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SOME REMARKS ON THE OPERATION OF THE SELF-CONTROLLING INFRA-RED SPECTROPHOTOMETER

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ABSTRACT

In order to operate the infra-red spectrophotometer automatically, proper attention should be given to the facts that the resolving power, scanning speed of wavelength and the signal-to-noise ratio of the spectrometer are not mutually independent but are related in a complicated manner. It will be shown, however, that their mutual dependence can be expressed by a somewhat simple formula.

1. Introduction

The sources of limitations in the resolving power of a recording monochromator may be divided into two groups; namely, those concerning with the optical conditions of the monochromator, which are present even at infinitely narrow slit-width, and those relating to the electrical conditions, such as the signal-to-noise ratios of the receiving system and the scanning speed of wavelength of the recording spectrophotometer.

The optical factors have already been discussed in detail by Brodersen (**1**). Moreover, in practice a considerably wide slit-width has to be chosen in order to maintain a certain value of the signal-to-noise ratio of receiving system, so that there is no meaning to pursue along this way indefinitely.

Therefore, the second group, i. e. electrical conditions will be mainly discussed in the following pages in order to get conditions for good resolution and recording accuracy.

2. Condition for wavelength scanning

The most important condition for driving a monochromator is to scan the wavelength with constant time T per spectral slit-width. Let the dispersed image of the entrance slit be moved past the exit slit at a linear speed of $fd\phi/dt$, where $d\phi/dt$ is the rate of rotation of the scanning Littrow mirror and f the focal length of collimator (see Fig. 1).

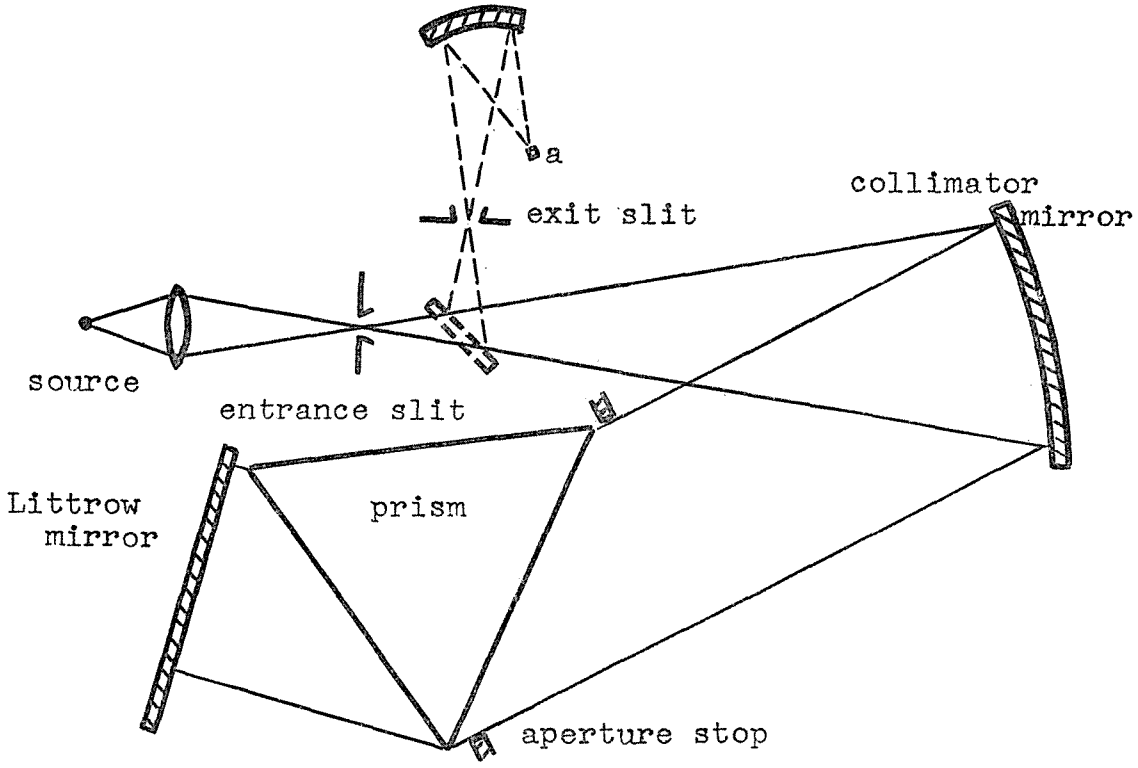

Fig. 1. Optical layout of infra-red monochromator.

The spectral slit-width s is proportional to the ratio of the geometrical slit-width W_λ to the linear dispersion L_λ of the prism taken as constant over the wavelength interval concerned in the plane of the exit slit, namely:

$$s=a_1 W_\lambda / L_\lambda , \tag{1}$$

where a_1 is a constant. Since, however,

$$L_\lambda = a_2 D_\lambda f , \tag{2}$$

where D_λ is the angular dispersion and a_3 is another constant, the spectral slit-width becomes

$$s=\frac{a_1 W_\lambda}{a_2 D_\lambda f} . \tag{3}$$

For the angle $\Delta\phi$ through which the scanning system must be turned in order to scan a spectral slit-width s, we have

$$\Delta\phi = a_3 D_\lambda s , \tag{4}$$

which, by (3), becomes

$$\Delta\phi = a_4 W_\lambda / f \,, \tag{5}$$

where a_3 and a_4 are both constants.

Therefore, in order to get a constant scanning time T per spectral slight-width, we should have

$$\frac{d\phi}{dt} = \frac{\Delta\phi}{T} = \frac{a_4 W_\lambda}{f\,T} \,, \tag{6}$$

namely, the rate of drive $d\phi/dt$ of dispersing system must be proportional to the geometrical slit-width, independently of dispersion.

3. Relation between wavelength scanning time T and response of electronic system

Tet τ be the response time of the receiving system, including the associated circuits, and $\Delta\lambda$ be the wavelength interval scanned in a time P. Then, the smallest wavelength interval $d\lambda$ by which two signals can be separated and clearly resolved, is determined by

$$\frac{d\lambda}{\tau} = \frac{\Delta\lambda}{P} \,.$$

Using the conventional optical definition for resolving power it follows that the resolving power R_{scan} in the scanning system is given by

$$R_{\text{scan}} = \frac{\lambda}{d\lambda} = \frac{\lambda P}{\tau \Delta\lambda} \,. \tag{7}$$

Since, on the other hand, $\Delta\lambda/P = f d\phi/dt$, we get, using (6),

$$R_{\text{scan}} = \alpha \frac{\lambda T}{\tau W_\lambda} \,, \tag{8}$$

where α is a constant of proportionality.

Thus, we see that the resolving power in the scanning system is proportional to wavelength λ and scanning time T and inversely proportional to response time τ and geometrical slit-width W_λ. It seems that this resolving power can be raised by decreasing both τ and W_λ, but one cannot decrease τ indefinitely not only from the practical standpoint but also for the reason that the signal-to-noise ratio decreases in proportion to $\tau^{\frac{1}{2}}$ (**2**). Also, the slit-widtlı W_λ cannot be decreased indefinitely, because the slit-width is controlled automatically in order to keep the energy passing through the second slit approximately constant in the recording spectrophotometer.

In this connection, therefore, the relation between the slit-width and the signal-

to-noise ratio is important. Referring to Fig. 1, which shows the optical design factors, the energy flux in the spectral band $d\lambda$ passing through the entrance slit and the aperture stop is given by $\pi J_\lambda hWN^2 d\lambda$, where J_λ is the source radiation per cm^2 per steradiation per unit $\Delta\lambda$ at wavelength λ, h the height of the slit, W the width of the slit and N the numerical aperture of the collimator and aperture stop. The dispersing element spreads this spectral band over a width $fD_\lambda d\lambda$ in the plane of the exit slit, but the portion falling on the second slit passes to the receiver. Thus, the flux which generates the signal in the receiver is given by

$$E_s = \frac{W}{fD_\lambda d\lambda} \times \Phi \pi J_\lambda hWN^2 d\lambda ,$$

where an optical transmission factor Φ has been added in order to account for losses due to absorption and unwanted reflections. Since the real slit-width W is proportional to the geometrical slit-width W_λ, we may finally put

$$E_s = \beta \frac{J_\lambda W_\lambda^2}{D_\lambda} , \tag{9}$$

where β is a constant of proportionality.

Empirically the thermal agitation noise E_n in the receiver of optimum design is given by (2)

$$E_n = ka^{\frac{1}{2}} , \tag{10}$$

where a is the area of receiver, E_n is expressed in terms of the incident flux required to produce a signal voltage equal to the RMS value of the noise voltage, and k is a constant depending on the type of construction, materials employed and the speed of response of measuring system. Dividing (9) by (10), we obtain

$$\frac{E_s}{E_n} = \frac{\delta J_\lambda W^2}{D_\lambda k \sqrt{a}} , \tag{11}$$

where δ is a constant of proportionality. Since, as mentioned before, E_s/E_n decreases in proportion to $\tau^{\frac{1}{2}}$, we may ultimately put the relation between the slit-width and the signal-to-noise ratio in the form:

$$\frac{E_s}{E_n} = \kappa \frac{\tau^{\frac{1}{2}} W_\lambda^2}{D_\lambda} , \tag{12}$$

where κ is a constant of proportionality. We see from this equation that the signal-to-noise ratio becomes large when W_λ is large, but, according to Eq. (8) R_{scan} becomes small in this case.

Taking the above two formulae (8) and (12) into consideration, we obtain the following conditions for operation of recording spectrophotometer.

(a) High resolution is obtained by slow scanning speed, fast response time and narrow slit-width.

(b) Accurate transmission value is obtained by slow response time and wide slit-width.

These two conditions are not consistent with each other, however. The optimum solutions may be obtained by widening the slit of the spectrometer until the optical and electrical resolving power become equal to each other for a particular scanning time T. So, the most desirable condition for the user, i. e., high resolution, fast scanning as well as accurate transmission value may be established only by the suitable arrangement of T, τ, W_λ and moreover signal amplifier gain factor G as in the case of the Beckman Spectrophotometer IR-2T, which will be described precisely in the next paragraph.

3. Application to the Beckman Spectrophotometer

We had the opportunity to handle with thd Beckman IR-2T Infra-red Spectrophotometer and examined its construction in detail. Now, we shall begin with the main feature of this instrument.

The Beckman Infra-red Spectrophotometer is a single beam monochromator instrument employing "*Memory Standardization*" to obtain direct transmittancy recordings on the pen recorder. The 100% reference level for direct transmittancy recording is automatically determined by making a "standardization run" against the definite light source, especially containing the empty or solvent filled sample cell in the optical path of the monochromator. The automatic slit control system maintains the amplified photoreceiver signal E_λ at a constant value E_0, and is so arranged that the electric signal for the function of the slit-width versus wavelength is recorded on a tape recorder. Thus, the following relation for E_λ is obtained:

$$E_\lambda = E_0 = \gamma W_\lambda G F(W_\lambda), \tag{13}*$$

where G is the thermocouple signal amplifier gain factor and γ is a constant.

On subsequent "play back", the signal from the tape recorder controls the slit and wavelength servo-motors, precisely reproducing the standardizing conditions so that absorption spectra from a sample are recorded in transmittancy when the sample is inserted into the optical path of the spectrometer at "play back run". So, in the case of the Beckman Spectrophotometer, high resolution and accurate transmission

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* $F(W_\lambda)$ is the correction term of G as introduced according to the following reason. In the Beckman IR-2T control system, it is necessary to drive an adjustable attenuator with the slit-motor, so that the percent error per revolution of the slit-motor is constant regardless of slit setting, since the slit-width versus rotation is non-linear. The factor is automatically controlled according to the slit-width.

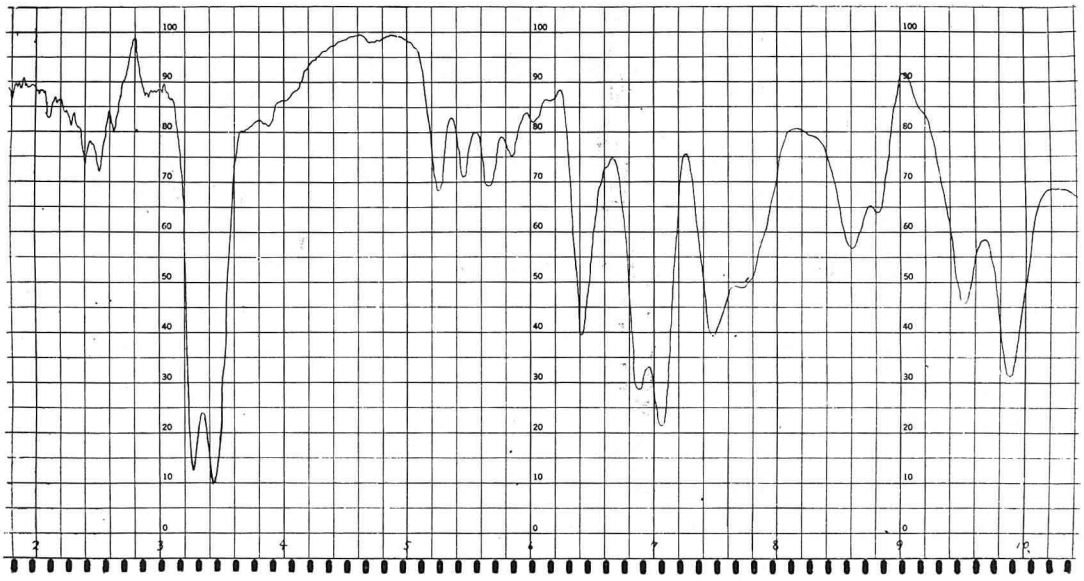


Fig. 2. Infra-red absorption of polystyrene film taken by the Beckman

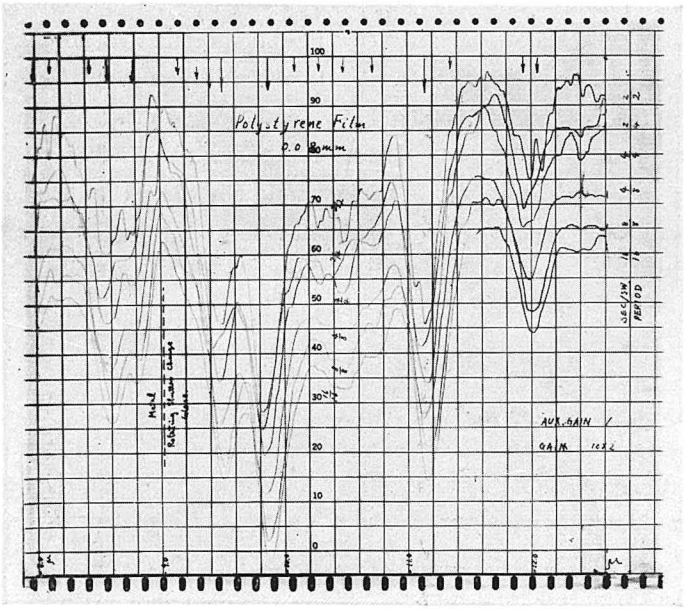
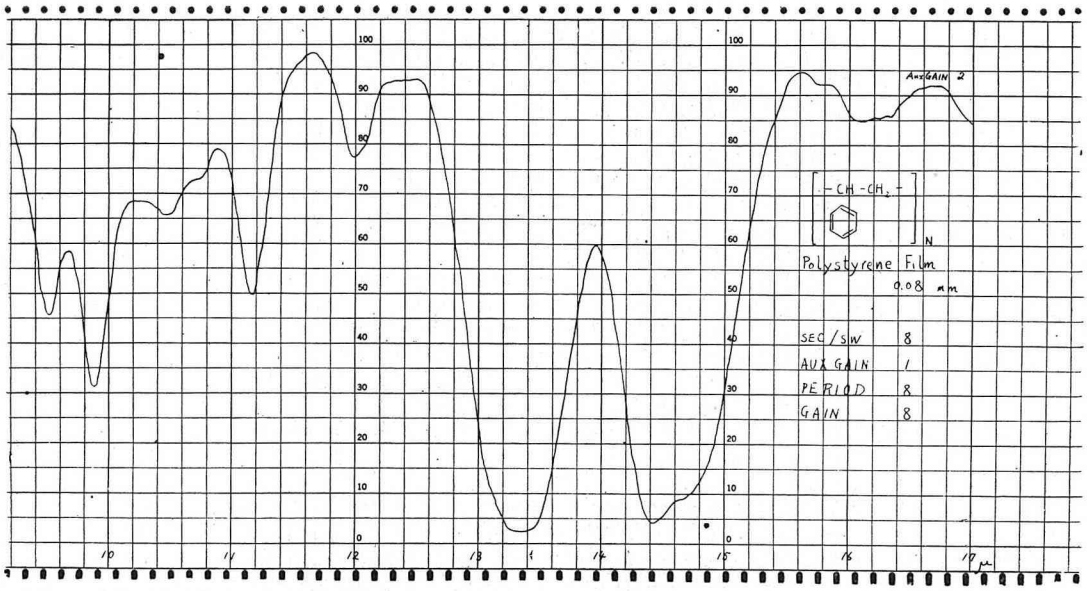


Fig. 3. Infra-red absorption curves of polystyrene film taken with the gain factor 1, 2, 7 and 10.

are obtained, considering the above-described formulae (8), (12) and (13).

By using the Beckman Infra-red Spectrophotometer IR-2T, we measured the absorption spectra of polystyrene film at various values of the scanning speed T, the



Infra-red Spectrophotometer IR-2T (using KBr 60° prism).

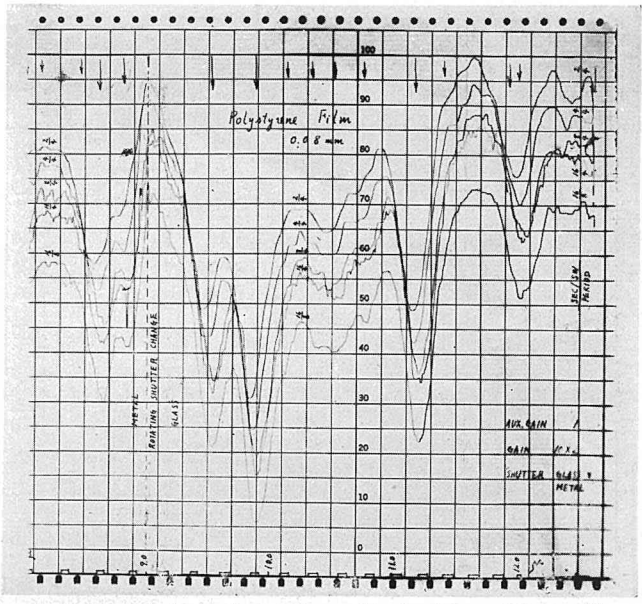


Fig. 4. Infra-red absorption curves of polystyrene taken with $\frac{\text{Sec./SW}}{\text{Period}} = \frac{16}{8}, \frac{16}{4}, \frac{8}{4}, \frac{4}{4}$ and $\frac{2}{4}$.

response time τ and the gain G. The results are shown in Figs. 2, 3, 4 and 5, as well as in Tables 1, 2 and 3. In these tables are given the absorption values of the polystyrene film, which have been measured from Figs. 3, 4 and 5.

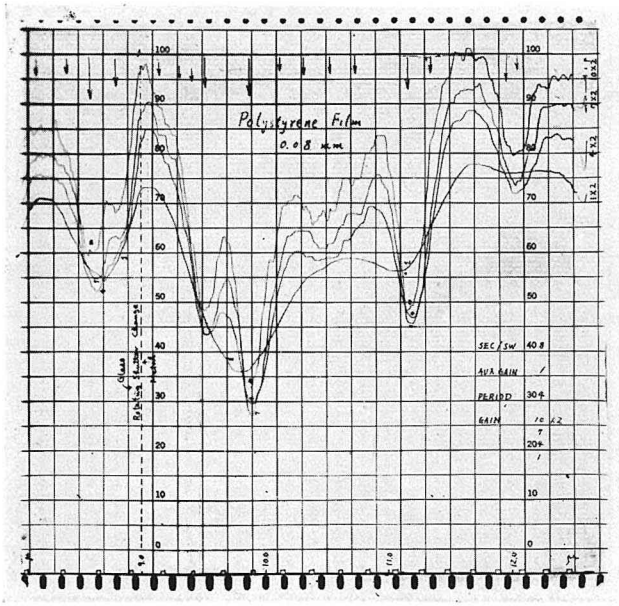


Fig. 5. Infra-red absorption curves of polystyrene taken with $\frac{\text{Sec./SW}}{\text{Period}} = \frac{16}{16}, \frac{8}{8}, \frac{4}{8}, \frac{4}{4}, \frac{2}{4}$ and $\frac{2}{2}$.

Table 1. Absorption of polystyrene film (0.08 mm)

Wavelength in microns	Gain			
	1	4	7	10
8.6	18	28	30	31.5
8.8	—	—	14	16.5
9.5	30	23.5	29.7	32.5
9.9		25	33	37.5
	—	6.3	—	—
10.5	—	—	10	15
	—	—	3	6
11.1	12	31.8	40.3	43.7
12	1.1	14.9	17.6	18.1

Aux. Gain $\frac{1}{2}$, Sec./SW(T) 8, Period (τ) 4.

Table 2. Absorption of polystyrene film (0.08 mm)

Wavelength in microns	T/τ				
	16/8	16/4	8/4	4/4	2/4
8.6	35	33	34	32.5	29.5
8.8	16.5	15	20.3	16.5	15.7
9.5	33.5	34	33.5	30	27.5
9.9	35.5	37.5	36.5	35	38
	2	—	2	1	—
10.5	11.5	11.5	12.5	10.5	10.5
	5	4	5	4	3
11.1	42.7	42	43.7	42.7	41.5
12	20.5	20.7	20.5	22	22.5

Aux. Gain $\frac{1}{2}$, Gain 10.

From these results it can obviously be seen that the user of the infra-red spectrophotometer must control the three variables: (1) resolution, (2) signal-to-noise ratio, and (3) speed of scanning over wide ranges, in order to obtain full power and flexibility from the spectrophotometer.

Resolution R_{scan} is the first of the three important variables. We need high resolution if we wish to study highly detailed spectra. If we scan fast at high

Table 3. Absorption of polystyrene film (0.08 mm)

Wavelength in microns	T/τ					
	16/16	8/8	4/8	4/4	2/4	2/2
8.6	36.5	34	31.5	34.5	28	30
8.8	16	15.5	14.7	16.5	13.5	18
9.5	30.5	34.5	28.5	33.5	26.5	30
9.9	35	36.5	29.5	35.9	29	37.5
	—	—	—	3	—	5
10.5	10.5	10	8.5	12.5	12	15
	4	3	—	4	—	7
11.1	43	41	40	46.5	42.5	44.5
12	19	20	18.5	22	19.5	21.5

Aux. Gain $\frac{1}{2}$, Gain 10.

resolution (i.e., R_{scan} is large and T is small in the formula (8)), we must accept a chart record with relatively inaccurate transmission value, because the record will be noisy (i.e., τ is small and then E_s/E_n becomes small in (12)). In Fig. 4, the record is very noisy when T/τ is equal to 16/4. If we scan slowly at high resolution (i.e., both R_{scan} and T are large in (8)), the chart record will be free of noise and will have accurate transmission values, but it will take somewhat longer time to make the spectrogram (see Fig. 5). These compromises will be made with any spectrophotometer.

The signal-to-noise ratio E_s/E_n is the second of the three important variables. If the signal is large compared with the noise, the chart record will be smooth and successive spectrograms of the same sample will match each other closely, and so we can obtain accurate transmission readings or the highest resolution (see Table 1). We cannot have all these advantages at high scanning speed. Accurate transmission readings combined with high scanning speed give rise to the loss of resolution, because E_s/E_n is large and T is small and hence R_{scan} is small: high resolution combined with high scanning speed results in a noisy record and hence results in the loss of accuracy in transmission readings, as described before. In Figs. 4 and 5, the values of T/τ are compared with each other, and these relations may be understood easily.

Scanning speed T is the last of the three important variables, and refers to the time required for the light of any particular wavelength to traverse the exit slit as the infra-red spectrum sweeps across the slit plates. The scanning speed for a series of runs is measured in seconds per spectral slit-width. The instrument automatically changes the speed of the wavelength drive as the slit-width changes to give the selected speed in seconds per slit-width. This allows us to traverse each slit-width in the time proportional to the response period of the recording system, where the proportional constant depends on the nature of the spectrum. Such scanning rates will give maximum efficiency (**3**).

Moreover, we lose accuracy if the response period is longer than the time taken to scan one spectral slit-width, because the chart will not be able to follow the changes in absorption fast enough. Empirically, in our instrument, when for sharp spectra

as in the case of gases the proportional constant T/τ is equal to unity, we have good recording (see Fig. 5). For broad spectra as in the case of liquids, T/τ is equal to 2, except in regions of strong sharp back ground absorption where the constant is equal to unity.

Then, in addition to the three important variables mentioned above, we must especially refer to the relations between amplifier gain factor G and slit-width W_λ according to the formula (13).

In order to keep high resolution, we must use narrow slit, high amplifier gain and a short response period of the recording system, according to formulae (8) and (13). The combination of high amplifier gain and short response periods causes noisy or randomly irregular chart record.

We can obtain a quiet chart record, i. e., accurate transmission values, by using low amplifier gain together with either of wide slit and long response periods of the recording system or together with these two, according to the formulae (12) and (13). Wide slits, though giving quiet records, reduce resolution (see Fig. 3). Thus it is evident that we lose resolution or accuracy of transmission readings if we go to the case of extremely fast scanning. Nevertheless, if we are more interested in finding the main absorption peak of the sample than in exact transmission values or resolution and want to obtain results in a hurry, rapid scanning may be most useful.

5. Summary

(1) Resolution is automatically kept to a maximum as determined by the chosen amplification G, response period τ and scanning speed T.

(2) Transmittancy recording accuracy is limited only by signal-to-noise ratio and linearity of the used amplifier in the single beam optical system such as the Beckman IR-2T Spectrophotometer.

(3) Recording speed may automatically be maintained at a maximum consistent with the resolving power of the spectrophotometer and chosen recording condition.

To get versatility in the infra-red spectrophotometer, its user must change the speed of scanning T, the response time τ and the gain factor G over wide range and must set the spectrophotometer in the best condition as stated above.

The planning of this work was stimulated when the opportunity was given to the writer to handle with the Beckman Infra-red Spectrophotometer purchased for Professor Yôichi Uchida with a grant-in-aid for scientific research of the Ministry of Education. The writer wishes to express his cordial thanks to Professor Uchida for his kind advices during the course of this work.

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