Journal of Research of the National Bureau of Standards Vol. 46, No. 5, May 1951 Research Paper 2206

Ultraviolet Spectral Distribution of Radiant Energy From the Sun

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This paper gives the results of some preliminary measurements on the ultraviolet spectral energy distribution of direct solar radiation at Washington, D. C. Data are given for wavelengths extending below 300 millimicrons for air masses approximating $M=1.4$. The new equipment and method employed in this work permit the rapid acquirement of a prismatic ultraviolet spectral energy curve at sea level showing greater Fraunhofer structure than previously obtained even at desert and mountain stations.

Other applications of this equipment, for example, in the study of total ozone and in sky-light spectral-energy distributions are suggested.

I. Introduction

The determination of the ultraviolet spectral radiant energy of sunlight has long been a subject of considerable interest. Nevertheless, but few measurements for wavelength regions shorter than about 330 or 340 mμ have been recorded in the literature [1 to 7].[1] This is easily understandable, since double quartz prism spectrometers suitable for the automatic and rapid recording of low spectral intensities have not been generally available until quite recently. The best radiometric data previously published, extending to wavelengths shorter than 300 mμ, are those of Pettit [1]. Although they were obtained at high altitudes the low sensitivity of the radiometer necessitated the use of wide optical slits (spectral width usually 5.0 to 10.0 mμ) and long response times.

The solar spectrum, when photographed with a good grating spectrograph, shows a continuous spectral energy distribution on which are superimposed thousands of Fraunhofer lines and bands [8, 9]. These features are much too numerous to be detected separately by a prism spectrometer. The prism averages the spectral energy over a wavelength interval corresponding to the effective slit width of the instrument. Hence in spectral regions in which the Fraunhofer lines are numerous and have intense absorption, depressions will occur in the energy curve observed with a prism spectrometer. The character of the observed curve will be significantly affected by the slit width employed. In general, the narrower the slit width the more detailed will be the structural character of the observed spectrum.

The data on the ultraviolet solar energy curve recorded in this paper were obtained between 10:00 a. m. and 12:00 noon during October 1950, when the sun was shining through clear atmosphere associated with high-pressure conditions. Since the purpose of this investigation was primarily to determine the possibilities of the available equipment in work of this type rather than to acquire extensive data, the instruments have not been removed to a location having day-long clear access to direct solar rays.

[1] Figures in brackets indicate the literature references at the end of this paper

II. Instruments and Methods

The apparatus employed in this investigation consists of a Farrand double quartz prism spectrometer, RCA type 935 phototube, 510-cycle light modulator, tuned amplifier and auxiliary meters, and recording apparatus (see fig. 1), set up and calibrated as described elsewhere [19], except that a heliostat was employed for keeping sunlight reflected into the entrance slit of the instrument. For this purpose the entrance slit of the instrument was placed toward the south and the heliostat arranged so that a beam of direct sunlight reflected from a plane chrom-aluminized mirror fell upon the center of the first lithium-fluoride-quartz collimating lens of the instrument. The spectral energy response characteristic of the complete instrument, including the heliostat mirror and phototube, were determined by using a standard tungsten-filament-in-quartz lamp [19, 20] calibrated for color temperature [11] and evaluated for spectral emission in the ultraviolet with the application of spectral emissivity data for tungsten [12 to 15] (see table 1). In this calibration the radiant energy from the standard lamp was reflected into the spectrometer by the heliostat mirror. The lamp distance was arranged so that the illuminated area of the collimating lens approximated that illuminated by direct sunlight.

No refracting lens or mirror was employed to produce an image of the sun on the entrance slit of the spectrometer because an integrated solar energy spectrum was desired. Although a small area of the sky surrounding the sun contributed to the total energy response, its effect is necessarily small since it probably did not at any time exceed 1 percent of the total and did not differ radically in spectral quality from sunlight as observed in check measurements on the sky only, near the sun.

In the present investigation the high sensitivity of the detecting and recording apparatus permitted the use of relatively narrow slit widths (spectral width 2 to 3 mμ), with noise levels less than 1 percent, to about 305 mμ. Hence, with this equipment somewhat narrower spectral slit widths could be practically employed at the altitude of the Bureau's

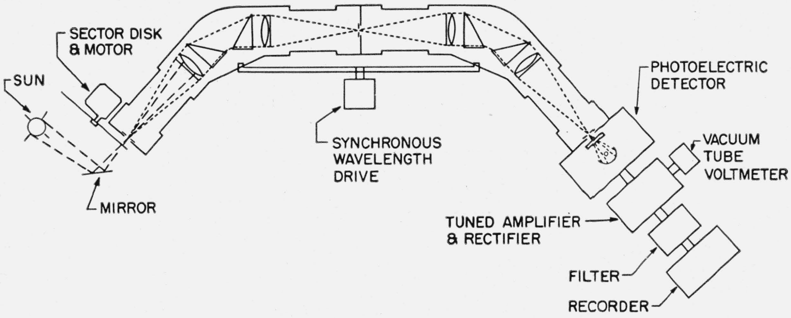

FIGURE 1. *Block diagram showing instrumental lay-out.*

TABLE 1. *Black-body data and emissivity factors for tungsten at operation temperature of standard tungsten-filament-in-quartz lamp; relative spectral energy emission of standard lamp, based on tabulated values of tungsten emissivity; relative spectral transmissive factor (response factor) of Farrand spectrometer, including heliostat mirror, phototube and all other components of the instrument; transmission coefficients of 0.18 cm of ozone per unit air mass through an air mass of M-1.43; and the calculated Rayleigh scattering spectral transmission coefficients for air mass, M=1.43, at Washington (approximately sea level, 355 ft)*

Wave-length	Relative energy black body, 2,945° K, c_2=1.438	Emis-sivity of tungsten	Relative energy tungsten lamp, 2,945° K	Relative spectral response factor of spectrom-eter, 0.25-mm slits	Transmis-sion coeffi-cient of 0.18-cm ozone, *ntp* M=1.43	Rayleigh scatter-coefficient, M=1.43
mμ						
300	100	0.422	422	48	0.060	0.197
305	-----	.425	509	59	.217	.219
310	143	.4275	611	82	.457	.242
315	-----	.430	728	96	.653	.265
320	199	.433	862	139	.814	.287
325	-----	.436	1,007	169	.903	.310
330	269	.4385	1,180	199	.953	.332
335	-----	.441	1,367	241	.980	.354
340	358	.443	1,586	271	.997	.376
345	-----	.4445	1,825	307	.998	.399
350	469	.446	2,092	335	.999	.421
355	-----	.447	2,369	405	.999	.444
360	598	.448	2,679	407	1.000	.466
365	-----	.449	3,017	444	---------	-------
370	752	.450	3,384	458	---------	-------
375	-----	.4505	3,776	479	---------	-------
380	931	.451	4,199	507	---------	-------
385	-----	.451	4,605	549	---------	-------
390	1,137	.4515	5,134	579	---------	-------
400	1,369	.452	6,188	630	---------	-------

Radiometry Laboratory (355 ft) and much narrower ones at mountain elevations. The rapid spectral scanning rate (300 to 400 mμ in about 3 min) permits the completion of an ultraviolet spectrogram before a significant change occurs in the air mass [2] even for air masses M=2.0 to M=3.0.

Within the wavelength range extending from about 299 to 330 mμ the spectral intensities increase so rapidly with wavelength that in order to evaluate the data properly the instrumental sensitivity must be changed at intervals of 10 to 30 mμ. For example, below about 304 mμ for an air mass M=1.4 an increase of 1 mμ in wavelength results in nearly 100-percent change in the intensity of solar radiant energy reaching the earth's surface. This rapid increase of intensity with wavelength made difficult the accurate interpretation of recorder records below 320 or 330 mμ. Hence, within this spectral region, supplementary readings were usually made by manual operation of the wavelength drive of the instrument and by recording the energy values as indicated on a Ballantine alternating-current VTVM or by the Leeds & Northrup recorder.

[2] In this paper air mass, represented by M, refers to the amount of air between the observer and the sun; air mass, M=1, being assigned to a single thickness of atmosphere above the particular station. For any solar position air mass is nearly proportional to the cosecant of the angle the sun's rays make with the earth's surface. For sunlight outside the earth's atmosphere, air mass, M=0. The reader must not confuse this use of the term, air mass, with the same term used to designate air of a particular origin, temperature, or other property.

III. Ultraviolet Solar Energy Curve

The data on which the solar energy curves displayed in figures 2 and 3 and in table 2 are based were obtained in the Radiometry Laboratory at this Bureau, which is located in the northwest section of Washington away from a large part of the city smoke. The air mass penetrated by the direct solar rays ranged from approximately M=1.35 to M=1.50 during the course of the mesasurements. Representative data for specific air masses are given for a few days during the early part of October. On some of the days on which 10 to 20 spectral determinations were rapidly made within the spectral range from 299 to 315 (or 320) mμ considerable variation was noted in the shorter wavelength intensities relative to that at 315 or 320 mμ. As the Rayleigh scattering factor is not greatly different (see table 1) between the limits of this wavelength interval, it is to be concluded that the greater fluctuations at the shorter wavelengths must be primarily associated with rapid changes in the amount of ozone penetrated. The data in table 2, and for the shorter wavelengths in figures 2 and 3, are the averages of three to seven sets of measurements at air masses approximating the values applied to the curves.

The solar energy curves displayed contain numerous absorption bands varying in magnitude both in spectral width and in intensity of absorption. If reference is made to the Rowland maps and wavelength data [8] and to the Utrecht photometric atlas of the solar spectrum [9], it is found that each band

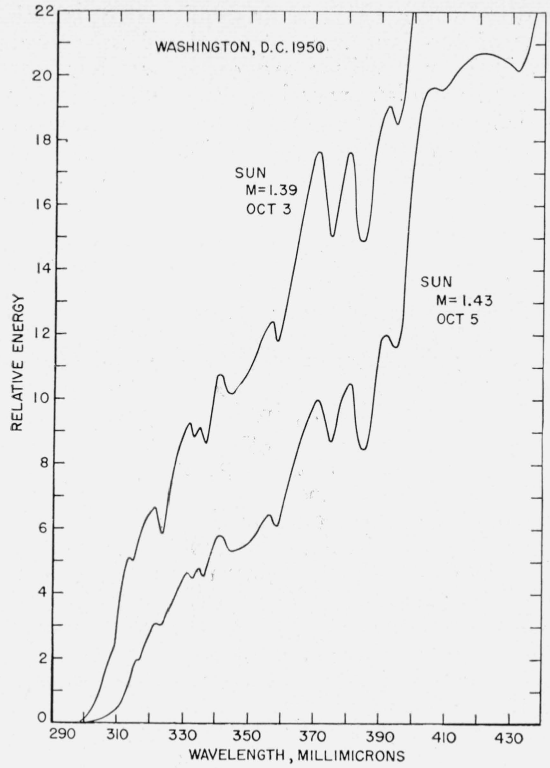

FIGURE 2. *Spectral distribution of radiant energy at Washington, D. C., from the sun for 2 days in October 1950; ordinates arbitrary.*

results from one or more groups of intense Fraunhofer lines. Some of these result mainly from one or two elements in the solar atmosphere—others from several elements. For example, in the spectral region of 309 mμ the principal absorbing elements are the neutral metals, Ni, Mn, Al, and Fe, accompanied by OH, while at 315 to 316 mμ, Cr, Fe, Ti and others are present. Again at 322 to 323 mμ Fe and several other metals have strong absorption lines, while at 335 to 337 mμ NH shows additional absorption. At 345 to 348 mμ Fe is the principal absorbing element, although many lines of Mn, Ni, and other elements are present. At 358 to 359 mμ and at 375 to 376 mμ the absorption bands result mainly from many strong Fe lines. The strong CN band (at 388 mμ) accompanied by many strong Fe lines (around 385 mμ), together with Mg absorption results in the strong band centered at about 386 mμ. The band at 395 mμ is a combination of the intense H and K Fraunhofer lines located at about 393.5 and 396.8 mμ and results primarily from absorption by ionized Ca and H atoms in the solar atmosphere. At 408 mμ and again at 432 mμ Fe and H are primarily responsible in producing two of the important absorption bands of the visible spectrum of the sun. Two relatively weak bands occurring at 465 and 489 mμ are caused principally by Fe and H, respectively, while the strong band between 520 and 530 mμ results mainly from Mg absorption in the solar atmosphere. A more detailed listing of the principal

TABLE 2. *Observed relative spectral-energy distribution of direct sunlight at Washington, D. C. on 3 days in October 1950*

Wavelength	October 3 $M=1.37$	October 6 $M=1.43$	October 6 $M=1.41$	October 11 $M=1.51$
mμ				
299.2	5	---------	3	4
300.2	10	4	7	8
301.2	18	9	13	15
302.2	35	20	29	30
303.2	59	37	45	51
304.2	89	60	74	74
305.2	109	82	99	98
306.2	131	105	120	121
307.2	172	145	156	161
308.2	201	181	192	179
309.2	223	202	210	224
310.2	286	280	283	280
311.2	374	361	359	352
312.2	431	430	421	411
313.2	473	460	461	435
314.2	502	502	510	478
315.2	498	507	519	497
316.2	534	---------	---------	534
317.2	572	---------	---------	---------
318.2	605	---------	---------	---------
319.2	629	---------	---------	---------
320.2	646	---------	---------	---------
Number of settings	3	4	6	7

Fraunhofer lines responsible for the observed absorption spectrum is given in table 3. The wavelength position of the absorption bands is found to be in close agreement with that of the main concentrations of the winged lines [10] in the solar spectrum.

The large drop in solar radiant energy intensity at about 390 mμ, previously noted by Pettit [1], is very interesting.

When consideration is given to the winged lines [10] of the solar spectrum and their effect upon the observed intensity as vividly displayed on the Utrecht

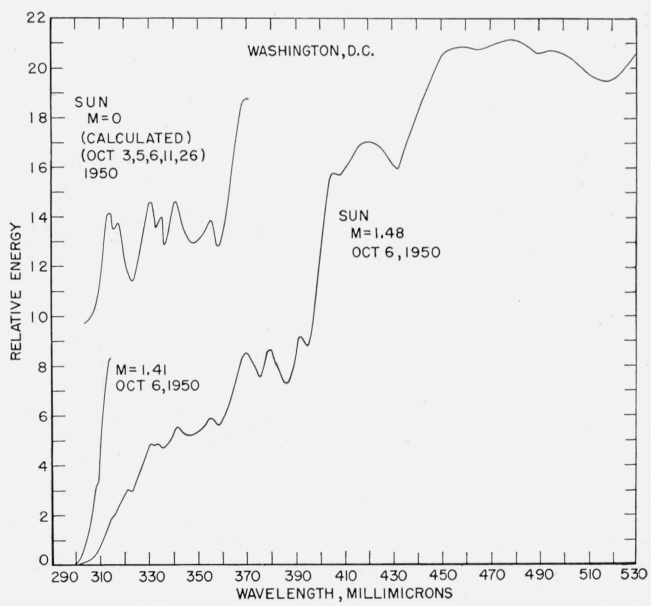

FIGURE 3. *Spectral distribution of radiant energy at Washington, D. C., for 1 day in October 1950; and calculated mean outside the atmosphere for several days; ordinates arbitrary.*

TABLE 3. *Relationship between the location of winged and other strong Fraunhofer lines and the observed minima in the spectral solar energy curve*

Very strong lines result from absorption by the italicized elements

Wavelength Rowland and Utrecht maps	Principal absorbing elements	Observed absorption band
$m\mu$		$m\mu$
308 to 310	Fe, Ni, Mn, Al, OH	308 to 309
316 to 317	Fe I and II, Cr II, Ni, Ti II, OH	315 to 316
323	Fe I and II, Ti II, Ni	322 to 323
331.5	Fe, Zr II, Na I, Ti II, Fe II	---
334	Mg, Ti I, Ti II, Fe, Cr II	335 to 337
336	NH, Ti II, Ni, Cr II	---
344	Fe, Mn II, Ti II, Ni, Co	345 to 348
358	*Fe*, Ni, V II, Sc II, Co, Ti II, Cr II	358 to 359
374	*Fe*, Ni, Ti, Ti II	375 to 376
385	*Fe*, Mg, *CN*	386
394	*Ca* II, Al, Hϵ	395
410	Hδ	408
427	Fe	---
434	Hγ	432
476	Mn, Fe, Ti II, Ni	465
490	Hβ, Fe	489
520	Mg	520 to 530

maps [9], the drop is adequately explained. As a matter of fact the other intensity depressions and resulting plateaus, for example in the regions of 315 to 360 mμ, 370 to 390 mμ, and 405 to 435 mμ simply represent departures from what would otherwise be a smooth approximate black body curve representative of the mean solar surface temperature, and result primarily from absorption by the winged lines of Fe, Mg, Ca, Ni, H, Ti and Al [9, 10].

The large calculated decrease in solar energy outside the earth's atmosphere for wavelengths shorter than about 310 mμ is probably not entirely real. At least an absorption band occurs at about 304 mμ, as can be detected by the inflection in the observed data at this wavelength. Its magnitude may be overrated in the calculated curve. Pettit's data also indicate a sharp decrease in solar radiant energy for wavelengths below about 310 mμ and probably for the same reason; namely, a lack of correct knowledge of the ozone absorption coefficients for these wavelengths. Data obtained by personnel of the Naval Research Laboratory [6] with apparatus transported by rockets into the stratosphere show no sharp decrease in solar energy at this wavelength except for a strong absorption band near 300 mμ. It is readily understandable that in these calculations, wherein small energy values are divided by extremely low ozone transmittance coefficients, errors in the ozone transmittance are greatly magnified in the short wavelength solar energy curve.

IV. Conclusions

As previously noted the data recorded herein on the solar energy curve, principally in the ultraviolet spectrum, are based on a few measurements made on a few days under similar air mass conditions, both as to time of day (similar values of air mass) and as to type of pressure pattern. Although these data were carefully obtained, their value lies principally in illustration of the use of new equipment and of the method employed in their acquirement, especially in view of the fact that at sea level solar radiant energy intensity values are extremely low at the shorter ultraviolet wavelengths. The quality of these data indicate the practicability of using much narrower spectral slit widths if the apparatus were installed at mountain or desert locations. At suitable stations much valuable solar spectral data should be obtainable.

Data of the type obtained with this instrument have long been urgently needed for use in ozone determinations by means of the phototube and filter method [16 to 18]. Previously a smooth curve best representing the filter measurements has been employed. The limited data recorded herein should serve to permit the use, in future phototube-filter ozone work, of a solar energy curve closely approximating in shape the true spectral energy curve outside the earth's atmosphere.

The use of spectroradiometric equipment of the type employed in the present investigation appears highly promising of producing precise data in total ozone determinations. The presence of numerous Fraunhofer absorption lines in the solar spectrum, resulting in a number of plateaus or inflections in the prismatic curve, furnish wavelength calibration indices that acquire significant importance in ascertaining the correct wavelength positions in the ultraviolet spectrum for use in the ozone calculations. Proper instrumental temperature corrections for use with double monochromator ozone meters ordinarily require unusual precautions. Often outdoor conditions of wind, varying sunlight, etc., render temperature correction next to impossible. With this equipment a solar curve covering the spectral region of the two or three wavelengths necessary for use in the ozone calculation may be made within a few minutes and it will include, on the same chart, the correct wavelength indices in the form of the Fraunhofer bands.

Tests on sky-light indicate a sensitivity of the equipment, as used on direct sunlight, sufficient to observe the spectral energy distribution down to about 310 mμ before noise becomes excessive. For practical use the full aperture can be employed. The small mirror employed with the sun (3 by 5 in.) and situated at a distance of about 6 ft from the spectrometer allowed use of only a small part of the total instrumental aperture in the tests to which reference is made. Wider spectral slit widths might also be employed. Hence, it would appear to be feasible to employ this equipment in the study of the spectral quality of the scattered radiant energy present in small areas of sky light.

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WASHINGTON, November 27, 1950.