

# Spectrophotometric studies of ultra low loss optical glasses I: single beam method

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**Abstract** A single beam spectrophotometer has been developed for the measurement of spectral attenuation

coefficients of very low loss optical glasses in the wavelength range 400–1000 nm. The instrument has an accuracy to  $\pm 0.00005 \text{ cm}^{-1}$  when sample thicknesses of 20 cm are used. The basic stability of the instrument and the sources and effects of systematic errors have been investigated in detail. Some results are presented in the form of attenuation curves for four different low-loss optical glasses.

## 1 Introduction

The developments in fibre optics and the possible use of a fibre surface waveguide for optical communication purposes have given rise to the demand for ultra-low-loss optical glasses. In response to this demand, glass technologists are studying the mechanisms of loss in glass with a view to manufacturing glasses with absorption coefficients of  $0.0001 \text{ cm}^{-1}$  within the wavelength range 400–1000 nm. At the present time, low-loss glasses have absorption coefficients never much below  $0.001 \text{ cm}^{-1}$ . Spectrophotometric techniques are required to support this development. The existing quantitative photometric measurement techniques for glass samples claim resolutions, at best, of 1 part in  $10^3$ . Many of the factors influencing the reliability of the measured results (Harper 1965) have not been thoroughly studied. The work to be described here concerns: (i) the development of a spectrophotometer, specially suited to glass sample evaluation, of the single-beam type and having an intrinsic resolution (see § 4.2) of better than  $\pm 3$  parts in  $10^4$ ; (ii) the investigation into the systematic errors arising due to the method of measurement; (iii) the measurement and statement of some results for a number of samples.

The increased accuracy and sensitivity, over that obtained from commercial instruments, has been achieved by the use of thick samples together with good beam collimation, accurate alignment of the samples and an increased understanding of the effects of beam parameter changes.

## 2 Method of measurement

The attenuation of a bulk sample of glass is measured by an insertion loss method in which the sample attenuation is deduced from the difference in the insertion losses of two identically prepared samples of different lengths. The reference signal is required to be invariant.

With unit incident energy and taking the attenuation coefficient per unit length to be  $\alpha$  and the reflection coefficient per interface to be  $R$ , the transmitted energy for a sample of length  $L$  having parallel faces is

$$t = \frac{(1 - R)^2 e^{-\alpha L}}{1 - R^2 e^{-2\alpha L}} \approx \frac{1 - R}{1 + R}, \text{ for small } \alpha L,$$

and the reflected energy is

$$r = R \left\{ 1 + \frac{(1 - R)^2 e^{-2\alpha L}}{1 - R^2 e^{-2\alpha L}} \right\} \approx \frac{2R}{1 + R}, \text{ for small } \alpha L.$$

The ratio of the transmitted energies through two samples of lengths  $L_1$  and  $L_2$  is

$$\frac{t_1}{t_2} = e^{-\alpha(L_1 - L_2)} \left( \frac{1 - R^2 e^{-2\alpha L_2}}{1 - R^2 e^{-2\alpha L_1}} \right).$$

Neglecting the fraction  $\left( \frac{1 - R^2 e^{-2\alpha L_2}}{1 - R^2 e^{-2\alpha L_1}} \right)$  introduces an error of about 1 part in  $10^5$  for a typical case. Since  $\alpha(L_1 - L_2)$  is small, by expanding and neglecting higher order terms,

$$\frac{t_1}{t_2} = 1 - \alpha(L_1 - L_2)$$

$$\text{hence } \alpha = \left( \frac{1}{L_2 - L_1} \right) \left( \frac{t_1 - t_2}{t_2} \right).$$

Hence the measurement of  $t_1$ ,  $t_2$ ,  $L_1$  and  $L_2$  can be used to evaluate  $\alpha$ .

## 3 Description of the instrument

The spectrophotometer is a single beam instrument and the method of measurement requires the maximum possible stability of source output and detector sensitivity during the period of an attenuation measurement. Figure 1 is a schematic diagram of the apparatus.

### 3.1. The light source and the monochromator

The white-light source is a 55 w tungsten-halogen projector lamp run from a regulated d.c. power supply. The short term stability of the voltage across the lamp has been checked with a digital voltmeter and found to be better than 1 part in  $10^4$ . The lamp is slightly under-run in order to increase its operational life, but not to affect substantially its stability.

A system of mirrors focuses the coil filament of the lamp on to the entrance slit of a double monochromator fitted with  $\text{CaF}_2$  prisms. The monochromator slits can be adjusted and set to give the required resolution. Typically, the bandwidth is arranged to be less than 20 nm over the wavelength range 500–1000 nm. The light source and the monochromator are contained in a light-tight housing of sufficient size to allow adequate ventilation.

### 3.2 The collimating system

The first lens  $L_1$  forms a demagnified image of the exit slit of the monochromator on to a  $100 \mu\text{m}$  diameter pinhole. The pinhole is then used as a 'point source' in conjunction with a collimating lens  $L_2$  to produce a well-defined beam.

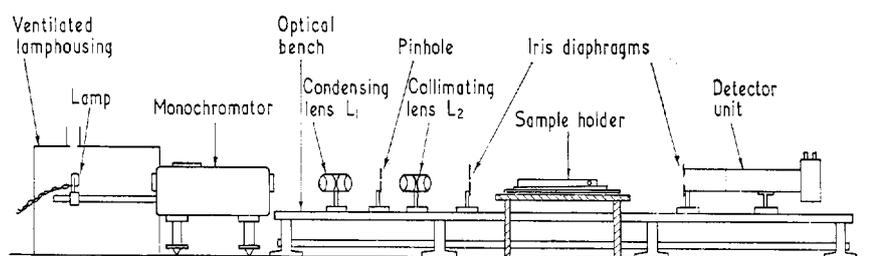


Figure 1 Schematic of the spectrophotometer apparatus

The arrangement can produce a collimated beam of 8 mm diameter (circular cross section) and with a total divergence of not more than 1 mrad. An iris diaphragm is used to reduce the beam diameter to any convenient size. Compound photographic objectives are chosen for both the lenses. These minimize aberration effects and have been found to behave reasonably achromatically throughout the wavelength range.

The size of the iris diaphragm aperture and the position of the pinhole are responsible, together with the slit setting of the monochromator, for defining the resolution or bandwidth of the apparatus. Any relative movement can introduce an uncertainty in the wavelength and resolution as well as the absolute intensity of the beam and beam intensity distribution. This requires that the apparatus is assembled with good mechanical stability.

### 3.3 The sample holder

The sample holder has been designed to allow accurate, repeatable and rapid insertion of two different lengths of a sample into the light beam. It consists of two sample carriers on a reference plane, which is movable over a base-plate, and can accommodate samples with lengths up to 25 cm. The whole assembly is mounted on a rigid stand separate from the optical bench carrying the collimating system. This is to ensure that any mechanical vibration set up by moving the samples is not transmitted to the collimating system.

The details of the assembly are as shown in figure 2. The sample carriers are accurate V sections with fine screw adjustments at one end, providing  $2^\circ$  of angular adjustment in planes parallel and normal to the reference plane. The other ends are at fixed locations on the reference plane, which is a ground steel plate. The plate is engaged along precision grooves by two silver steel rods mounted on the base-plate, so that the reference plane may be moved in the direction normal to the light beam. The grooves are designed to provide three line contacts for light, precise and smooth movement of the plate on the rails.

Provision has been made to locate the reference plane at one of three positions. Two of the positions allow the light beam to travel through the centre of either of the two samples, while the third position allows the beam to proceed uninterrupted between the sample carriers. This direct beam can be used as a reference signal.

The complete assembly is placed over the optical bench with the sample carriers approximately parallel to the axis defined by the light beam. In this position, the reference plane can be moved along an axis approximately normal to the light beam. Fine adjustment of the sample carriers can then be made to accurately align the samples with respect to the light beam (see § 4.2.4).

### 3.4 The detector assembly and recording apparatus

A photomultiplier tube is used as the detector in this spectrophotometer (see § 4.1.2). The complete assembly (figure 3) also includes a diffusing screen mounted in front of the photocathode and separated from it by a cylindrical tube with a highly reflecting inner surface. The diffusing screen is a disk of opal glass, depolished on both sides and mounted parallel to the photocathode. Together with the reflecting tube, its purpose is to reduce the sensitivity of the detector to any change in incident beam size, shape, position or direction which might be produced by the insertion of a glass sample. An integrating sphere with suitable beam divergence optics may be a more effective means of reducing this sensitivity, but only at the expense of reducing the signal level. The diffuser-to-photocathode distance is the result of a compromise between positions for high output signal and low sensitivity to beam changes.

For measurement in the wavelength range 500–800 nm, an EMI 9558 B tube was chosen because of its S20 photocathode and low noise level. Above 800 nm, a RCA 7102 photomultiplier, with S1 photocathode, is used. The photomultiplier is mounted in a brass tube with an internal mu-metal shield. The dynode resistor chain is situated in a separate metal box at the base of the tube. This is an arrange-

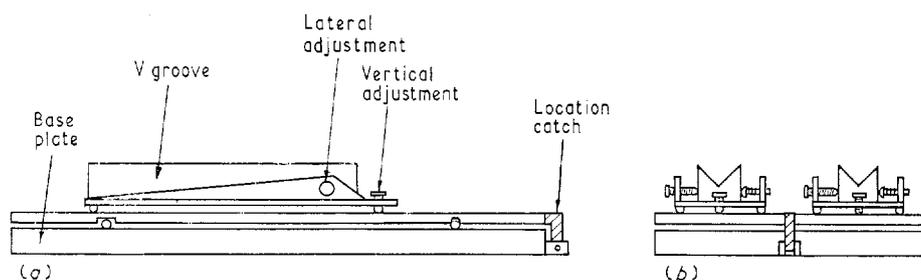


Figure 2 Sample holder. (a) Side elevation showing short sample mount in position; (b) end elevation showing both sample mounts in position

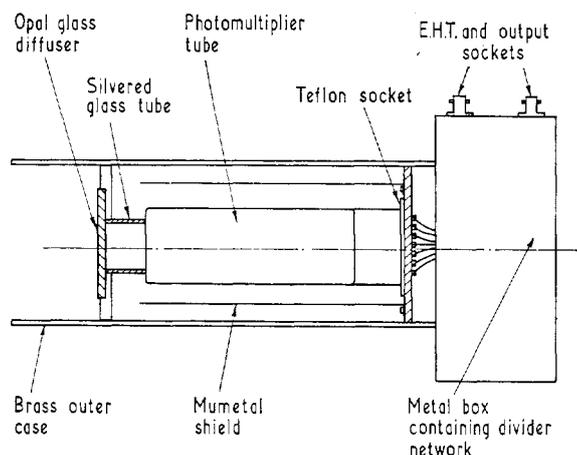


Figure 3 Detector assembly

ment to minimize the effect of the small amount of heat dissipated in the resistors on the photocathode temperature stability.

The photomultiplier is supplied by an e.h.t. unit, chosen for its high stability and, in particular, for its freedom from a.c. ripple and spurious pulses. The specified a.c. ripple is less than 2 mV peak-to-peak and the total drift is less than 0.1% in 24 h, after a suitable stabilizing period.

For convenience and ease of operation, and to minimize unwanted light inside the darkroom housing the main unit of the spectrophotometer, the photomultiplier load resistor and the measurement recording apparatus are situated outside the room. All connections have been made using shielded cable where possible. A five-window digital voltmeter is used to measure the voltage developed across the high stability load resistor. The voltmeter has a maximum resolution of better than 4 parts in  $10^5$  and an accuracy to  $\pm 0.0033\%$  of full scale or  $\pm 0.005\%$  of reading. The binary-coded decimal output from the voltmeter is used to operate a paper-tape punch, via a logic unit. The photomultiplier signals are then in a form suitable for statistical processing by a computer.

#### 4 Evaluation of the performance

The performance of the spectrophotometer has two aspects; the basic stability of the unit and the measurement accuracy. The latter includes the uncertainties due to systematic errors.

##### 4.1. Basic stability

The basic stability of the instrument depends on the stability of the light source and the detector. The factors influencing the choice of the source and detector for maximum stability are the spectral range, the intensity of the source and the sensitivity of the detector.

**4.1.1 Source** A wide variety of sources are available. For optimum choice exhaustive tests are necessary. A near optimum choice can be made based on the following facts. It is known that the arc sources have a tendency for the arc position to wander, and the emission usually contains distinct lines. These are not desirable characteristics for this application. Among hot body sources, a high temperature filament is preferred as it gives good emission in the visible as well as at the infra-red wavelength. The tungsten sources fulfil many of the requirements. Under steady ambient conditions the tungsten light source stability is governed by the supply stability. A relationship sometimes quoted (Walsh 1958) is  $\delta F/F = k\delta V/V$  where  $F$  is the output flux (or intensity) and  $V$  is the supply voltage. The factor  $k$  is quoted to be 3.8 for the light source running at normal rated voltage and varies gradually if it is over or under run. The lamp housing is

required to be draught proof, but ventilated to allow normal convection to take place.

**4.1.2. Detector** In the spectral range concerned, the photoemissive detectors have reasonable quantum efficiencies (about 1%). Photomultipliers with high gain and a relatively large photosensitive area are suitable for this application. The solid-state detectors have high efficiencies and are good in the longer wavelength part of the spectrum of interest. However, the low intensity of light available would result in thermal noise being predominant, giving a small signal-to-noise ratio. The stability of the photomultiplier is dependent on the stability of the potential at the dynodes and also on the operating conditions with respect to the voltage between dynodes and the magnitude of the cathode current.

##### 4.2 Determination of systematic errors

The resolution of the spectrophotometer has a limiting value (the intrinsic resolution) which is governed by the stability of the source-detector combination and the observation time. The reliability of the loss measurements, however, is governed by the systematic errors if these predominate. Before accurate loss measurements can be made on glass samples, it is necessary to determine the causes and consequences of any systematic errors in the readings.

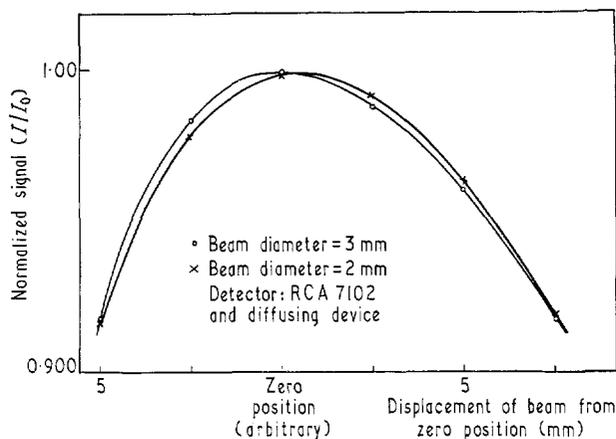
The essential requirement for the accurate determination of bulk loss is that the differences in the transmitted signals for the two lengths of glass be due only to absorption and scattering within the bulk of the sample. (The forward scattered energy is taken to be transmitted energy.) Other factors causing a change in the detected signal are considered as systematic errors. These include, for example, the difference in the reflection losses of the two samples, variation in the detector output caused by beam diameter change, etc. In the experimental studies of these errors, steps are taken to ensure that the number of variables are reduced to a minimum in order that meaningful results may be obtained.

**4.2.1 Sample preparation** It is important to have the surface conditions the same on both sample lengths so that the end-face reflection and scattering losses are nearly equal. The sample preparation adopted is as follows. The two lengths of the particular glass sample are cut from the same rod. Their end faces are polished by the same operator. Each pair of ends is polished simultaneously to a flatness of better than  $\lambda/20$  and a parallelism of 10 seconds of arc. This mode of preparation yields samples with a surface refractive index consistent to 1 part in  $10^3$  as measured using an ellipsometer. This gives a variation in the theoretical reflection loss of about 1 in  $10^4$  and it is assumed that this can be considered to yield insignificant errors in surface losses. The parallel end-faces are convenient for alignment purposes. In addition to the initial polishing, the sample faces are subjected to a standard cleaning process before each set of measurements. This involves gentle polishing with a lens tissue and a preliminary wash in a mild solution of liquid detergent in de-ionized water. After rinsing in de-ionized water and drying with a lens tissue, the sample is placed for an hour in an acetone vapour degreasing apparatus. The samples are kept in a desiccator until required for measurements.

**4.2.2 Measurement of beam divergence** During initial alignment procedure it was found that careful movement of the collimating lens  $L_2$  can provide a reliable means of changing the beam divergence. The lens position on the optical bench can be accurately determined by using the vernier on the bench saddle. Calibration of the lens position against beam divergence or convergence is conveniently carried out by direct photographic recording of the beam cross section at two points with a measured separation along the optical bench. Positive-negative Polaroid film is used. The beam

diameters at the two positions can be accurately measured, by using a vernier microscope, and the divergence calculated. It is important to compare the diameters only of images which have had, as nearly as possible, equal exposures. As a result of the lower intensity towards the edge of the light beam, an overall attenuation of the beam will mean that the image diameter can appear to be less than that for the unattenuated beam at the same exposure.

**4.2.3 Sensitivity of detector system to changes in beam parameters** Preliminary tests have shown that a diffusing screen placed in front of the photocathode, with an internally silvered tube separating the screen from the photocathode, gives adequate photocurrent for a shot noise level in the region of 2 parts in  $10^4$ . The transverse movement of such a detector unit across a normally collimated beam produces an output signal variation of the form shown in figure 4.



**Figure 4** Variation of detector signal with beam displacement

This variation is essentially independent of the beam diameter, for diameters between 2 and 6 mm. The position of least sensitivity to transverse displacement is also the position of maximum signal. Hence, by tuning the detector position for maximum signal, it is possible to align the apparatus so that any beam shift caused by the sample insertion will have minimum effect. The effect is not linearly related to the magnitude of the shift, but at the maximum signal position a beam movement of 1 mm produces 0.1%, or less, change in signal. The detector unit is also sensitive to beam diameter changes, resulting in another possible source of systematic error. A change in beam diameter can be produced by the focusing effect of a sample intercepting a non-parallel beam. The change in focal length for paraxial rays of a non-collimated beam passing through a parallel-ended sample is  $(d - d/n)$ . A direct attempt to determine the effect of the  $(d - d/n)$  focal length change has been made by moving the detector assembly along the axis defined by the beam. After taking account of changes in background signal produced by moving the detector, there is no detectable change in signal introduced by the change in path length, provided the best collimated beam is used. Any possible signal change is below the noise level of the photomultiplier, i.e. it is much less than 0.1%.

**4.2.4 Sample alignment** The alignment of a parallel-ended sample with respect to a collimated beam can affect the detected signal in two significant ways:

(i) The presence of the sample can produce a lateral displacement of the beam if the angle of incidence at the first face is not normal.

(ii) The relative alignment of the beam and the sample end-faces determines the total transmitted energy as outlined in §2. The change in the magnitudes of the first and second reflections is negligible up to an angle of incidence of about  $6^\circ$ . The cavity effect, of which the third reflection is the most significant part, can give a theoretical error of about 2 in  $10^3$ .

The sample alignment procedure is in two parts: the second is a fine adjustment. The course alignment of each sample is carried out using a thin front-silvered piece of glass with an elliptically shaped hole in its centre. At an inclination of  $45^\circ$ , the mirror presents a circular aperture to the beam. The first and second reflections of the collimated beam at the sample surfaces are reflected by the mirror on to the cathode of an image converter. The image converter can be used over the whole wavelength range 500–1000 nm in order to check any possible variation in alignment with wavelength. No such variation has been detected. The orientation of the sample is altered until the two reflected images coincide with the aperture in the mirror as seen on the screen of the image converter. The fine adjustment is made by tuning the sample position to give maximum detected signal. This proves to be a very sensitive technique capable of detecting less than 5 minutes of arc misalignment of the 25 cm long sample from the position of normal incidence. The calculated beam shift produced by this misalignment is less than 0.2 mm and likely to produce no noticeable signal change. The sensitivity of the fine adjustment is much greater than can be accounted for by alignment of the third reflection in the sample. The maximum effect of the third reflection is likely to produce a signal change of less than 0.1% over the range of adjustments available on the sample mount. However, it is observed that little misalignment is required to produce a signal change of up to 0.5%. This high sensitivity can be explained by the formation of a secondary source around the pinhole as a result of light reflected from the sample end-faces being focused by the collimating lens. Since the beam is not perfectly collimated, the contribution due to the secondary source is likely to be different for the two samples and therefore a possible source of systematic error. To reduce such an error to an insignificant level, measurements were made with a neutral density filter (e.g. 20% transmission) located between the collimating lens and iris diaphragm. The secondary source contribution is then attenuated twice before passing through a sample. It is important to use good quality filters that produce as little scatter as possible. Photographic verification of the calculated beam shifts has been obtained by using the image of crosswires as reference points.

**4.2.5 Errors in the wavelength setting of the monochromator** Although the bandwidth of light from the monochromator is determined by the slit widths, it is also governed by the pinhole and the aperture in the collimating system. However, the bandwidth calculated from the slit widths can be taken as the upper limit. The selection of the slit width is partly governed by the quality of the beam shape required from a particular pinhole. The manufacturer's calibration figures have been checked conveniently and sufficiently accurately with the aid of a number of calibrated narrow-band interference filters. The wavelength drum was rotated in a consistent direction while the photodetector output was recorded as a function of the drum setting. The drum setting for the peak signal was taken to correspond to the centre of the passband of the filter.

## 5 Results and discussion of accuracy

Bulk loss measurements have been made on a number of different optical glasses in the wavelength range 500–1000 nm. The procedure adopted was to take the readings in

the following order: reference beam transmission, attenuated beam transmission with the short sample in position, reference beam transmission, attenuated beam transmission with the long sample in position, reference beam transmission. Each of these five signals was recorded on punched tape. Some 25 readings were taken for each position at the rate of about six readings per second. The total time for taking the five sets of readings was under 1 min. This time was sufficiently short to ensure that any variation in signal due to photomultiplier drift is insignificant (see Appendix). Regular checks were made on the readings due to the dark-current, but these were small enough to require no correction of the readings due to the light-beam.

Computer analysis of the results involved the detection and rejection of erroneous results, averaging and calculation of the standard error of the mean for each set, and calculation of the attenuation and reflection losses for the samples.

The measured variation of the absorption coefficient with wavelength is shown for a number of glasses in figure 5.

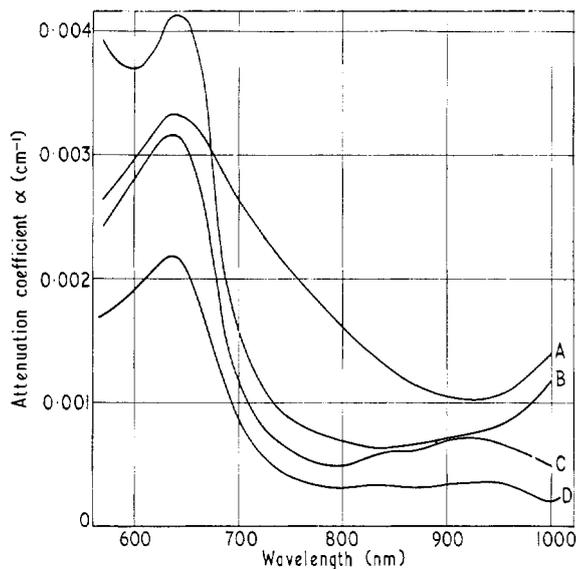


Figure 5 Variation of attenuation coefficients with wavelength

The samples were three different flint glasses (A, C, D) and a fluor-crown (B). The long and short samples of each glass differed in length by 20 cm. The wavelength resolution for these results is approximately  $\pm 10$  nm at the shorter wavelengths and  $\pm 20$  nm in the 1000 nm region. The intrinsic resolution of the instrument is 3 parts in  $10^4$  but this is reduced by systematic errors to a practical accuracy of 1 part in  $10^3$ . For high practical accuracy the systematic errors have to be assessed and controlled, as described in §4.2. The systematic error produced by the presence of dust on the end-faces of the samples can be large and errors of 2 parts in  $10^3$  have been produced by the presence of visible particles. The spectrophotometer is in fact housed in a clean-air tent to reduce the chances of significant dust collection on the samples. Any further reduction in the systematic errors will require more detailed studies.

Within the wavelength range 500–1000 nm, the main cause of optical absorption in glasses is the presence of relatively small amounts of transition metal ions (Bates 1962, Steele and Douglas 1965). The location and shape of absorption

bands due to a particular impurity ion depend on the chemical structure of the glass. As an example, it is known that ferrous ions give an absorption band centred at  $1.05 \mu\text{m}$  in silicate glasses and at 980 nm in borate glasses. Identification of particular bands is not always easy without prior knowledge of the chemical composition and production process of the glass.

The absorption coefficient  $\alpha$  at a particular wavelength is related to the molar concentration  $c$  of an absorbing ion by the equation  $\alpha = \epsilon c/lg e$  where  $\epsilon$  is the molar extinction coefficient due to the absorbing ion at the same wavelength. In the borate glasses, the molar extinction coefficient at the ferrous band peak is  $31 \text{ mole}^{-1} \text{ cm}^{-1}$ . Hence, a change of  $0.00005 \text{ cm}^{-1}$  in the absorption coefficient of a borate glass at 980 nm can be produced by a change of 0.15 p.p.m. in the concentration of ferrous ions.

## 6 Conclusions

The single-beam spectrophotometer described in this paper is capable of measuring the attenuation coefficient of suitably prepared samples with an accuracy to  $\pm 0.00005 \text{ cm}^{-1}$  over the wavelength range 400–1000 nm. The absorption length of the sample is 20 cm. The accuracy is limited by the basic stability of the light source and the detector and by the observation time. Increasing the observation time can reduce the errors due to random noise in the source and detector but only as long as the 'photomultiplier fatigue' effect is negligible. In practice, this means that the total time for a measurement is less than one minute and that the r.m.s. value of the random errors in an attenuation measurement (i.e. the intrinsic resolution) is  $\pm 3$  parts in  $10^4$ , or  $0.000015 \text{ cm}^{-1}$  for a 20 cm attenuation length.

Systematic errors are introduced into the measurements by the sensitivity of the detector to changes in the shape and position of the light beam which can be produced by the sample insertion. These errors have been minimized by careful preparation of the samples and their accurate alignment in a well collimated beam.

## Acknowledgements

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## Appendix

### Performance characteristics of the photomultiplier detectors

The photomultiplier output signal shows a time variation for constant illumination of the photocathode. The effect is shown in figure 6 for the EMI 9558 B tube. The signal reaches the most stable level after several hours and, in some instances, has been observed to start a slow increase after further illumination (e.g. 6 h after switch-on).

This signal 'fatigue' was observed by Keene (1963) who studied the effects of high cathode illumination which produced initial cathode currents greater than  $1 \mu\text{A cm}^{-2}$ . The illumination of the 9558B cathode used in the experiments produced cathode currents of less than  $10^{-3} \mu\text{A cm}^{-2}$  but a signal decrease of approximately 1% was observed after 5 h. It was not likely that this effect was due to heating of the last dynode since the anode current was always less than 1/40 of the stipulated maximum anode d.c. The cause was possibly a temperature-induced decrease in photocathode sensitivity.

The drift in signal level is not troublesome as long as a set of readings is taken sufficiently quickly and after the photomultiplier has been allowed to stabilize. Under such conditions the signal drift is not detectable above the noise for periods of less than two minutes.

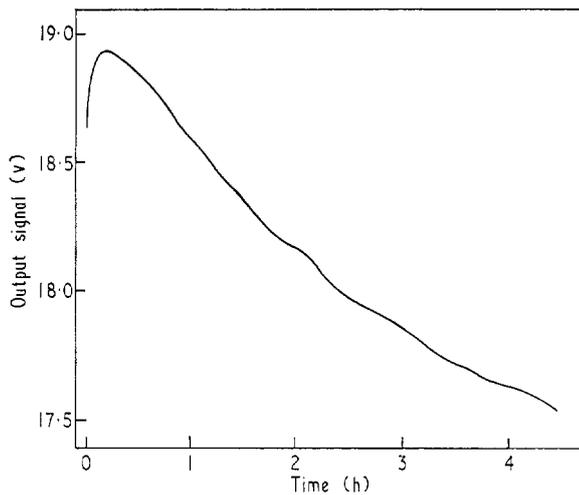


Figure 6 Drift of photomultiplier signal with time

The signal-to-noise ratio of a photomultiplier, calculated on shot noise basis, is given by

$$I_k \left\{ 2e(I_k + I_{0,k})\Delta\nu \left( \frac{\delta}{\delta - 1} \right) \right\}^{1/2}$$

where  $I_k$  is the photocurrent,  $I_{0,k}$  is the cathode dark current,  $\Delta\nu$  is the bandwidth of the measuring apparatus,  $e$  is the electronic charge and  $\delta$  is the average secondary-emission factor per stage. In this basic equation it is assumed that the dark current noise is 'white' i.e. frequency-independent. This is, in fact, not a generally valid assumption but the equation can be used for order of magnitude calculations, particularly in cases where  $I_{0,k} \ll I_k$ .

For the EMI 9558B, with SbCs dynodes, the relation for  $\delta$  is  $\delta = 0.2 V_s^{0.7}$  where  $V_s$  is the interdynode voltage. The overall gain of the tube is given by

$$G = \frac{\text{Overall sensitivity (A lm}^{-1}\text{)}}{\text{Cathode sensitivity (\mu A lm}^{-1}\text{)}}$$

The bandwidth of the detector circuit was obtained by using the equation  $\Delta\nu = 1/4RC$  where  $R$  and  $C$  are the measured values of output circuit resistance and capacitance. The measured values of  $R$  and  $C$  gave  $\Delta\nu \approx 0.5$  kHz.

By use of the above relationships and some typical observed values of anode current and dark current, the signal-to-noise ratio is calculated to be approximately  $2 \times 10^3$  for the 9558B. This agrees very well with the observed signal-to-noise ratio of approximately  $2 \times 10^3$ .

The other photomultiplier (RCA 7102) has an S1 cathode with a dark current considerably higher than that for a S20 cathode. Nevertheless, the ratio  $I_{0,k}/I_k$  is still small and the dark current is not the limiting factor in the signal-to-noise ratio.

To obtain the optimum performance from a particular photomultiplier used in spectrophotometric work, it is necessary to operate the tube under conditions which give the best signal-to-noise ratio and gain stability. The tube should have a high first-stage gain for best signal-to-noise ratio, and the anode current should be kept at or below 1/100 of the maximum value stated by the manufacturer for best stability and linearity. Loss of linearity due to space-charge effects is not a problem at low current levels.

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Appendix X