FINAL REPORT

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STUDY OF AIR POLLUTANT SIGNATURES FOR REMOTE SENSING

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Abstract

Experimental results are presented for a possible new, indirect signature for air pollutants: the spectral reflectivity of plant leaves. Sub-visual changes (up to 160%) in the spectral reflectivity of bean and tobacco leaves were observed over the range 475nm to 750nm in response to SO_2 exposures such as 2ppm/4hrs or 4ppm/16hrs, or to O_3 exposures such as 90pphm/21hrs or 7.5pphm/292hrs. Such changes might be observed from a satellite using either laser or sunlight as the illumination source. Inasmuch as the plants appear to become acclimated to some of these exposure doses, environmental changes may be most important for this type of plant-response.

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I. Introduction

The use of earth-orbiting satellites and conventional aircraft
to scan the earth's surface has proven to be an accurate and econom-
ical method for obtaining geographical and agricultural information
over large areas.[1,2]   Such information is often unique, leading to
the discovery of new features and producing an overview of correlated
features, the interrelationships of which would be unnoticed or not
measured from earth-surface data.

In order to obtain a maximum amount of useful data, many types
of sensors and analytical instruments are used, either simultaneously
or in rapid sequence. These sensors and instruments measure remotely,
and therefore use electromagnetic radiation in various parts of the
spectrum from microwaves through infrared and visible to the ultra-
violet.[3] The instruments include film cameras, television cameras,
radiometers and spectrometers. The aggregate of these data is a des-
cription of the earth in terms of the electromagnetic radiation arriv-
ing at the sensors as modified and limited by atmospheric transmission
and by the sensors' characteristics. Obviously, the description is
limited in scope and sensitivity, first, by our knowledge of the "sig-
natures" of the various earth characteristics, and second by our ability
to read (or sense) the signatures we know.

Most sensing instruments are "passive" in that they do not excite,
or interact with, the characteristic being sensed. On the other hand,
an example of an active technique is the laser backscatter measurement

of particulate matter in cloud banks. The successful use of active instruments is often difficult because of power requirements connected with the remote-sensing aspect. However, in certain cases it may provide the only reasonable way to obtain a signature.

The use of satellites and planes for both remote sensing and point sampling of air and water pollutants has the same advantages as their use in geographical and agricultural applications. The difficulty with pollutants, of course, is that more sensitivity is required since the concentration of the pollutants is low (usually in the range of parts per million or hundred million). Therefore, extra effort needs to be placed on developing more extensive knowledge of the possible signatures of pollutants for use with either active or passive sensors.

II. General Considerations on Remote Sensing

The term "remote sensing" has been used with a variety of meanings in the literature. Often a "remote" distance is taken to be about 1 kilometer, as in the ground measurement of effluents from smokestacks.[4] Here, however, we shall use "remote" with reference to earth orbiting satellites at altitudes of about 300 kilometers.

We have estimated the signal strengths available at 300 km for measurement of air pollutants using the laser-Raman radar technique.[5,6] This technique appears to be a promising one with respect to: specificity of pollutants, relative insensitivity to interferants and temperature fluctuations, sensitivity to actual number of molecules

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in the measured volume, and its single-ended nature (as distinguished, for example, from transmission absorption techniques). The equation for the power received is:

$$P_r = (\frac{P}{A})(\sigma_d)(N_v A \ell)(\frac{A_r}{R^2}) \qquad (1)$$

where P = peak power output of the laser per pulse, A = area of laser beam $\simeq$ independent of range, σ_d = Raman differential cross section of pollutant molecule, N_v = number of pollutant molecules per unit volume, ℓ = length of atmospheric path sampled by pulse, A_r = area of receiver aperture, R = range or distance between satellite (containing laser source and receiver) and sampled volume. For an order-of-magnitude calculation the following values of the parameters in equation (1) were assumed:

$P = 10^3$ watts

$\sigma_d = 4 \times 10^{-29}$ cm^2/sterad (from Ref. 7)

$N_v = 10^{12}$ cm^{-3} (from air density = 1.2×10^{-3} g/cm^3, molecular weight $\simeq$ 30, pollutant level = 0.1 ppm)

$\ell = 1 \times 10^4$ cm(1000 ft)

$A_r = 100$ cm^2

$R = 3 \times 10^7$ cm

One calculates that $P_r = 10^{-22}$ watts per pulse. This is a very small signal, well beyond detectable limits, but then we are attempting to detect directly the presence of 10^{-6} moles, or 7×10^{17} molecules, by a relatively weak scattering at a distance of 300 km (about 200 miles),

assuming a laser beam area of 10 cm^2. Hirschfeld and Klainer[5] give detectable limits of about 1 ppm at 250 m for various pollutants (using a cooled photomultiplier tube, phase lock detection and photon counting). They state that resonance Raman techniques could increase sensitivity by a factor of 10^6. Such resonance techniques would perhaps permit detection of 1 ppm at 300 km. However, the resonance Raman method needs the presence of absorption bands, and therefore pollutants such as SO_2, hydrocarbons, aldehydes, and CO_2 could not be detected, although nitrogen oxides and halogens might be.

Ludwig, et al[8] investigated the signal changes expected at a satellite by polluted atmosphere absorption of reflected sunlight or earth emission or laser radiation. They concluded that earth radiation, in the infrared (3.5 - 13μm), provided the best situation among these possibilities with signal changes ranging from a few percent to 27 percent (for example 27% for 2.5 ppm of CO at 4.6μm, 12% for 0.02 ppm of SO_2 at 7.4μm, 8% for 0.05 ppm of PAN at 8.6 m, and 3% for 0.03 ppm of O_3 at 9.5μm). Some of the limitations were: (1) the product concentration times thickness was measured, (2) the transmission did not necessarily follow Beer's law, (3) high resolution spectroscopy was needed to separate the spectral overlaps of the possible pollutants, (4) results depended upon the pollutant concentration profile and upon the difference between surface and low-level atmospheric (pollutant) temperatures.

It is well known that additions or contaminants of a few parts per million in a plating bath or crystal growing solution will drastically change the nature of the deposit or the shape of the crystal.

Such coupled effects in the atmosphere are not likely, however, because all the constituents are gaseous and there are no surfaces upon which the contaminant may concentrate or promote selective action. It was then reasoned that air pollutants could well influence some characteristic of the earth's surface and the coupled effect would constitute a "signature" for the pollutant. This of course, is just the sort of signature for the presence of disease or insect blight that is observed in infrared photographs of trees. The damage to plants and trees by long-term exposure to air pollutants is in evidence along most heavily travelled highways and city streets. However, much shorter-term visual effects have been noted.[9-13] We therefore set out to explore the possibilities for using changes in the characteristics of the light reflected from plants or trees (their albedo) as signatures for remote detection of air pollutants.

Rough calculations were made to determine the magnitude of the signal strength at a satellite of light reflected from leaves on the earth.

The first calculation assumed sunlight at sea level, of flux equal to 0.1 watts/cm^2, incident onto fields and grass of albedo equal to 10% (according to Reference 14, such albedos have the range 3-37%). Assuming that 1% of the albedo is in the spectral band of possible interest (such as the chlorophyll bands), the effective albedo is 10^{-3}. The power received is given by:

$$P_r = (\frac{P}{A}) \ (albedo) \ (\frac{A_r}{2\pi R^2}) \tag{2}$$

where P/A = incident flux, A_r = area of receiver aperture, R = range or distance between satellite and earth, A = area on the earth's surface that is resolved by detector. Assuming P/A = 10^{-1} watts/cm^2, A_r = 100 cm^2, R = 3×10^7 cm, and A = 2×10^6 cm^2 (about 50 ft x 50 ft), one computes $P_r = 3 \times 10^{-12}$ watts. If one integrates over 600 seconds, the total energy received would be about 2×10^{-9} joules.

The second calculation assumed that a laser beam from the satellite is reflected from the plant. With the following values: laser power output of 10 watts, reflection coefficient of 0.5 (according to Reference 15, in the band 0.5-0.6μm the reflection coefficient of green pears or peaches is about 0.5 and green crepe paper is about 0.5) and a further reduction in reflection coefficient of 10^{-2} for a specific band, and values of A_r and R as above, one may compute $P_r = 10^{-13}$ watts. This received power is close to that of the previous computation

An estimate was made of the power needed to expose a photographic plate. For a photographic density = 1 = $\log(\frac{\text{inc. flux}}{\text{trans. flux}})$, λ = 600 nm, and a 5 minute development time, one finds a log exposure = log (It) = -2 from the D-log E (Hurter-Driffield) curve,[16] where I = incident power flux and t = exposure time. For an exposure of 600 seconds, I = $10^{-2}/600 \approx 10^{-5}$ erg/sec-cm^2 = 10^{-12} watts/cm^2. Since each pertinent resolvable area on the plate would have 10^{-13} to 3×10^{-12} watts incident on it, there should be sufficient power for an exposure.

It is concluded than that sufficient detectability exists for a base signal. However, the detectability of changes due to pollutants remains a major question.

Reference 9 details some of the visual effects of various air
pollutants on plants (the leaf is the primary indicator) and in-
cludes some "threshold values" for pollutant exposure effects. For
example, exposure of certain tobacco plants to ozone at a concentration
of $2x10^{-7}$ for 2 hours, or $5x10^{-8}$ for 4 hours, produces visible damage;
25 ppm of NO_2 for several hours will injure most indigenous vegeta-
tion; 0.3 ppm of SO_2 for 8 hours causes abnormalities in leaves.
Apparently the pollutants cause rapid changes in the chlorophyll.

In view of the above, we directed our efforts to an examination
of the spectral reflectance of plant leaves, especially in the region
of the chlorophyll absorption bands,[17] and the possible changes in
this spectrum with plant exposure to pollutants.

There are obvious disadvantages to this indirect approach to pol-
lutant measurement: (1) it may not be sufficiently specific as to
pollutant type; (2) it is susceptible to strong synergistic effects
(i.e. 0.03 ppm O_3 + 0.24 ppm SO_2 for 2 hours has yielded 38% leaf
damage whereas the individual pollutants gave no damage[9]); and (3)
temperature and humidity conditions may affect the extent of injury.
However, some account might be taken of these effects.

III. Experimental Details

A. Apparatus

An integrating sphere reflectometer[18] was used to measure the spectral
reflectance of leaves before and after exposure to specific pollutants.
In this device monochromatic radiation from a Perkin-Elmer doublepass
monochrometer and a tungsten-iodine light source is directed through a

port in the wall of an 8 in. diameter aluminum sphere coated on the inside with a two millimeter thick layer of magnesium oxide. By means of a rotatable plane mirror and two concave mirrors, the light can either be focused onto a specimen suspended at the center of the sphere or allowed to impinge directly on the inner wall of the sphere. The light reflected from the specimen is scattered by the magnesium oxide coating onto a photomultiplier tube set in the wall of the sphere and a reading of the photomultiplier current is taken. The plane mirror is then rotated so that the light strikes the wall of the sphere direct-ly and another current measurement is made. The ratio of the two read-ings then gives the absolute spectral reflectance of the specimen if the photomultiplier is operating within its linear range, and if, as assumed, the magnesium oxide coating on the sphere is perfectly diffus-ing. The spectral reflectivity of MgO is essentially uniform in the wavelength interval between 330nm and 2.5µm.

The specimen holder can be rotated about an axis perpendicular to the incoming beam so that reflectance as a function of the angle of incidence can be obtained. If the specimen is specularly reflecting (a shiny leaf) angles of incidence near normal cannot be used since the reflected light goes back out the entrance port.

The absolute reflectance was obtained for leaves unexposed to contaminants. Absolute reflectance was obtained by dividing the photo-multiplier output (corrected for background readings at low levels) of the integrating sphere with the light beam incident on the sample at a

30° grazing angle by the output with the beam passing by the sample and hitting the white wall of the integrating sphere.

The integrating sphere can also be used to measure relative reflectance. A reference sample is placed on the back of the specimen holder and by rotating the holder through 180° with an electric motor the reference is brought into exactly the same configuration relative to the incident beam as was the original specimen. A current reading is made with the specimen in position, the holder is rotated by 180° and another current reading is taken with the reference in position. The ratio of the two readings gives the relative reflectance without the danger of errors due to replacing specimens or resetting the monochrometer.

Figures 1 and 2 show the auxiliary optics and the details of the integrating sphere.

Two transparent plexiglass boxes were constructed to serve as exposure and control chambers, respectively. The boxes are each 59 cm wide, 60 cm deep, and 45 cm high (160 liters capacity, each). The controlled input gases (air plus pollutant) were mixed by passing them through a column of glass beads. The gases were then admitted through two series of holes along one side of the box and removed through similar sets of holes on the opposite side to be "scrubbed" if necessary and vented to a chemical hood. At the top inside of each chamber is a fan 20 cm in diameter that was rotated about 50 rpm to avoid stratification of the atmosphere in the chamber. The two boxes were placed side-by-side

and a fluorescent light fixture spanned the tops. Two 40-watt Gro-
Lux bulbs (No. F40-GRO-WS, Sylvania Electric Company, Danvers, Mass.)
each 48 inches long provided suitable illumination for plant growth.
Figure 3 is a photograph of these chambers.

B. Specimens

Leaves from both bean and tobacco plants were used in this in-
vestigation. The former were Eastern Butterwax Yellow Bush Lima
Bean, and the latter were Wisconsin Tobacco. These plants were grown
at the Northeastern University Greenhouse and were about 4-5 weeks
old when measured. Leaves for examination were affixed to the specimen
holder of the integrating sphere by double-stick adhesive tape. Exposed
and unexposed leaf specimens were placed in the rotating sample holder of
the integrating sphere so that they could be measured in rapid suc-
cession. The reflectivities of only the top side of the leaves were
measured, since the top side would furnish the signal to the satellite.
Less than one hour usually elapsed between snipping the sample from
the plant and taking the reflectivity data. However, no change in re-
flectivity readings occurred even several hours after snipping the
leaf from the plant.

C. Procedures

Plants were kept for about 24 hours in the closed, lighted test
chambers to become acclimated before the exposure to the pollutant.
The atmosphere in both chambers was changed continuously at the rate

of one to two liters per minute. For the SO_2 experiments the air was obtained from compressed gas cylinders. (The commercial compressor was located in the country about 30 miles from Boston. The air contained no oil and was filtered through aluminum oxide at the compressor.) The air atmosphere for the O_3 experiments was laboratory air obtained from a small pump (Model 1513-P107-288, Gast Manufacturing Co., Benton Harbor, Michigan).

The desired concentration of SO_2 (parts per million) was obtained by a flow-rate dilution of about 1000:1 starting from a cylinder of compressed nitrogen containing 930 ppm SO_2. Typical flow rates of 2 ml/min for the SO_2 and 1 ℓ/min for the air resulted in an SO_2 concentration of about 2 ppm. The cylinder concentration was checked by a time-of-flight mass spectrometer measurement (courtesy of Dr. Eugene J. Rapperport).

The ozone was introduced via an ultra-violet type generator (model 3 Ozone Generator, Biozonics Corporation, Natick, Mass.) with appropriate flow rate dilution. This generator produces ozone at the rate of 5 to 6 mg/hour with an air throughput of 1.5 to 2 liters/minute. The ozone concentration in the test chamber was monitored with an ozone meter (MAST Model 724, Mast Development Company, Davenport, Iowa) whose output was connected to an x-y recorder. A limit-switch arrangement astride the recorder pen functioned as a feed-back device to turn the ozone generator on and off, thereby controlling the ozone concentration in the desired range.

Attempts were made similarly to control the ozone during simul-

taneous introduction of SO_2 and O_3 into the test chamber. The SO_2 "poisons" the O_3 detector and various filter designs incorporating iodine crystals were tried. None of our designs functioned long enough for satisfactory monitoring, and these runs were considered as very qualitative.

Leaf samples were taken from about 2/3 up the stalk and were measured immediately after a given exposure and at various subsequent times, the plants meanwhile being kept in the chambers with air only being put through.

Plants were seldom kept more than two weeks, and were watered and fertilized. No controls were put on humidity, but the chambers were quite humid (about 80%) and the temperature was about 77°F.

IV. Experimental Results

Erratic behavior was noted for the spectral reflectivity of these plants when there was a change in their general environment, i.e. replacement of greenhouse with laboratory, or experimental chamber in place of laboratory. After a day or so, however, the reflectivity behavior would settle down as the plant apparently ac-climated itself. Data for the absolute reflectivity of 5 unexposed bean plant leaves is given in Fig. 4. It may be seen from this Figure that the standard deviation about the mean value of reflectance at any wavelength is ±5-10%.

Figures 5-11, inclusive, are graphs of the relative spectral reflectivities versus wavelength (in nanometers) for bean plants

exposed to SO_2. The ordinates are the reflectivity ratio (S/R) of specimen leaf to reference leaf (from plant in "unexposed" box which had a similar environment as the specimen but without the pollutant). Because of the frequently occurring rapid changes between data points (which are plotted on the graphs) the points have simply been connected by straight lines. The various curves on each graph are for data taken at the indicated times after exposure (t=0 means within 30 minutes after the flow of pollutant had been stopped). In some cases a curve has been included showing unusual relative reflectivity before exposure. Each Figure represents a new plant except for cumulative exposures. Figure 8 presents data after an additional exposure of 4 ppm for 16.5 hours for the plants of Figure 7; a time lapse of 176 hours occurred between the end of the original exposure and the beginning of the second one (data is presented in Fig. 7 out to 149 hours of this time lapse). In a similar fashion there is a time lapse of 146 hours between Figs. 9 and 10, and 170 hours between Figs. 10 and 11. Figures 12-17, inclusive, present data for tobacco plants similar to the data of Figs. 5-11. There are time lapses of 128 hours between Figs. 13 and 14, 123 hours between Figs. 14 and 15, and 123 hours between Figs. 16 and 17.

Figures 18 and 19 present data for bean leaves exposed to O_3. The exposure for Fig. 18 consisted of 70 pphm (parts per hundred million) O_3 for 4.7 hours followed immediately by 90 pphm for 20.5 hours.

Figures 20 and 21 show data for tobacco leaves exposed to O_3.

In both exposures the control circuit, or ozone meter, malfunctioned and the actual concentration of O_3 exceeded 100 pphm (i.e. was off-scale on the recorder). The lower leaf of Fig. 18 was badly spotted, whereas the higher leaf was less spotted.

Figure 22 presents data for bean leaves exposed simultaneously to 2 ppm SO_2 and to more than 100 pphm O_3 for 18 hours.

Figures 23 and 24 are plots of S/R at dial readings 660 and 700, respectively, versus time for various sets of data. The data coding refers to the following Figures in this report: 1.1-Fig. 5, 2.1-Fig.7, 2.2-Fig. 8, 5.1-Fig. 9, 5.2-Fig. 10, 5.3-Fig. 11, 6a.1-Fig. 6.

Figures 25 and 26 are plots of the ratios $(S/R)_{660}/(S/R)_{770}$ and $(S/R)_{700}/(S/R)_{770}$, respectively, versus time for the same data sets as Figs. 23 and 24. In order to "normalize" the ordinates to data points that did not change very much with exposure, data at the dial reading of 770 was chosen.

At first glance it may seem difficult to sort out any systematic trends from the data in view of the individualistic behavior of the plants. There is no doubt, however, that the reflectivity is affected by exposure to pollutants and by changes in the environment. The variations in reflectivity reported here are not noticable by visual inspection, except for a few cases especially with O_3. Hence, the plant responses documented here are precursors to the visual damage reported in the literature (for example, references 9-13), and they occur at lower exposure doses.

However, some trends are discernable in the data and they are

listed below:

1. Bean plants exposed to SO_2, on the order of 5 ppm for 16 hours, show increased reflectivity over the range 500-700nm. This may be as large as 1.6 times that of an unexposed reference leaf. Subsequent to exposure, the reflectivity is variably-cyclical, usually increasing at first and then decreasing (often below that of the reference leaf) and increasing with time over periods such as 6, 24, 48 and 55 hours depending on exposure level. Recovery to pre-exposure values occurs after 60 to 120 hours.

   Larger effects accompany larger exposure doses in this experimental region. In many cases, the plants seemed to adjust to the pollution, since the data taken immediately after exposure showed mimimal effects, whereas much wider swings were observed some hours later. It would appear that environmental changes may be as important as the actual level of pollutant in these responses.

2. Tobacco plants exposed to SO_2 in doses similar to those of the bean plants behave in a roughly similar manner. However, the initial response is a decrease in reflectivity in the 500-700nm region, followed by a variably-cyclical behavior. Reflectivity increases as high as 1.8 times that of the reference leaf were observed (at 5 ppm for 17 hours). Recovery occurred after about 60 hours.

3. Bean plants exposed to O_3 (80 pphm for 25 hours or 7.5 pphm for 292 hours) show very much smaller changes than exposure to SO_2. The reflectivity is not prone to cycling. At large exposure the reflectivity over the region 500-700nm is raised to about 1.2 times that of a reference leaf.

4. Tobacco plants exposed to O_3 were more sensitive than the bean plants, although exact doses are not known: at the highest exposure (greater than 100 pphm for 40 hours) the reflectivity was about 2.5 times that of the reference leaf at 675nm and 500 nm. Some cyclical behavior was noted. Recovery occurred in the order of 60-100 hours. In these plants the visual damage (widely separated shiny, gold-brown spots) was evident before changes in reflectivity were observed.

V. Conclusions

This exploratory and limited program has demonstrated that plants can display a sensitivity towards pollutants that is detectable at sub-visual thresholds by spectral reflectivity measurements in the range 475-750nm. These effects constitute possible new signatures for the remote detection of pollutants. However, the utility of those signatures for satellite monitoring remains to be shown. Although detectability does not appear to pose a problem here other aspects may, viz.: sensitivity, response calibration, synergistic

effects, effects of temperature and moisture.

On the basis of the rapid spectral variations seen in our re-
sults, we suggest   that in future work there should be continuous
recording of reflectance (or S/R) versus wavelength (or wavenumber).
Important spectral regions may be narrow and we may have missed
them. Such "windows" could lead to greater sensitivity and more
specific identification of pollutants. If an in-situ, continuous,
measurement could be developed it would be even more useful than
the before-after measurements.

Further, more detailed, study of these effects may be valuable
to the plant physiologist in understanding the reactions of plants
to pollutants. The discoveries of this program may provide him with
a new investigative tool. Reflectivity changes could be correlated
with metabolic or other physiological changes. Clues to what these
other changes might be could be obtained from the wavelengths associated
with the reflectivity changes, especially if narrow "windows" were
identified.

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VII. Acknowledgements

OPTICAL PATH IN POSITION FOR
ILLUMINATING SPECIMEN OR
REFERENCE

ROTABLE
PLANE MIRROR

P-E MODEL 112
MONOCHROMETER

INTEGRATING
SPHERE

EXIT SLIT

ENTRANCE
SLIT

SPECIMEN
HOLDER

OPTICAL PATH IN REFERENCE
POSITION FOR ABSOLUTE
REFLECTANCE MEASUREMENT

LIGHT SOURCE
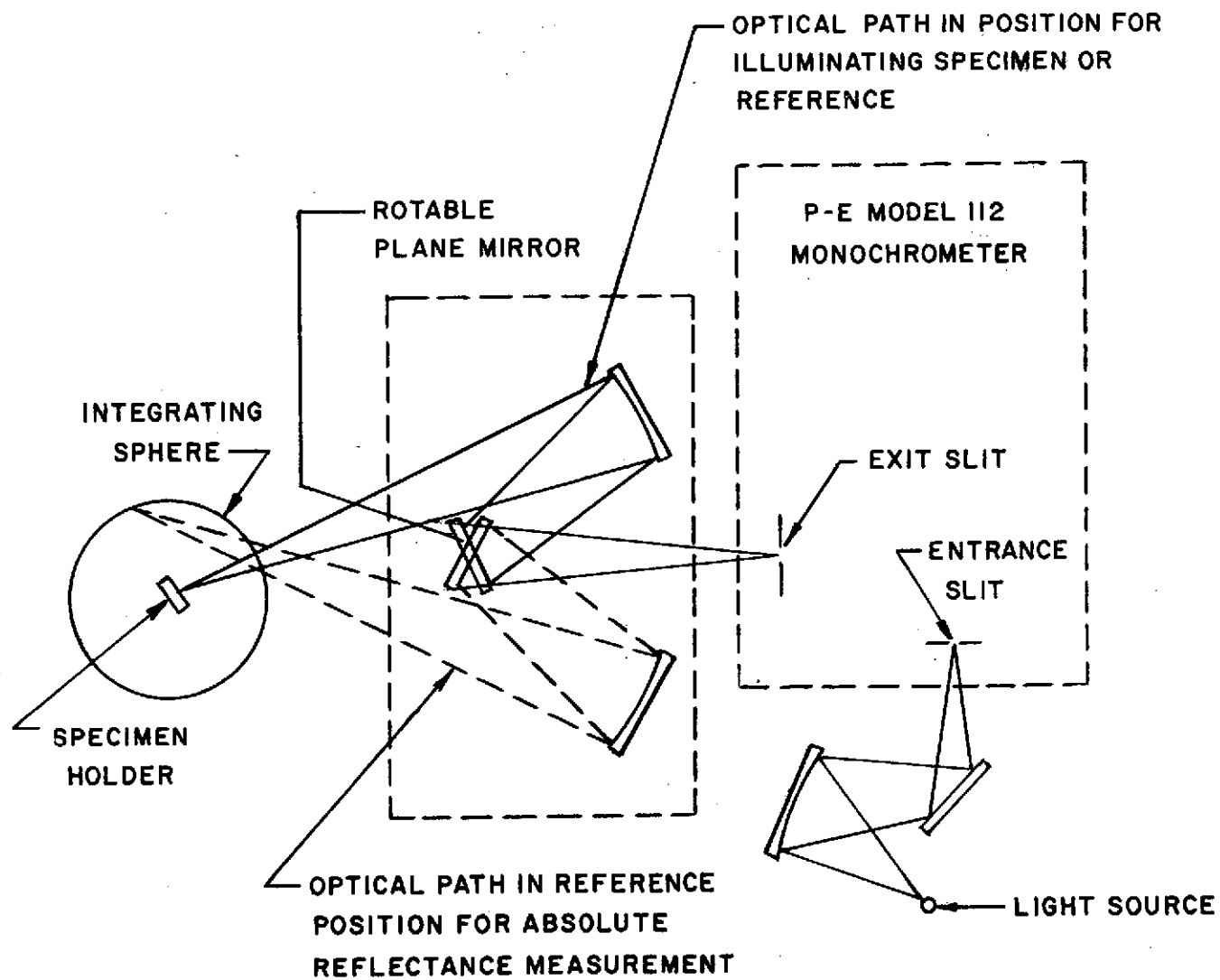
Fig. 1 Auxiliary optics.
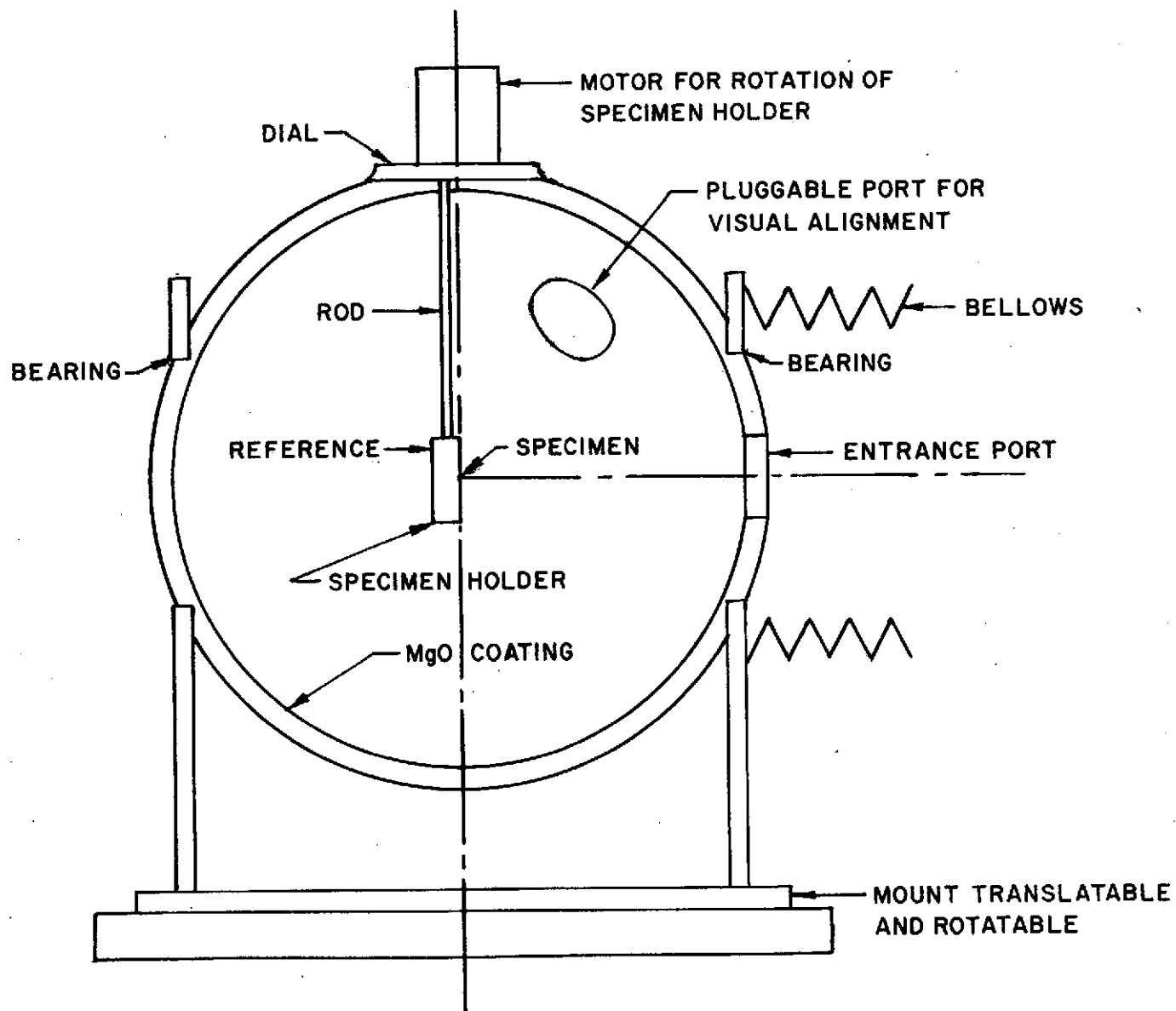
Fig. 2 Detail of integrating sphere.
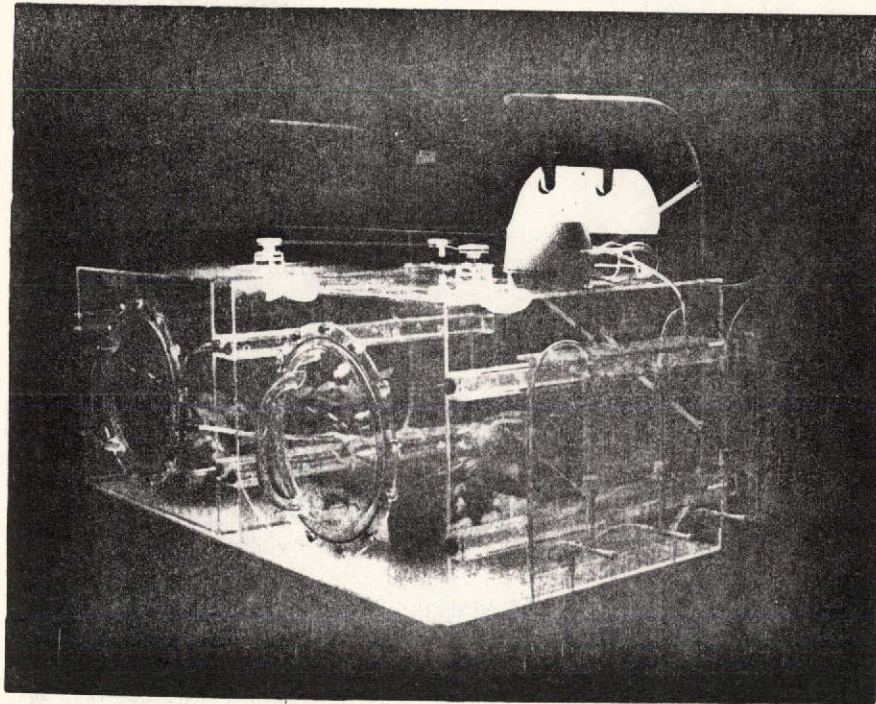
Fig. 3   Photograph of exposure and reference
          chambers. Flow meters and glass bead
          mixing column are mounted on reference
          chamber. Ozone generator is small
          round unit on top.
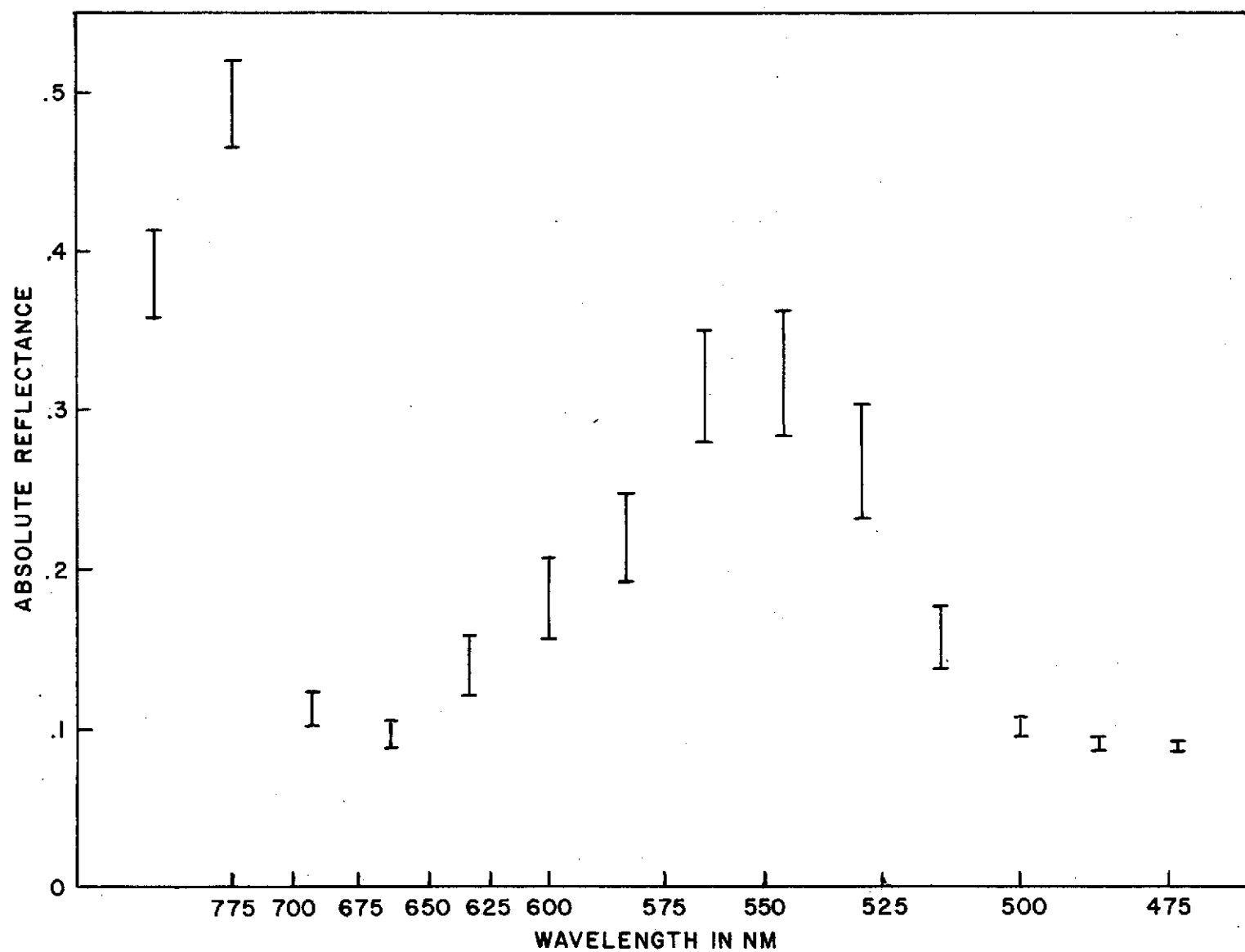
Fig. 4   Absolute reflectance of 5 bean plant leaves.
Error bars show RMS deviation.
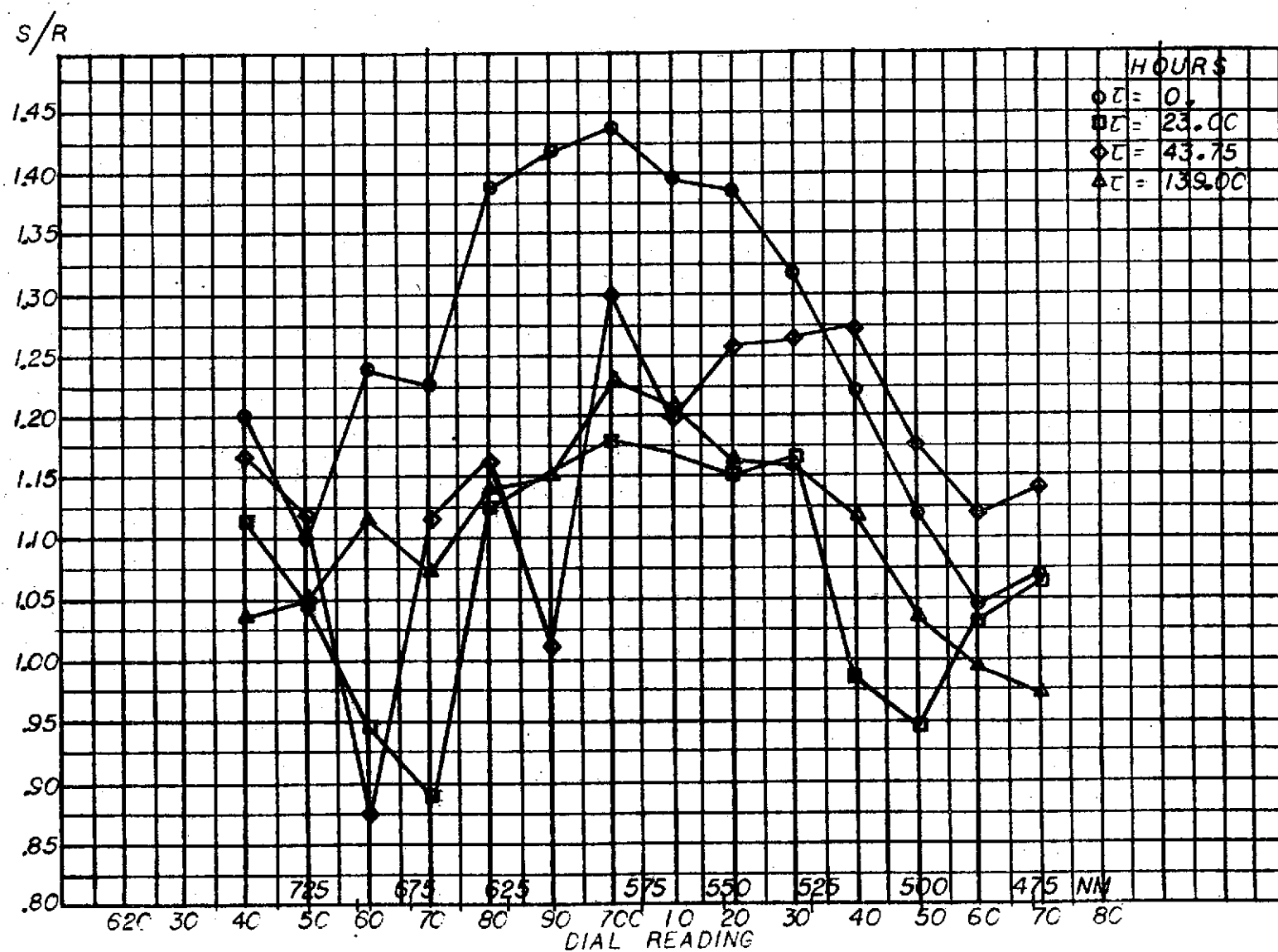
Fig. 5   Relative spectral reflectivity of bean leaves. SO_2. 5 ppm/2 hrs.
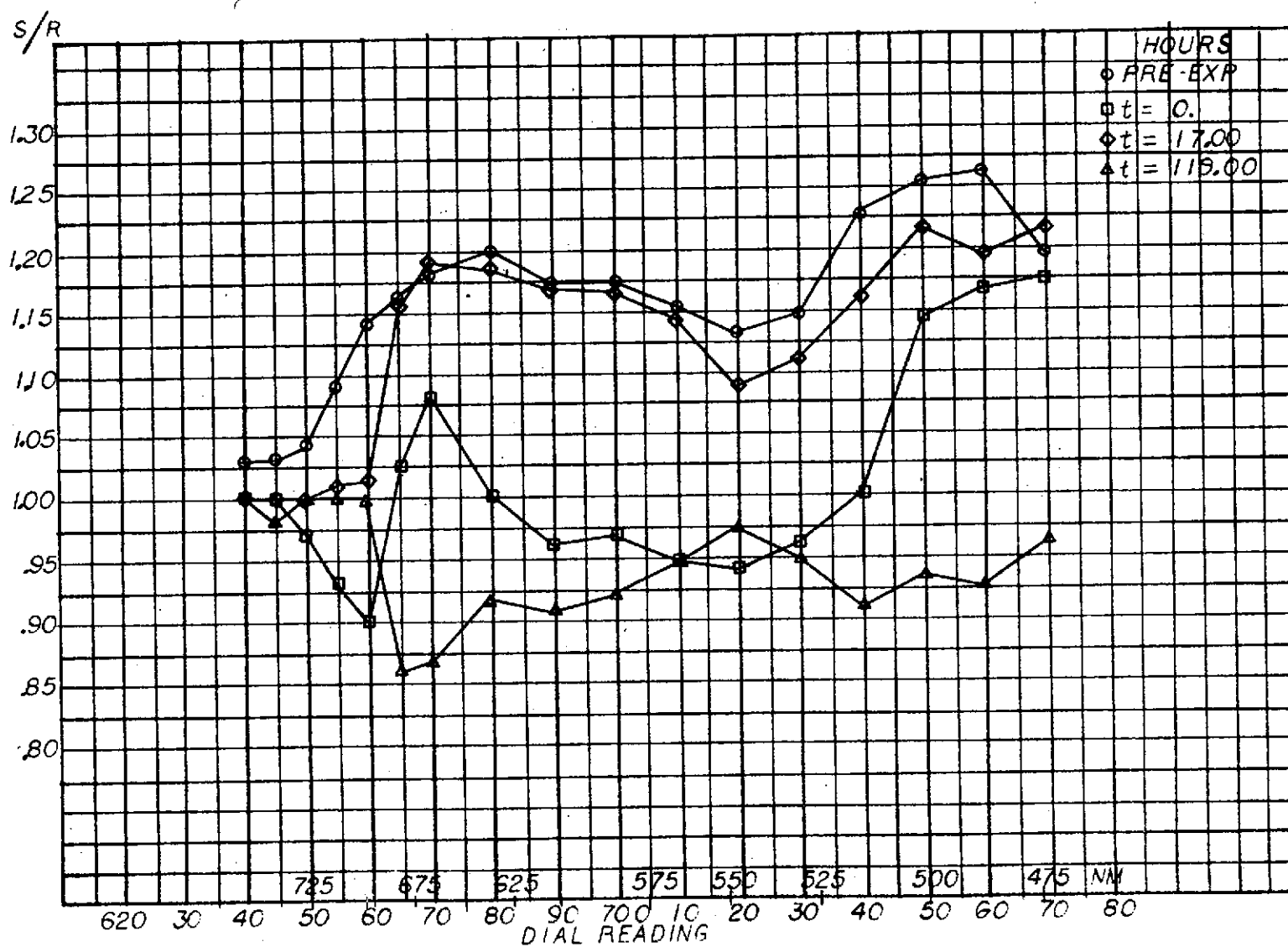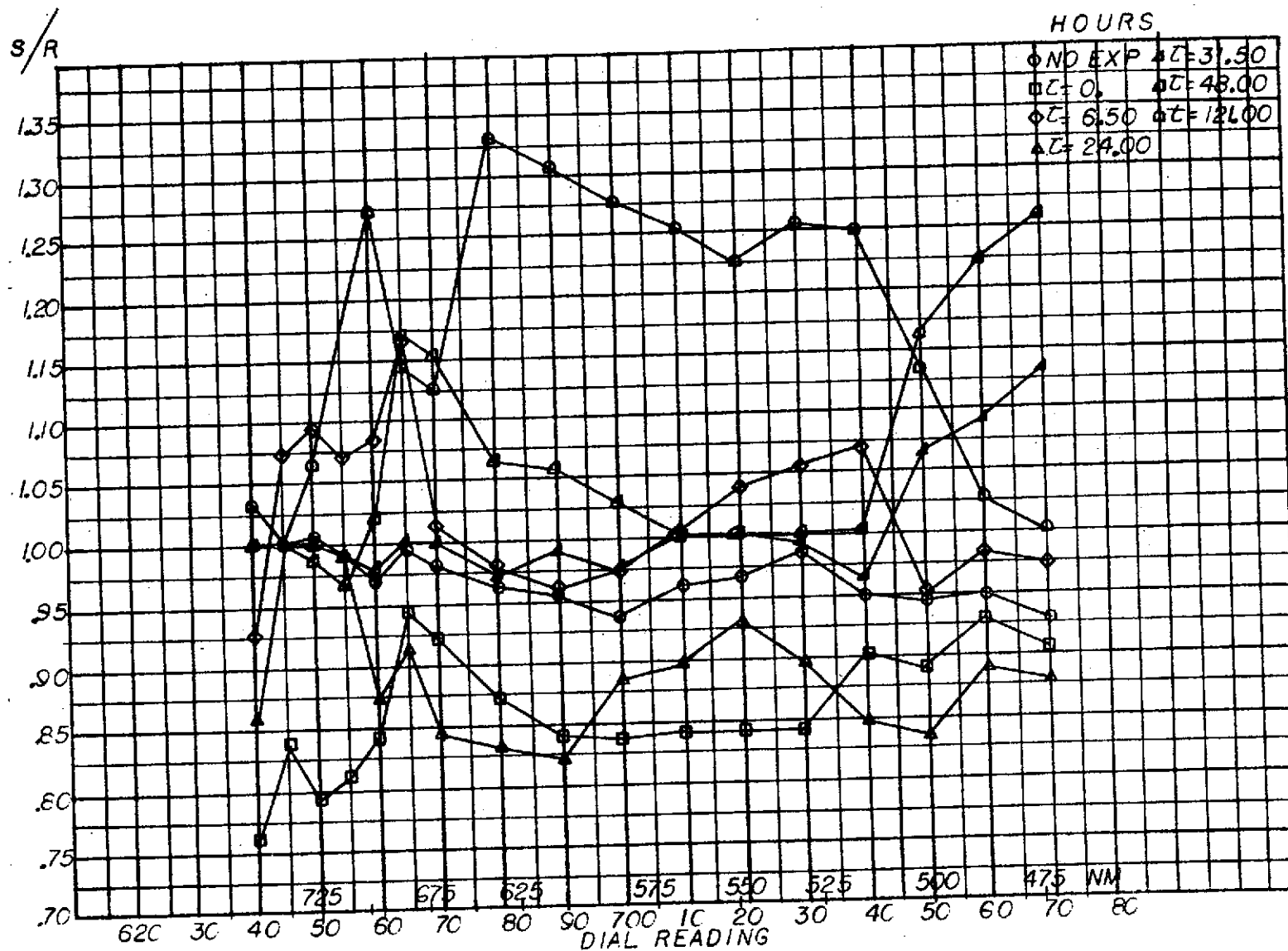
Fig. 6 Relative spectral reflectivity of bean leaves. SO_2. 2 ppm/4 hrs.
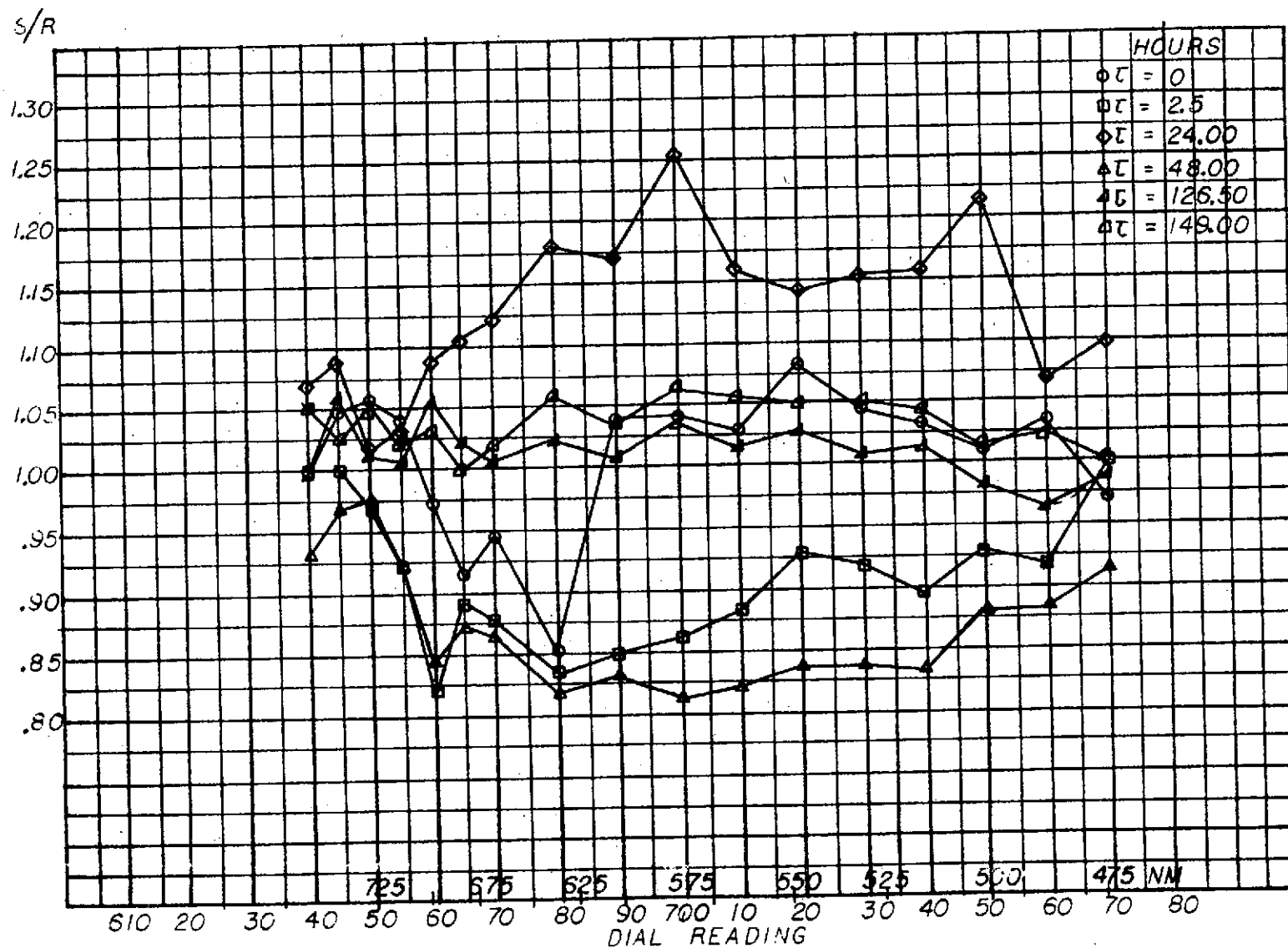
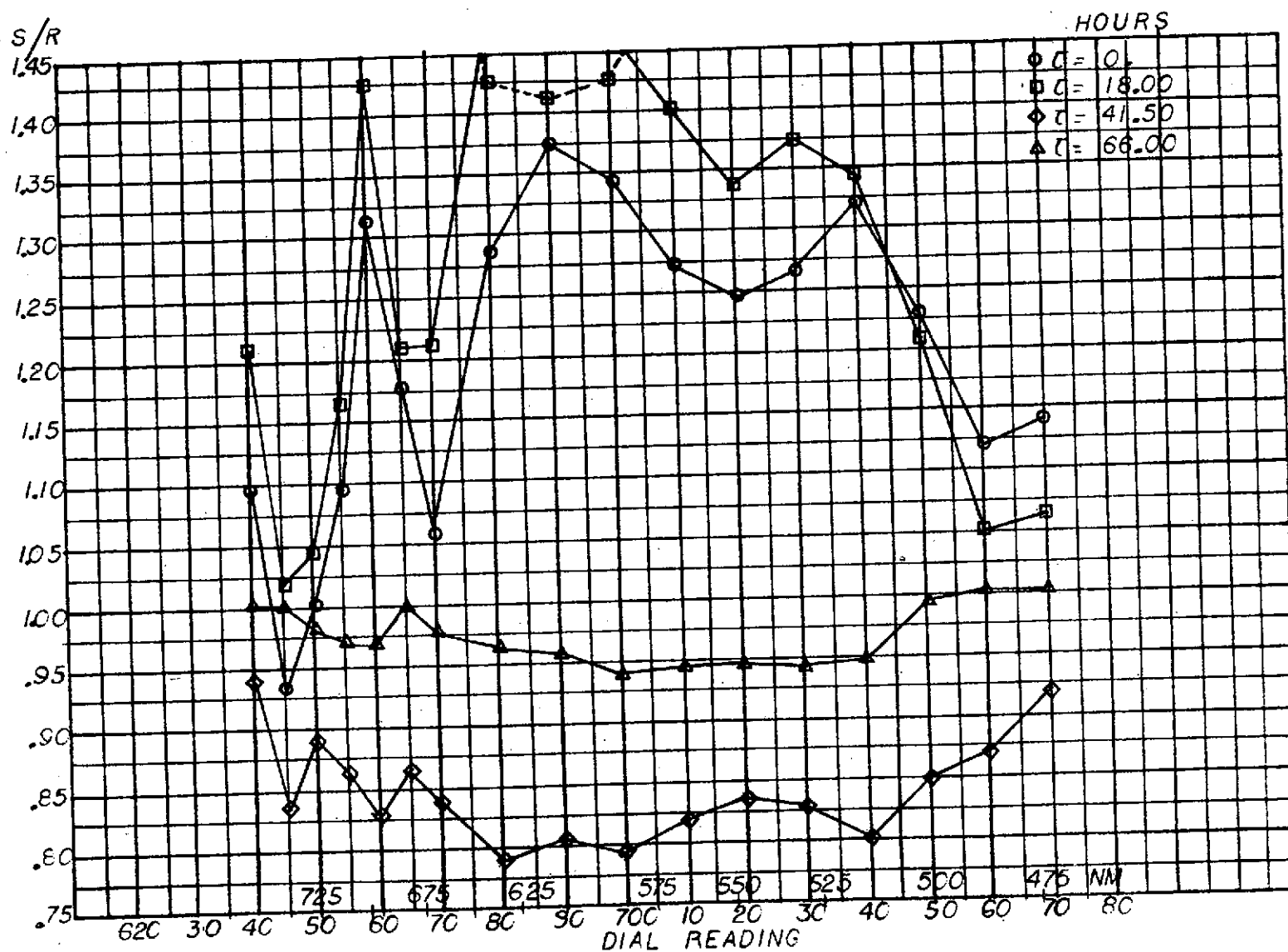Fig. 7 Relative spectral reflectivity of bean leaves. SO_2. 2 ppm/16hrs.

Fig. 8 Relative spectral reflectivity of bean leaves. SO_2. 2 ppm/16 hrs. -
0 ppm/176 hrs - 4 ppm/16.5 hrs.
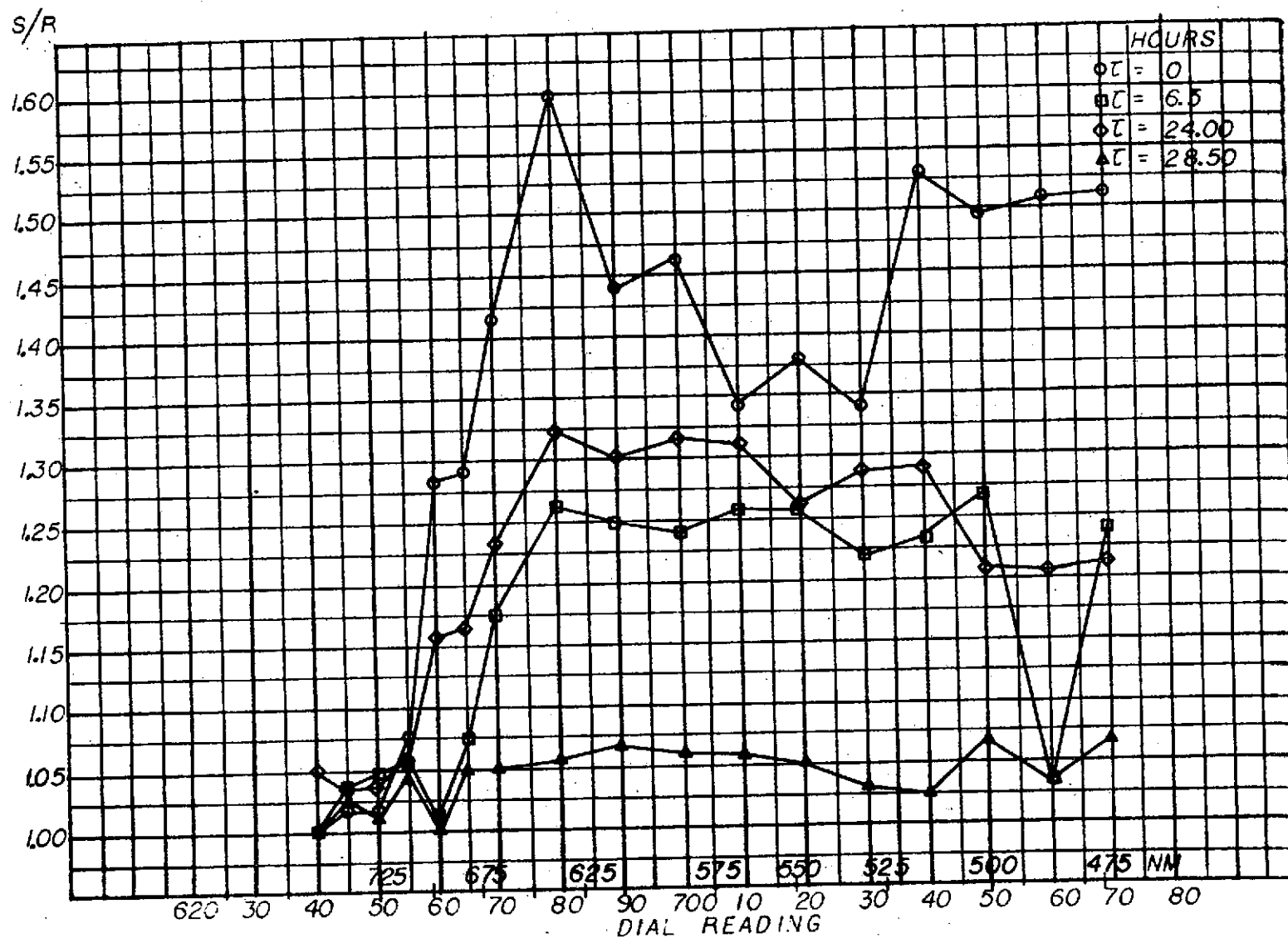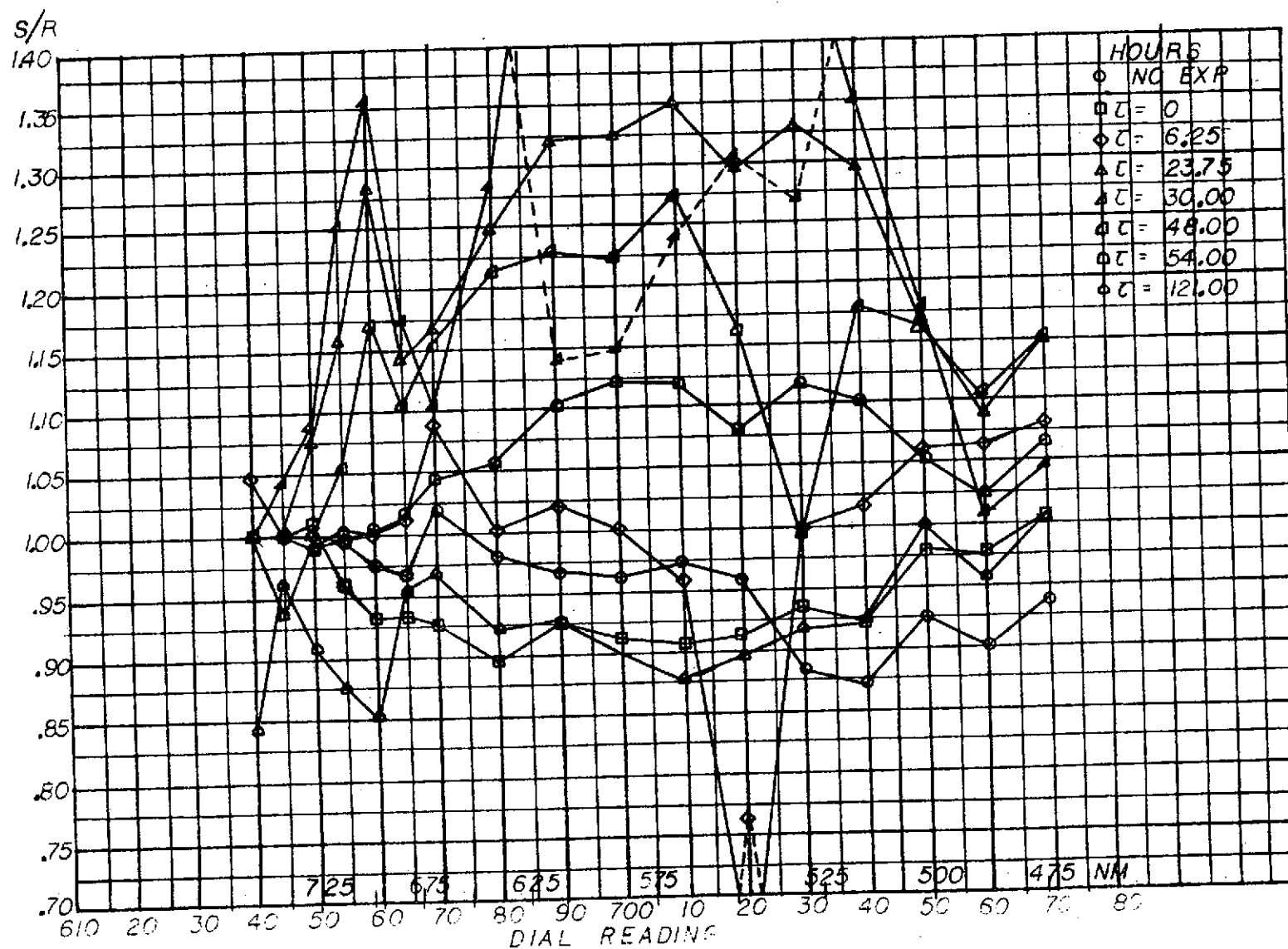
Fig. 9   Relative spectral reflectivity of bean leaves. SO_2. 4 ppm/16 hrs.
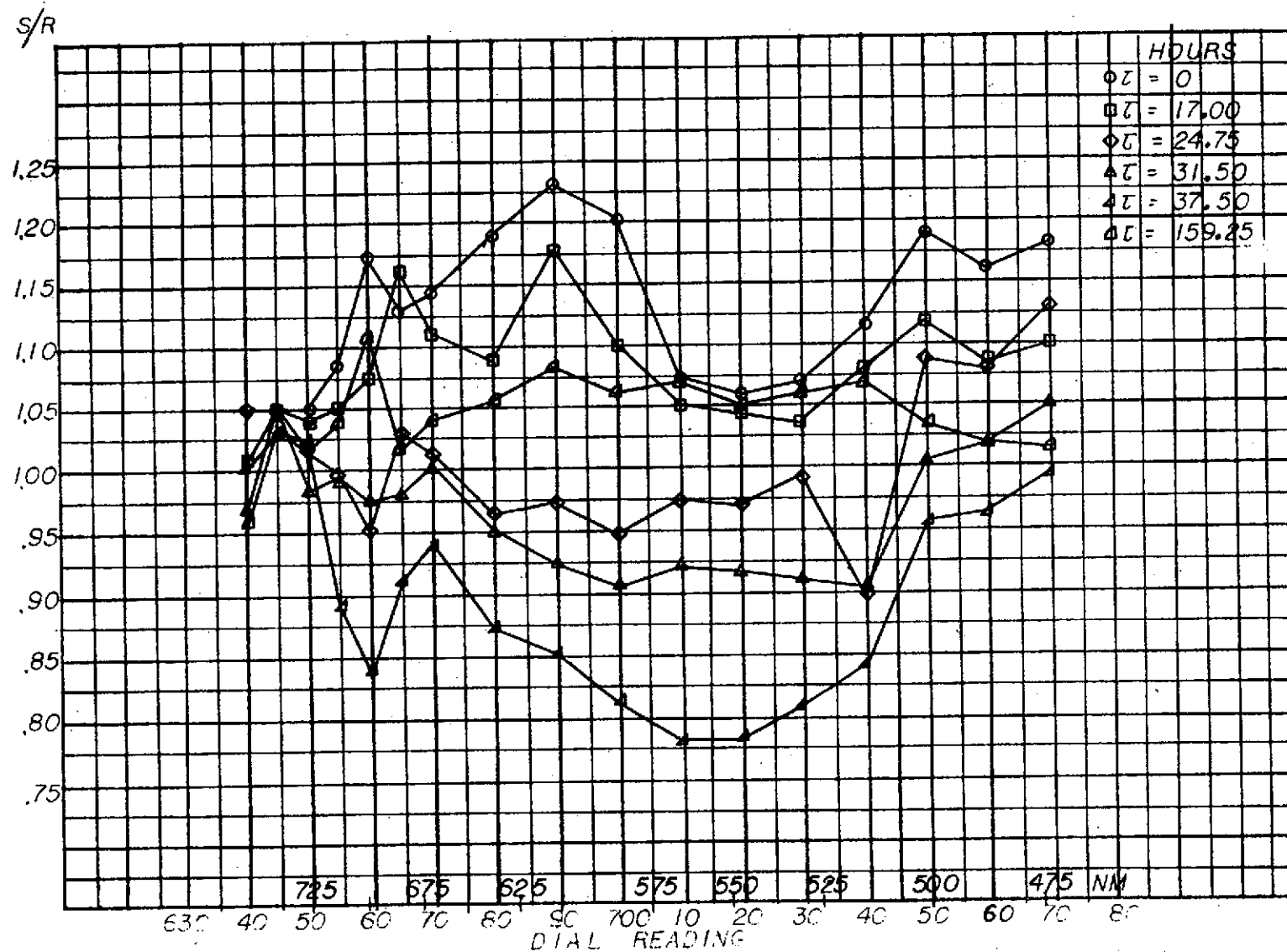
Fig. 10 Relative spectral reflectivity of bean leaves. SO2.
4 ppm/16 hrs. - 0 ppm/146 hrs. - 4 ppm/4 hrs.
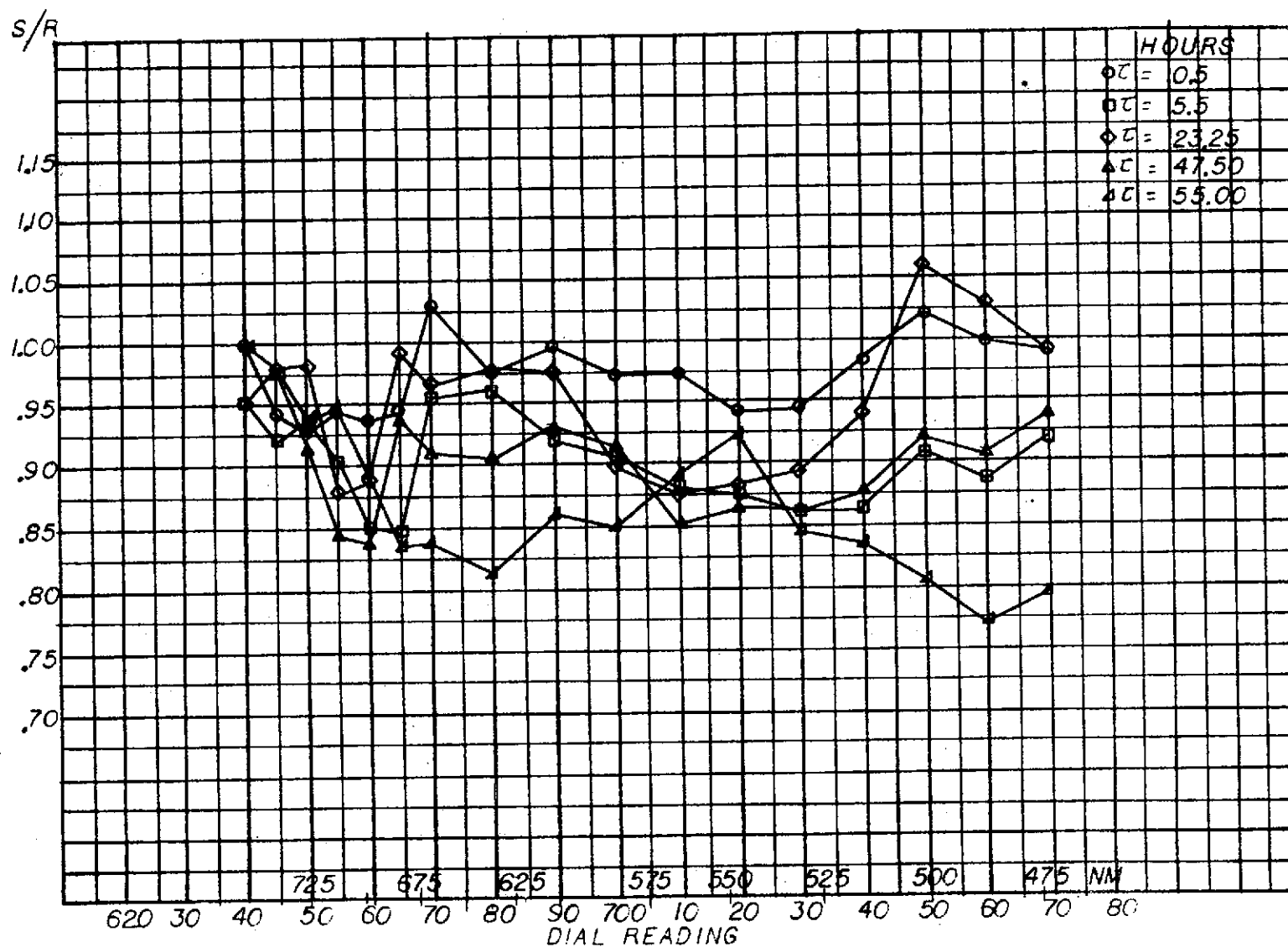
Fig. 11   Relative spectral reflectivity of bean leaves. SO_2.
4 ppm/16 hrs. - 0 ppm/146 hrs. - 4 ppm/4 hrs. -
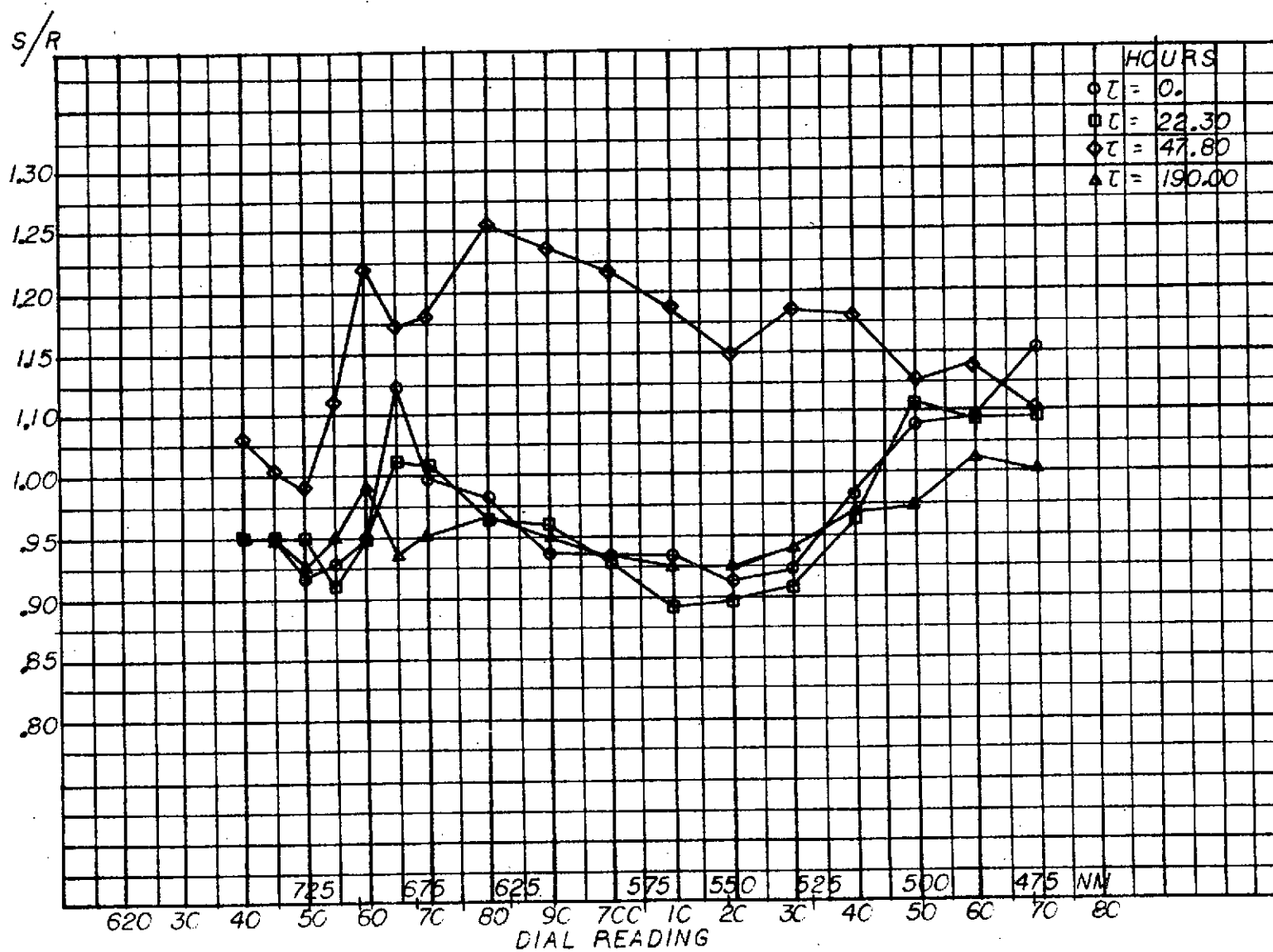0 ppm/170 hrs. - 2 ppm/16 hrs.
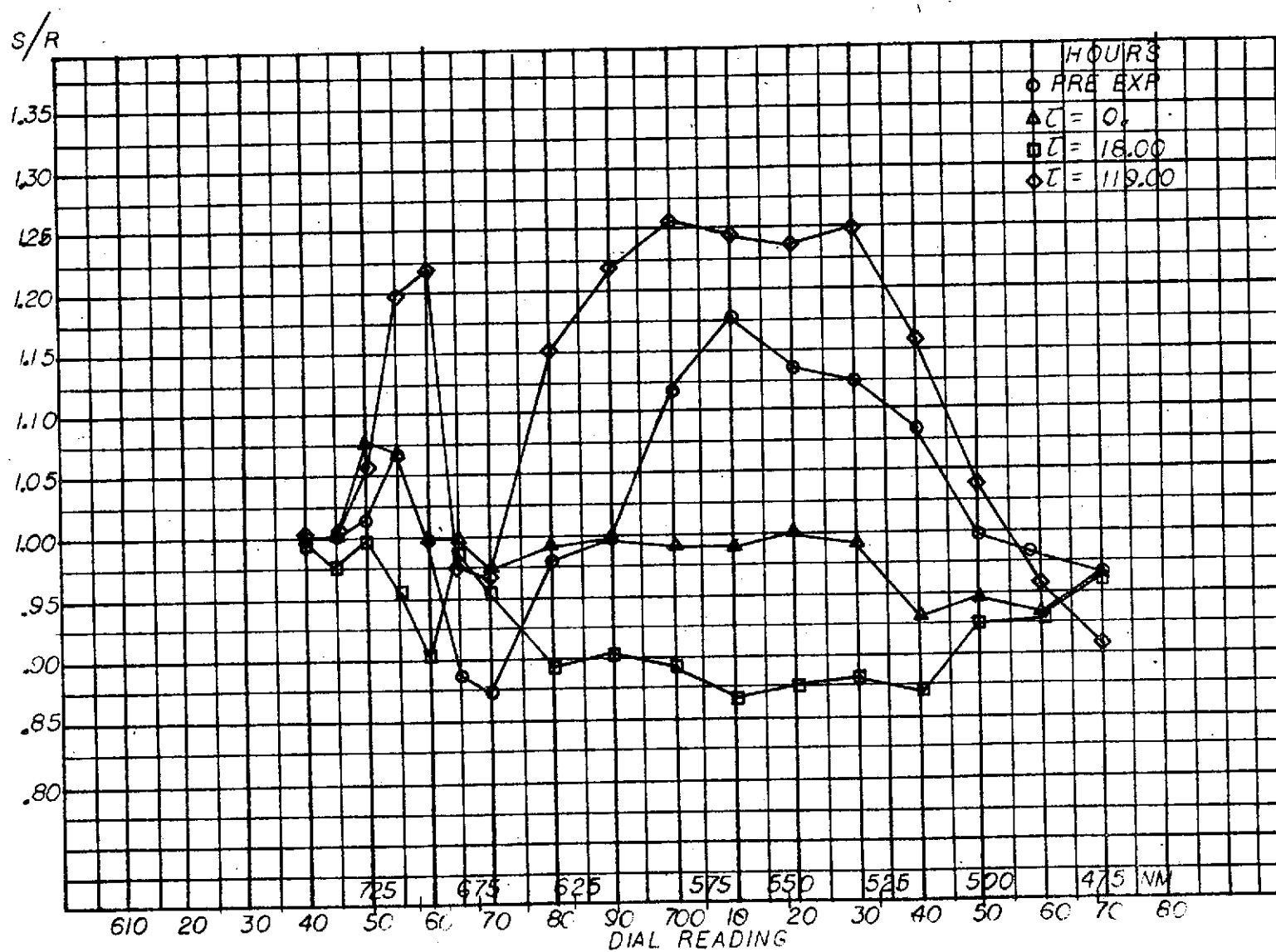
Fig. 12 Relative spectral reflectivity of tobacco leaves.
SO_2. 2 ppm/4 hrs.
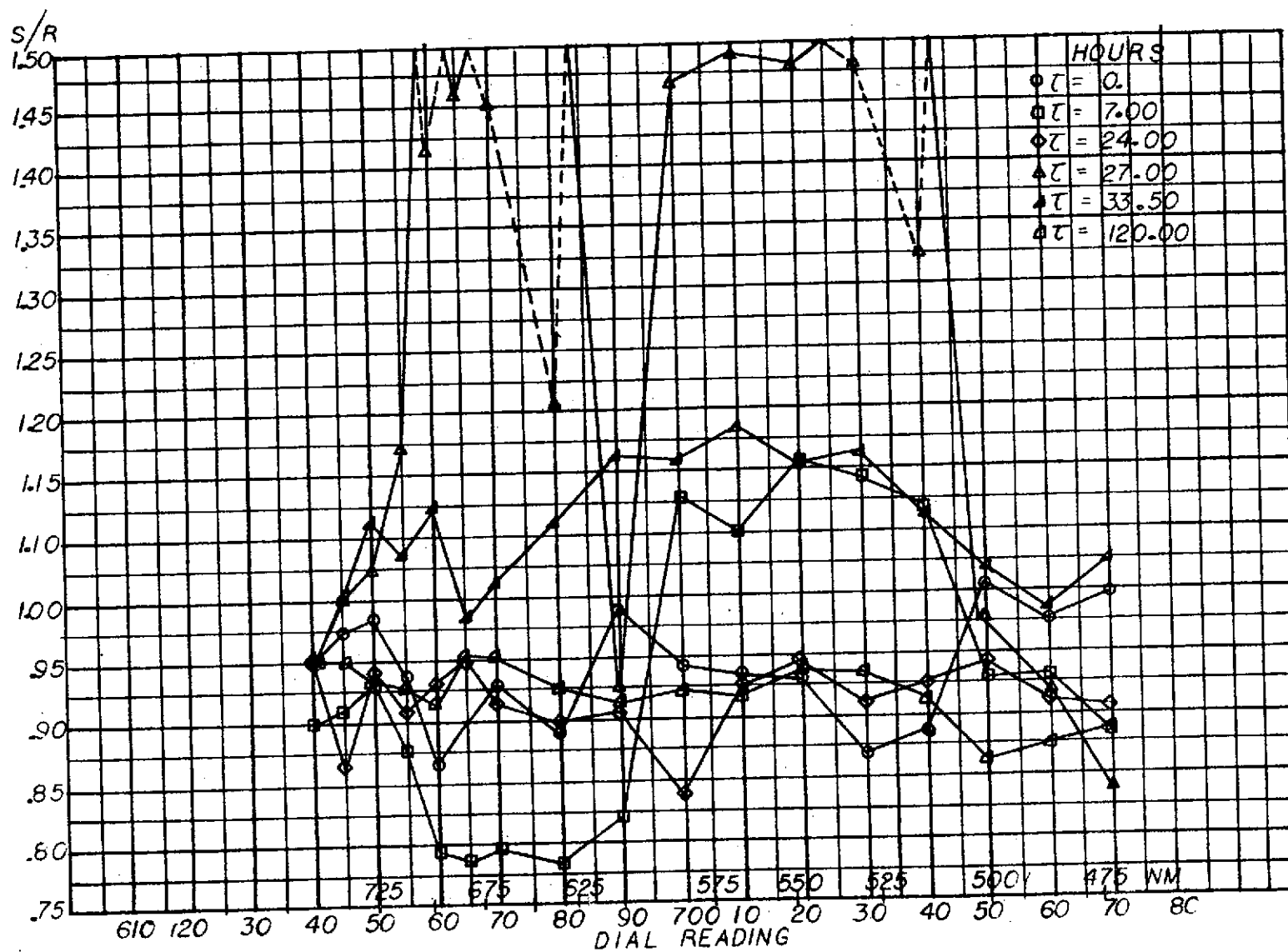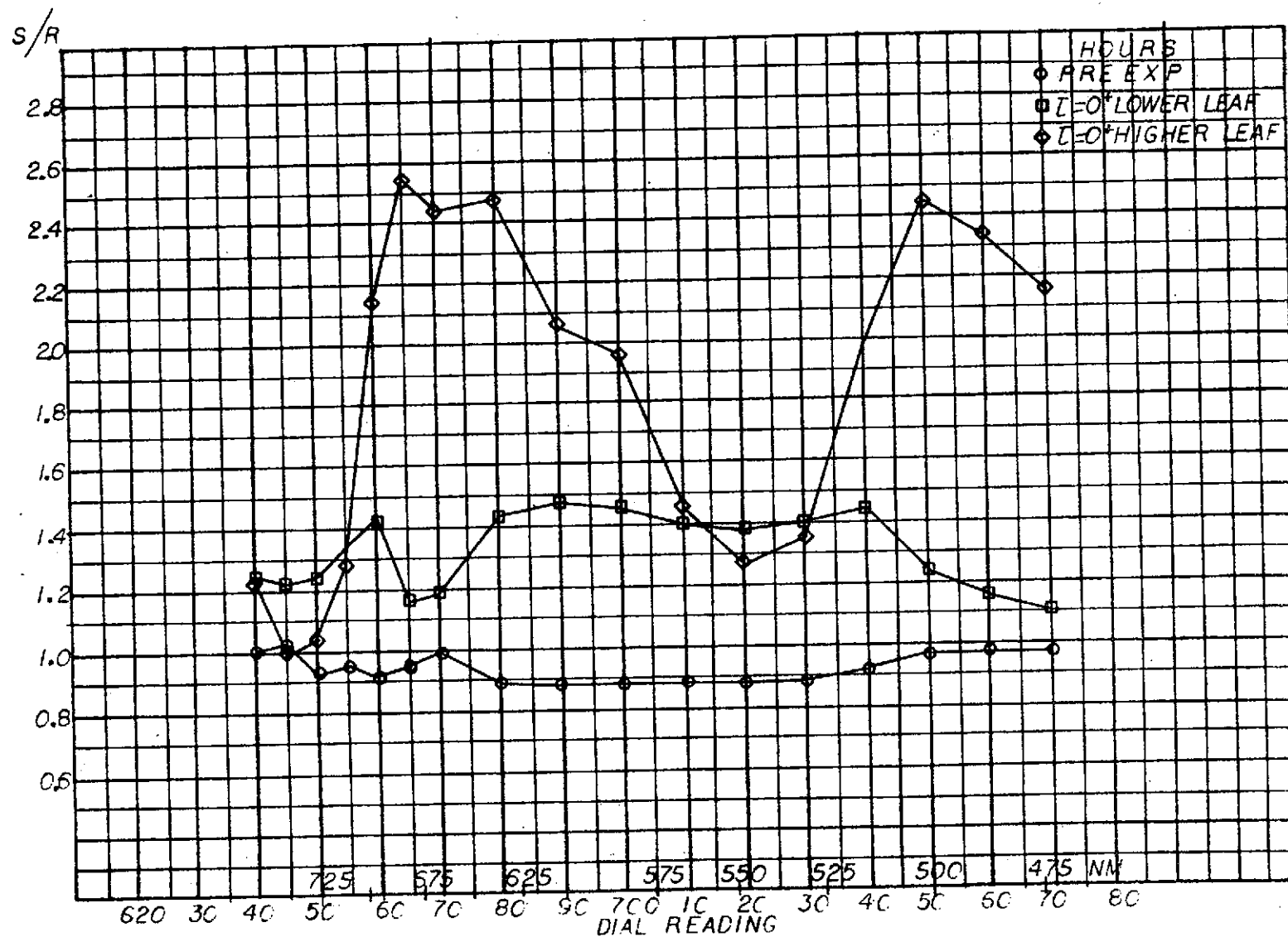
Fig. 13 Relative spectral reflectivity of tobacco leaves.
SO_2 5 ppm/17 hrs.
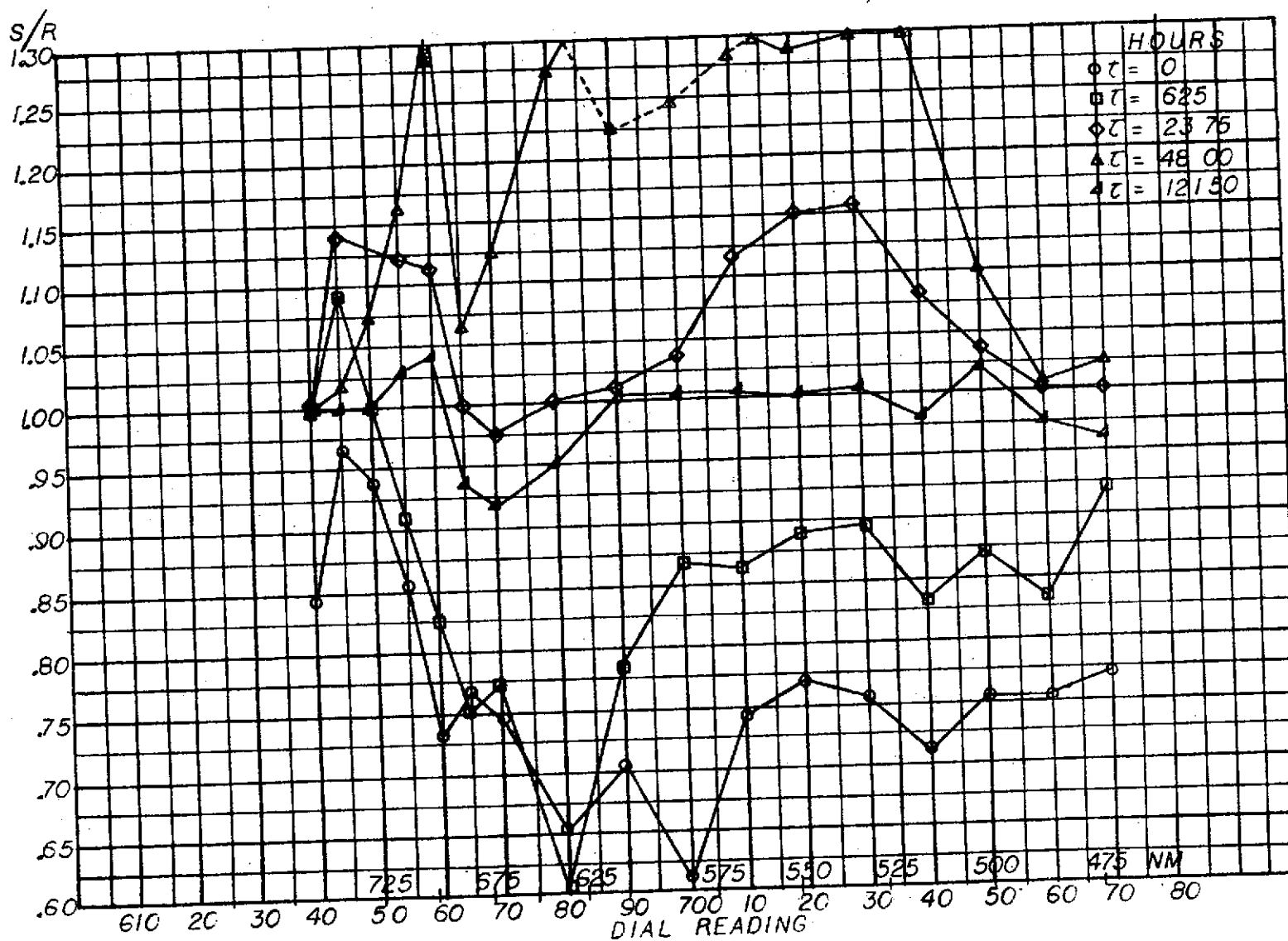
Fig. 14 Relative spectral reflectivity of tobacco leaves.
SO_2. 5 ppm/17 hrs - 0 ppm/128 hrs. - 4 ppm/16 hrs.
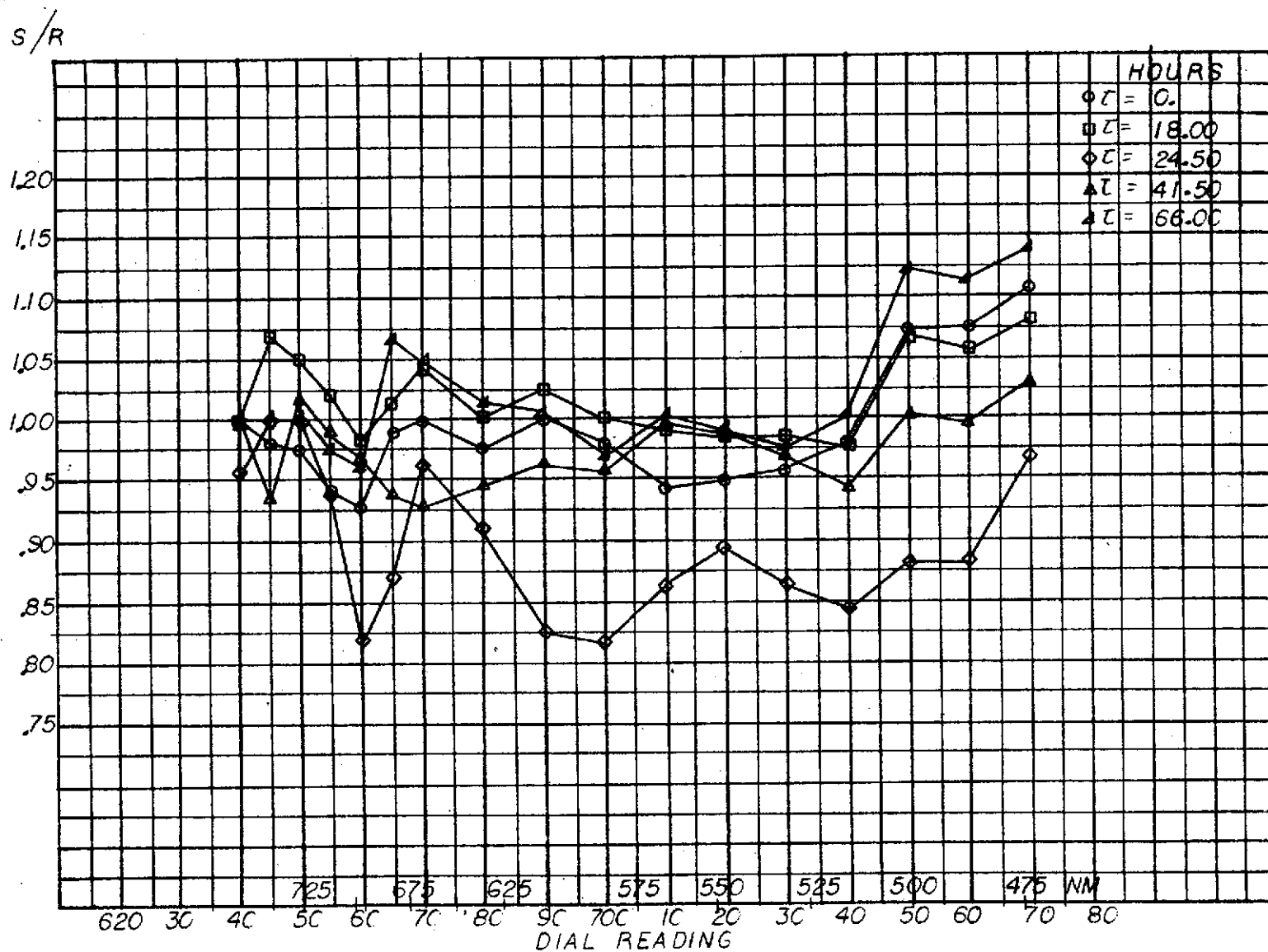
Fig. 15 Relative spectral reflectivity of tobacco leaves.
SO₂. 5 ppm/17 hrs. - 0 ppm/128 hrs. - 4 ppm/16 hrs. -
0 ppm/123 hrs. - 5 ppm/3.2 hrs.

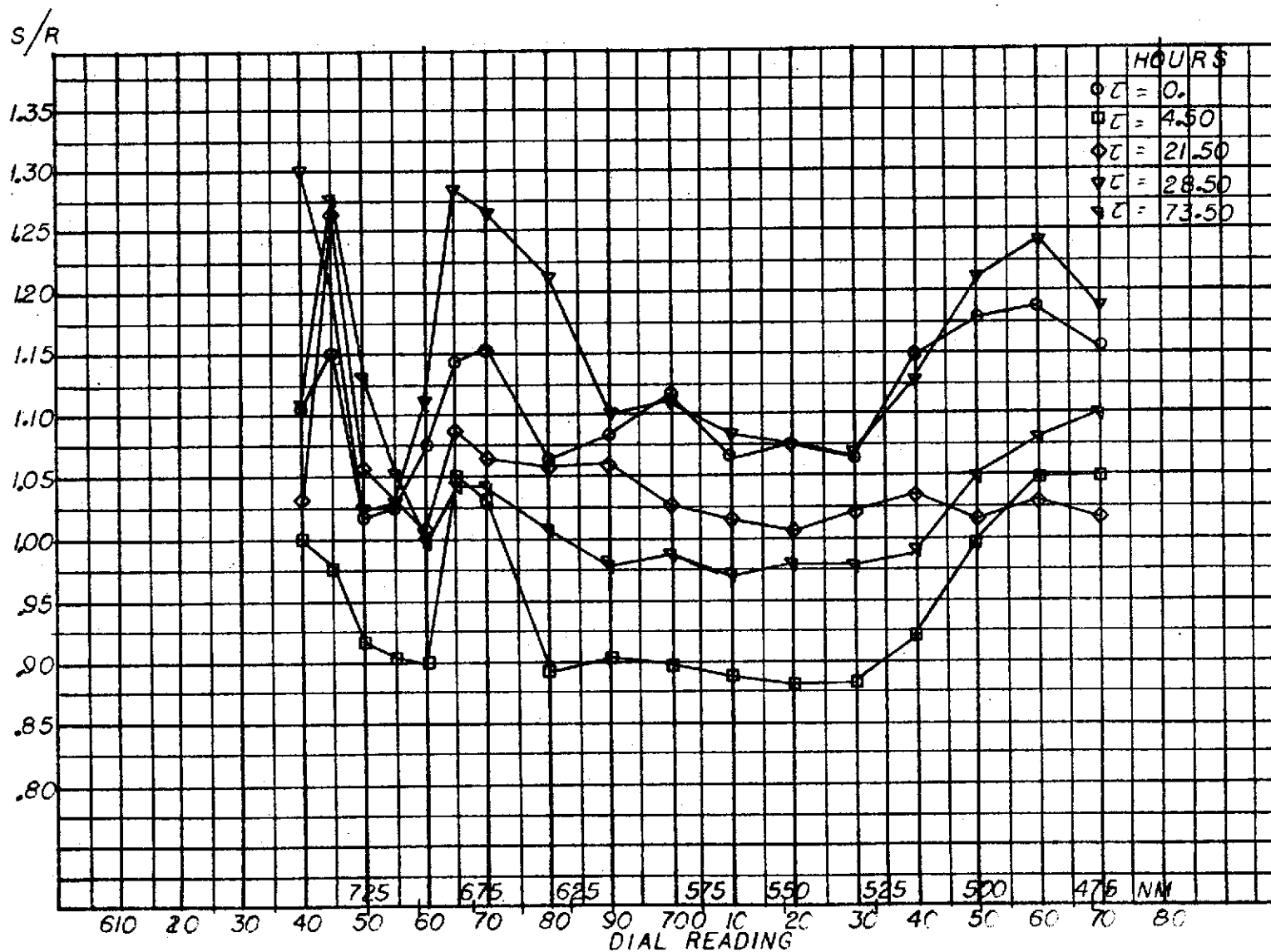Fig. 16 Relative spectral reflectivity of tobacco leaves.
SO_2 4 ppm/16 hrs.

Fig. 17   Relative spectral reflectivity of tobacco leaves.
SO$_2$.   4 ppm/16 hrs. - 0 ppm/123 hrs. - 5 ppm/3.2 hrs.
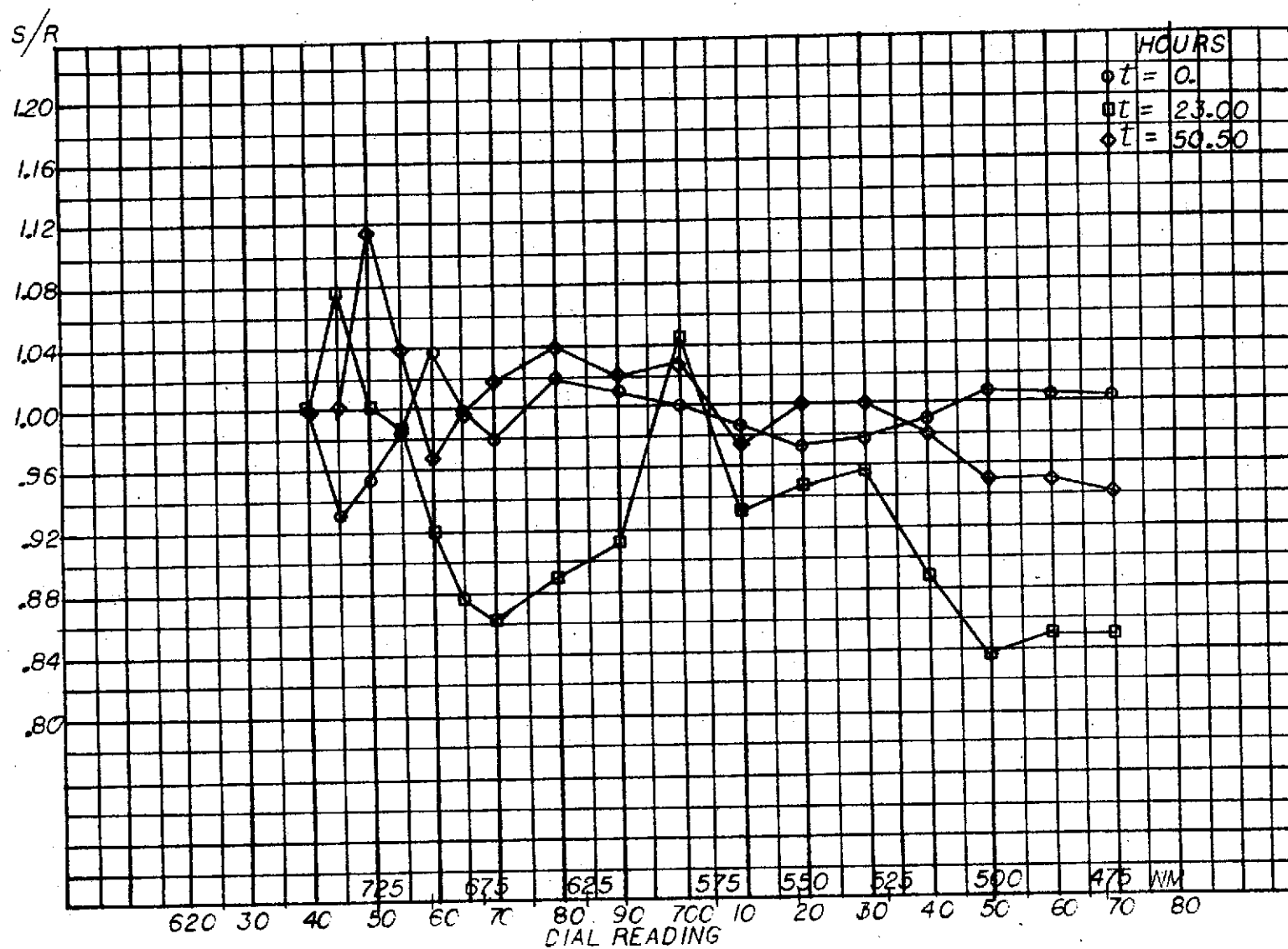
Fig. 18 Relative spectral reflectivity of bean leaves.
O$_3$. 70 pphm/4.7 hrs. plus 90 pphm/20.5 hrs.

Fig. 19   Relative spectral reflectivity of bean leaves.
O_3. 7.5 pphm/292 hrs.

Fig. 20 Relative spectral reflectivity of tobacco leaves.
O_3. 95 pphm/24 hrs. plus > 100 pphm/41 hrs.

Fig. 21 Relative spectral reflectivity of tobacco leaves.
$O_3 > 100$ pphm/16 hrs.
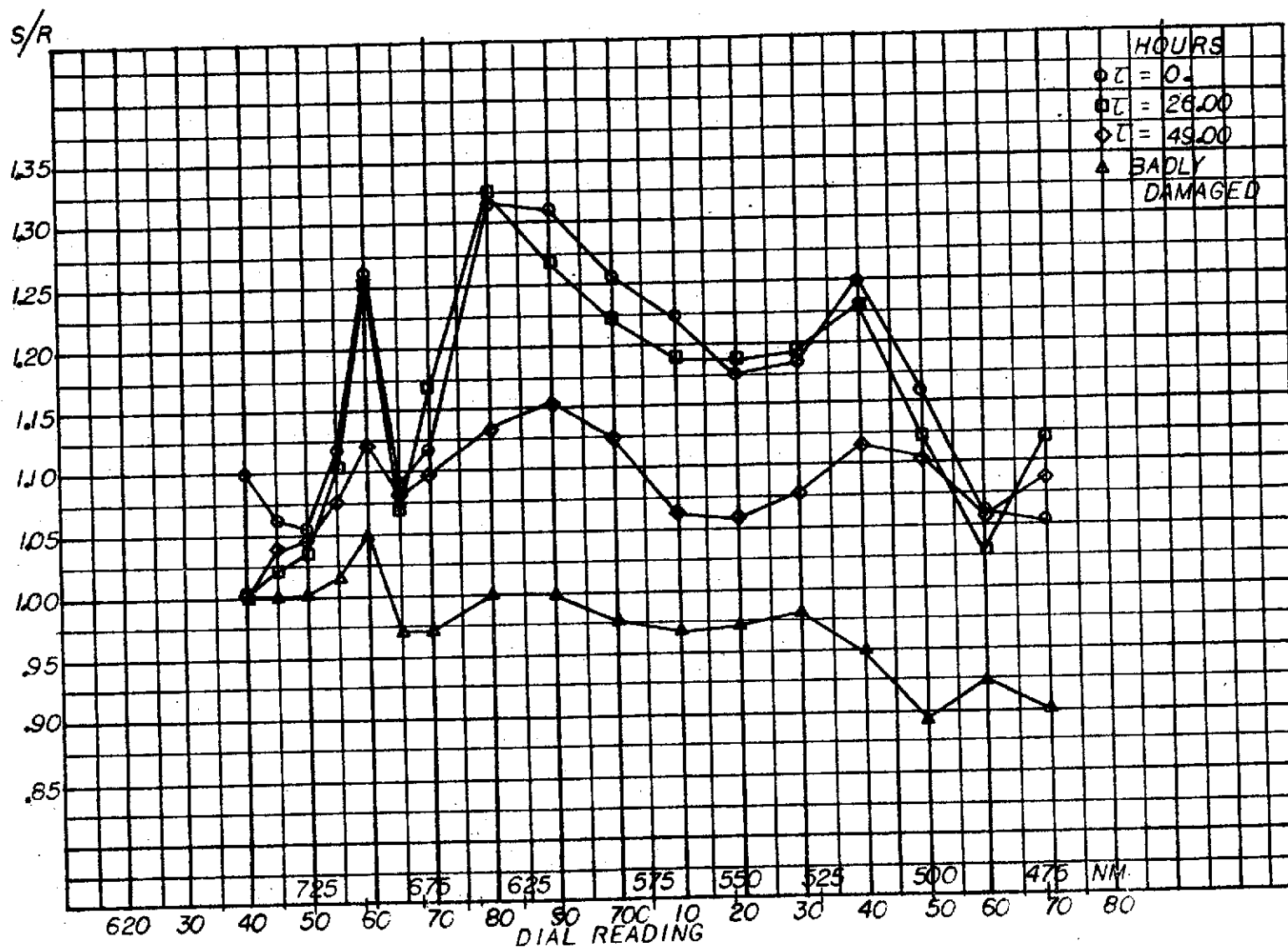
Fig. 22 Relative spectral reflectivity of bean leaves.
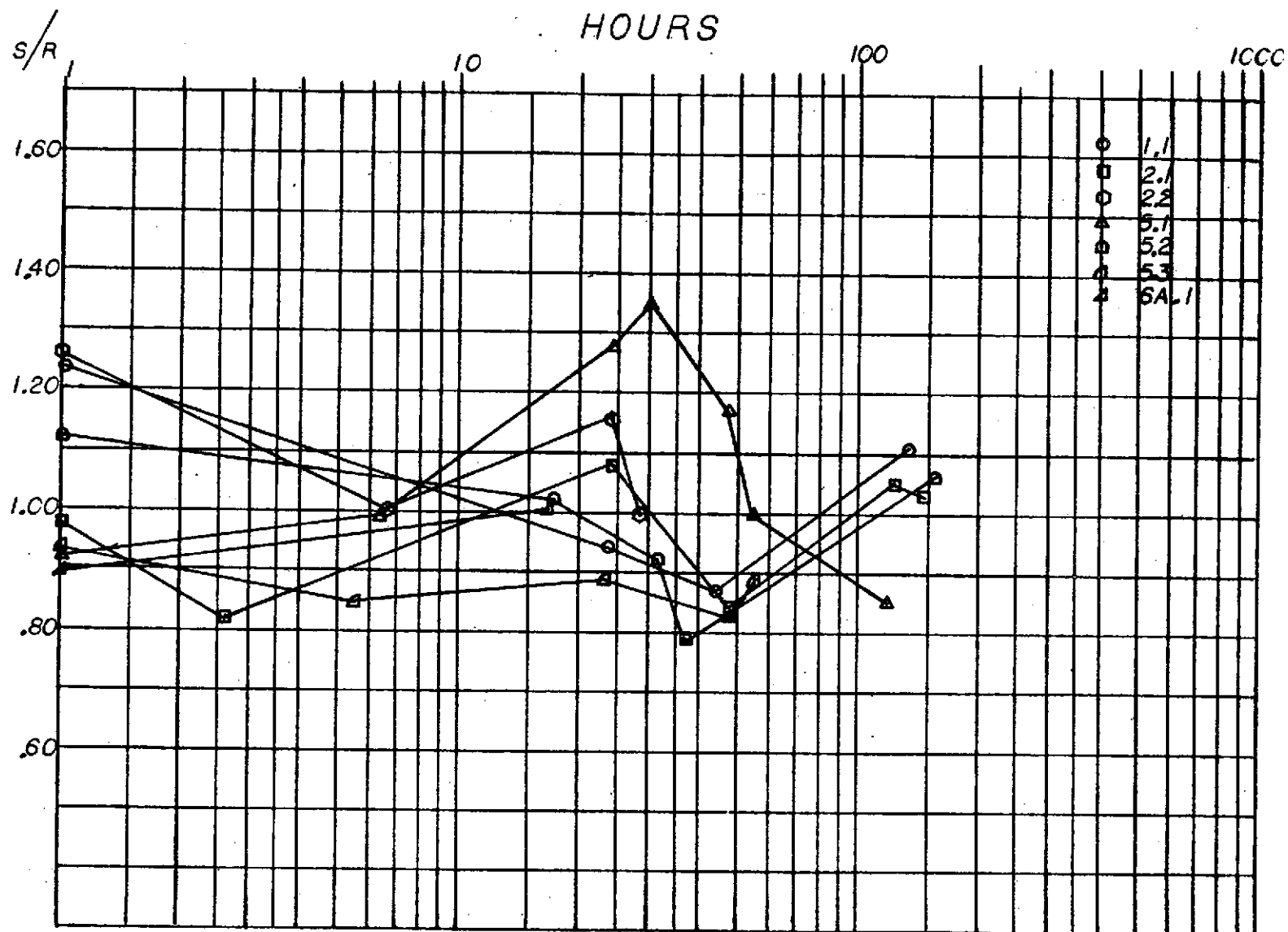2 ppm SO_2 + > 100 pphm O_3 for 18 hrs.

Fig. 23   Relative reflectivity at 697nm versus time for
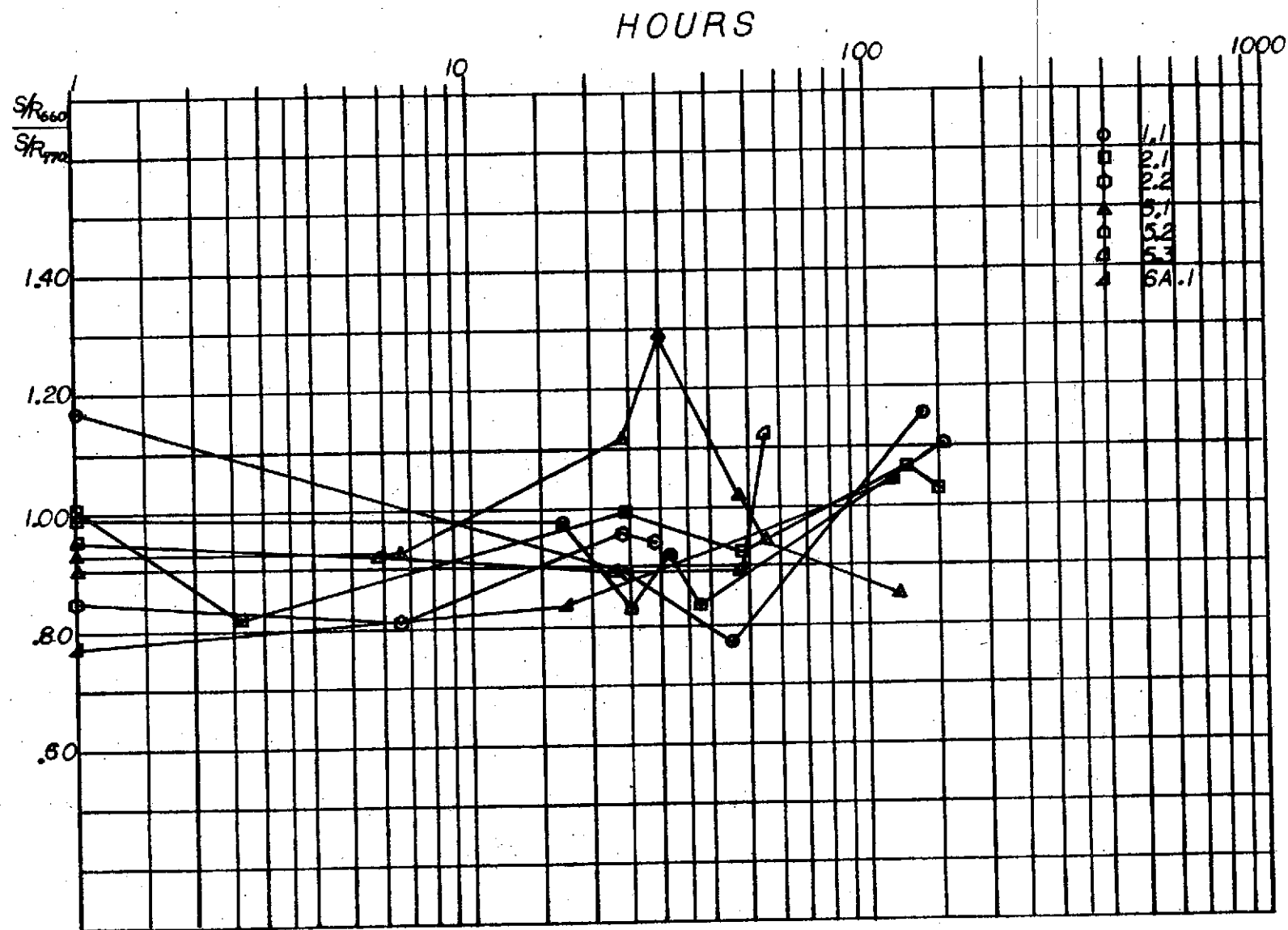bean leaves. SO_2. See text for curve coding.

Fig. 24 Relative reflectivity at 579nm versus time for
bean leaves. SO_2. See text for curve coding.
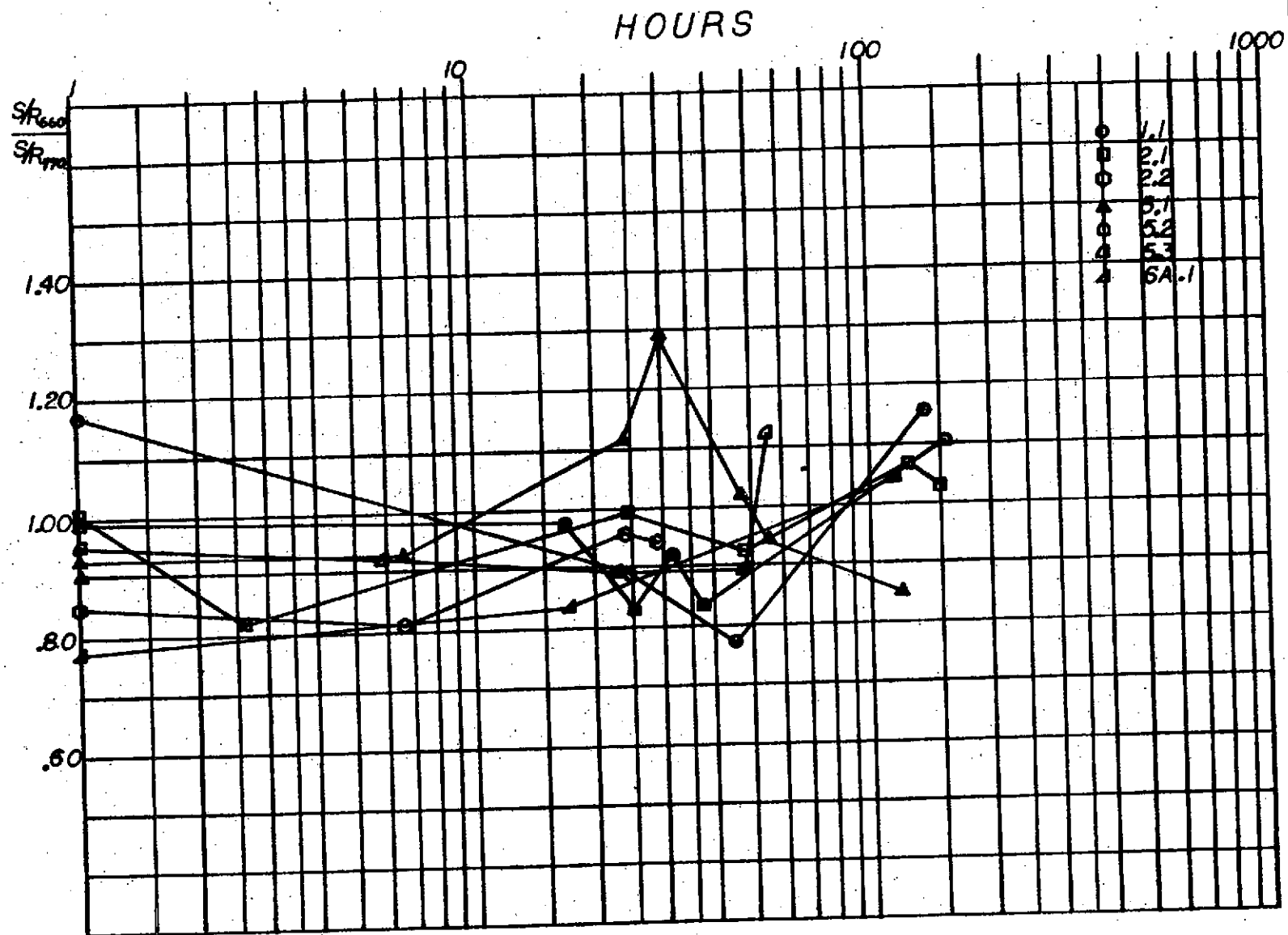
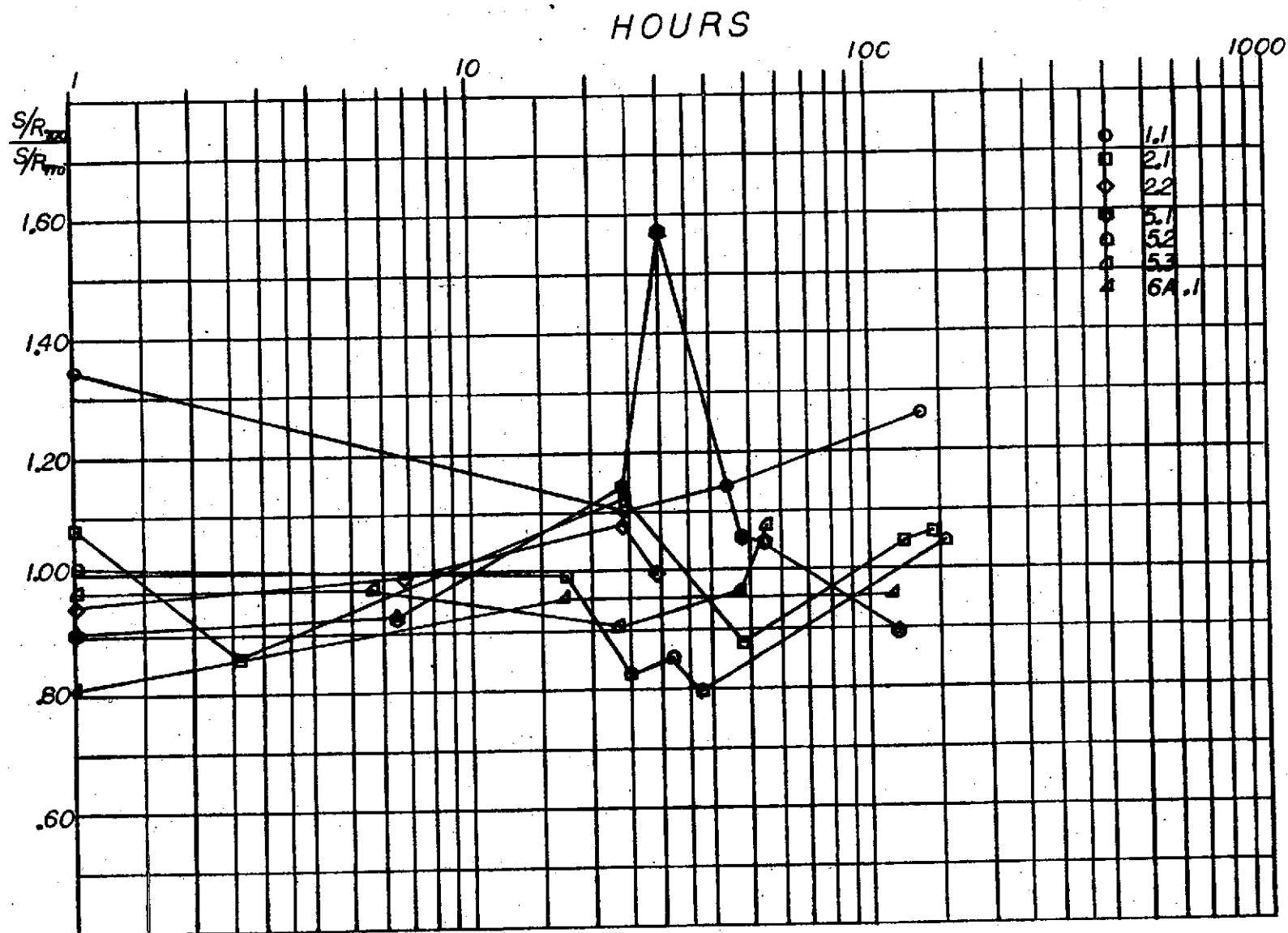Fig. 25   Data of Fig. 23 normalized by relative reflectivity at 474 nm.

Fig. 26   Data of Fig. 24 normalized by relative reflectivity at 474nm.