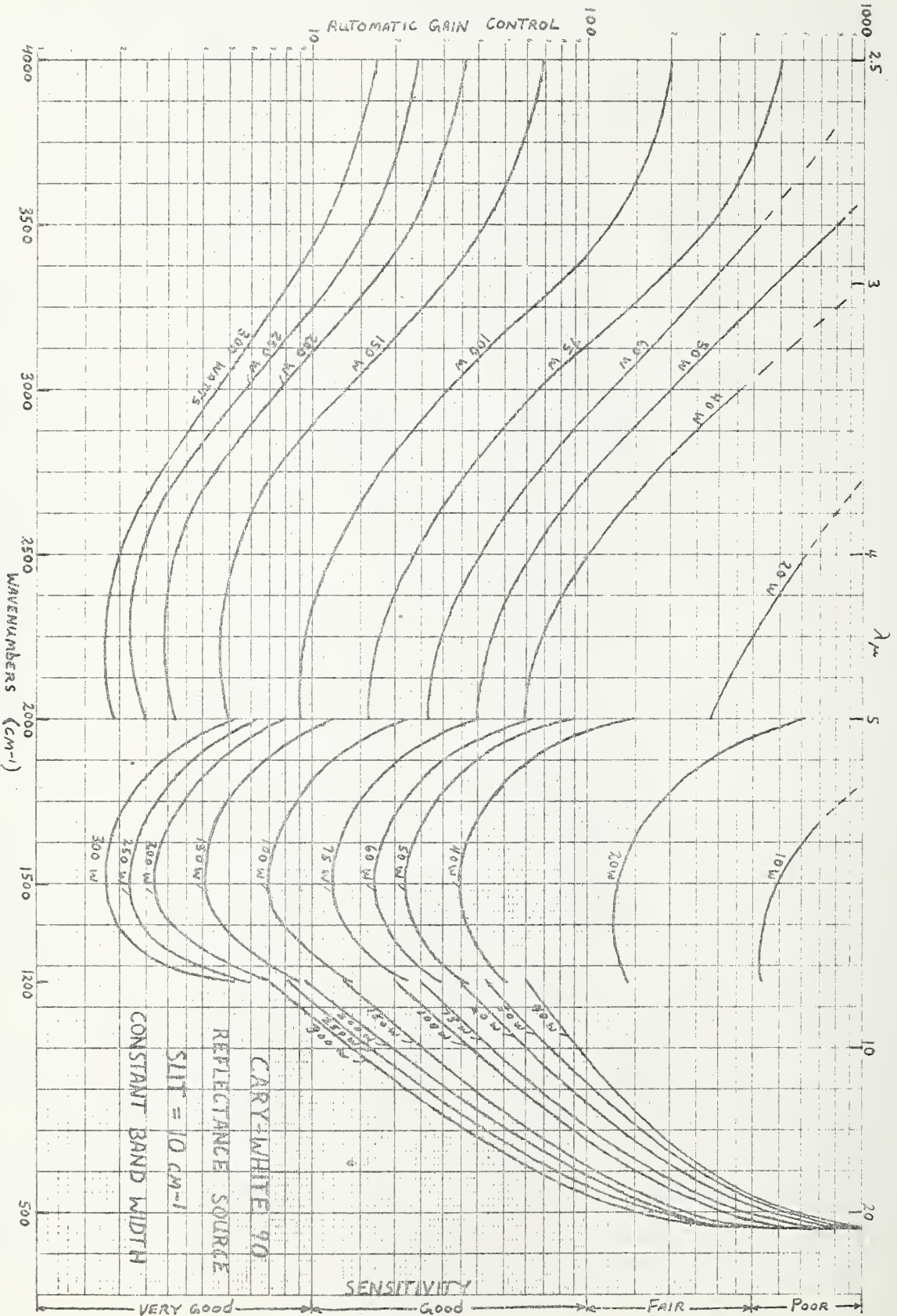


Figure 14. Correlation between reflectance source input power and sensitivity, as indicated by the automatic gain control meter, for a constant slitwidth of 10 cm^{-1} wavenumbers

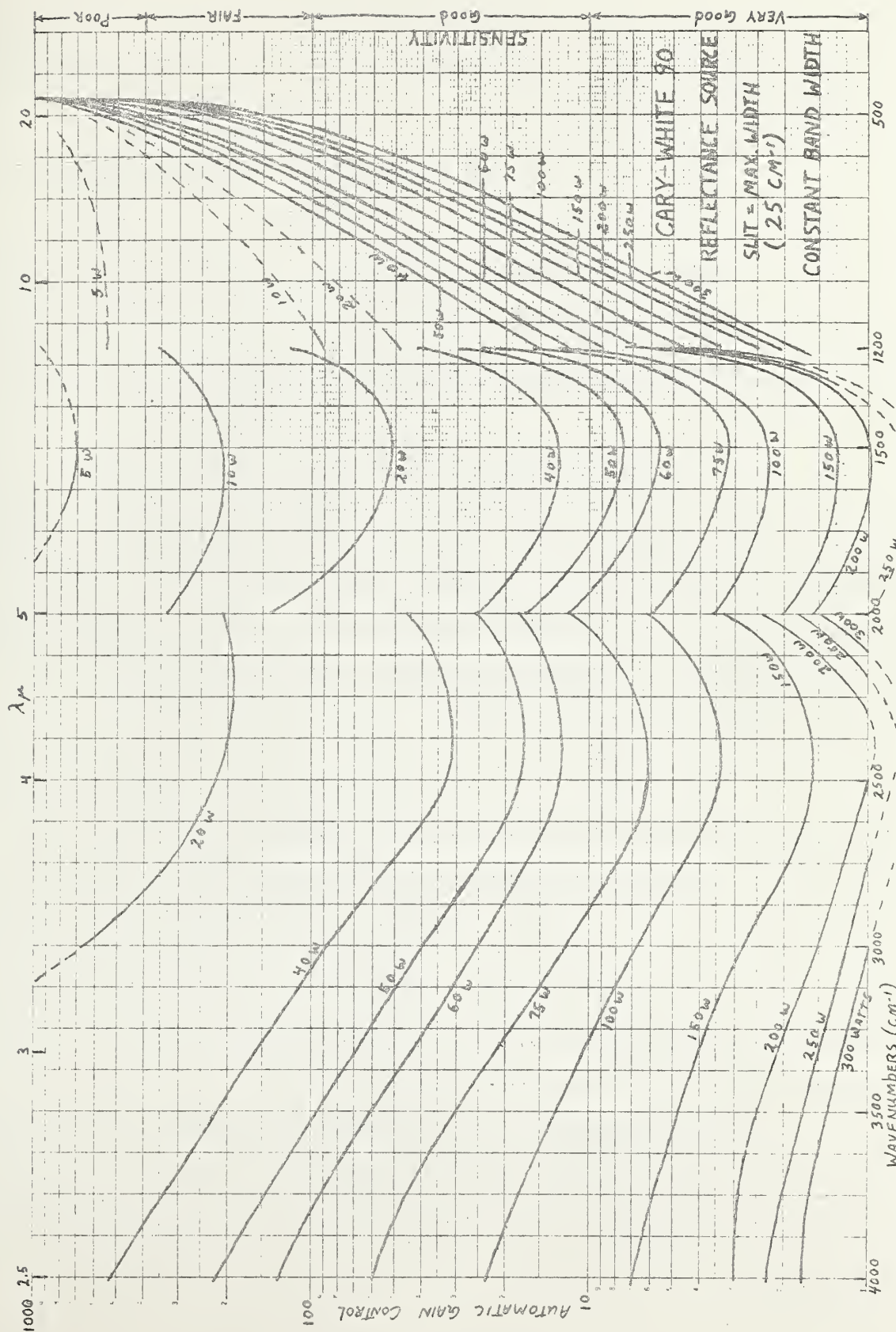


Figure 15. Correlation between reflectance source input power and sensitivity, as indicated by the automatic gain control meter, for a constant slitwidth of 25 cm⁻¹ wavenumbers

(ii) Let also $T_2 = T_1^m$, where m is greater than one but not necessarily an integer, and define the quantity $F = (E_2 E_1) (E_2 - E_1)^{-1}$.

(iii) Then T_1 is a solution of the equation

$$T_1^{m+1} + (F-1)T_1^m - (F+1)T_1 + 1 = 0.$$

(iv) The zero-order solution of this equation is

$${}_0T_1 = (F+1)^{-1},$$

which is clearly valid for the extreme values $E_1 = E_2 = 0$ and $E_1 = E_2 = 1$.

(v) For intermediate values of E_1 and E_2 , the zero-order solution is in error by an amount which has a maximum at the values of E_1 and E_2 for which $F = 2(m-1)^{-1}$. The value of the maximum proportional error in ${}_0T_1$ is given by the quantity $4(m-1)^{m-1} (m+1)^{-m-1}$. As an example, if $m = 3$, the maximum error is 0.063.

(vi) If the more accurate first-order solution, ${}_1T_1$, is desired, it is obtained by substituting ${}_0T_1$ for T_1 in the first two terms of the above equation, substituting ${}_1T_1$ for T_1 in the third term, and then solving the equation for ${}_1T_1$. By induction, we see that the higher order solutions, ${}_2T_1$, ${}_3T_1$, etc., are obtained in a similar manner.

(vii) Once T_1 has been computed to the desired degree of accuracy, the normal surface reflectance can be calculated easily from either of the original McMahon equations.

B. The effect of surface reflectance on the value of the sample internal transmittance which yields minimum error in the computed value of the normal absorption coefficient, has been calculated. The formula is

$$\ln(T_{\text{opt}}^{-1}) = 1 - 0.087 R,$$

where T_{opt} is the internal transmittance which yields minimum error and R is the surface reflectance. The effect of surface reflectance is thus quite small for materials of index of refraction less than 2.

C. The radial temperature distribution of a disc sample, placed symmetrically in a cylindrical, isothermal sample holder, has been computed approximately taking account of:

- (i) radial heat conduction through the sample rim;
- (ii) radiant heat transfer between sample and sample holder.

The calculation neglects air conduction and convection, so that it overestimates the temperature gradients in the sample. The resulting formula for the temperature difference between the sample rim and center is useful in estimating the error in emissivity measurements where the sample temperature must be measured at the rim. This is the case for emissivity measurements on transparent materials, since large errors will arise if the radiometer field of view is obstructed by a thermocouple.

D. Some work has been done on deriving McMahon's equations (which relate the normal surface reflectance and internal transmittance of a plane parallel lamina to its externally measured normal reflectance and transmittance) from interference theory.

E. Formulae have been derived which give the normal spectral emissivity of cylindrical and spherical blackbodies in terms of the normal hemispherical wall reflectance and coefficients dependent on the blackbody geometry. The formulae neglect terms of the third order in the blackbody wall reflectance; the wall is assumed to reflect diffusely and to be isothermal. In addition, approximate viewfactors were used. It was found that the DeVos (ray tracing) method and the Gouffe (isotropic radiation distribution after second reflection) method give identical results to the second order for a spherical blackbody, but significantly different results for a cylindrical blackbody.

The normal spectral emissivity of a cylindrical-conical blackbody was also computed by the DeVos method to terms of the second order in the wall reflectance and using the assumptions above.

Some work has been done in calculating the general formula for the internal and external viewfactors of conical segments.

II. Data Analysis:

The experimental data on the normal spectral absorption coefficient of single-crystal calcium fluoride at 6, 8, and 10 microns wavelength, and at room temperature (Rubens' data), 500°C and 600°C., has been analyzed. It has been found that the data at 8 and 10 microns fit a power law of the form

$$a = bT^n,$$

where, a , is the absorption coefficient, b , a wavelength dependent constant, and T , the absolute temperature. The value of n varies with the wavelength; $n = 2.06 \pm 0.02$ at 8 microns, and $n = 1.58 \pm 0.01$ at 10 microns. Figure 16 shows the closeness with which the data fit the preceding formulae. It is interesting that the preceding values for n are consistent with the Born and Huang theory of crystal lattices.

III. Experimental Results:

Due to the move to the Gaithersburg facility in March, 1966, no experimental data have been obtained.

IV. Equipment Setup and Additions:

The new Gaithersburg laboratory for infrared normal spectral emissivity measurements has provided satisfactory space to set up the equipment. The Perkin-Elmer 13U spectrophotometer, external optics, and the blackbody and

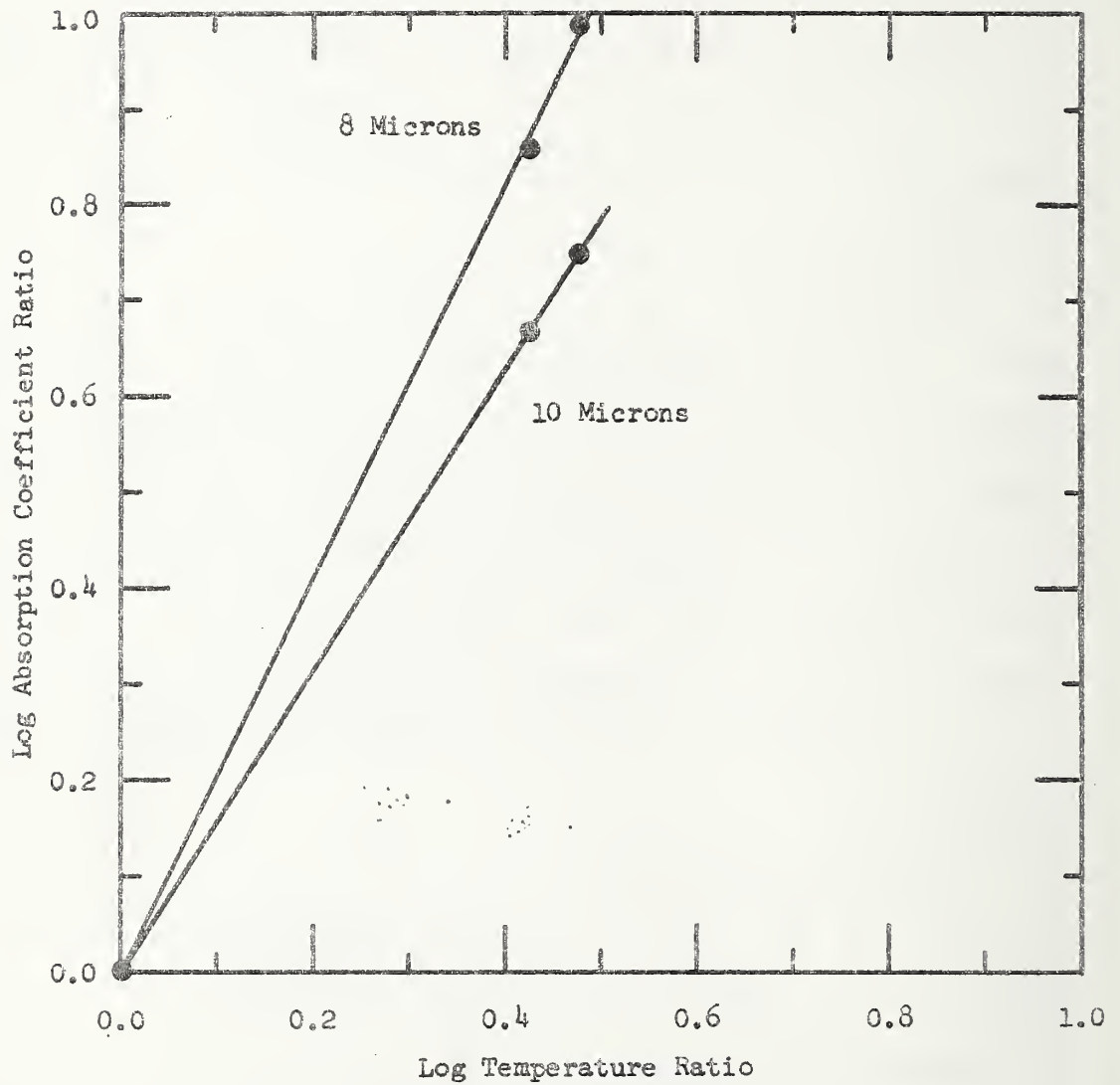


Figure 16. Infrared absorption coefficient as a function of temperature at 8 and 10 microns for a single crystal of calcium fluoride

sample ovens, have been set up and aligned. The two 2kva Sola voltage regulators for the radiometric system have been installed. A technique for rapid alignment of the three external optics mirrors has been achieved by permanently mounting a G.E. H100 mercury arc lamp near the back exit port of the 13U spectrometer.

A Brower 129 thermocouple amplifier, with calibrated zero-offset and a 13 cps. chopper with optical commutator, will be delivered shortly. This equipment will increase the sensitivity and improve the linearity of the present radiometric system.

An additional Leeds & Northrup 10877 current-adjusting-type automatic oven temperature control system has been ordered. This will permit more accurate oven temperature control.

A potassium bromide prism for the 13U has been delivered. This will extend the long-wavelength limit of the 13U spectrometer to about 25 microns.

V. Publications:

The calcium fluoride paper was returned by the NBS Editorial Review Board to the authors (Fussell and Geist) in January for extensive revision. The paper has since been completely rewritten and will shortly be resubmitted for publication.

12. Listing of Naturally-Occurring and Man-Made Objects Spectrophotometered this Year; also List of Reports to ARPA-DOD

H. J. Keegan

During this reporting period, the spectral transmittance of 5 specimens has been measured and the spectral directional reflectance of 86 specimens has been measured for all or part of the spectral range 0.2 to 22.2 microns. In table VII are listed some of the specimens of naturally-occurring materials which have all been measured for spectral directional reflectance and in table VIII are listed some of the man-made materials which have been measured for either spectral transmittance or spectral directional reflectance (as indicated) together with the instrument used and the wavelength region covered.

The NBS Test Reports issued during this half-year period are listed in table IX by test number and title.

Table VII

Partial listing of naturally-occurring materials measured for spectral reflectance on the Cary-White 90 recording spectrophotometer over the spectral range 2.5 to 22.2 microns.

Specimen
Identification

Basalt (4 specimens)

Clay, "Sinton" (5 specimens)

Crater, glass

Dunite (7 specimens)

Dunite at 0°, 75°, 150°C (2 specimens)

Granite (5 specimens)

Granite at 0°, 75°, 150°C (2 specimens)

Mixture of serpentine-basalt-granite-dunite (3 specimens)

Obsidian (4 specimens)

Sand

Serpentine (4 specimens)

Tektite (2 specimens)

Tuff at 0°, 75°, 150°C. (2 specimens)

- 46 -
Table VIII

Partial listing of man-made materials measured for spectral transmittance (T) or spectral reflectance (R) on the indicated recording spectrophotometers for the indicated wavelength range.

Sample Identification	Recording Spectrophotometer		
	Cary 14	Beckman IR-4	Cary 90
Chemicals, inorganic			
Barium sulfate	----	----	2.5-22.2 μ (P)
Calcium carbonate	----	----	" "
Calcium carbonate (with H ₂ O frost coatings) (2 specimens)	----	----	" "
Dysprosium oxide	----	----	" "
Erbium oxide	----	----	" "
Europium oxide	----	----	" "
Gadolinium oxide	----	----	" "
Holmium oxide	----	----	" "
Magnesium carbonate	----	----	" "
Neodymium oxide	----	----	" "
Praseodymium oxide	----	----	" "
Samarium oxide	----	----	" "
Sodium borate	----	----	" "
Terbium oxide	----	----	" "
Tin oxide on silicon	0.9-2.65 μ (T)	1.5-15 μ (T)	----
Ytterbium oxide	----	----	" "
Crystal			
LaF ₃	0.2-2.65 μ (T)	1.5-12.5 μ (T)	----
Frost			
CO ₂	----	----	" "
H ₂ O (2 specimens)	----	----	" "
N ₂ O ₄ (2 specimens)	----	----	" "
NH ₃	----	----	" "
Frost Mixtures			
CO ₂ and N ₂ O ₄	----	----	" "
H ₂ O and CO ₂ (3 specimens)	----	----	" "
H ₂ O and N ₂ O ₄ (2 specimens)	----	----	" "
Ice			
NH ₃	----	----	" "
Oil	----	----	" "
Oil on water	----	----	" "
Paint, 25°C to 400°C (8 specimens)	----	----	" "
Plastics			
Mylar	0.2-2.65 μ (T)	1.5-15 μ (T)	----
Polyethylene (2 specimens)	" "	1.5-14.5 μ (T)	----
Quartz, GE 106 powdered	----	----	" "
Water, distilled (3 specimens)	----	----	" "
Water, salt	----	----	" "

Table IX

Reports issued to ARPA
July, 1965 to August, 1966

Test No. 12.11P-	Title	Submitted by	Date
110/65	Spectral directional reflectance of 3 polished SiO ₂ plates	Cleek Keegan NBS	6-22-65
2/66	Spectral directional reflectance of one sample of mylar backed gold mesh	Keegan NBS	7-7-65
5/66	Spectral transmittance of one sample of mylar plastic	Keegan NBS	7-7-65
8/66*	Spectral directional reflectance of 17 specimens of naturally occurring minerals and 3 reagent grade inorganic materials	NASA Goddard	7-12-65
19/66	Energy study of Cary-White 90 reflectance source	Keegan NBS	7-29-65
20/66	Infrared spectral reflectance of frost 4000 to 450 cm ⁻¹ (2.5 to 22.2 microns) formed at temperatures approximating minus 100°C	Keegan NBS	8-24-65
29/66*	Spectral directional reflectance of 12 specimens of naturally occurring minerals and 4 specimens of man-made quartz	NASA Goddard	9-24-65
30/66	Spectral directional reflectance of 10 rare-earth oxide powders before and after heating at 900°C	Keegan NBS	9-28-65
31/66	Spectral hemispherical-directional reflectance of distilled water	Keegan NBS	9-29-65
37/66	Spectral transmittance of one LaF ₃ crystal	Keegan	11-8-65
38/66	Spectral hemispherical-directional reflectance of 8 specimens of one paint sample over the temperature range 25° to 400°C	Keegan NBS	11-9-65
39/66	Spectral hemispherical-directional reflectance of ammonia frost and ammonia ice	Keegan NBS	11-15-65

46/66	Spectral directional reflectance of white oak, sycamore, and redbud leaves collected during the spring, summer and autumn of 1965	Keegan NBS	12-3-65
47/66*	Spectral hemispherical-directional reflectance of 2 specimens of tuff, 2 specimens of granite, and 2 specimens of dunite at temperatures of approximately 0°, 75°, and 150°C	NASA Goddard	12-3-65
48/66*	Spectral hemispherical-directional reflectance of calcium carbonate powder and H ₂ O frost on calcium carbonate powder	NASA Goddard	12-3-65
49/66*	Spectral hemispherical-directional reflectance of 2 specimens of tektite, one specimen of crater glass and 4 specimens of obsidian	NASA Goddard	12-3-65
50/66	The temperature control of reflectance samples on a Cary-White 90 infrared spectrophotometer over the temperature range of 50°C to 850°C	Keegan NBS	12-6-65
54/66	Infrared spectral transmittance and infrared spectral hemispherical-directional reflectance of 2 types of chalcogenide non-oxide glasses	Keegan NBS	1-10-66
55/66	Infrared spectral hemispherical-directional reflectance of cupric oxide	Keegan NBS	1-12-66
60/66	Spectral hemispherical-directional reflectance of one sample of epoxy cement on copper, 2 samples of platinum black in epoxy cement on copper and 2 samples of "3M" black enamel paint on copper	Keegan NBS	2-3-66
63/66	Infrared spectral hemispherical-directional reflectance of one sample of electrolytically deposited gold on copper and 2 samples of platinum black on gold	Keegan NBS	2-16-66
65/66	Spectral hemispherical-directional reflectance of one sample of "3M" black paint and one sample of "Sicon" black paint at room temperature and 200°C	Richmond NBS	2-18-66

56/66	Spectral hemispherical-directional reflectance of graphite at 20°C, 232°C, 420°C, 650°C, 825°C, and 1012°C	Richmond NBS	2-23-66
57/66	Infrared spectral hemispherical-directional reflectance of 2 samples of graphite at 232°C, and 420°C	Fussell NBS	4-4-66
58/66**	Infrared spectral hemispherical-directional reflectance of 9 specimens of herbicide chemicals and 2 specimens of sand	USAF Eglin AFB	4-18-66
59/66	Spectral directional reflectance of cryogenic deposits of NO	Keegan NBS	5-16-66
73/66	Spectral hemispherical-directional reflectance of 8 "black" materials in the infrared spectral range 2.5 to 20 microns	Keegan NBS	6-1-66
76/66*	Infrared spectral hemispherical-directional reflectance of 6 sandstone specimens	NASA Goddard	6-16-66
82/66	Infrared spectral hemispherical-directional reflectance and infrared spectral transmittance of polytetrafluoroethylene	Nutting ARPA	7-13-66
87/66	Spectral transmittance of 3 interference filters	Nutting ARPA	8-15-66
Test			
097***	Spectral hemispherical-directional reflectance of 12 infrared gray scale samples	Data Corp.	3-31-66
098***			
208****	Spectral directional reflectance of 4 samples of Ponderosa pine foliage	USDA Forest Service	7-6-66

* Measurements financed by NASA, Goddard Space Flight Center, Greenbelt, Maryland

** Measurements financed by U.S. Air Force, Eglin Air Force Base, Florida 32543

*** Measurements financed by Data Corporation, 7500 Xenia Pike, Dayton, Ohio 45432

**** Measurements financed by U.S. Dept. of Agriculture Forest Service, Berkeley, California 94701

APPENDIX A

Infrared Spectral Reflectance of Frost*†

HARRY J. KEEGAN AND VICTOR R. WEIDNER
National Bureau of Standards, Washington, D. C. 20234
(Received 27 September 1965)

INDEX HEADINGS: Infrared; Spectral reflectance; Frost; Carbon dioxide; Spectrophotometry.

THE infrared-reflectance spectra of water frost and of two forms of solid carbon dioxide ("frost" and crushed commercial "dry ice"), were obtained over the spectral range 4000 to 450 cm^{-1} on a high-resolution spectrophotometer with a reflectance attachment.¹

To avoid melting the frost samples, or vaporizing the "frost"

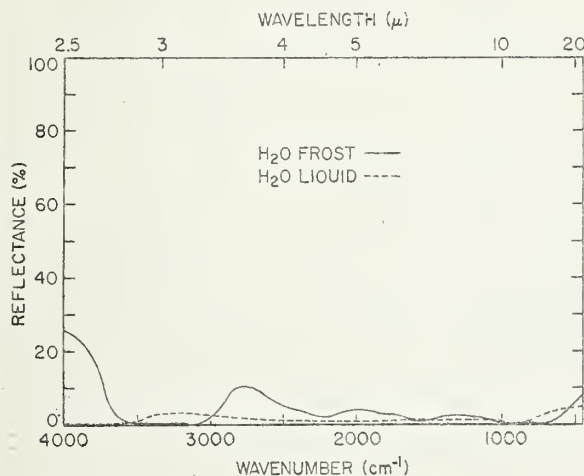


FIG. 1. Infrared spectral reflectance, 4000 to 450 cm^{-1} , of water frost (solid curve) at approximately the boiling point of nitrogen (-196°C). Also shown (dashed line) is the infrared spectral reflectance of a pool of distilled water (50-mm deep) at room temperature (approximately 25°C).

form of solid carbon dioxide, the power input to the source of radiation was reduced from a maximum of 300 to approximately 45 W. The frost was deposited on a super-cooled substrate consisting of crushed ice in a polystyrene-foam cup filled to its depth of 50 mm with crushed ice and liquid nitrogen.

Frost was allowed to collect from atmospheric water vapor to a depth of approximately 2 mm on the super-cooled crushed ice that extended above the level of the liquid nitrogen in the cup. The

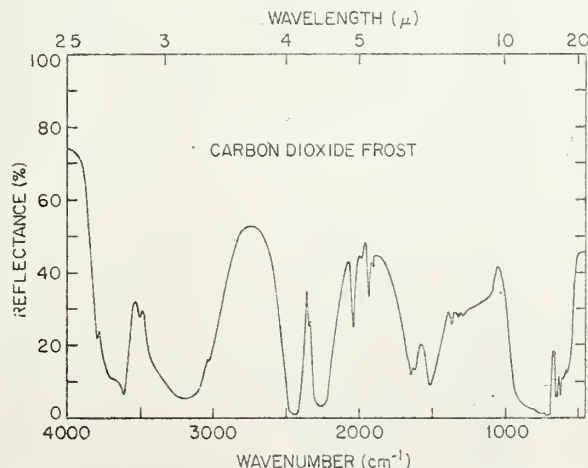


FIG. 2. Infrared spectral reflectance, 4000 to 450 cm^{-1} , of carbon dioxide frost (2-mm thickness) at approximately the boiling point of nitrogen (-196°C).

infrared spectral reflectance of this frost sample is shown as the solid curve in Fig. 1; also shown is the spectral reflectance of a pool of water (50-mm deep) at room temperature (dashed curve).

The solid carbon dioxide sample in "frost" form was prepared by placing a similar supercooled substrate in a closed container with evaporating dry ice. The infrared spectral reflectance of this solid carbon dioxide sample is shown in Fig. 2. For comparison, a measurement of the spectral reflectance of solid carbon dioxide in the "crushed dry ice" form was made by placing crushed commercial dry ice alone in the polystyrene cup (without the liquid nitrogen); see Fig. 3.

Note the great similarity between the infrared spectra reflectance curves for the "frost" and the "crushed dry ice" form of carbon dioxide (Figs. 2 and 3), and the lack of similarity between water frost and carbon dioxide "frost" (Figs. 1 and 2), although to the eye they appear to be identical whites of the same texture.

There is a possibility that the CO_2 frost may contain traces of H_2O frost, and vice versa, because both samples were exposed to some atmospheric CO_2 and H_2O vapors during their formation as well as during the time required to make the measurements. The

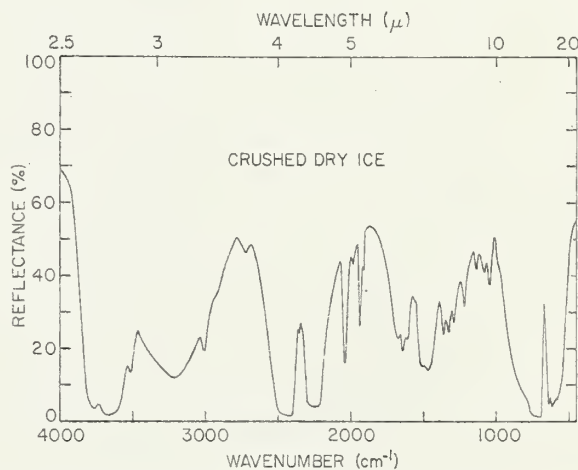


FIG. 3. Infrared spectral reflectance 4000-450 cm^{-1} , of crushed commercial carbon dioxide "dry ice" (10-mm deep) at approximately the sublimation temperature of CO_2 (-78°C).

influences of these impurities on the spectral curves are not known. The H_2O frost, however, shows practically none of the complex absorption features found in the CO_2 frost and crushed dry ice. These features are quite pronounced and possess what appear to be some strong reststrahlen spectra² in the 15- to 22.2- μ region.

Although the experimental procedures employed in obtaining these measurements do not assure that the samples of H_2O frost and CO_2 frost are completely pure, they do overcome some major difficulties in maintaining samples in the solid state in a double-beam infrared spectrophotometer while irradiating them at a sufficiently high rate to accomplish measurements of spectral reflectance. Further refinements in the procedures have made possible similar measurements of "frost" formed from other materials which exist as gases at ordinary temperatures. The results of these measurements will be described in later communications.

These measurements were made at the request of John D. Strong³ to assist him in setting up heat budgets for planets such as Venus that have H_2O and CO_2 clouds.

* Presented at the 1965 Fall Meeting of the Optical Society at Philadelphia [J. Opt. Soc. Am. 55, 1567A (1965)].

† Supported in part by the Advanced Research Projects Agency, DOD, and by Goddard Space Flight Center, NASA.

¹ J. U. White, J. Opt. Soc. Am. 54, 1332 (1964).

² W. M. Sinton and W. C. Davis, J. Opt. Soc. Am. 44, 503 (1954).

³ Laboratory of Astrophysics and Physical Meteorology, The Johns Hopkins University, Baltimore, Maryland.

APPENDIX B

SPECTRAL REFLECTANCE AND PLANETARY RECONNAISSANCE

David M. Gates, Harry J. Keegan, and Victor R. Weidner

(Proceedings of Third Goddard Memorial Symposium, American
Astronautical Society, Peter C. Badgeley, NASA Headquarters, Editor.)

ABSTRACT

The spectral reflectance of selected vegetation, animal integuments, and minerals from 0.26 to 22.2 microns was measured and reported. Strong absorption by the material of incident radiation is caused by pigmentation at ultraviolet and visible wavelengths due to electronic quantum transitions. Strong absorption in the infrared beyond about 2.0 microns are caused by vibration-rotation quantum transitions due to water and organic molecules. A distinct absorption gap exists in the spectrum between these two wave-length regions which is exhibited by a strong reflectance in the 1.0 to 2.0 micron region. Plants with chlorophyll pigmentation display a very abrupt change in reflectance at 0.7 micron. Animal integuments and the bark of some trees do not exhibit this sharp edge. The reflectance spectra of plants and animals have a characteristic absorption band at about 3.5 microns due to C-H stretching.

If there is life on Mars it may be detected by searching with spectral reconnaissance for the presence of a sharp edge in the spectrum of reflected sunlight. The spectral characteristics of sunlight reflected from vegetation on the Earth's surface is described and the expected reflectance from Mars is discussed.

SPECTRAL REFLECTANCE AND PLANETARY RECONNAISSANCE

David M. Gates*, Harry J. Keegan**, and Victor R. Weidner***

INTRODUCTION

The search for life on other planets requires the application of many techniques, one of which is to obtain the spectral characteristics of sunlight reflected from the planetary surface. The reflected sunlight will have a unique spectral quality resulting from the spectral quality of the incident sunlight, the spectral transmittance of the planetary atmosphere, and the spectral reflectance of the surface. It is the purpose of this paper to discuss the spectral properties of plant, animal and mineral substances as they pertain to the spectral reconnaissance of a planetary surface. The main questions to answer are: Do plant and animal integuments exhibit unique spectral reflectance properties which are distinct from mineral reflectances? Why do the spectral reflectances of plants, animals or minerals have specific characteristics? By means of spectral reconnaissance of the Earth's surface from satellite altitudes could one recognize vegetation on the surface and recognize it as living substance? If

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***National Bureau of Standards.

substantial areas of the surface of Mars are covered with living substance what would one expect to observe with spectral reconnaissance?

SPECTRAL REFLECTANCE MEASUREMENTS

The spectrophotometric reflectance properties of plant and animal surfaces and of some minerals were measured for wavelengths from 0.26 to 22.2 microns. The following instruments of the Spectrophotometry Unit, Photometry and Colorimetry Section, National Bureau of Standards were used:*

A Hardy (General Electric II) recording spectrophotometer for spectral ranges of 0.4 to 0.75 micron and 0.73 to 1.08 microns with spectral slit widths of approximately 10 and 20 millimicrons respectively; a Cary 14 recording spectrophotometer with a Cary 1411 reflectance attachment from 0.26 to 0.4 micron and from 0.6 to 2.5 microns; and a Cary-White 90 recording spectrophotometer over the spectral range 2.5 to 22.2 microns; for most of the measurements both the specular and diffuse reflectance were observed. Each instrument utilized a different technique for the illumination and observation of the sample. Where the spectrum from one instrument joined with the spectrum from another instrument there may be small differences in the reflectances. The two spectra were forced to agree by

*These commercial instruments are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment identified is necessarily the best available for the purpose.

averaging the individual values for a small wavelength distance to either side of the position of overlap or juncture.

Spectral reflectance measurements may be considered as qualitatively accurate as a function of frequency or wavelength. The shapes of the curves and character of the features are valid, but the photometric value of reflectance cannot be considered as representative. The value of reflectance is correct for the particular measurement, but represents the nature of the sample used and the conditions under which the measurement was made. The reflectance will change for different angles of illumination, whether a point source or extended source is used, and other measurement conditions. For the present discussion the interest is to compare features and not to determine photometric values of spectral reflectance. Earlier measurements on the spectral properties of plants were reported by Gates, Keegan, Schleter, and Weidner (1965). Further details and references concerning the instrumentation may be found in that article.

SPECTRAL REFLECTANCE RESULTS

The spectral reflectance properties of selected minerals, animals, and plants are shown in figures 1, 2, and 3 for the wavelength range 0.26 to 14.0 microns. It is evident in all the curves that the ultraviolet reflectance

is very low for most substances. Nearly all materials exhibit a peak reflectance in the visible and/or the near infrared at wavelengths between 0.4 to 2.7 microns. The infrared reflectances beyond 3.5 microns are for all substances substantially less than the visible or near infrared reflectances. The reflectances of feldspar and malachite exhibit reststrahlen peaks in the long wave infrared beyond 7.0 microns. Such reststrahlen reflectances occur only for crystalline-type materials and not for more amorphous substances.

The general features of the reflectance curves presented in figures 1, 2, and 3 can be easily understood. The lack of strong reflection at any wavelength is the result of strong absorption of the incident radiation with the molecular structure of the material. At high frequencies, and as a general rule at wavelengths shorter than 1.0 micron, the absorption is caused by electron transitions within atoms or molecules. These electron transitions require a definite amount of energy in order to raise the electron from one quantum level to a higher quantum level. Since a quantum of radiation has an energy equivalent of $h\nu$, the energy available is proportional to the frequency of the radiation. Radiation of wavelengths longer than about 1.0 micron possess too little energy per quantum to produce a direct electron transition. Every

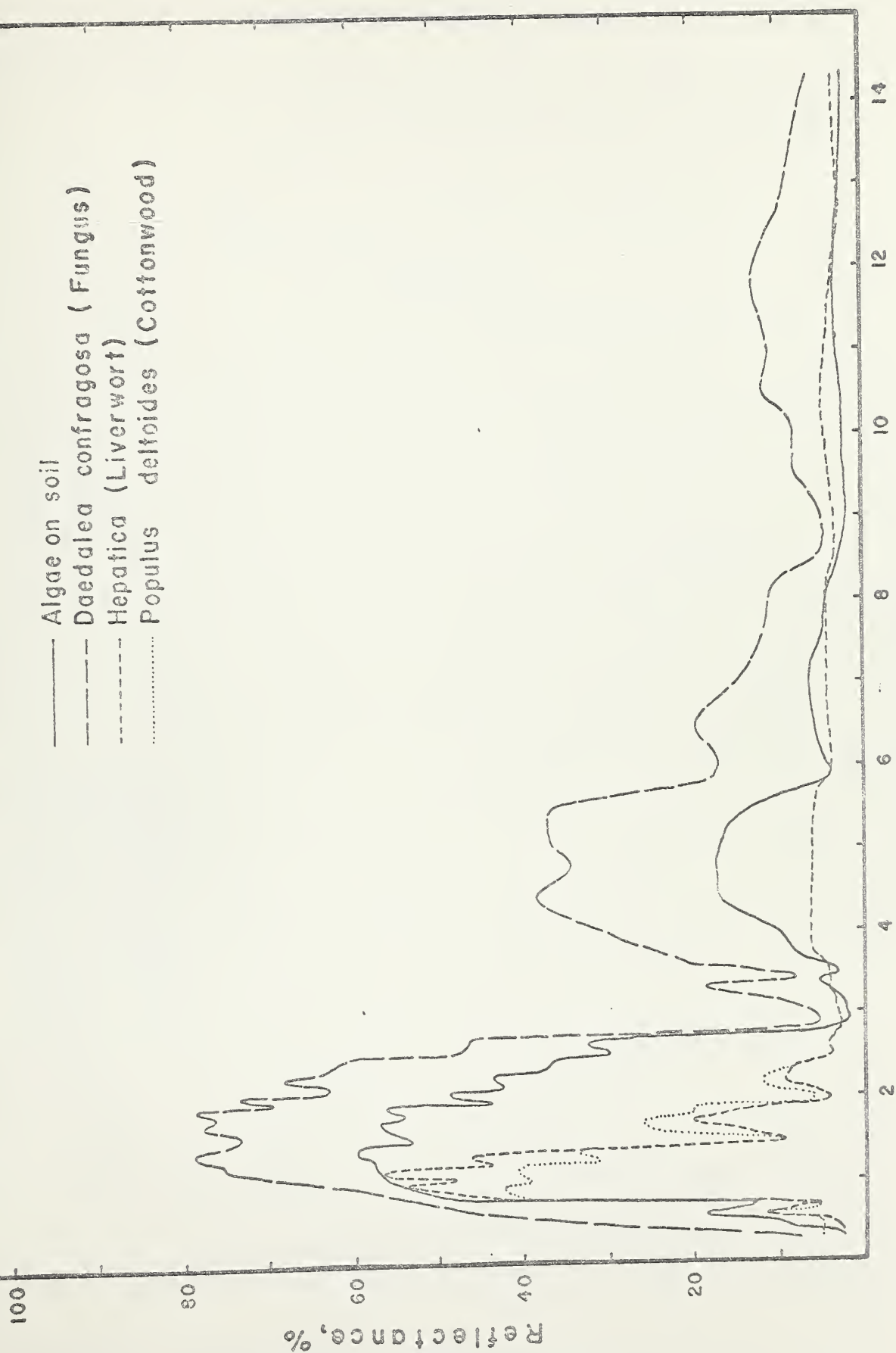


Fig. 1 The spectral reflectance of plants as a function of wavelength.

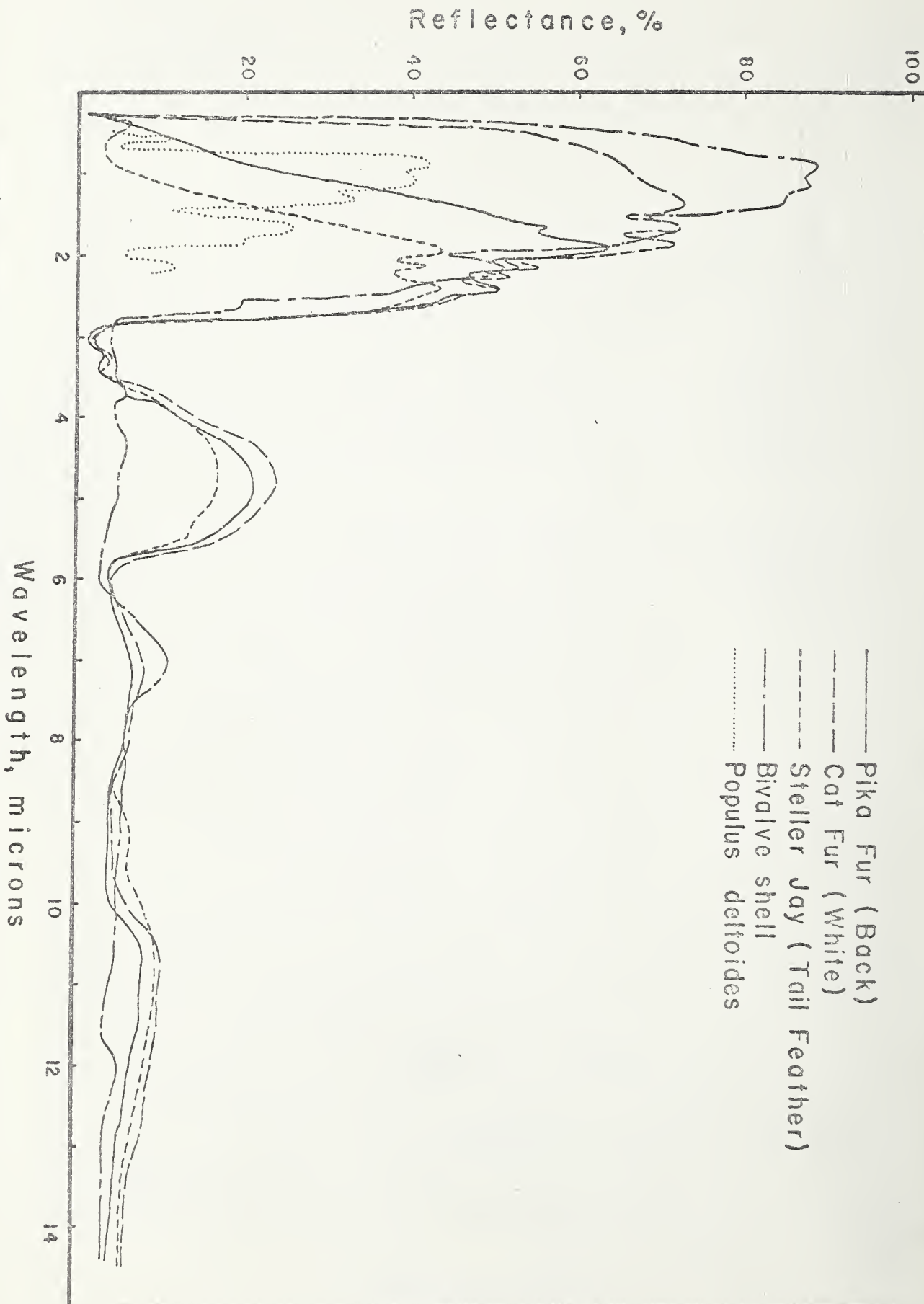
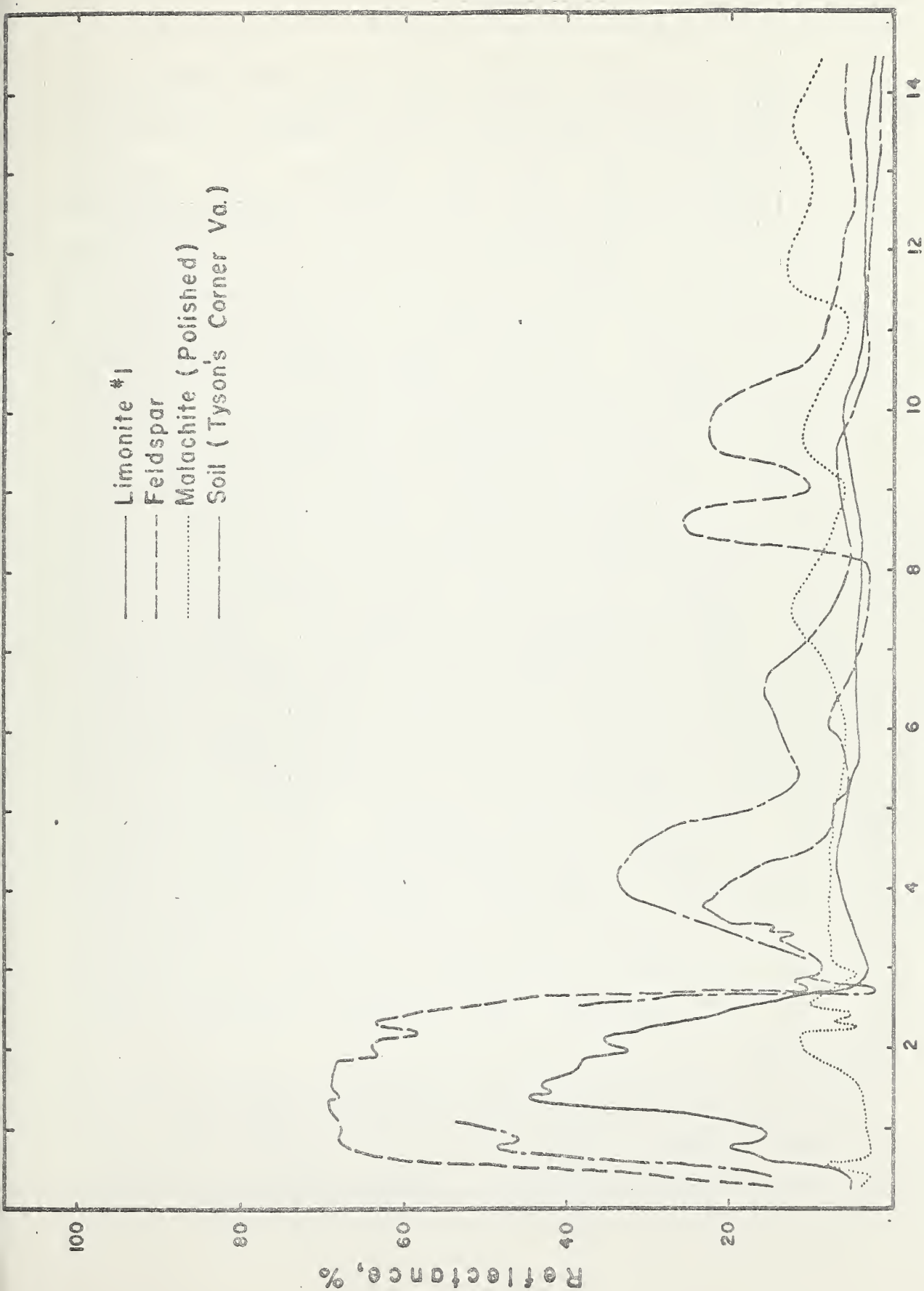


Fig. 2 The spectral reflectance of animal integuments as a function of wavelength and the reflectance of a green leaf for comparison.



Wavelength, microns

Fig. 3 The spectral reflectance of minerals and soil as a function of wavelength.

substance, gas, liquids or solids, has a specific absorption response to incident radiation as the result of electron transitions within its specific molecular or atomic structure. Most pigments will absorb selectively and render an object blue, green, yellow, or red in appearance depending upon which frequencies it does not absorb. Ultraviolet radiation contains a high amount of energy per quantum and thereby produces electron transitions in nearly all substances. Hence the ultraviolet, particularly the far ultraviolet, is strongly absorbed. The low reflections and hence strong absorptions, which occur at the long infrared wavelengths beyond 1.0 micron, have another origin than electronic. These absorptions are caused by vibration and rotation quantum transitions of single molecules or portions of molecules comprising a substance. These transitions are of low energy and hence require the interaction with low frequency, long wavelength radiation. The fundamental quantum transitions of many molecules occur at wavelengths greater than 2.0 microns, but often overtone and combination transitions occur with much reduced intensity at wavelengths short of 2.0 microns and produce relatively weak absorptions.

The fact that the physical world of absorption and reflection spectra divide into two distinct frequency regions, e.g. the high frequency electronic transitions and

the low frequency vibration-rotation transitions means that there may be in between the two a nearly absorption-free region. This is indeed the case and the fact that most substances possess a peak reflectance in the visible or near infrared is the result of this phenomenon. If a material, such as the bivalve shell, the white cat's fur, or the feldspar is reasonably free of pigments, strong absorption will occur only in the ultraviolet and the substance will be reflective throughout the visible. On the other hand the pigments contained in the brown fur of the Pika, the plant leaves, the Steller Jay feathers, and some of the minerals cause the absorption edge to shift into the visible or the near infrared. The long wave infrared absorptions (regions of low reflection) seen in the curves of figures 1, 2, and 3 are primarily caused by bound water. Liquid water and water vapor have absorption bands in the wavelength vicinity of 1.1, 1.4, 1.9, 2.7, and 6.3 microns. Water also absorbs strongly in the pure rotation band which begins to be in evidence beyond 12 microns wavelength. The greater the water content of the material the stronger are the absorption bands and the lower the amount of reflection between the bands. An absorption band possesses wings which extend far beyond the band center and therefore the regions between the band centers are primarily influenced by absorption. If bound water is totally lacking from a substance these absorption bands will be absent and the

infrared reflectance will be considerably higher.

Special note should be made of the absorptions in the vicinity of 3.5 microns. The interesting aspects of the feature in the vicinity of 3.5 microns is that it occurs so very strongly in the reflectance of the bracket fungus, Daedalea confragosa, but much less strongly in the algae and even less in the reflectance of Hepatica, the liverwort. This feature is of particular interest since a similar feature was reported by Sinton (1957) in the reflection spectrum of Mars. It is very interesting to note by comparison with figure 2 that a similar feature appears in the reflectance spectra of animal integuments. From figure 3 it is seen that a similar feature does not appear in the reflectance spectra of most mineral substance, although there is a different type feature slightly shifted in wavelength for the spectrum of feldspar. Sinton (1957) attributed the band origin to organic C-H bonds and showed similar bands in the reflection spectra of Mars, Sinton (1961). Colthup has refined this interpretation to be an aldehyde C-H and probably due to acetaldehyde (CH_3CHO). Rea, O'Leary, and Sinton (1965) have recently revised the interpretation to show that there may not be reason to believe these are surface features of Mars but may be contaminations due to H₂O in the Earth's atmosphere.

REFLECTANCE OF PLANT VERSUS ANIMAL SUBSTANCE

One wonders whether the spectral reflectances of plants are clearly distinctive when compared with the reflectances of animals. The answer is only partially in the affirmative. The reflectance spectra of selected plants and animals is shown in figures 4 and 5. All plant parts containing chlorophyll exhibit a very sharp absorption edge at 0.7 micron or 700 millimicrons. This is because the plant pigment, chlorophyll absorbs very strongly the blue and red wavelengths. A weak reflection maximum occurs in the green and by this we see plants as green. The absorption by chlorophyll ends very abruptly at 0.7 micron. Absorption by bound and free water does not occur until longer wavelengths. Hence plants exhibit a very dramatic and strong reflection at wavelengths between 0.7 and 1.4 microns. Plant barks not containing chlorophyll do not possess the abrupt absorption edge at 0.7 micron and continue to reflect strongly in the visible. This is seen for the bark of Acer rubrum (red maple) and Quercus alba (white oak) shown in figure 5. A lichen represents the symbiosis of algae and fungus. The food production and chlorophyll development is carried on only within the algae

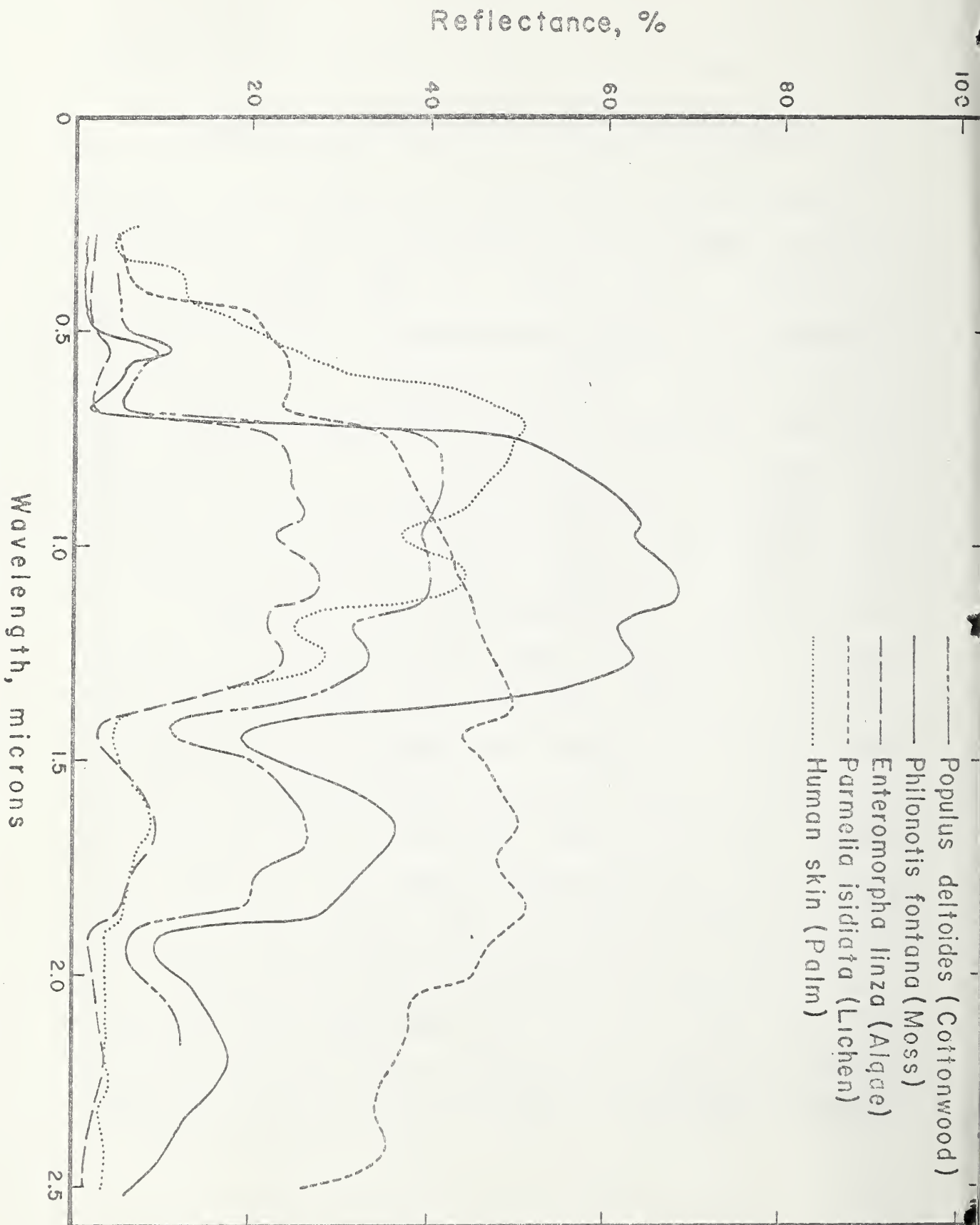


Fig. 4 The spectral reflectance of plants as a function of wavelength and the reflectance of human hand for comparison.

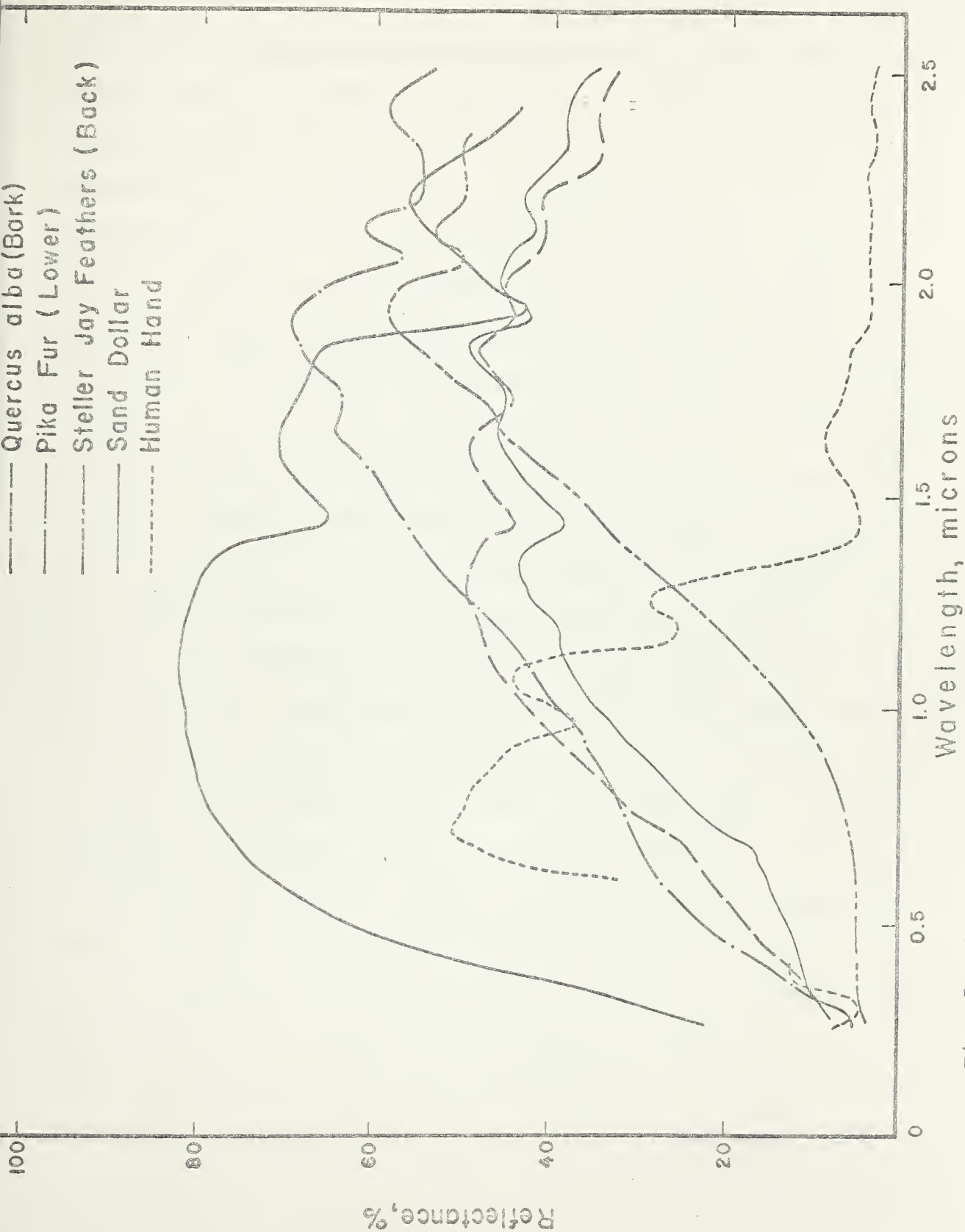


Fig. 5 The spectral reflectance of tree bark (Pica and Quercus) and of animal integuments as a function of wavelength.

and the fungus in turn encases the algae and protects it from dessication. Pigments may be present in the fungus which produces the main body of the lichen. These pigments may contribute the primary color appearance of the lichen, but the influence of chlorophyll in the algal component may show through in reflection spectra. This is clearly seen to be the case for the curve of Parmelia insidiata shown in figure 4. This is also shown in the curves for lichens published by Gates, Keegan, Schleter, and Weidner (1965). However, as also seen in those curves the pigment in the fungus may completely hide the chlorophyll pigment and cause a reflectance versus wavelength to be without the appearance of a sharp absorption edge. This occurred for the reflectance from the very black lower surface of a foliose lichen reported in the paper just mentioned. This situation is unusual and not the general reflectance behavior of lichens. The only other fresh plant material which did not exhibit a sharp absorption edge at 0.7 micron was Daedalea confragosa, a dry bracket fungus, where its reflectance spectrum is shown in figures 1 and 6. The bracket fungus also exhibited much less water absorption and substantially higher reflectance throughout the infrared than did other plant materials. Dried leaves also have reflectance spectra resembling more closely that of the bracket fungus than of green leaves.

It is interesting to note from figure 5 that none of the spectral reflectance curves for animal integuments displayed an abrupt absorption edge in the visible or near infrared. The water bands clearly showed up in the reflectances of the animal materials, but interestingly enough the strongest were associated with the sand dollar. Clearly the animal materials have other absorption bands in the near infrared in addition to those originating with water.

A more detailed comparison of the spectral reflectances of plant and animal materials is made by comparing figures 6 and 7. In figure 6 are shown the reflectance spectra of species from most of the major plant groups. The similarity of all the curves except for that of the bracket fungus is striking. It certainly can be argued that any plant material containing chlorophyll will exhibit this sharp absorptance or reflectance edge at 0.7 micron. The reflectance curves shown in figure 7 for the animal materials also display no sharp edges. The pigments comprising the animal integuments produce a much more neutral absorption and reflection than do the plant pigments.

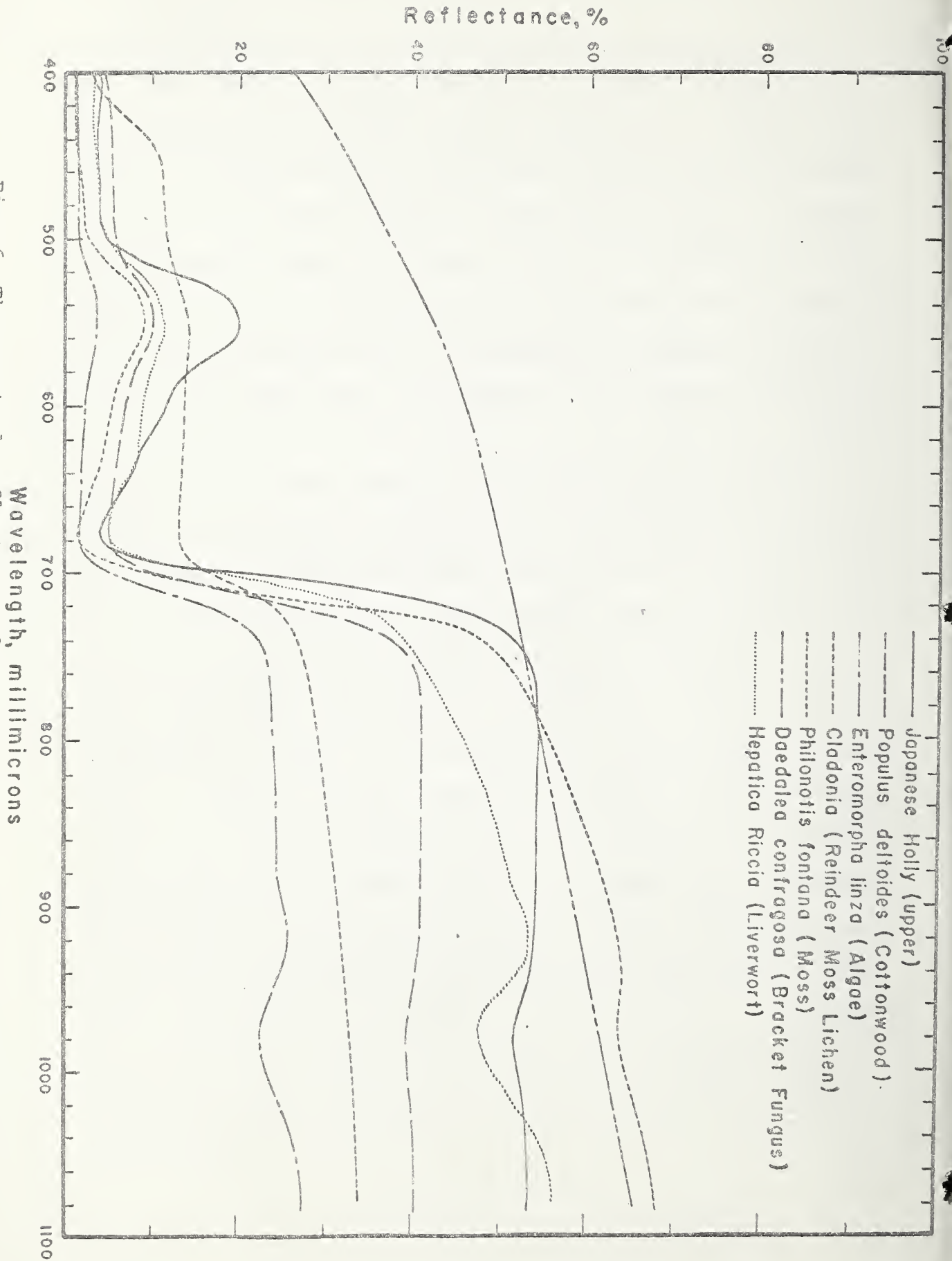


Fig. 6 The spectral reflectance of several plant groups as a function of wavelength in the visible and near infrared.

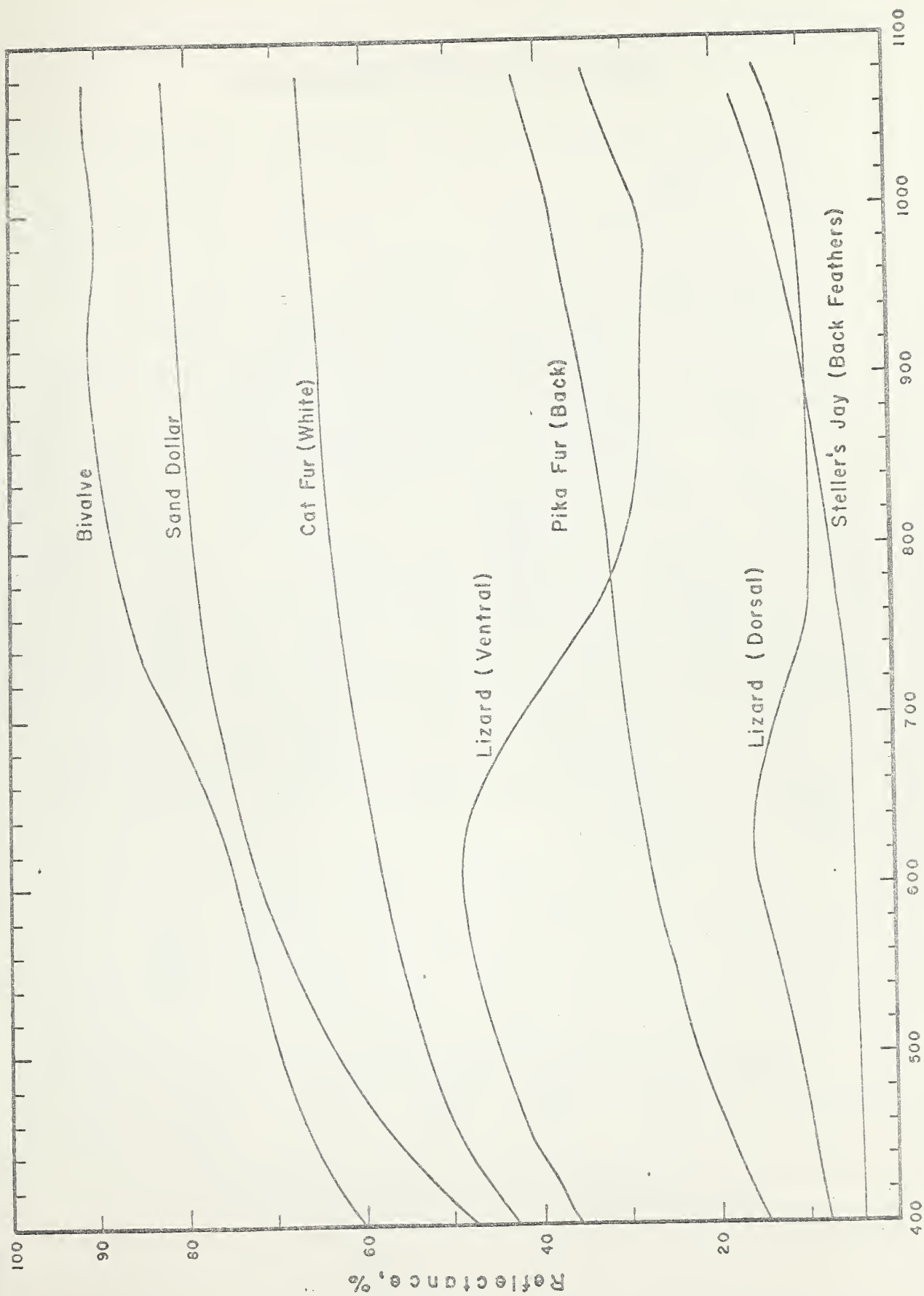


Fig. 7 The spectral reflectance of animal integuments as a function of wavelength in the visible and near infrared.

SUNLIGHT REFLECTED FROM PLANTS

Sunlight penetrating the Earth's atmosphere to illuminate vegetation at the surface has a characteristic spectral distribution on a clear day similar to that shown in figure 8. This is the solar intensity per unit wavenumber as a function of the wavenumber (frequency) of the radiation. When this incident sunlight is reflected from a vegetated surface on the reflected sunlight as seen from near the Earth's surface will have the spectral distribution shown in figure 8. The sharp absorption-reflection edge at 0.7 micron remains. Many of the absorption bands in sunlight produced by water vapor in the atmosphere are further enhanced by their appearance in the reflectance spectra of plants. If the Earth's surface is viewed from a satellite these absorption bands are further intensified by one additional passage of the radiation out through the atmosphere.

If the day is overcast, and the Earth's surface is being viewed from near the ground, the absorption-reflection edge of plant materials is only very weak in the spectrum of reflected cloudlight as shown in figure 8. This is because the cloudlight spectral distribution is being rapidly attenuated in the red and near infrared by the high

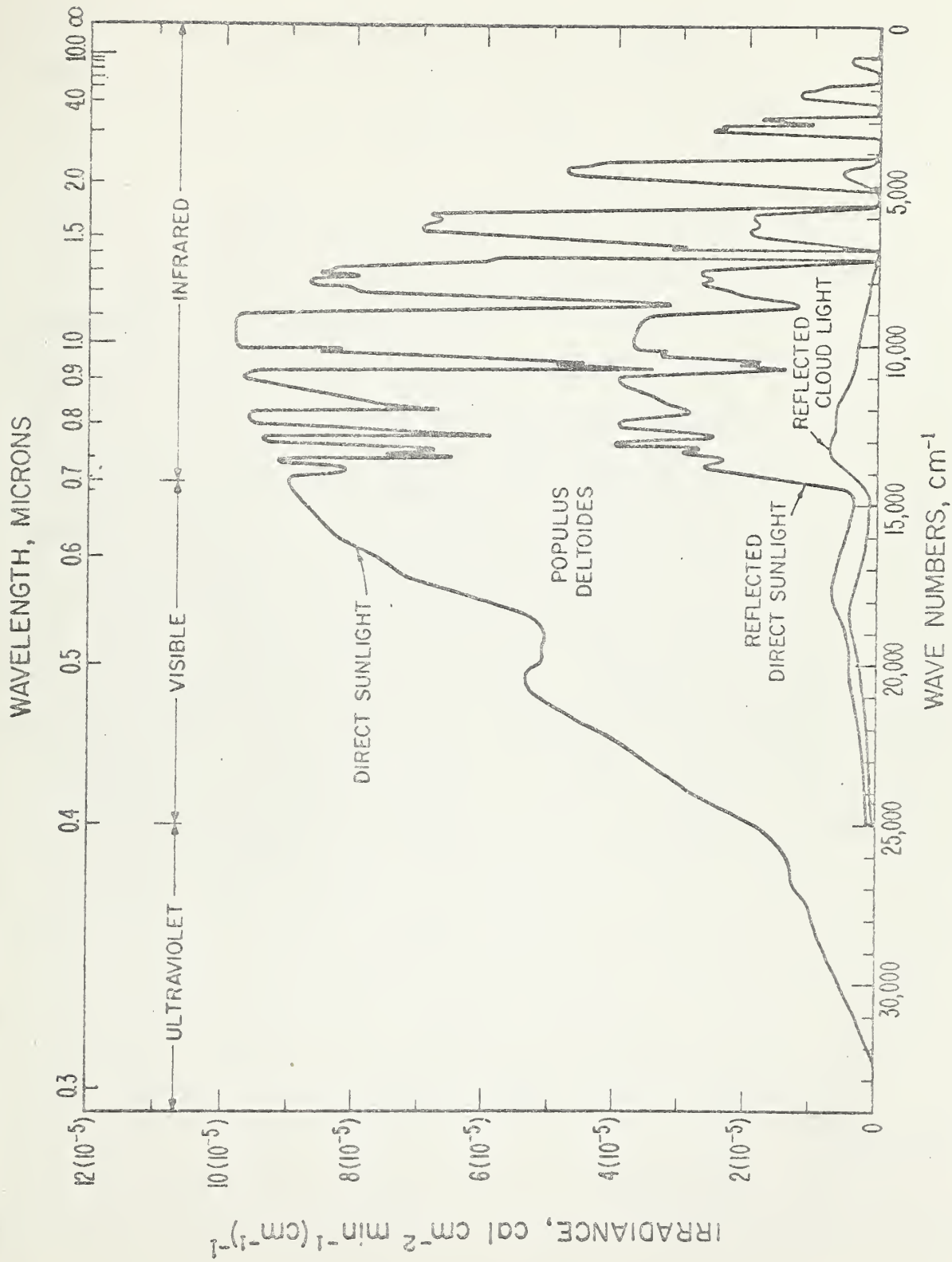


Fig. 8 The spectral distribution of incident direct sunlight at the Earth's surface as a function of wavenumber. A wavelength scale is shown at the top of the graph. The spectral distributions of sunlight reflected from a vegetated surface or a clear day and on an overcast day are shown.

concentration of water vapor and water droplets in the clouds. These properties of sunlight, cloudlight, and reflected light have been discussed in detail by Gates (1965).

If the characteristic reflectance spectra of plant materials were known, it is likely that observed reflection spectra could be interpreted as representing a vegetated surface or not a vegetated surface, if an unknown area of the Earth's surface were viewed from a satellite with a spectral scanner. This would only be true during the growing season for deciduous vegetation. For a surface covered with conifers this would be true throughout the year. For deciduous vegetation the dried plant leaves or exposed bark of trees would not show a sharp absorption-reflection edge at 0.7 micron and could not be readily distinguished from a soil or mineral surface. Certainly there would be seasons when deciduous living plants on the surface could not be recognized uniquely as plants as observed by spectral reconnaissance from a satellite. However, if spectral observations could be made throughout a complete year then seasonal changes in the spectral quality of the reflected light might reveal the surface as vegetated.

SPECTRAL RECONNAISSANCE OF MARS

If there is life on Mars it will be probably very difficult to detect from an artificial satellite of Mars. However, an attempt must be made to observe the surface of Mars in every possible detail. One such means of observation is to obtain spectral information concerning the quality of sunlight reflected from the surface as observed from a Mars probe such as Mariner. The relatively low atmospheric pressure on Mars (approximately 25 mb), the apparent extremely low amount of water vapor, if any, and the very low temperatures prevailing much of the time (240 K), except for seasonal maxima near the equator as high as 300 K, make the likelihood of life improbable. Also the possibility of a substantially greater amount of ultraviolet irradiation on the surface of Mars, because of less atmospheric ozone, would make life less probable. However, from our present lack of knowledge concerning the requirements of organisms, one cannot rule out the possibility of life on Mars. Organisms on Mars may occupy isolated niches where conditions may be locally suitable. Such a niche might be a thermal hot spring where ample moisture might be available. If one assumes that life may exist on Mars, then one should ask what might be the appearance of reflected sunlight from the Martian surface. If one first assumes

organisms resembling vegetation on Earth, then one can ask what their reflectance spectrum may be. They may possess pigments resembling chlorophyll or they may be quite different. However, if they are to have photochemical food production then they must possess pigments to absorb the incident sunlight. The Martian atmosphere transmits somewhat different wavelengths of radiation than the Earth's atmosphere. The short wavelength cutoff may be about 2900 Å if there is atmospheric ozone. The long wave length end should be without much water vapor absorption but with strong carbon dioxide absorption at 2.0, 2.7, 4.3, and 14.0 microns. This has been discussed in detail by Sagan, Weaver, and Kaplan (1961). Hence if vegetation on Mars is to be photochemically active the plant pigments must absorb very much as they do on earth. The intensity of sunlight on Mars is approximately one-half of the intensity at the Earth because of the greater distance from the Sun. Hence plant pigments on Mars may extend their absorption over as broad a band of wavelengths as possible. It could be expected that the Martian pigments would absorb the near ultraviolet and all of the visible. Because of the fact that electron transitions are not generated by quanta at infrared frequencies, it is doubtful that plant pigments on Mars absorb strongly the infrared beyond 1.0 micron. Since the water vapor content of the Martian atmosphere is very low the plants would be expected not to contain much water. The

reflectance of plants on Mars should exhibit strong absorption at ultraviolet and visible frequencies and strong reflection at infrared frequencies. A sharp absorption-reflection edge should appear between about 0.7 to 1.0 micron. A broad peak of reflection should occur between wavelengths of about 0.7 or 1.0 micron to the vicinity of 2.7 microns or even beyond. The sunlight reflected from a vegetated surface on Mars should show this same sharp absorption-reflection edge and bright reflectance to 2.7 microns where very strong atmospheric carbon dioxide absorption will occur. Beyond this wavelength further bright reflection may occur until strong atmospheric absorption occurs at 4.3 microns.

Much of the speculation regarding the possibility of organic molecules on the surface of Mars results from the spectroscopic observation of Mars by Sinton (1957) in which he reported interesting features at wavelengths 3.43, 3.56, and 3.67 microns. The original interpretation by Sinton attributing these features to C-H bands of organic origin has been modified more recently by Rea, O'Leary, and Sinton (1965) to attribute them to HDO absorption in the Earth's atmosphere. Nevertheless, such bands do exist in the reflection spectra of plant and animal materials and must be carefully investigated as a possible unique feature of living substance.

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