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V. DETERMINATION OF CONSTANTS etc. USED IN THE CALCULATION OF THE AMOUNT OF OZONE FROM SPECTROPHOTOMETER MEASUREMENTS AND AN ANALYSIS OF THE ACCURACY OF THE RESULTS

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(For Notation see Part III "Observers Handbook for the Ozone Spectrophotometer")

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1. INTRODUCTION

1.1 Object of this report.

The photoelectric spectrophotometer for measuring the amount of atmospheric ozone is described in detail, together with its method of use, in the "Observers Handbook"[1] /Annals of the IGY, 5, 46, 1957/ while the details of its adjustment and calibration are described in the "Adjustment & Calibration Manual",[2] /Annals of the IGY, 5, 90, 1957/. However given an instrument which has been properly adjusted and accurately calibrated (so that, for example, the instrument can be set exactly at the desired wavelengths and a table is available for converting dial readings to values of (Log I/I' + k) - where k is an unknown constant,) it is still not possible to obtain a measure of the ozone from readings on the sun, the clear sky or the cloudy sky, until certain constants have been determined and charts constructed. It is the purpose of this report to record exactly how these constants and charts are obtained and to assess the accuracy of the observations.

1.2 The 1957 Series of Observations at Oxford.

During the spring and early summer of 1957 in a period of good weather an extensive series of observations was made at Oxford, measurements being made on the A, B, C, and D wavelengths on both sun and clear zenith sky whenever possible, when μ was roughly equal to 3.0 and 2.0 in the morning and a little before noon and again a little after noon and when μ was roughly equal to 2.0 and 3.0 in the afternoon. When the zenith was not clear the measurements were made on the cloudy zenith sky. This series of observations was used to check the constants and charts previously made and is used here to illustrate these methods. It is hoped that those in charge of other instruments will be encouraged to make a similar analysis of their observations.

1.3. Procedure.

When determining these constants and constructing the charts it is necessary to proceed in a definite order. First, we calculate the value of $(\beta - \beta')$ for each pair of wavelengths using the work of Rayleigh and Cabannes[1], /Cabannes, J. 1929 La Diffusion Moleculaire de la Lumiere, p. 86, Paris./; next, using the tables prepared in the laboratory calibration, we determine the extra-terrestrial constant for each pair of wavelengths, i.e. the value of $(\log I/I' + k)$ which would be obtained if measurements could be made on sunlight outside the atmosphere. Thirdly, we must calculate the values of the ozone absorption coefficients for the selected wavelengths from laboratory data, allowing for the finite slit-widths used. Here the absorption coefficients given by Vigroux[2] have been adopted. (Annales de Physique 12 Serie, Tome 8, 1953).

In order to obtain the amount of ozone from measurements made on the clear zenith sky it is necessary to construct a chart or table relating the readings of the instrument to the amount of ozone as determined by direct sunlight for every height of the sun. When measurements are made on the cloudy zenith sky further charts are required and the construction of these is also described.

1.4. Accuracy of the measurements.

An attempt has been made to assess the standard error under normal working conditions of the measurement of the ozone as found from observations on sunlight, clear zenith sky light and cloudy zenith sky light. The effect of haze in the atmosphere is also considered.

2.0 MEASUREMENTS USING DIRECT SUNLIGHT.

2.1. Molecular scattering coefficients of Air.

The work of Rayleigh and Cabannes enables the scattering coefficients for an atmosphere containing only air molecules to be calculated with sufficient accuracy, the actual figures adopted being given in table 1 Observers' Handbook p. 47.

2.2. Calculation of the pathlength of sunlight through the ozone region.

The pathlength of sunlight through the ozone region (μ) for any zenith distance of the sun (Z) is of fundamental importance in calculating the amount of ozone and depends on the height of the ozone region above the surface. It is usually expressed as the ratio of the pathlength for a given value of Z to that when the sun is overhead (Z = 0, $\mu = 1.0$). Measurements of the vertical distribution of ozone in the atmosphere by the Götz "umkehr" method and from solar spectra taken from rockets and balloons indicate an average height of the ozone region of about 22 kms. and that height is used in this work. If h be the height of the ozone region above m.s.l. and R be the radius of the earth then

$$\sin \zeta = \sin Z \frac{R}{R+h}$$

where $\sec \zeta = \mu$. If later work should show that the value of 22 kms is not correct - as may well be the case in other parts of the world - then the value of μ will have to be altered accordingly. However, except when the sun is low, a small change in the adopted height makes little difference to the values of μ. When $\mu = 4.0$ a change of 4 kms in the height only makes a 1% change in μ. In all the measurements used in the present work μ was less than 4.0. No appreciable error in μ should therefore arise from variations in the vertical distribution of the ozone.

2.3. Extra-terrestrial Constant.

2.31 Method of Determination.

In order to be able to measure the amount of ozone from an observation made at a single time of the day it is necessary to know the "Extra-terrestrial Constant" for the instrument, i.e. the value of ($\log I_0/I_0' + k$) (or L_0) which would be found if observations could be made on sunlight outside the atmosphere and the dial reading (R) converted to the value of (L + k) by use of the wedge calibration table provided by the laboratory calibration. It is assumed that this value (L_o) remains sensibly constant from day to day though possible changes over a long period of time (e.g. any changes which might occur during a sunspot cycle) can be allowed for by measuring the value of the constant from time to time.

The only way in which this constant can be determined is by making measurements at two or more values of μ and extrapolating back to $\mu = 0$. This assumes that the amount of ozone and the haziness of the atmosphere remain constant during any one set of observations. (As a consequence a diurnal variation of the ozone which varies roughly as cos Z cannot be found.) Equation (2) of the Observers' Handbook i.e.

$$L = L_o - (\alpha - \alpha')\mu x - (\beta - \beta')m - (\delta - \delta')\sec Z$$

shows that if we plot L against μ we should obtain a nearly straight line, but since 'm' and Sec Z are also involved it will not be quite straight. We therefore eliminate 'm' by subtracting $(\beta - \beta')m$, since we know the value of $(\beta - \beta')$ accurately. We can only eliminate the Sec Z by making the observations at a place where the atmosphere is very clear and therefore $(\delta - \delta')$ is very small. Then, on plotting $[L + (\beta - \beta')m]$ against μ, we should obtain a straight line from which we should get an accurate value of L_o, if the amount of ozone remains constant. This last condition restricts the places where useful observations can be made to stations in low latitudes where the day-to-day changes in ozone are very small. In practice, owing to errors of observation, small real changes in the amount of ozone and possibly slight changes in haze, the observed points on the graph will not lie exactly on a straight line and the estimated best line through the points is used.

While the value of L_o may be obtained arithmetically from the observations, a graphical method is often convenient but the graphical extrapolation as described above requires a large sheet of accurate squared paper and very careful plotting since, if the errors of the calculation are to be small compared with the errors of observation the values of L must be plotted to 0.001 over a range of about 1.500, with similar accuracy for the values of μ. However, provided we have a rough estimate of the extra-terrestrial constant, a much easier method is possible. Let the assumed value of the extra-terrestrial constant be L_o^* while the true value is L_o and let $[(L_o^* - L) - (\beta - \beta')m]/\mu = P^*$. Then, if we plot P^* against μ we shall get a horizontal straight line if $L_o^* = L_o$ so that a very open scale of P^* can be used and no great accuracy in μ is required. If L_o^* be not equal to L_o, a curved line will be obtained from which the correction to L_o^x could be obtained. However if the error in L_o^x is S, then

$$P^* + S\left(\frac{1}{\mu}\right) = \left[(L_o - L) - (\beta - \beta')m\right]/\mu$$
$$= (\alpha - \alpha')x + (\delta - \delta')$$

= a constant, under the conditions assumed.

Therefore if P^* be plotted against $1/\mu$ the observed points should lie on a straight line, of which the slope is S; see fig. 2.31(a). It will be seen that the whole graphical extrapolation can be done on quite a small piece of square paper with no great accuracy of plotting

2.32. Observations for the determination of the value of L_o made at Oxford in 1957.

2.321. Calculation of L_o

During a period of good weather in the spring and summer of 1957 observations were made using the wavelength A, B, C and D on sunlight, as well as on the zenith skylight, whenever possible at $\mu = 3$ and $\mu = 2$ in the morning and an hour before and after noon, also when $\mu = 2$ and $\mu = 3$ during the afternoon. There were 31 half days when observations were possible at all three heights of the sun during the morning or the afternoon and these will be used to illustrate the method of finding the value of L_o.

In order to reduce errors due to changes in the ozone content during the course of any set of three observations, the upper air pressure maps were examined and those days when large changes in ozone might be expected were eliminated. Any day when there was a large change in ozone content between the day before it and the day after it was also omitted; nor were days of great haziness used. Unfortunately the conditions at Oxford were such that, after this selection, only 17 half days (a.m. or p.m.) remained for use in finding the value of L_o.

Plots of the value of P^* against $1/\mu$ for the A and D wavelength pairs and for the double pairs AD are shown in Figs. 2.321(a), 2.321(b) and 2.321(c) while Fig. 2.321(d) gives the mean results. Although the days used in these plots had been selected, as stated above, the results show great variability which makes it impossible to place much reliance on the value of L_o deduced from them. (Compare results at Mauna Loa § 2.33). The plots for the AD wavelengths, in which the effects of haze are largely eliminated, are noticeably less variable than those for the A wavelengths although they include the observational errors of the D wavelengths in addition to those of the A wavelengths. This indicates that changing haziness is a contributary cause of the variations. Those variations remaining in the AD plots are largely due to variations in the amount of ozone during the observations; this is indeed clear from the fact that variations in the 'D' wavelengths (which are less affected by ozone) are much smaller than those of the 'A' wavelength.

As stated in 2.31, we should expect that if atmospheric conditions remained constant during a set of measurements, then the three points plotted would lie on a straight line. This is clearly not the case and there is a systematic tendency for the low sun value to be below that expected from the other two observations. This holds for all wavelengths - though more marked for some than for others - and for both morning and evening observations. No instrumental cause has been found for this effect and it is difficult to suggest any reason for it other than a regular diurnal variation in the amount of ozone which does not vary as Cos Z (At Mauna Loa, § 2.33, a small effect of this sort is found but in the opposite direction).

The fact that the values of P^* for the three heights of the sun do not lie on a straight line makes it impossible to deduce a definite value of L_o. We have therefore taken the value of P^* for high sun and the mean of the other two points and used the line through these to deduce the value of L_o, which gives us the following values for the A wavelength

<u>Aλλ</u>

	(1)	(2)	(3)	Mean of (2) & (3)
$1/\mu$ =	0.835	0.525	0.310	0.417
P^* =	0.601	0.615	0.614	0.6145

Difference of $1/\mu$ = 0.835 - 0.417 = <u>0.418</u>

Difference of P^* = 0.601 - 0.6145 = - 0.0135

∴ Slope of line = - 0.0135/0.418 = - <u>0.032</u>

which indicates that the value of L_o^* used in the provisional table of R : N_A^* is too small by 0.032 and 0.032 must be added to all values to give 'N', so that N = L_o - L, the true difference between the observed value, 'L', at ground level and 'L_o' outside the atmosphere.

The corrections to L_o^* for the different wavelength pairs are given below together with similar corrections calculated for 14 half days which had been rejected in the above work as being liable to large variations in ozone or as being very hazy.

Corrections required to L_o^*

Wavelength	A	B	C	D
From 17 selected days	+0.032	+0.021	0	-0.003
From 14 other days	+0.013	-0.005	-0.012	-0.017

2.322. Accuracy of the value of L_o found from the Oxford observations

The table below shows the standard deviation of the differences between two adjacent values of P^* at the three sun heights for each set of a.m. or p.m. observations which have been used to obtain L_o. While the number of observations is too small to allow a statistical analysis to be of much value, some points stand out clearly and are of interest.

(1) All values of the standard deviation decrease regularly with wavelength from A to D wavelengths. This shows that at least a part of the standard deviation is due to real changes in ozone during the period of the three observations.

(2) In all cases the values for $1/\mu$ from 0.8 to 0.5 are less than those for $1/\mu$ from 0.8 to 0.3, showing that the differences increase with the length of time between the observations as would be expected whether the differences were due to changes in haze or ozone.

(3) It is found that the differences in P^{x} between the observations of a set of three, are very similar on all four wavelengths A, B, C and D. This would suggest that the differences are largely due to atmospheric changes and not random errors.

(4) It is found that $\sigma(\Delta P^{x}_{AD})$ is less than $\sigma(\Delta P^{x}_{A})$ but greater than $\sigma(\Delta P^{x}_{D})$. This would follow if changes in ozone were the chief cause of the variations.

Table

Standard Deviation of the difference between two adjacent values of P^{x} and estimated Standard Error of L_o

	$\sigma(\Delta P^{x})$		$\sigma(L_o)$	
$1/\mu$ =	0.8 to 0.5	0.8 to 0.3	0.8 to 0.5	0.8 to 0.3
A	0.011	0.014	0.032	0.028
B	0.009	0.010	0.030	0.020
C	0.007	0.008	0.020	0.016
D	0.006	0.006	0.018	0.012
AD	0.008	0.009		

(5) The general value of the standard error of a single determination of L_o may be taken as about 0.020 to 0.030 so that the

error of the mean of the 17 sets may be about ±0.010 or less. The difference in the values obtained for the 17 selected days and those for the 14 omitted days is about double this amount.

The analysis shows definitely that much of the error in L_o is due to changes in the atmosphere (whether in ozone or haze) during the course of a set of observations. Oxford has a most unsuitable atmosphere for this work.

2.33. Observations at Mauna Loa. (see also § 2.642)

By the courtesy of the United States Weather Bureau, we are able to show in Fig. 2.33(a) and 2.33(b) the results of measurements made at the Observatory at Mauna Loa (Hawaii) which can be used to find the value of L_o for the AD wave-lengths. These figures may be compared with Figs. 2.321 (c) and (d) which give the results at Oxford. The scales in all the figures are the same. It should be noted that the days chosen in the Mauna Loa results were these on which observations were made right through the day, both morning and afternoon and not morning or afternoon as had to be accepted at Oxford. Fig. 2.33 (a) shows the results of individual days in Feb. 1958 while Fig. 2.33 (b) gives the mean results for the different months, about twelve days being included in each monthly mean. The means for the whole 70 days are also given.

The regularity of the results from Mauna Loa compared with those at Oxford is striking and is clearly due to the constancy of the ozone and to the very clear atmosphere.

Mauna Loa appears to have an ideal climate for the determination of the value of L_o.

As in the case of the Oxford measurements the three points in a plot for Mauna Loa do not lie exactly on a straight line but the departure is much less than that at Oxford and is in the opposite direction. Using the mean noon value of P^* = 0.830 at $1/\mu$ = 0.91 and the average of the two results for lower sun, i.e. P^* = 0.846 at $1/\mu$ = 0.42, we find the slope of the line P^* against $1/\mu$ = 0.007 which is the correction to be applied to L_o^* of AD wavelength. The probable error of this value is very small. The fact that the three values of P^* do not lie on straight lines makes it difficult to say whether the observations indicate any change in the value of L_o during this period.

2.34. Constancy of the Extra-terrestrial Constant.

It is possible that the real value of the Extra-terrestrial constant may change with time, for example during the course of a sunspot cycle. It is therefore very desirable that frequent measurements should be made at some place with a suitable climate, e.g. at Mauna Loa. If there is any real change in L_o it will apply to all instruments and all values in the "R : N" tables of every instrument will need correction by a constant amount in N. Arrangements are necessary for informing all observatories if such a change does take place; it should also be agreed to make the necessary change for all instruments at the same time so that their results may be comparable.

Since the calibration of all instruments has so far been done in England where the atmospheric conditions for this work are poor, it is possible that the "R : N" tables sent out with the instruments may not be very accurate. At the present time, if there exist an instrument e.g. at Mauna Loa, for which there are accurate "R : N" tables (i.e. with accurate value of L_o) the only way in which this value can be transferred to another instrument is by bringing the two instruments together and taking simultaneous measurements on both. This is very inconvenient and expensive and there is danger of the calibration of the instrument changing during transit.

At first sight it would seem possible to take a set of three or more standard lamps and determine their mean values of N on the standardised instrument and then transfer the lamps to another instrument and adjust its "R : N" tables so that the mean reading of the lamps gave the same value of N on the second instrument. (The use of three or more lamps is to avoid possible changes in one lamp). In this way the set of lamps could go the round of all the instruments. Unfortunately, for some reason which has not yet been found, results differ slightly when two instruments are compared by means of the standard lamps and by sunlight. Thus all that we get through the medium of standard lamps is a rough approximate estimate of L_o, not an accurate value.

2.35. Errors due to Light scattered within the Instrument.

When taking observations for the determination of L_o it is desirable that they should extend over as great a range of μ as possible, but, as pointed out in § 4.14 of the "Observers' Handbook for the Ozone Spectrophotometer", when the sun is low the intensity of the shorter wavelengths of sunlight may be so small compared with that of the longer wavelengths that, in spite of the precautions taken in the design of the instrument, light of the longer wavelengths which is scattered by the optical surfaces may still cause serious errors. It is suggested in the Handbook that observations be made from time to time to see when this error becomes appreciable. For this purpose observations using the focussed image are continued until the sun is low. The ozone values are then calculated in the usual way and plotted against N or μ . The ozone values which should, of course, remain constant except for real changes with time, will be found to begin to decrease rather suddenly at some value of N or μ as the error becomes serious. It is important when taking observations for L_o that they are not continued until this error is appreciable. Fig. 1.35(a) shows two sets of measurements made to find the point at which this error begins. In the figure the ozone values calculated from the C wavelengths are plotted against N_C and the values of μ are also shown. It will be noted that while the error began to be serious when N_C was about 2.30 on the 3rd August, there was little error up to the last observations at N_C = 2.65 on the 4th February, this being due to different amounts of haze and ozone.

The figure also shows the errors produced if the ground quartz plate is used at low sun. (See Handbook § 4.12).

2.4. Absorption Coefficient of Ozone.

2.41. Calculation of absorption coefficients for the A, B, C and D Wavelengths.

Since the beginning of the International Geophysical Year (1st July 1957) the absorption coefficients of ozone measured in the laboratory by Vigroux have, by general agreement, been used at all stations. Previous to this the values given by Ny and Choong were used, the values of Ny and Choong being about 1.36 times greater than those of Vigroux. In calculating the appropriate values for use in this work it is necessary to allow for (1) the temperature of the ozone in the atmosphere and (2) the finite band-width of wavelengths passed by the monochromator. In fixing the absorption coefficients to be used it has been supposed that the ozone in the atmosphere was at a temperature of -44°C. Fortunately at these wavelengths a difference of 10°C does not make a serious difference to the values.

The equivalent widths of the relevant slits in A.U. of the monochromator are:-

S_1 = 9 A.U. S_2 = 9 A.U. S_3 = 30 A.U.

The weighting of the absorption coefficients for the different wavelengths is therefore that shown in the small diagrams of Fig. 2.41(a).

The published absorption coefficients relate only to the wavelengths having maximum and minimum absorptions and a smooth curve must be drawn through these values with the best judgment possible but such a curve leaves room for some uncertainty (this uncertainty is however much smaller than the differences that will be discussed in 2.42.) Figure 2.41(a) shows the absorption coefficients given by Vigroux and also those by Ny and Choong in the region of 3114.5 A.U. (the shorter wavelength of the 'C' pair). The Ny and Choong values have been divided by 1.36 to make them approximately equal to the Vigroux values. Owing to the absence of measurements by Vigroux between 3113 A.U. and 3130 A.U. some uncertainty exists in drawing the curve in this region, though the values of Ny and Choong are of some help. This particular wavelength is used to illustrate the method of finding the absorption coefficients because it presents the greatest difficulty, other wavelengths having less uncertainty.

Owing to the presence of Fraunhöfer lines the solar spectrum may not be uniform over the band of wavelengths passed by any slit and this may invalidate the weighting. A test to see if such an error could occur was made using the 'A' wavelengths which seemed to be the most likely to be affected in this way. A vessel with quartz windows and containing ozonised oxygen could be placed in front of the entrance slit of the instrument and the absorption by the ozone in the vessel was measured using alternately the zenith sky and a tungsten lamp as the source of light. As no difference in the measured absorption was found in the two cases it seems that non-uniformity of the solar spectrum causes no appreciable error.

2.42. Absorption Coefficients of the Ozone in the Atmosphere.

It has been shown that when using two pairs of wavelengths e.g. AD, the effect of haze is largely eliminated and an accurate value of $[(\alpha-\alpha')_A-(\alpha-\alpha')_D]x$ should be obtained from such an observation. Clearly if the absorption coefficients and the measurements are correct, the same value of x should be obtained whichever set of wavelengths is used, but this is not found to be the case. The mean values from a large number of measurements made for the determination of L_o gave the following results:-

Wavelength	AD	AC	BD
Ozone	0.345cm	0.375cm	0.331cm

Since observations in two different years and observations made at quite different values of μ all show the same differences and since any errors arising from the calibration of the instrument are likely to be quite small, it appears that they must be real and the only explanation seems to be that the absorption coefficients measured in the laboratory do not apply to the ozone in the atmosphere. We may look at the matter in a different way and calculate the value of $(\alpha - \alpha')_{AC}/(\alpha - \alpha')_{BD}$ from a set of observations when figures as those given in the table below are obtained.

Values of $(\alpha - \alpha')_{AC}/(\alpha - \alpha')_{BD}$

μ	Mean Value	Maximum	Minimum
≈ 3	1.196	1.241	1.154
≈ 2	1.204	1.246	1.155
≈ 1.2	1.196	1.238	1.147
All	1.187	1.246	1.147

The mean deviation, regardless of sign was 0.016. The laboratory value of $(\alpha - \alpha')_{AC}/(\alpha - \alpha')_{BD}$ is 1.056 and it is seen that even the lowest atmospheric ratio is much greater than the laboratory ratio.

These differences in the absorption coefficients would be accounted for if there were another gas in the atmosphere which had absorption bands in the region of the spectrum used in this work. Oxides of nitrogen are an obvious suggestion. Until we have further information all we can do is to use adjusted values of the absorptions coefficients for the B and C wavelengths which will make the average values of x equal for all wavelengths used.

The maximum and minimum ratios given in the table differ from the mean value by about $\pm 3\%$ and errors of this magnitude are unlikely to be exceeded in the values of ozone as found from the standard measurements. Further the AD wavelengths having the largest value of $(\alpha - \alpha')$ are likely to be the least affected. However a study of the absorptions of such gases as are likely to exist in the atmosphere is needed.

So far we have used only the results from a double pair of wavelengths thus eliminating the effect of haze. It is, however, desirable to fix the value of $(\alpha - \alpha')$ for one pair of wavelengths. This is much more difficult in a climate such as that of Oxford owing to the effect of haze. Assuming Sec Z = μ and $(\delta - \delta')_{AD} = 0$, we have

$$(\delta - \delta') = P_C - P_{AD}(\alpha - \alpha')_C/(\alpha - \alpha')_{AD}$$

and $$(\alpha - \alpha')_C = (\alpha - \alpha')_{AD}\ x[P_C - (\delta - \delta')]/P_{AD}$$

Thus, accepting, say the value of $(\alpha - \alpha')_{AD}$ we can determine either $(\delta - \delta')$ assuming $(\alpha - \alpha')_C$ or we can determine $(\alpha - \alpha')_C$ assuming $(\delta - \delta')$. What we have done is to calculate the value of $(\alpha - \alpha')_C$ which will make $(\delta - \delta')$ = zero on the clearest days since $(\delta - \delta')$ is not likely to be negative. We can thus arrive at a probable mean value of $(\delta - \delta')$ for all the days on which the observations were made, which can be used

Table illustrating adjustments to values of absorption coefficients that lead to consistent estimates of ozone from atmospheric observations.

Wavelengths	A	B	C	D	AD	AC	BD
$P-(\delta - \delta')$	0.615	0.404	0.280	0.124	0.491	0.335	0.280
Accepting Vigroux's values as published we get $(\alpha - \alpha')$	1.762	1.223	0.865	0.374	1.388	0.897	0.849
which give values of x	0.349	0.329	0.324	0.332	0.354	0.374	0.330
Accepting $(\alpha - \alpha')_A = 1.762$ we get $(\alpha - \alpha')$	1.762	1.158	0.800	0.357	1.405	0.961	0.801
which give values of x	0.349	0.349	0.350	0.347	0.349	0.349	0.350
Accepting Vigroux's $(\alpha - \alpha')$ for mean B & C we get $(\alpha - \alpha')$	1.849	1.215	0.840	0.375	1.474	1.009	0.840
which give values of x	0.333	0.332	0.334	0.331	0.332	0.332	0.333
Accepting $(\alpha - \alpha')_A - (\alpha - \alpha')_D$ from Vigroux we get $(\alpha - \alpha')$	1.741	1.144	0.791	0.353	1.388	0.950	0.791
which give values of x	0.353	0.353	0.354	0.351	0.354	0.353	0.354

with the mean results of the observations. The accompanying table gives at the top the mean value of P-(δ - δ') for a set of observations at Oxford, while the second line shows the absorption coefficients as given by Vigroux and the corresponding mean ozone values. The other lines show possible adjustments to the ozone absorption coefficients to make the values of ozone equal from all sets of wavelengths. We have actually used that in the last line, accepting the absorption for the AD wavelengths as that given by Vigroux. This work should be repeated in a clear climate where the effect of haze is negligible.

2.5. Accuracy of Direct Sun Observations of Ozone.

2.51. Accuracy of Reading.

Measurements using a constant weak artificial source of light show that the errors in reading the records made on the dial are given approximately by

$$\sigma_R = 0.1 \times \text{Trace width.}$$

Except for observations made on the 'A' wavelengths when μ is greater than about 3 and the atmosphere is hazy, trace widths for D.S. observations are usually less than 2° so that σ_R from this cause will be less than 0.2° (σ_N being less than 0.002). When μ is small, trace widths are of the order of 0.5° to 1.0°. Occasionally, in very hazy conditions and with low sun, the 'A' wavelength trace widths might be 5°. Dial readings are normally recorded to the nearest 0.1°.

In general for the 'AD' wavelengths, where the difference of two readings is involved, we may say that $\sigma(N_{AD})$ may be expected to be about 0.003 while occasionally going up to 0.005 in poor conditions.

2.52. Constancy of the Instrument.

The monthly routine tests with the 'Standard Lamps', made to check the constancy of the instrument, show (apart from steady drifts for which allowance is made) a variability of $\sigma(R) = 0.1^{o}$ i.e. $\sigma(N) = 0.001$. There is a strong tendency for values of the dial reading with the Standard Lamp on all four wavelengths to be high or low together at any one time. Whether this is due to a change in the standard Lamp or to real changes in the instrument, it is clear that values of N_{AD} will be little affected.

2.53. Atmospheric Conditions.

Using two pairs of wavelengths (e.g. A & D) any change in atmospheric conditions between the observations on the 'A' and 'D' wavelengths will cause an error in N_{AD}. It is the usual practice to make the measurements in the order, A, D, A to eliminate the effect of changing height of the sun and any regular changes in haziness. The change in the dial reading (R) to be expected between the two 'A' readings (made about one minute apart) due to change in the height of the sun is usually much less than 1^{o}, yet it is very seldom that the recorded change is not in the direction expected. When the sky is covered by patchy cloud observing is difficult and the errors may increase.

Summarising the above three sections, we may say that $\sigma(N_{AD})$ is not likely to exceed 0.005 and is usually less (possibly 0.003).

2.54. Observational Checks on Accuracy.

2.541. Oxford.

Fig. 2.541(a) is given to show the agreement between observations made with three different instruments at the same time. The observations were made during the calibration of instruments Nos. 15 and 18 to deduce their value of the extra-terrestrial constant by comparison with instrument No. 1 for which the value was already known. Since the dial reading (R) is only taken to the nearest 0.1° corresponding to about 0.001 in N, it is seen that the agreement is good. The steady increase in N with time is, of course, due to the decreasing value of μ.

Some 40 pairs of measurements are available where the two observations were made within about 20 minutes of each other using the same instrument. These show

$$\sigma\left[x_{AD}^{DS}(1) - x_{AD}^{DS}(2)\right] = 0.004\text{cm}$$

In another similar set of measurements were made in which the two observations of a pair were made on two different instruments and yet showed the same standard deviation. This would indicate that $\sigma(x^{DS}_{AD}) = 0.003$cms. The standard error in N_{AD} corresponding to a value of $\sigma(x^{DS}_{AD}) = 0.003$cm varies with μ and is

μ	1	2	3
$\sigma(N_{AD})$	0.004	0.008	0.013

When μ is small the value agrees with that expected from 2.53, but when the sun is low the observed error is greater than expected.

When we come later (§ 4) to consider the observed accuracy of observations made on the cloudy zenith sky we shall have to use pairs of observations made up to three hours apart. It will therefore be useful to have the corresponding $\sigma(x)$ figure for two D.S. observations also made three hours apart and this is found to be $\sigma\left[x^{DS}_{AD}(1) - x^{DS}_{AD}(2)\right] = 0.0055$cm compared with the value of 0.004cm for nearly simultaneous observations.

2.542. Results from Mauna Loa.

The Observatory at Mauna Loa, situated at a height of about 11,000 ft. in the Pacific high pressure area, has a climate which, for such work as the determination of the value of 'L_o', is probably unsurpassed at any other station where there are instruments for measuring atmospheric ozone by the spectroscopic method used in this work. Owing to its low latitude (20°N) and rather constant pressure conditions, the day-to-day changes in ozone are small while its altitude ensures a haze-free atmosphere. By the courtesy of the United States

Weather Bureau we have been supplied with the measurements made at this station.

The following discussions apply only to the measurements made with the 'AD' wavelengths using direct sunlight.

(1) The differences (irrespective of sign) between two observations of a pair made at intervals of one hour, four hours, nine hours, eleven hours, thirteen hours and fifteen hours are shown below. They include all observations made in the three months May, June and July 1958.

Average change (irrespective of sign) of measured ozone

Values of μ	Time Interval (t)	$\sqrt{t}$	Average difference in ozone
$\mu \simeq 2$ and $\mu \simeq 3$, a.m. or p.m. same day	1 hr.	1.0	0.0017 cm
$\mu \simeq 1$ and $\mu \simeq 2$ same day	4 hrs.	2.0	0.0028 "
$\mu \simeq 2$ and $\mu \simeq 2$ " "	9 hrs.	3.0	0.0038 "
$\mu \simeq 3$ and $\mu \simeq 3$ " "	11 hrs.	3.3	0.0041 "
$\mu \simeq 3$ (p.m.) and $\mu \simeq 3$ (a.m. next day)	13 hrs.	3.6	0.0043 "
$\mu \simeq 2$ (p.m.) and $\mu \simeq 2$ (a.m. next day)	15 hrs.	3.9	0.0045 "

The difference in ozone value from observations made one hour apart are remarkably small although the values of μ, and therefore the dial readings of the instrument, were quite different at the times of the two observations of a pair.

(2) The average value of the ozone measured at the same value of μ for morning and afternoon observations are almost identi-

cal indicating that there is no appreciable diurnal variation in ozone which is asymetrical about noon. (This result does not, of course, depend on an accurate knowledge of the value of L_o). The significance of the slightly higher value of the measured ozone at $\mu = 3$ has not yet been determined.

(3) If the average difference between two observations of ozone (irrespective of sign) made t hours apart is plotted against the square-root of t the points lie nearly on a straight line. This, of course, is what would be expected if the changes in ozone with time were random. If it is justifiable to extrapolate this line back to zero time interval we obtain the very small value of 0.001 cm for the difference between two observations made nearly at the same time. This would indicate errors in N_{AD} at the different values of μ of the order of

μ	1	2	3
N_{AD}	0.001	0.0015	0.0025

2.6. Atmospheric Haze.

2.61. Discussion of Methods of Measurement.

The haziness of the atmosphere can be measured with the ozone spectrophotometer in two different ways. In the first method, using observations with direct sunlight, we find the value of $(\delta - \delta')$ which will make $x^{DS}_{D} = x^{DS}_{AD}$ (and similarly for any other two pairs of wavelengths) using equations (4) and

(5) (see Observers' Handbook, page 48). In the second method we use observations on the zenith sky and find the difference $\Delta N_{C'}^{ZB}$ between the observed value of $N_{C'}^{ZB}$ and the value of the same quantity which had been measured on very clear days with the same height of sun and the same ozone value. (On very clear days the value of $\Delta N_{C'}^{ZB}$ is therefore zero). This value is similar to the "cloud correction" discussed in § 4.2 except that haze takes the place of cloud.

When designing the spectrophotometer we wished to make the effect of haze on the measurement of ozone by direct sunlight small and with this object the wavelengths passing slits S_2 and S_3 (see Observers' Handbook, page 51) were kept as close together as possible while maintaining a sufficiently large difference in the absorption coefficients of ozone $(\alpha - \alpha')$. Hence the instrument cannot be expected to give accurate values of $(\delta - \delta')$. On the other hand it was desired to measure the effect of cloud as accurately as possible and slits S_3 and S_4 were fixed approximately 1000 AU apart. The value of $\Delta N_{C'}^{ZB}$ should therefore give a good measure of the 'whiteness' of the sky.

It will be clear that these two methods of measuring haze do not measure quite the same thing. $(\delta - \delta')$ depends only on the differential scattering of the two wavelengths involved and is thus a measure of those particles in the atmosphere whose size is comparable to the wavelength of light; large particles, which scatter all wavelengths equally, will have no effect as is seen in the case of observations taken through thin cirrus cloud. The value of $\Delta N_{C'}^{z\theta}$ depends on the amount of sunlight added to the zenith blue sky light through scattering by all particles which are not so small that they scatter in the same way as pure air.

2.62. Measurement of Haze by Observation on Direct Sunlight.

In principle, having fixed the constants discussed above (§ 2.1 to 2.4), we can obtain an estimate of $(\delta - \delta')$ from observations with any two pairs of wavelengths for which we can assume that the values of $(\delta - \delta')$ are equal. For the A and D wavelengths, for example, we have

$$x_{D}^{DS} = P_D/(\alpha - \alpha')_D - (\delta - \delta')_D/(\alpha - \alpha')_D$$

$$\text{and} \quad x_{AD}^{DS} = P_{AD}/(\alpha - \alpha')_{AD} - (\delta - \delta')_{AD}/(\alpha - \alpha')_{AD}$$

$$\text{or } (\delta - \delta')_D = P_D - P_{AD} \times (\alpha - \alpha')_A/(\alpha - \alpha')_{AD},$$

$$\text{if } (\delta - \delta')_{AD} = 0.$$

If we put in the values of $(\alpha - \alpha')$ found suitable for atmospheric ozone we have $(\delta - \delta')_{D-AD} = P_D - 0.254\, P_{AD}$.

$$(\delta - \delta')_{C-AC} = P_C - 0.833\, P_{AC}$$

$$(\delta - \delta')_{D-BD} = P_D - 0.440\, P_{BD}$$

$$(\delta - \delta')_{D-CD} = P_D - 0.806\, P_{CD}$$

However, as stated above, it is not to be expected that very accurate values for $(\delta - \delta')$ will be obtained. In § 2.541 it was shown that the standard error in N_{AD}/μ was about 0.004. This error would lead to a standard error in (δ - δ') of about 0.005. In Fig. 2.63(a) values of (δ - δ') as obtained from the A and C wavelengths are plotted against the value from the B and D wavelengths measured at the same time. The scatter of the points is about what we should expect.

2.63. Measurements of Haze by Measurements on the Zenith Sky.

As stated above, the chief effect of haze on the value of $\Delta N_{C'}^{zb}$ will be the scattering into the instrument of light of approximately the spectral composition of sunlight in addition to the normal, bluer, zenith light. Clearly particles which are large compared to the wavelength of light will produce an effect. A hazy day on which the haze is composed of large particles (e.g. a winter day with high relative humidity) will give a large value of $\Delta N_{C'}^{zb}$ but may have a small value of (δ - δ'). On the other hand with low relative humidity the haze particles will probably be of all sizes and we may expect some relation between $\Delta N_{C'}^{zb}$ and (δ - δ'). Fig. 2.63(b) shows the relation actually found at Oxford and also the relation with the estimated visual haziness.

3.0. Observations on the Zenith Blue Sky.

3.1. Construction of the chart for the zenith blue sky.

The total amount of ozone cannot be obtained directly from observations on the light from the zenith blue sky unless the vertical distribution of the ozone be known (and even then there is great difficulty in making the calculations) but it is possible to make an empirical chart (charts I_C and I_{AD} of Handbook) using nearly simultaneous observations with the AD wavelengths on the direct sun and with the AD or C wavelengths on the zenith blue sky. Such charts may be made with N_{AD}^{ZB} or N_C^{ZB} as ordinate and with μ as abscissa when lines of equal ozone run roughly diagonally across the chart. It is rather more convenient to use N_{AD}^{ZB}/μ or N_C^{ZB}/μ as ordinate since the lines of equal ozone are then roughly horizontal and a more open ordinate scale can be used since the range is smaller. Figs. 3.1(a) and 3.1(b) show such charts (drawn on a reduced scale) for the AD and C wavelengths. As days with an amount of ozone well above, or well below, the average are few, there is always difficulty in drawing the lines for very high or very low ozone values. Extrapolation from the more frequent values is easier when using N/μ rather than N as ordinate.

On a simple theory which neglects the effects of multiple scattered light, the separation of the lines of equal values of x at $\mu = 1$ should be equal to $(\alpha - \alpha')_{AD}$ or $(\alpha - \alpha')_C$. In the case of the AD chart this appears to be the case. In the case of the C wavelength chart the separation for a difference of x = 1.00 c.m. is 0.98 compared with the value of $(\alpha - \alpha')_C$ from Vigroux's work of 0.865 or the value suggested in § 2.42 of 0.791. Presumably the larger value observed for the C wavelengths is due to multiple scattering but it is not known why the AD wavelengths do not show a similar increased value. Possibly the range of ozone on the days of observations was too small.

The values of $N^{ZB} - N^{DS}$ may vary from instrument to instrument since this difference involves the scattering by the G.Q.P.s and these are not quite neutral and differ slightly from one to another. The effect will be small in the case of the AD. wavelengths since both wavelengths will generally be affected nearly equally, but the C wavelength chart for one instrument may not quite suit another instrument for this reason.

In the case of the AD wavelengths, if we plot the value of $\left[N^{ZB}_{AD}/\mu - N^{DS}_{AD}/\mu\right]$ for nearly all simultaneous observations against the value of μ, it is found that all the points lie on a narrow band (see Fig. 4.11(a)) and are almost independent of the ozone value for values of μ less than about 2.2. (It is convenient to plot N/μ rather than N since the former changes little with μ and it is not necessary to correct the observations of a pair for small differences in μ.) Since we can calculate the value of N^{DS}_{AD}/μ for any value of x this relation allows us to calculate any value of N^{ZB}_{AD}/μ when the sun is fairly high. This is very useful when constructing the zenith chart for the AD wavelengths (see fig. 4.11(a)). It is not found worth while to extend the zenith chart for AD wavelengths beyond $\mu = 2.2$ since the results are variable, presumably because differences in the vertical distribution of the ozone begin to affect the values.

3.2. Observations on the zenith blue sky with the 'AD' wavelengths.

3.21. Haze effect.

It has been shown in § 2.0 that observations using two pairs of wavelengths (e.g. AD.), have a great advantage over those using one pair of wavelengths (e.g. A or C) since, while the latter are seriously affected by the haziness of the atmosphere, the values from the double pair of wavelengths are almost unaffected. In the case of the zenith sky the effect of scattering by the large particles of haze will be to add an amount of light, which is nearly of the spectral composition of sunlight, to the light from the clear blue zenith sky, i.e. light from a hazy zenith sky will have more long wavelengths relatively to short wavelengths and the deduced ozone value will be too great (see Fig. 3.31(b)). When a double pair of wavelengths is used the effect of haze will be similar on each pair and the difference of the two values will be but little affected. A plot for the AD wavelengths similar to 3.31(b) indicates a small effect when the sun is high, but little effect when μ exceeds about 1.5.

3.22. Accuracy of measurement of x_{AD}^{ZB}

The value of x_{AD}^{DS} is the most accurate estimate that we have of the value of x and we may obtain an indication of the errors of x_{AD}^{ZB} by comparing them with the values of x_{AD}^{DS} made nearly at the same time. Such a comparison indicates that

$$\sigma\left[x_{AD}^{ZB} - x_{AD}^{DS}\right] \approx 0.005 \text{ cm.}$$

If $\sigma\left(x_{AD}^{DS}\right) = 0.003$ cm (see § 2.4) then $\sigma\left(x_{AD}^{ZB}\right) = 0.004$ cm. A value of $\sigma\left(x_{AD}^{ZB}\right) = 0.004$ cm corresponds to a value of $\sigma\left(N_{AD}^{ZB}\right)$ at different values of μ :-

μ =	1	2	3
$\sigma\left(N_{AD}^{ZB}\right)$ =	0.006	0.010	0.010

which are very similar to the corresponding values given in § 2.4 for observations using direct sunlight.

3.3. Observations on the zenith blue sky using the 'C' and C' wavelengths.

3.31. Effect of Haze.

As mentioned in 3.21 the value of N_C^{ZB} is much influenced by haziness of the zenith sky. Three possible measures of this haziness are available:-

a. Measurements of $(\delta - \delta')$ from nearly simultaneous D.S. observations.

b. The value of N_C' as compared with the same value on very clear days.

c. Visual estimates of the haziness - whiteness of the sky or visibility.

The most convenient measure of the haziness is obtained from the value of $N_{C'}^{ZB}$ (as used in the "cloud correction", - see section 4). Apart from a small effect depending on the value of the total ozone which is easily allowed for, the value of this quantity should be the same on all good clear days; the difference between the value on any given day and that on very clear days will be a measure of the haziness on that day. Fig. 3.31(b) shows how the error in x_C^{ZB} depends on the haze as measured in this way. Clearly a correction depending on the observed value of N_C^{ZB}, (equivalent to a "cloud correction" - see section 4) should be used to correct for haze. In the earlier work when X_C^{DS} was used as the most reliable value of the ozone, this error was overlooked since haze causes an almost similar error in x_C^{DS} (see section 2).

3.32. Accuracy of measurement of $x_{CC'}^{ZB}$

As in § 3.22 we can get an estimate of the errors of $x_{CC'}^{ZB}$ by comparing pairs of observations ($X_{CC'}^{ZB} - X_{AD}^{DS}$) made nearly at the same time. If the ZB observations are corrected for the haziness of the sky as described in § 3.31 then we find $\sigma\left[X_{CC'}^{ZB} - X_{AD}^{DS}\right] \simeq 0.006$ cm. indicating a standard error $\sigma\left(X_{CC'}^{ZB}\right) \simeq 0.005$ or almost the same as that for corresponding measurements using the AD wavelengths. It seems, however, definitely larger than the figure for $\sigma\left(X_{AD}^{DS}\right)$ (0.003 cm.)

4.0. Observations on the Cloudy Zenith Sky.

4.1. Measurements using the light from the Cloudy Zenith Sky and the 'A' and 'D' Wavelengths.

4.11. Principle of the Method.

The top of a cloud will be illuminated by (a) direct sunlight and (b) scattered light from the whole hemisphere of sky; the light which leaves the bottom surface of the cloud will be a mixture of (a) and (b) and there seems no reason to expect any differential absorption of any wavelength within the cloud, while, since the scattering is by relatively large cloud droplets, it may be expected to be the same for all the wavelengths. Since sources (a) and (b) have different spectral distributions and we do not know the proportions of light from (a) and (b) emerging from the lower surface of any cloud, we cannot in general use this light to obtain a measurement of the ozone.

However it is observed that, when the sun is not too low, the value of N_{AD} is very similar for the two sources (a) and (b) above; see Fig. 4.11(a). Strictly the values of N_{AD}^{ZB} shown in this figure should be the values obtained with the ground quartz plate in position, (since it is in position for observations on the direct sun) and using the light from the whole hemisphere of clear blue sky. However a direct comparison of the values of N_{AD}^{ZB} with simultaneous values using the hemisphere sky with ground quartz plate showed the difference to be small when μ is less than 2 and the hemisphere value of N_{AD} to be rather the greater, i.e. nearer the value for sunlight, when μ is greater than 2. In the special case when these two values are equal the value of N_{AD} as measured on light emerging from the lower surface of the cloud will be independent of the relative proportions of sunlight and sky light in it and we can use such measurements on the cloudy zenith sky as if they had been made on the clear blue sky. (It is found better to refer such measurements to the zenith sky rather than to direct sunlight). In practice the method is found to work reasonably well provided μ is not greater than about 2.5.

We may simulate the effect of a cloud by placing a ground quartz plate above the entrance slit of the instrument and exposing it fully to the light of the sun and sky. Such a test was made on a cloudless day as μ gradually increased. The result showed that the values of N_{AD} for the clear zenith sky and for the artificial 'cloud' were within 0.010 so long as the sun was fairly high.

Figure 4.11(b) shows how similar are the changes in N_A and N_D caused by cloud. In this case simultaneous observations were made on the zenith sky using two instruments, one set for the A wavelengths and the other for the D wavelengths. Values of N_A and N_D are plotted as ordinate with time as abscissa during a period when the zenith was partly clear and partly cloudy. The figure is drawn so that the values of N_A and N_D are equal for the clear blue periods. The two observations (the 5th and the last) when the values of N_A and N_D do not agree were taken when the cloud had rapidly changed and it is probable that the two instruments did not look at exactly the same part of the sky.

In Fig. 4.11(c) is seen the effect of cloud on the Zenith values of N_A, N_D and N_{AD}, two direct sun observations also being obtained. On this day a belt of rain lasting for some two hours cleared off about 10.50 with clearing skies and was followed later by a small cumulus shower. The first observations were taken on the cloudy zenith sky when the rear part of the cloud of the rain belt was overhead. Shortly after this a measurement with direct sunlight was obtained followed by an observation on the nearly clear zenith sky (only a little thin cirrus being present). Later as the small cumulus passed overhead, observations were taken continuously until rain began. Finally another observation was possible with direct sunlight though the zenith did not clear enough to allow a second measurement on the clear blue zenith sky. (In the figure the values of N/μ are plotted rather than N since N/μ is nearly independent of μ for both the sun and zenith measurements).

The following points are worth noting:-

(1) Cloud at 10.45 gave a value of N_{AD}^{ZC} identical with the later blue sky value of N_{AD}^{ZB}.

(2) At the beginning and at the end of the cumulus shower the values of N_{AD}^{ZC} were similar to the values of N_{AD}^{ZB}, but when the darkest part of the cloud was passing over and just before the rain, the value of N_{AD}^{ZC} increased by about 0.020 which would correspond to an increase in ozone of about 0.013 cms. This is an example of the "Cumulus Effect" discussed in § 4.3. The value of N for the 'A' wavelengths is affected by the cumulus cloud more than that of the 'D' wavelengths, which would happen

if there were a real increase of ozone within the cloud.

4.12. Accuracy of Zenith Cloud measurements by the 'AD' wavelengths.

We may estimate the accuracy of measurements made by use of light from the cloudy zenith sky by comparing these values with the values obtained when using sunlight as in § 3, but the time between two observations of a pair is of necessity much longer than when comparing zenith blue sky and direct sunlight measurements and will usually be about three hours. During these three hours real changes will have occurred so that not all the difference will be due to errors of measurement. The standard deviation for two measurements using sunlight and made three hours apart was found to be 0.005_5 cm. and this figure should be kept in mind when considering the accuracy of cloud observations.

Comparison of pairs of observations shows that for observations taken within three hours

$$\sigma\left[X_{AD}^{ZC} - X_{AD}^{DS}\right] \simeq 0.010 \text{ cm.}$$

so that for the standard error of an observation in the cloudy sky $\sigma\left(X_{AD}^{ZC}\right) \simeq 0.008_5$ cm.

This is about twice the figure for observations on the zenith blue sky. The greater inaccuracy of the cloud observations may be due to the following:-

(a) Ideally the observations on the 'A' and 'D' wavelengths should be made at the same time on the same piece of cloud.

This is not practicable and observations are actually made in the order A, D, A, D, A. Such a series occupies about two minutes. Care is taken to choose as uniform a piece of cloud as possible but appreciable variations not infrequently occur. An idea of the variability with typical stratocumulus cloud can be obtained from Fig. 4.12(a). In this case observations on the 'A' and 'D' wavelengths lasting about 25 seconds each were made alternately. The ozone values shown at the bottom of the figure were calculated from the mean of two values of N_A and the intermediate value of N_D. It is recommended that at least three measurements be made on the 'A' wavelength and two on the 'D' wavelength. This will clearly reduce the variability of the calculated ozone value. Some improvement may be made by taking still more observations but with increasing length of time the variability of the cloud will increase also. This variability undoubtedly causes a substantial part of the error of measurements using the cloudy sky.

(b) A further cause of inaccuracy may be that there is some real differential absorption of the wavelengths within the cloud. There is no information on this point.

(c) A small correction would be expected for those observations which are made at times other than when μ is about 1.65 (see § 4.11).

(d) The "Cumulus Effect" for which see below (§ 4.3).

4.2. Measurements using the light from the cloudy zenith sky, with the C and C' wavelengths.

4.21. Principle of the Method.

The light received by the instrument from the cloudy zenith sky will be a mixture of sunlight and sky-light and there is no reason to expect that within the cloud there will be any different absorption or scattering of one wavelength of a pair relative to the other. If it were possible to measure the relative proportions of sunlight and of sky-light received by the instrument we could correct the actual observation to what it would have been if only sunlight or only sky-light had been received. This can be done approximately if observations are made on another pair of wavelengths which are not absorbed by ozone. In practice the C and C' pairs of wavelengths are used (the small absorption of the C' wavelength - 3323 A.U. - is easily allowed for). We know $N_{C'}$ for both sunlight and sky-light from observations on clear, cloudless days, since the value at any given zenith distance of the sun will always be the same. The observed value of $N_{C'}$ on the cloudy sky will then allow us to find the proportion of sunlight and sky-light in these wavelengths reaching the instrument. It is reasonable to assume that the same proportion will also hold for the C wavelengths.

In practice a more empirical method is used; on days with some cloud and some clear blue sky, observations on the

C and C' pairs of wavelengths are made as patches of cloud and patches of blue sky pass across the zenith. If the observed differences between the blue sky and cloudy sky values are ΔN_C and $\Delta N_{C'}$ we find on plotting ΔN_C against $\Delta N_{C'}$ that the points cluster round a line for any given value of μ.

Figure 4.21(a) shows a set of observations which were made, first on the clear blue sky and later on the cloudy sky. The differences X and X' show the changes in N_C and $N_{C'}$ caused by the earlier part of the cloud while the changes due to the later part of the cloud, when there was slight drizzle, are shown by Y and Y'.

Figure 4.21(b) shows the results of a number of observations which were made with the object of constructing the "cloud correction" curves. Each point represents differences such as X and X' or Y and Y'. From many sets of observations such as these, "cloud correction" curves have been constructed for different types of cloud and different values of μ.

It will be noted that at YY' there was slight drizzle and also that the "cloud correction" given by YY' is greater than that given by XX'. This is frequently found in the case of very dark cloud and particularly when there is rain or drizzle and shows that no unique 'cloud correction' can ever be obtained.

The corrections to N_C are generally between 0.02 and 0.06

so that the whole correction corresponds (for average values of μ and x) to between 0.010 cm. and 0.025 cm. of ozone. The average error involved in the correction is probably not more than a fifth of this amount corresponding to errors in ozone of between 0.002 cm. and 0.005 cm.

4.22. Accuracy of measurements using the C and C' wavelengths and the Cloudy Zenith Sky.

A comparison similar to that given in § 4.12 between pairs of observations, one made on the A & D wavelengths using direct sunlight and the other on the C & C' wavelengths using the cloudy zenith sky, the two observations of a pair being made within about three hours, gives a value

$$\sigma (X^{ZC}_{CC'} - X^{DS}_{AD}) = 0.010 \text{ cm.}$$

Taking the standard deviation of two observations using the AD wavelengths and direct sunlight made within three hours of each other as 0.005_5 cm. (see § 2.65) we can estimate the standard error of one cloud measurement as 0.008_5 cm. ozone.

The following are probably the chief causes of error in the measurements on the cloudy zenith sky using the C & C' wavelengths:-

(a) The method assumes that the measurements on the C and C' wavelengths are made on the same cloud which, in fact, is not possible when using only one instrument and the best that can be done is to make a series of measurements on the C and C' wavelengths alternately, and to choose a time for the observation when the cloud is as uniform as possible. The conditions vary very greatly with the type of cloud and in many cases with, say, uniform alto-stratus cloud very good results can be obtained. On the other hand it may be almost impossible to take observations which are worth anything when alto-cumulus cloud with clear blue patches covers the sky. Figure 4.22(a) shows two typical series of observations on different types of cloud. It is usual to take at least three observations on the C wavelengths alternated with two observations on the C' wavelengths but, if time can be spared, there is an advantage in increasing the number.

(b) There is no doubt that the idea of using a "cloud correction" to correct an observation using the C wavelengths on the cloudy sky to the value it would have had if the sky had been clear, can only be realised very approximately and different individual clouds under different conditions (particularly if there are more than one cloud layer present) may require different corrections. The values used are those which seem to fit best the average clouds.

(c) The "Cumulus Effect" (see § 4.3).

4.3. The "Cumulus Effect".

It has always been found that if observations are made on the cloudy sky when a thunderstorm or a big cumulonimbus cloud is overhead (see Bakerian Lecture Proc. Roy. Soc. A Vol. 185, p. 165, 1946) the amount of ozone whether found by the AD or the CC' method is much greater than that from adjacent measurements with direct sunlight or on the clear zenith sky. In the case of thunderstorms the increase may be very large, up to 0.200 cm. or more, but the effect is also often shown by quite small cumulus clouds to a much smaller extent - of the order of 0.020 cm.

It has never been possible to find the cause of this apparent increase in the ozone or whether there is really a large concentration of ozone within the clouds. Attempts have been made to detect an increased concentration within the cloud by making direct sun observations when the sun was seen through dissolving false cirrus from a large cumulonimbus cloud, but only in one case was any increase found and this may not have been really connected with the presence of the cloud. While ozone might well be formed in thunderstorms, it is surprising that electrical potentials should be great enough in small cumulus clouds.

The increase in N_{AD}^{ZC} shown in Fig. 4.11(c) just before the rain occurred when a small cumulus was passing overhead would amount to about 0.010 cm. of ozone and is typical of the effect in small cumulus. It will be seen from the figure that the 'A' wavelengths are much more affected than the 'D' wavelengths as would be the case if there were really a concentration of ozone within the cloud. The apparent increase in ozone in cumulus clouds is roughly the same whether the CC' or the AD wavelengths are used.

For synoptic and climatological purposes it is generally the stratospheric ozone which is of interest and any local effects should be avoided. In the case of isolated cumulus and cumulonimbus this is easy but cumulus are often embedded in layer clouds such as stratocumulus when the only indications of their presence overhead may be that the cloud is very dark. It is therefore general practice to avoid any dark cloud when making the observations and particularly any cloud from which rain is falling, since abnormally high values may be expected in these conditions.

4.4. Comparison of cloudy zenith measurements with AD and CC' wavelengths.

A comparison of pairs of ozone values deduced from measurements on the cloudy zenith sky with the AD and CC' wavelengths made nearly at the same time gives a value of $\sigma(X^{ZC}_{AD} - X^{ZC}_{CC'})$ = 0.007 cm. This is only half the value which would be deduced from the standard error (0.010 cm) of the ozone values deduced from either the AD or the CC' wavelengths above, on the assumption (a) that the observations are "independent" and (b) that the value of 0.010 cm. is not unduly increased by the interval of time (some three hours) between the observations of a pair which were compared. It is difficult to estimate the relative importance of these two effects, but certainly at times, the "Cumulus effect" will be responsible for raising the ozone value deduced from both pairs of wavelengths.

LIST OF DIAGRAMS

ERRATA to DIAGRAMS

2.31(a) For $(L - L_o^*)$ read $(L_o^* - L)$

2.321(a), (b), (c), (d) For "P" read "P^*"

2.33(a), (b), For "P" read "P^*"

2.35(a) In caption, after "errors" add "due".

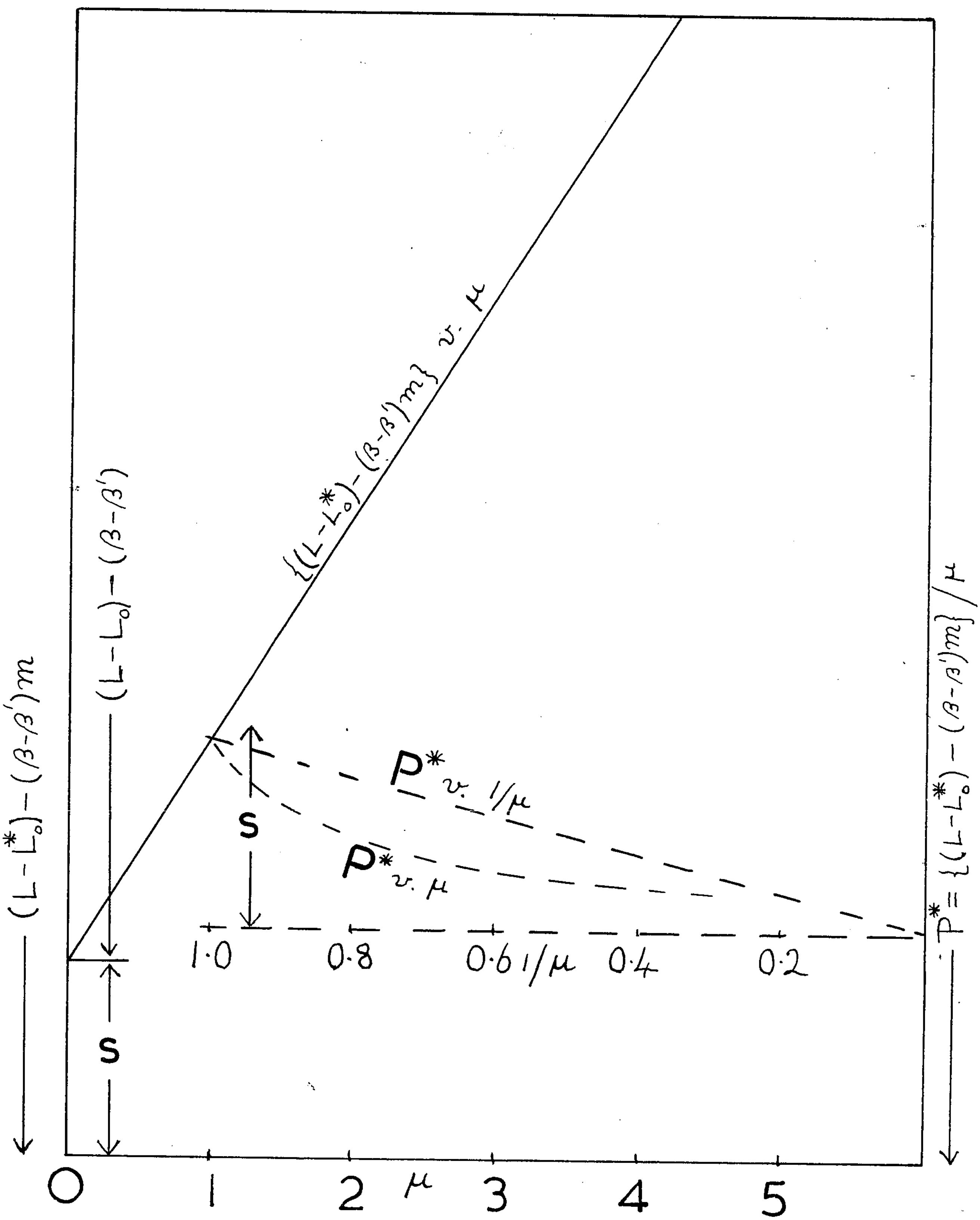

{(L-L*₀)-(β-β')m} v. μ
(L-L₀)-(β-β')
(L-L*₀)-(β-β')m
S
S
P* v. 1/μ
P* v. μ
1·0
0·8
0·6 1/μ
0·4
0·2
P* = {(L-L*₀)-(β-β')m}/μ
O
1
2
μ
3
4
5

Fig. 2·31 (a)

PLOT OF PA AGAINST 1/μ FOR CALCULATION OF L₀. OXFORD 1957

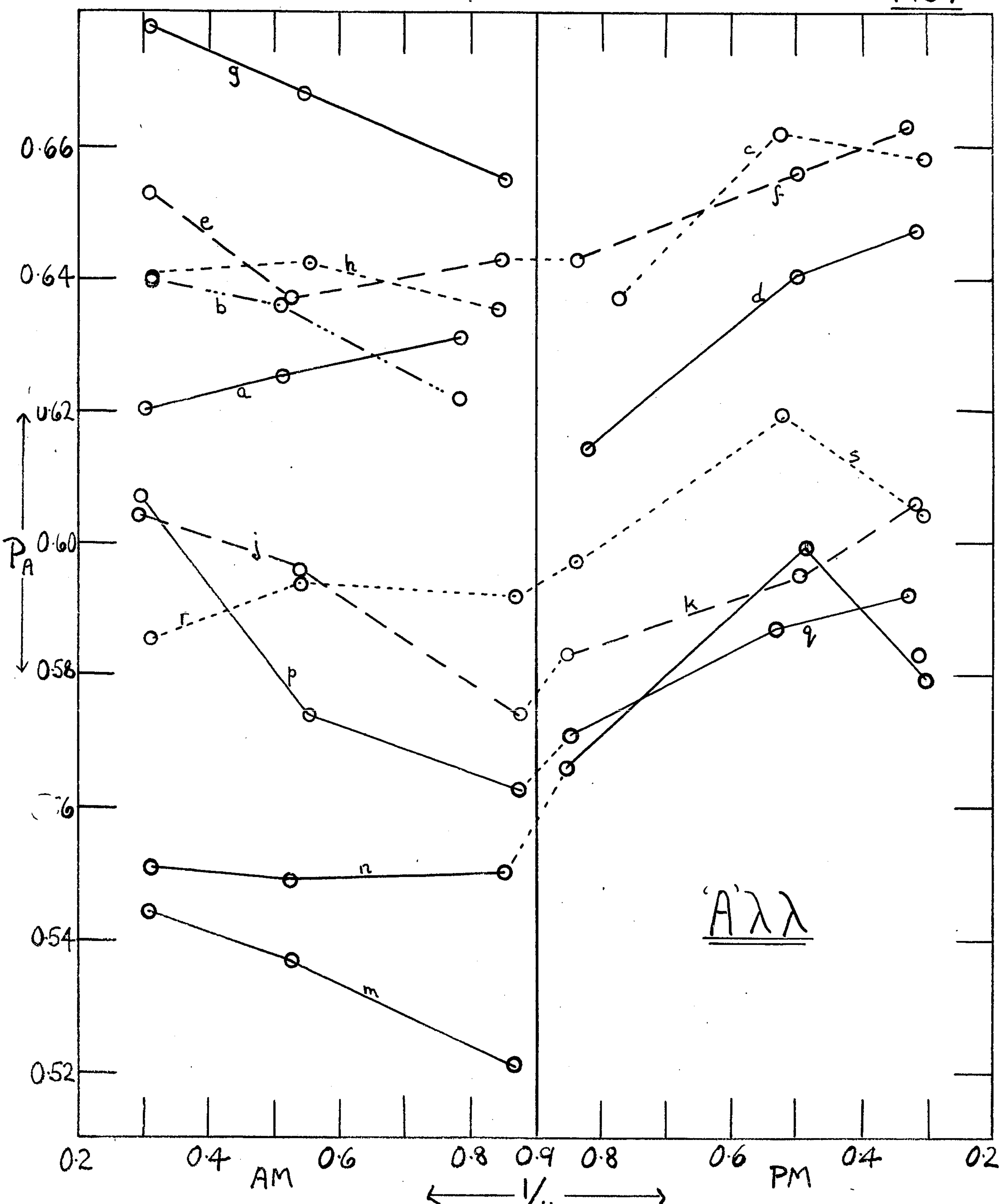


Fig. 2·321 (a)

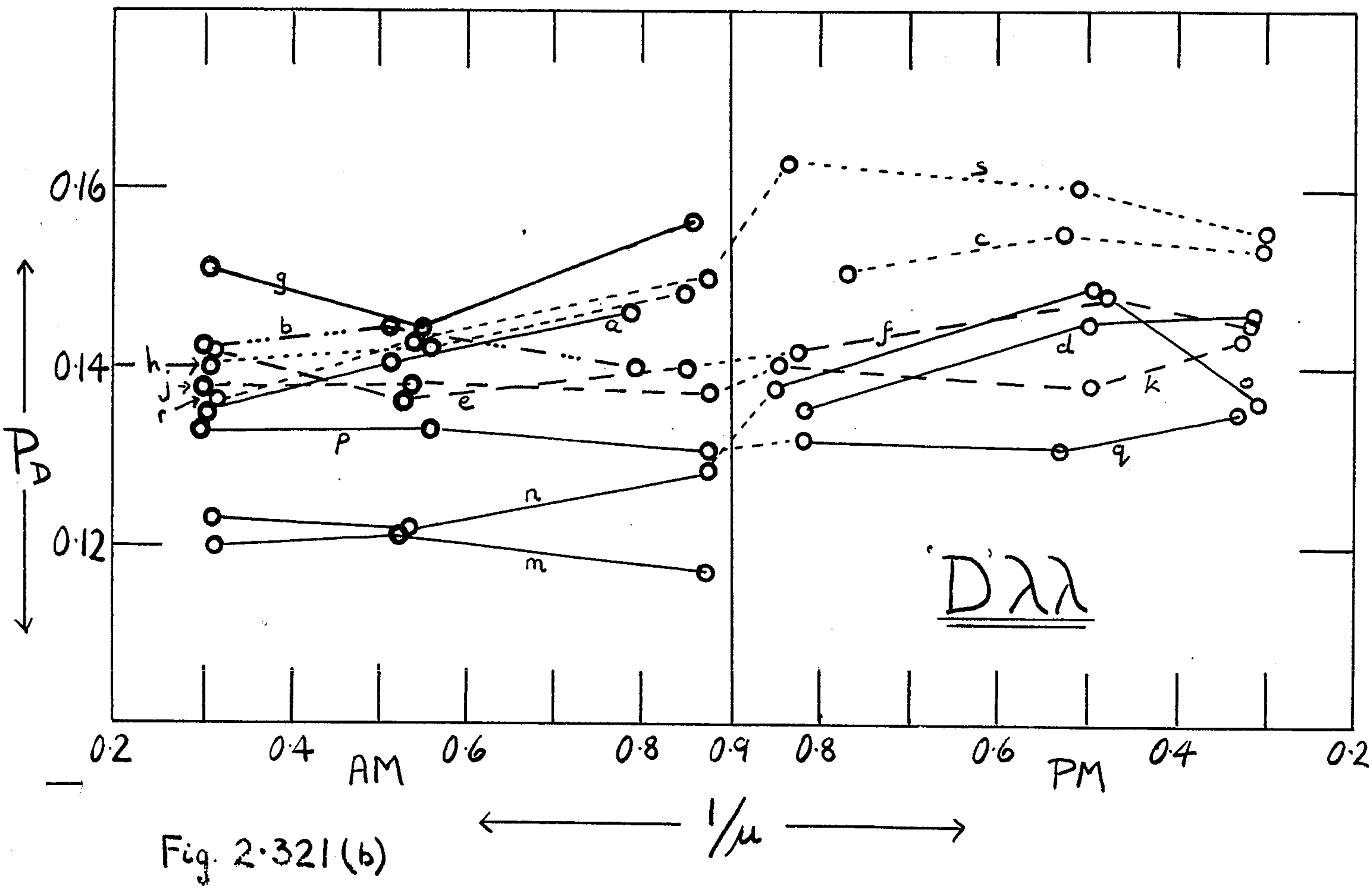


Fig. 2·321 (b)

PLOT OF P_D AGAINST $1/\mu$ FOR CALCULATION OF L_o.

OXFORD 1957

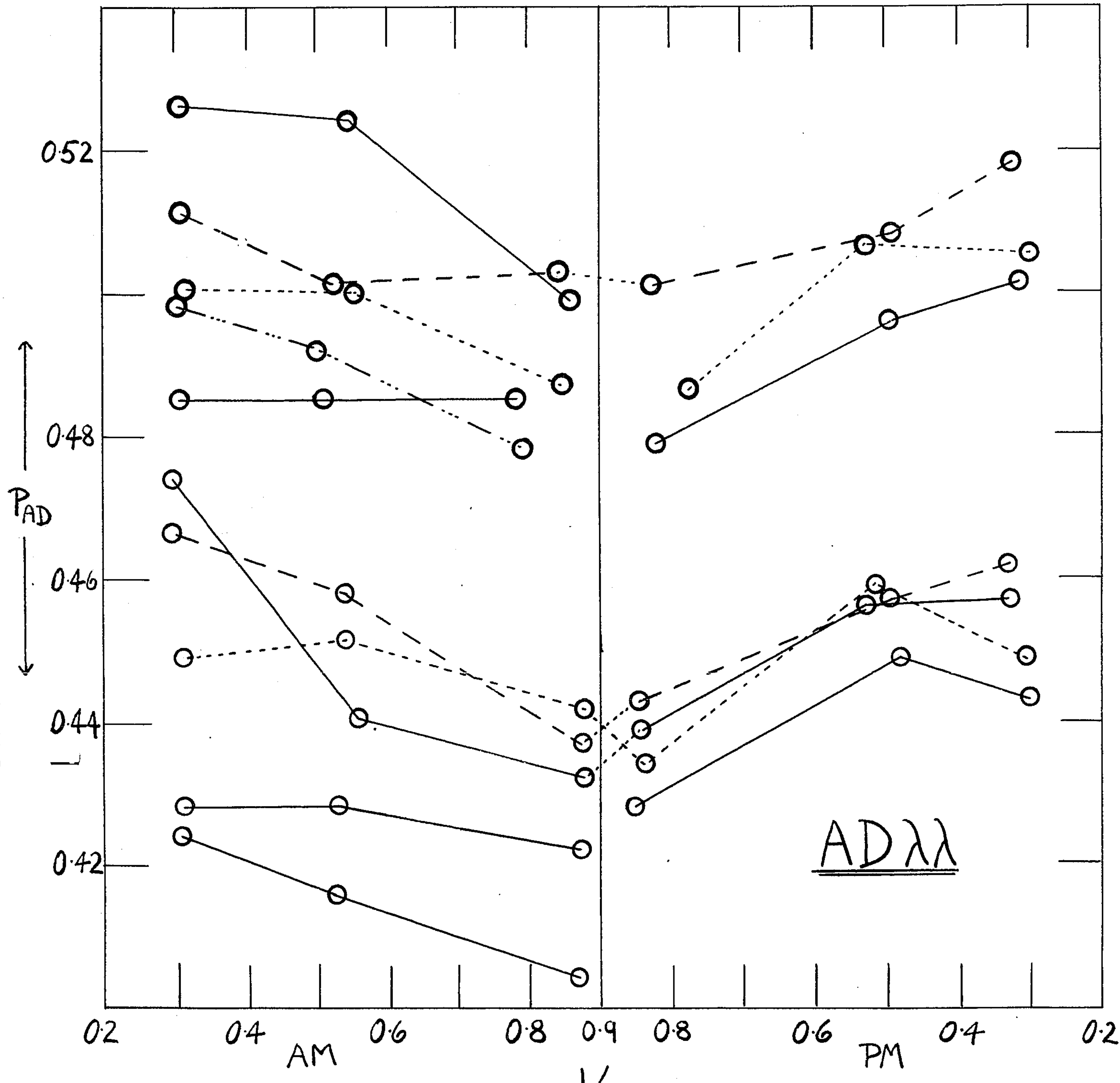


Fig. 2·321 (c)

PLOT OF PAD AGAINST 1/μ FOR CALCULATION OF L_o.

OXFORD 1957

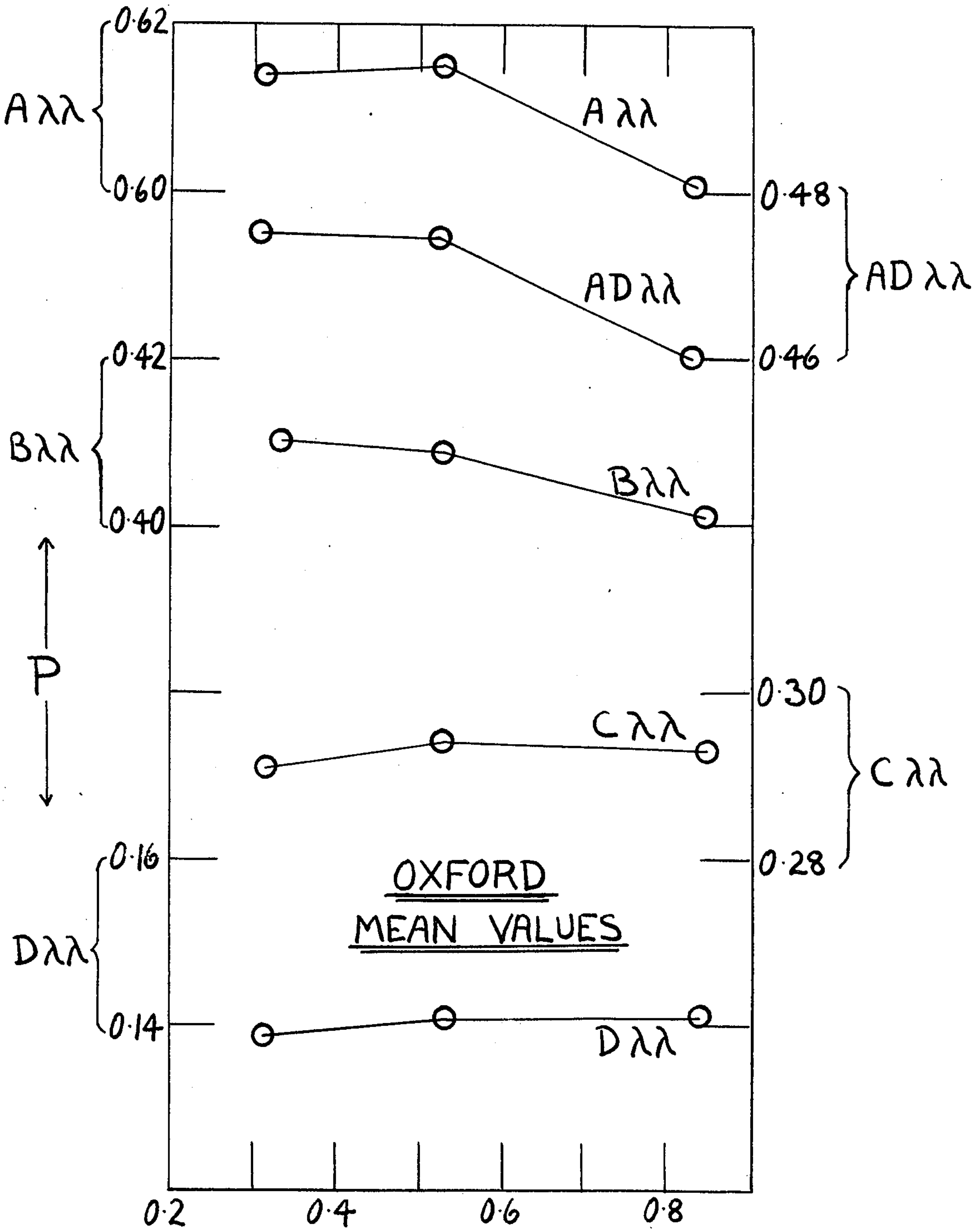
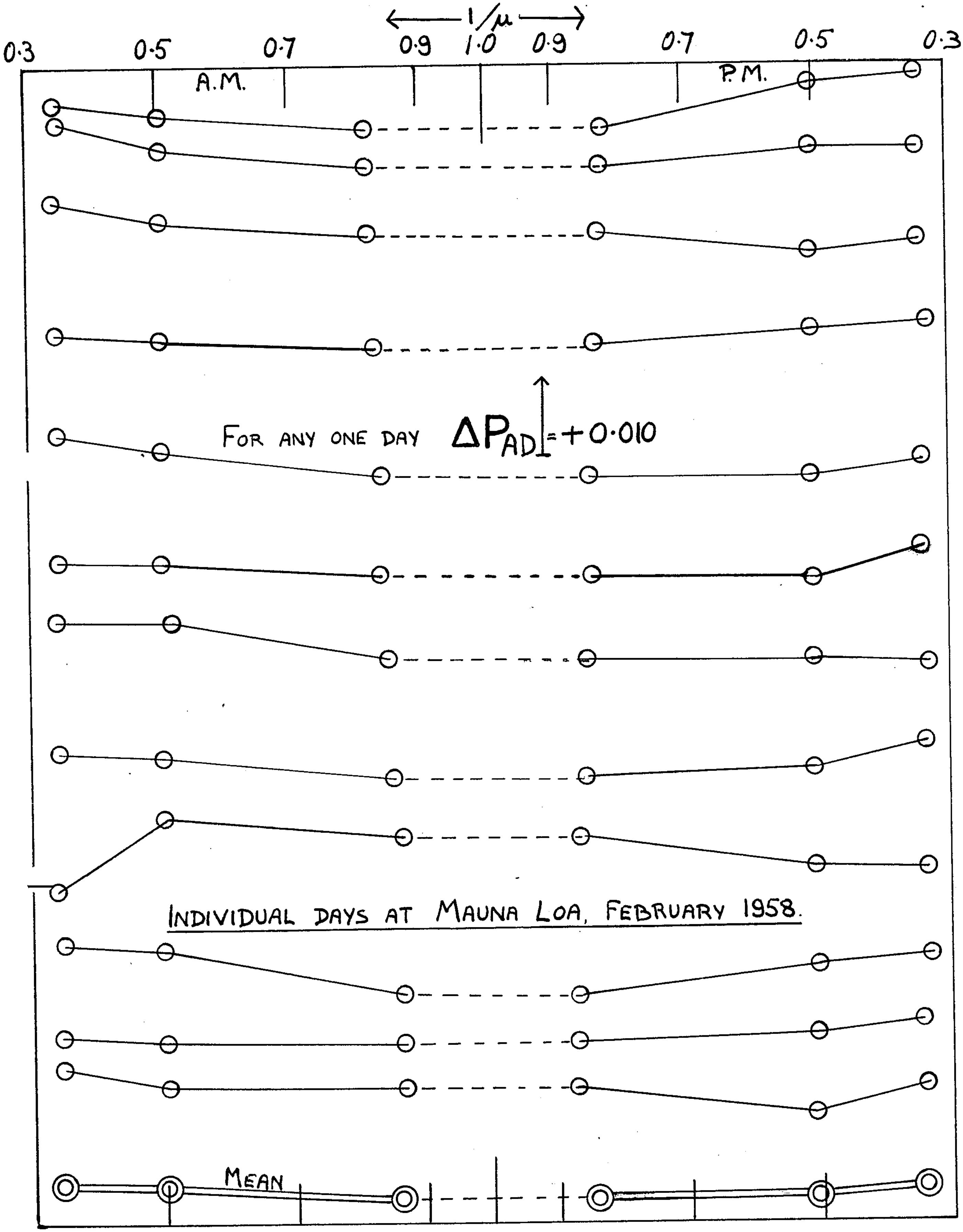


Fig. 2·321 (d)

PLOT OF MEAN VALUES OF P_A, P_B, P_C, P_D + P_{AD} AGAINST $1/\mu$

FOR CALCULATION OF L_o. OXFORD 1957



Zeros of each curve displaced to give approximately equal spacing.

Fig. 2·33 (a)

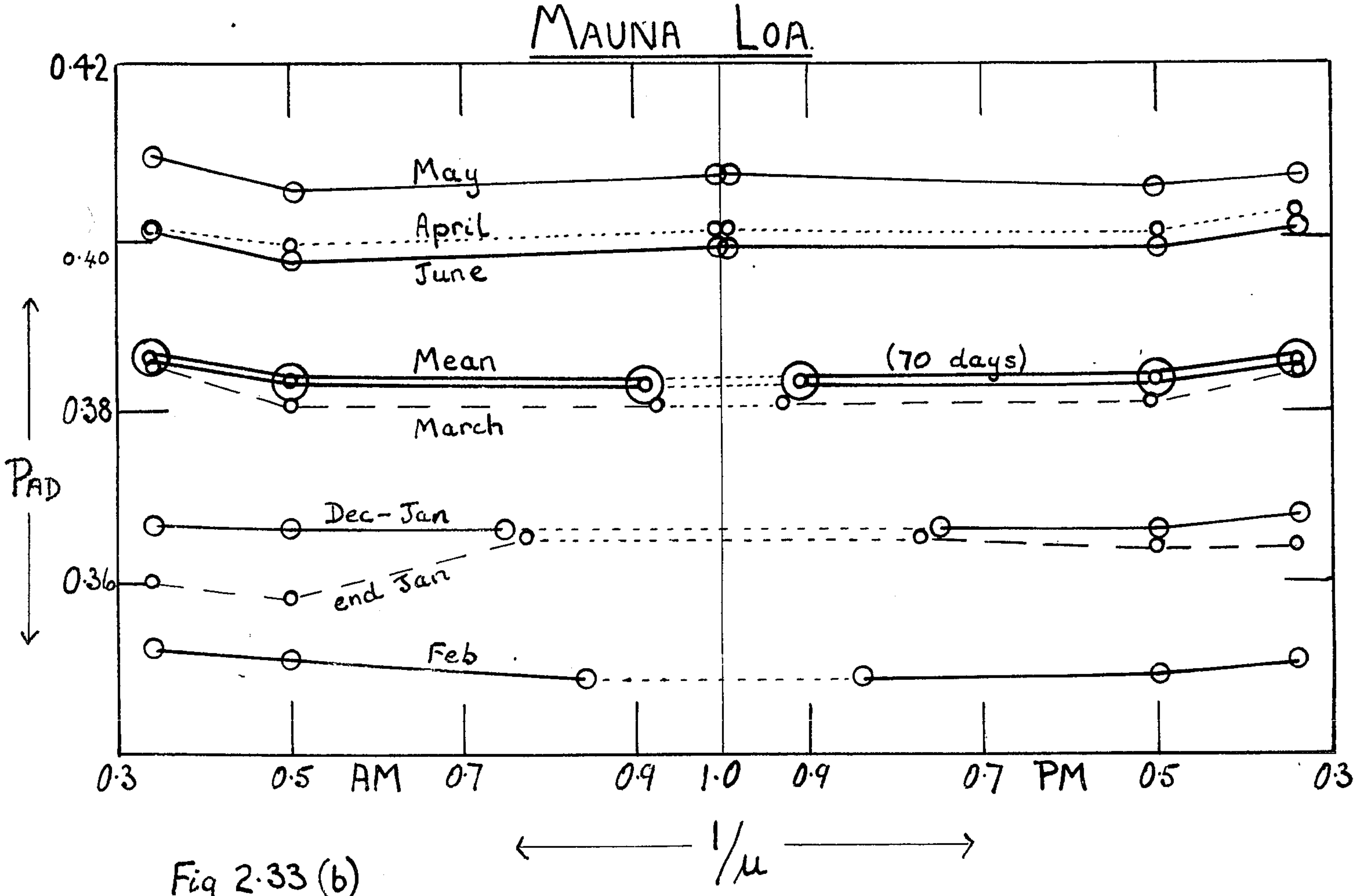


Fig 2·33 (b)

PLOT OF MONTHLY MEAN VALUES OF PAD FOR CALCULATION OF L_o.

MAUNA LOA. 1958

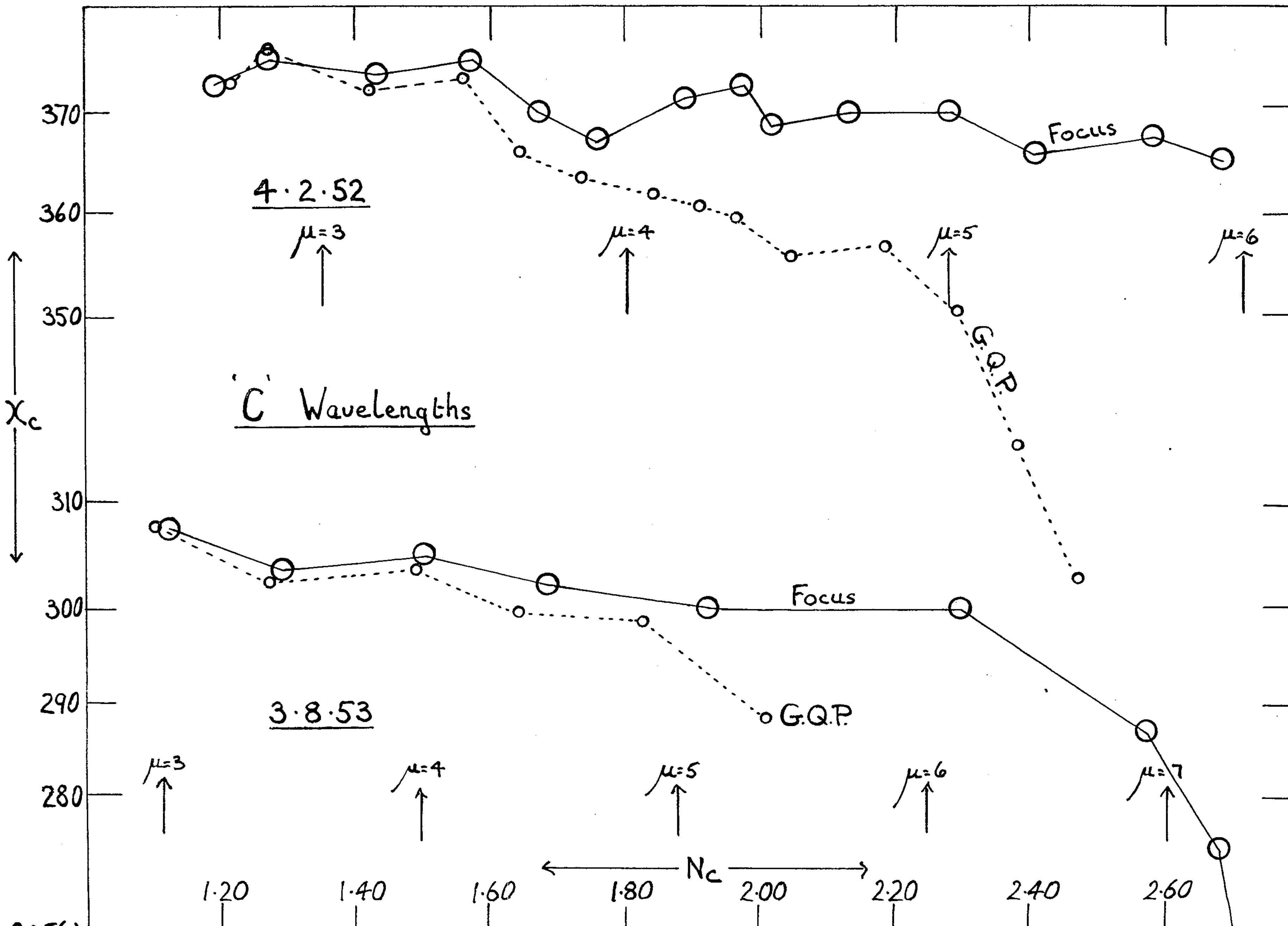


Fig 2·35(a)

OBSERVATIONS SHOWING ERRORS TO SKYLIGHT ON G.Q.P. AND SCATTERING OF LIGHT WITHIN INSTRUMENT AT LOW SUN. OXFORD.

ABSORPTION COEFFICIENTS OF OZONE DETERMINED BY VIGROUX AND BY NY & CHOONG FOR THE 'C' WAVELENGTHS

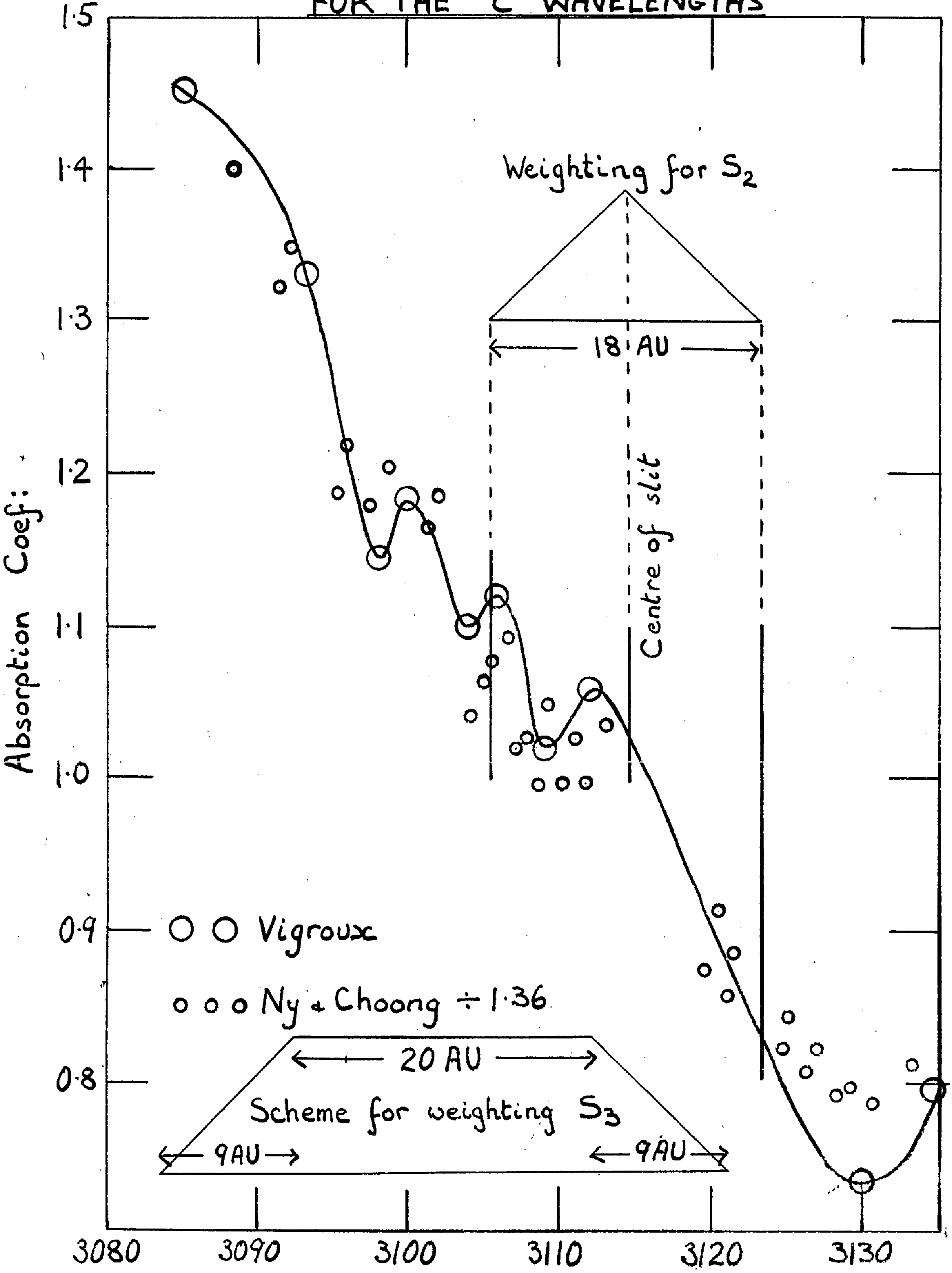


Fig. 2·41 (a)

SIMULTANEOUS OBSERVATIONS WITH THREE INSTRUMENTS USING A WAVELENGTH ON DIRECT SUNLIGHT.

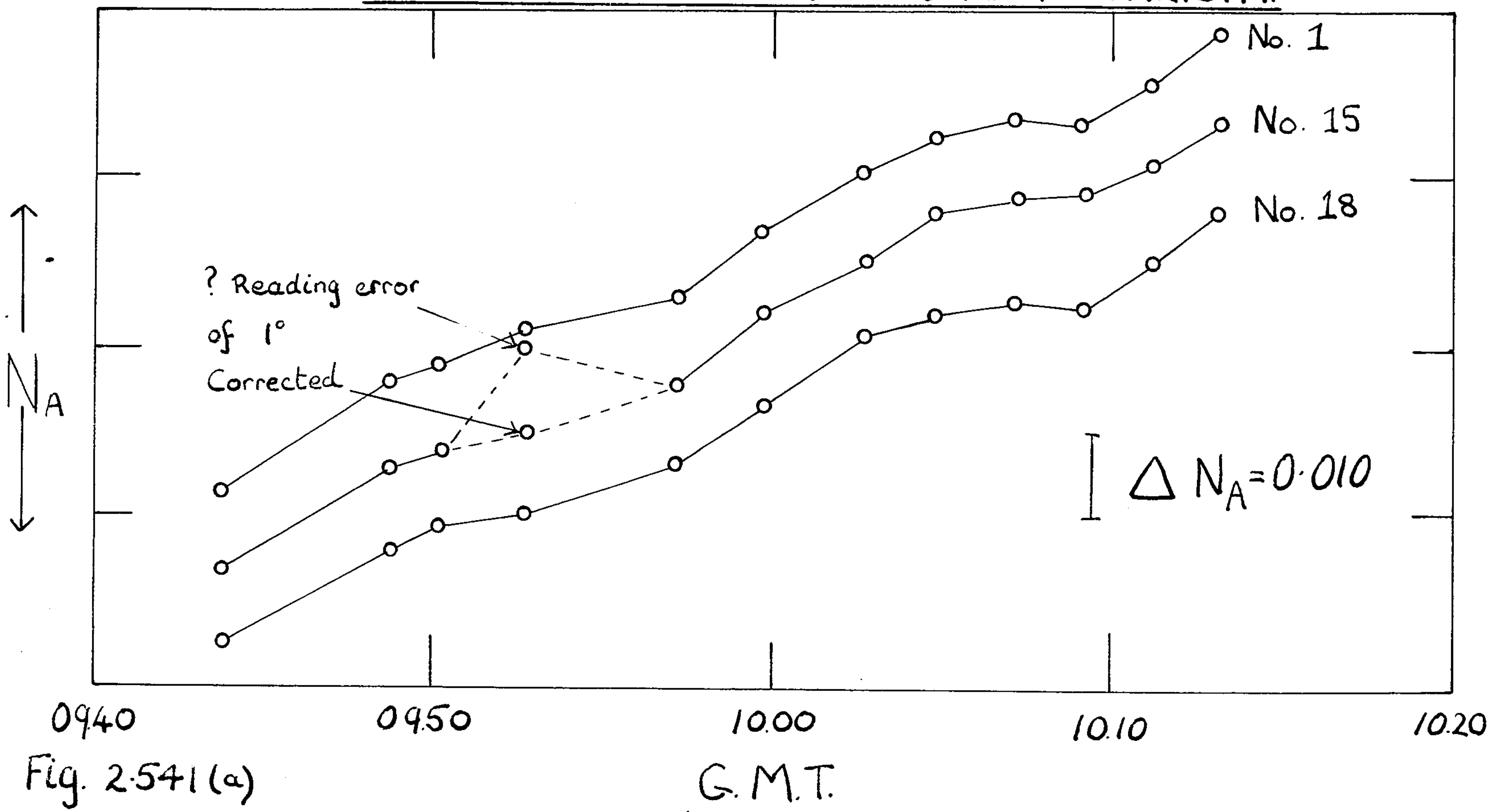


Fig. 2·541 (a)

Zeros of curves are displaced approx. 0·01 in N_A to avoid confusion.

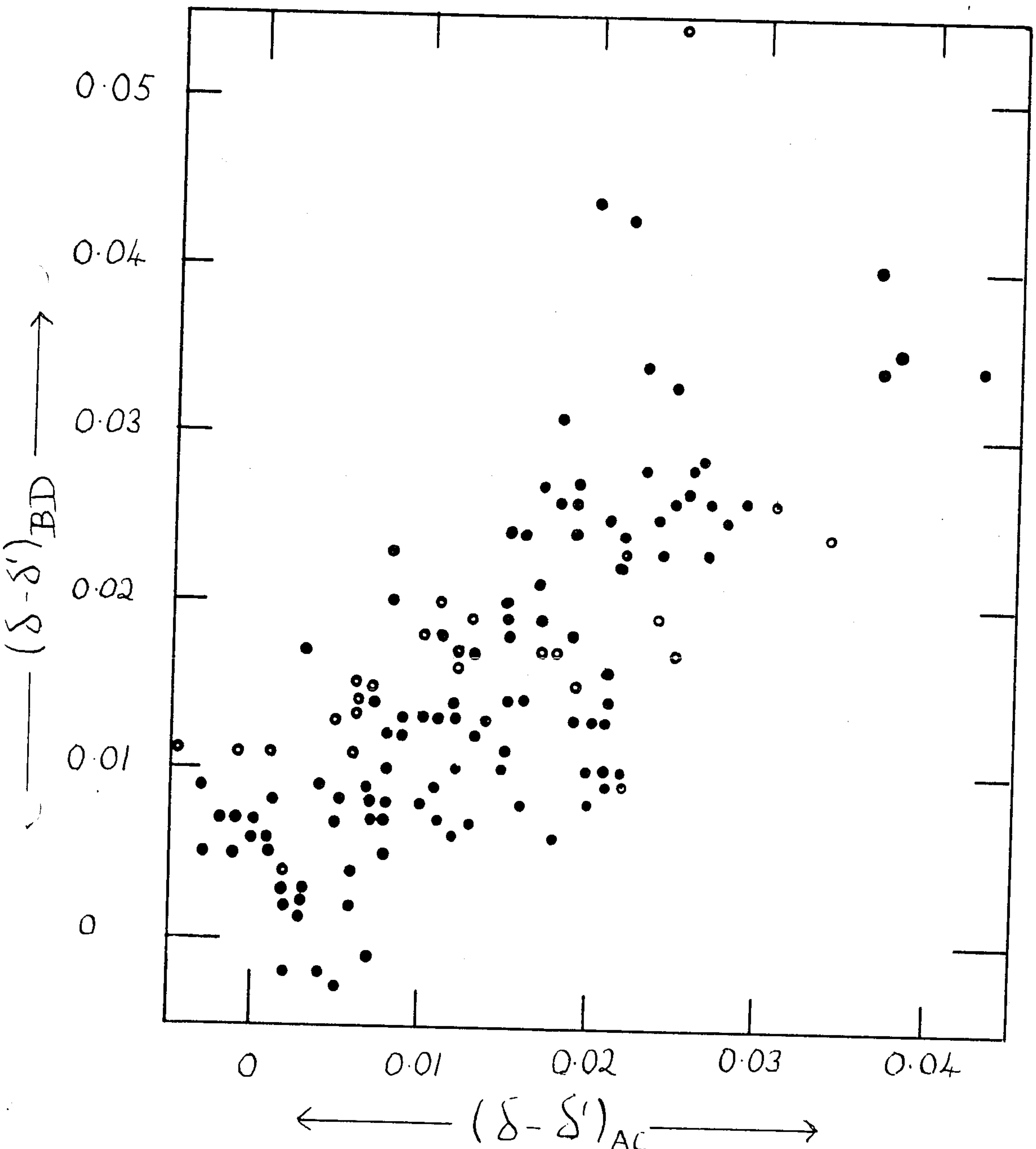


Fig: 2·63 (a) Comparison of $(\delta-\delta')$ obtained from different wavelengths.

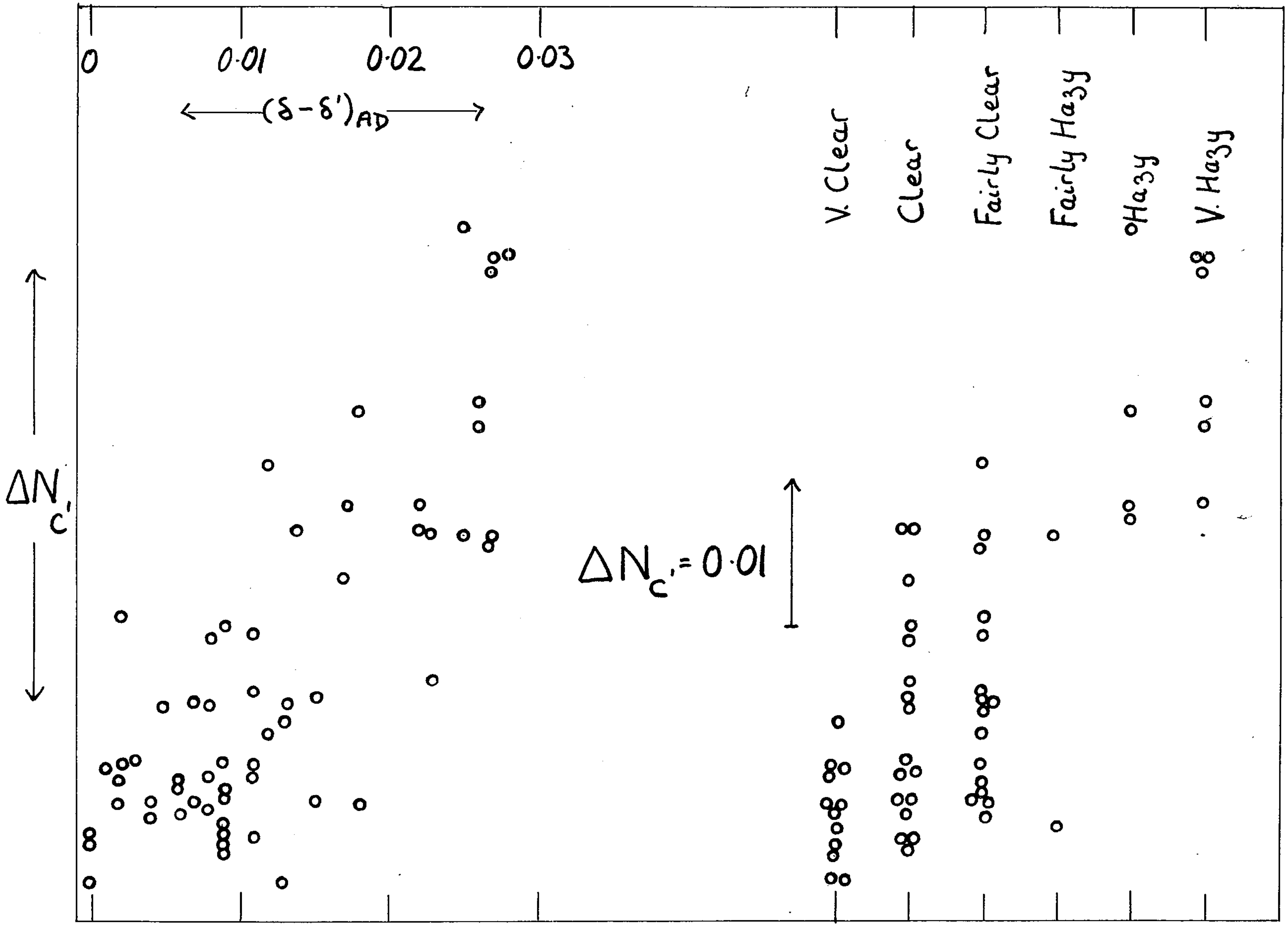


Fig 2·63 (b). OBSERVED RELATION BETWEEN $\Delta N_{c'}$ AND $(\delta - \delta')_{AD}$ OR VISUAL CLEARNESS. OXFORD SUMMER 1957.

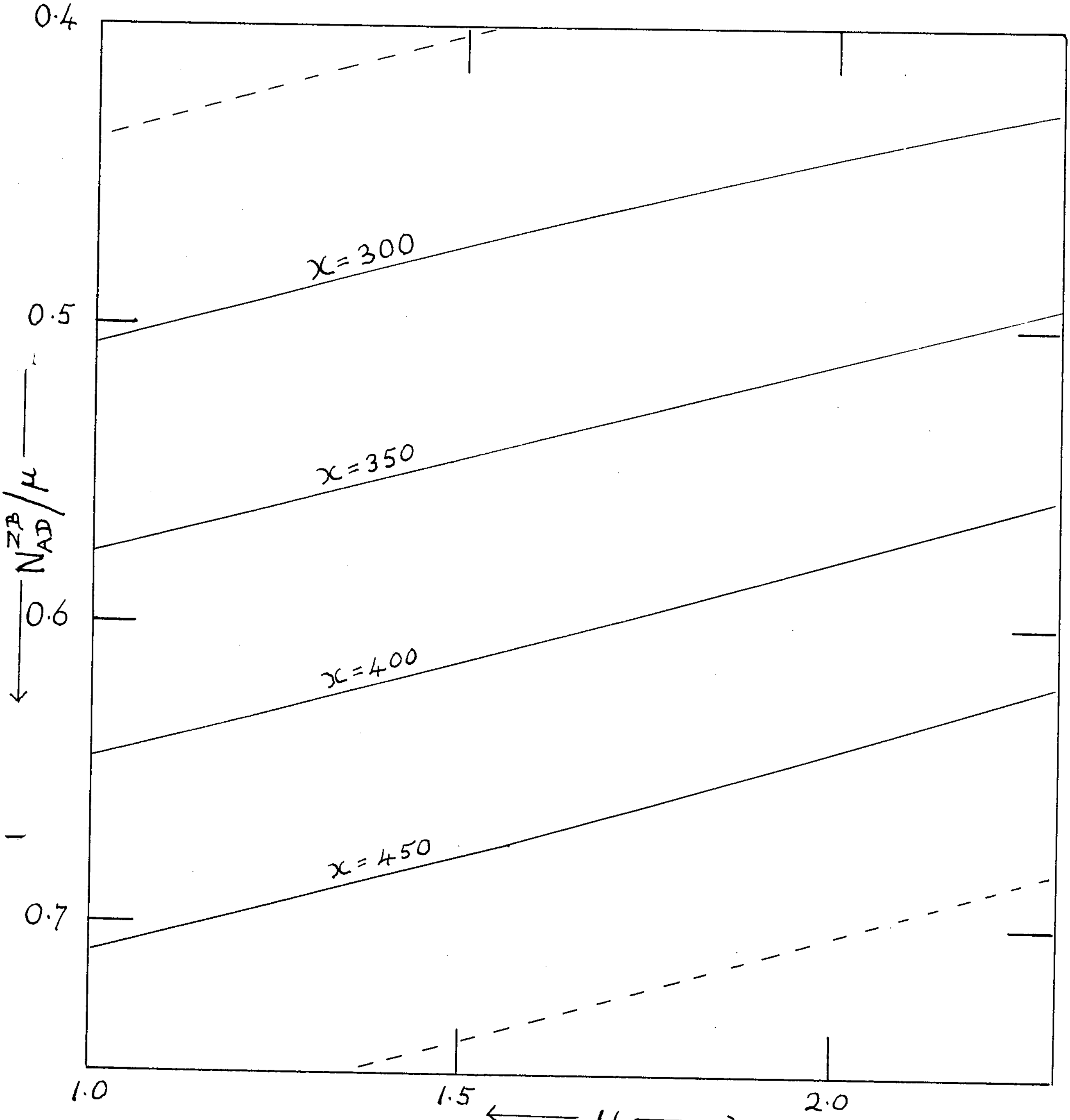


Fig. 3.1(a)

Zenith blue sky chart for AD λλ.

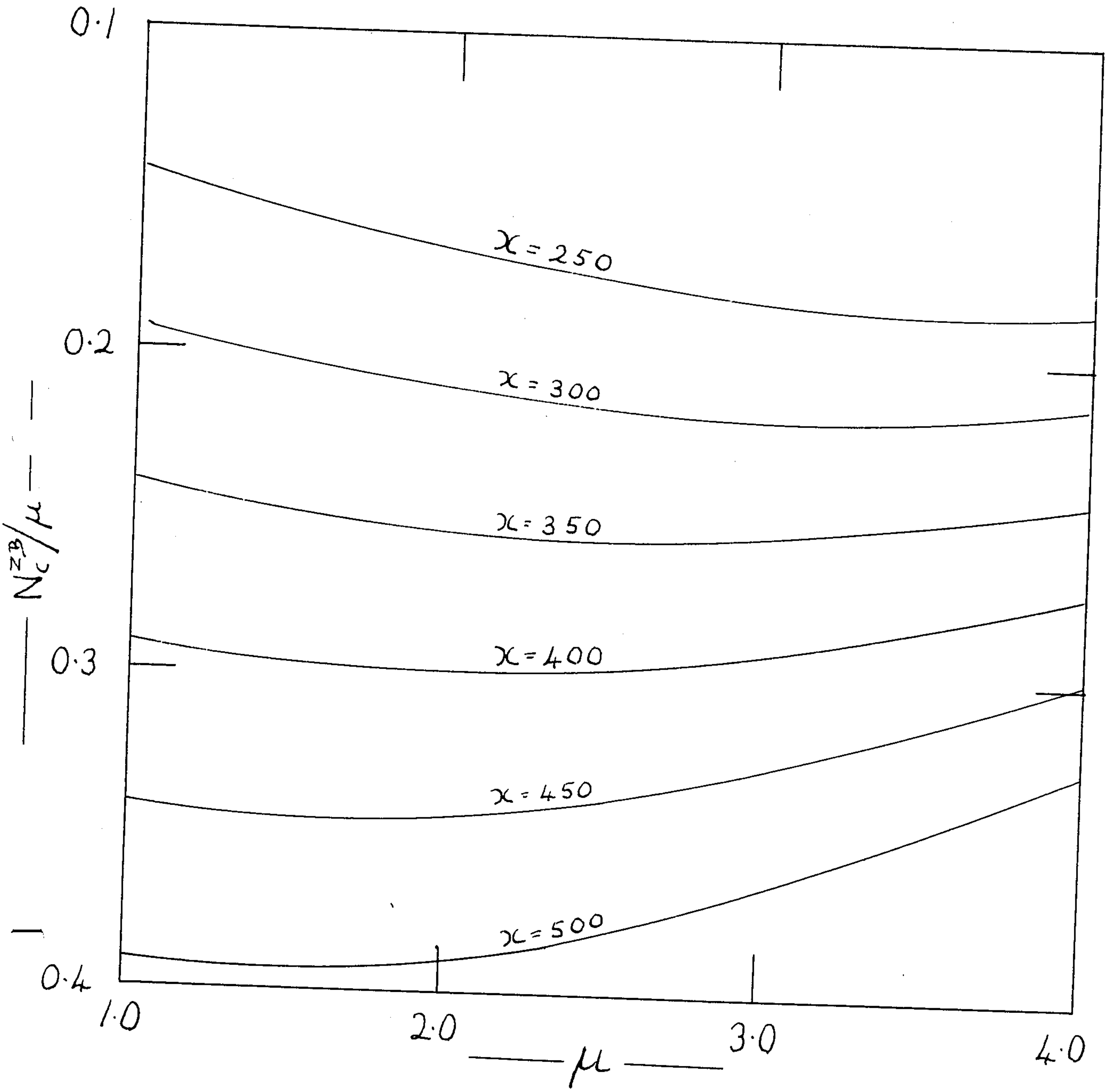


Fig: 3·1(b) Zenith blue sky chart. CλλPD

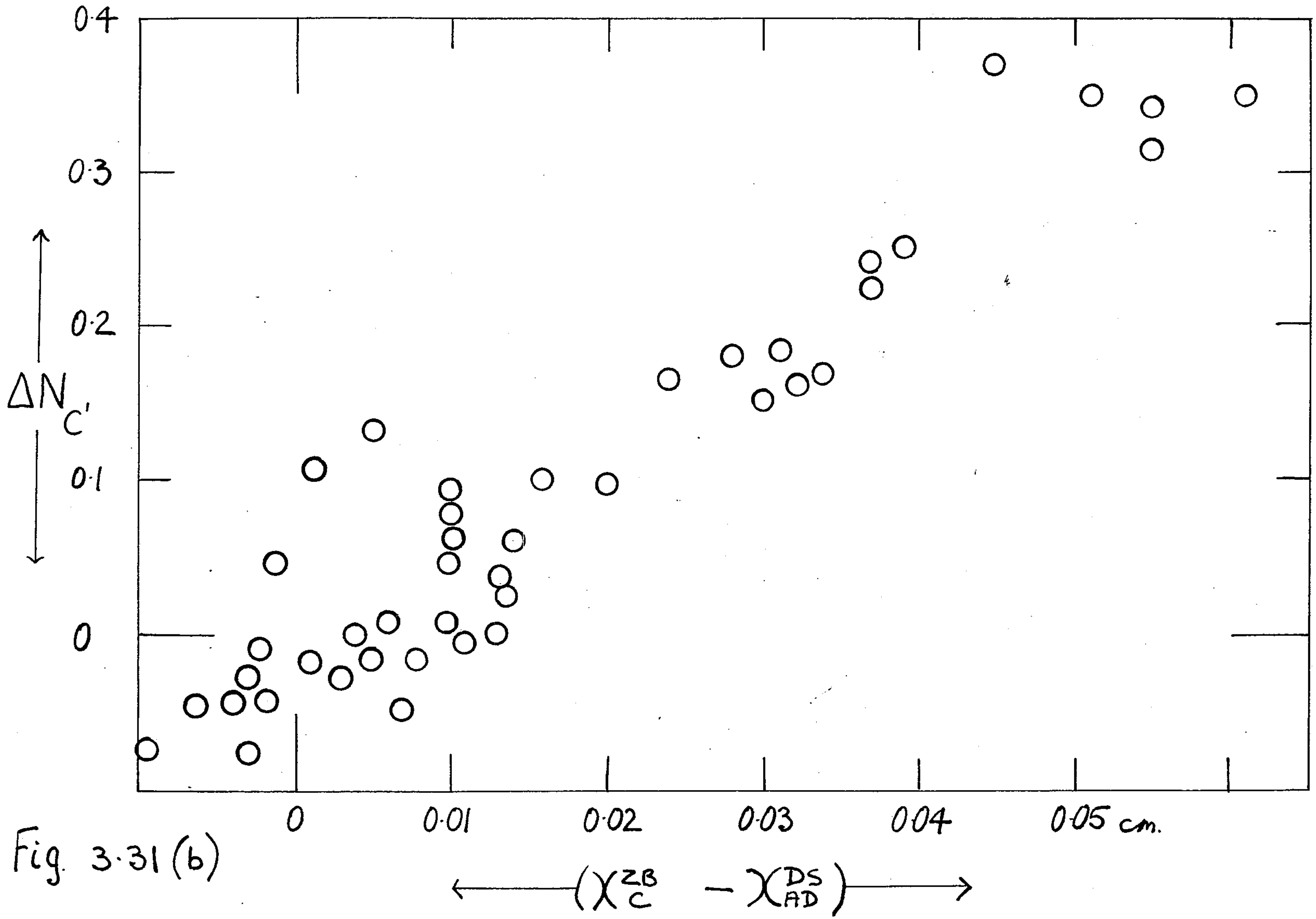


Fig. 3·31 (b)

EFFECT OF HAZE ON OZONE VALUE FOUND FROM ZENITH BLUE SKY. C λλ.

DIFFERENCE BETWEEN ZENITH BLUE SKY & SIMULTANEOUS DIRECT SUN MEASUREMENTS FOR AD WAVELENGTHS. ALL CLEAR DAYS OXFORD 1958.

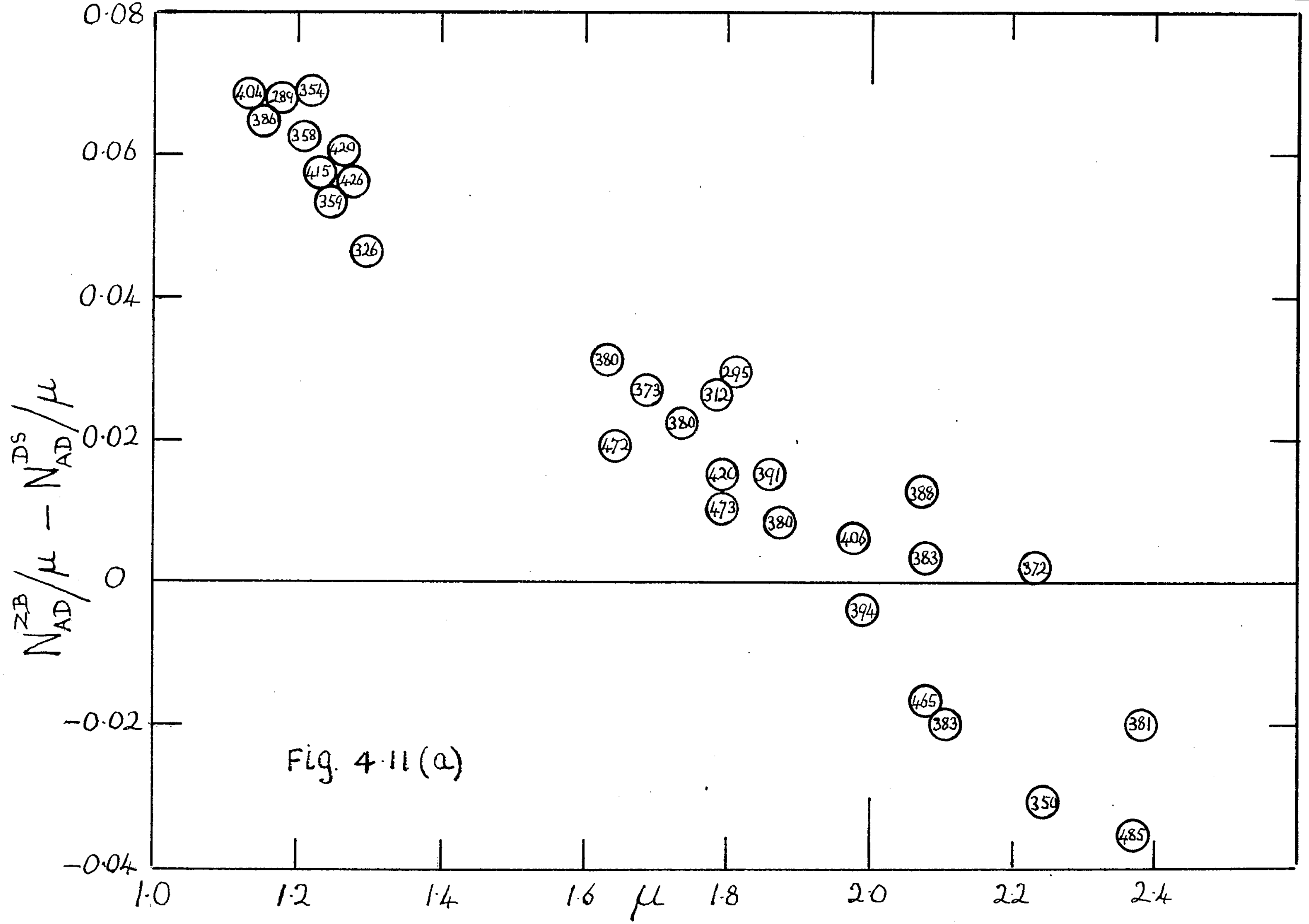
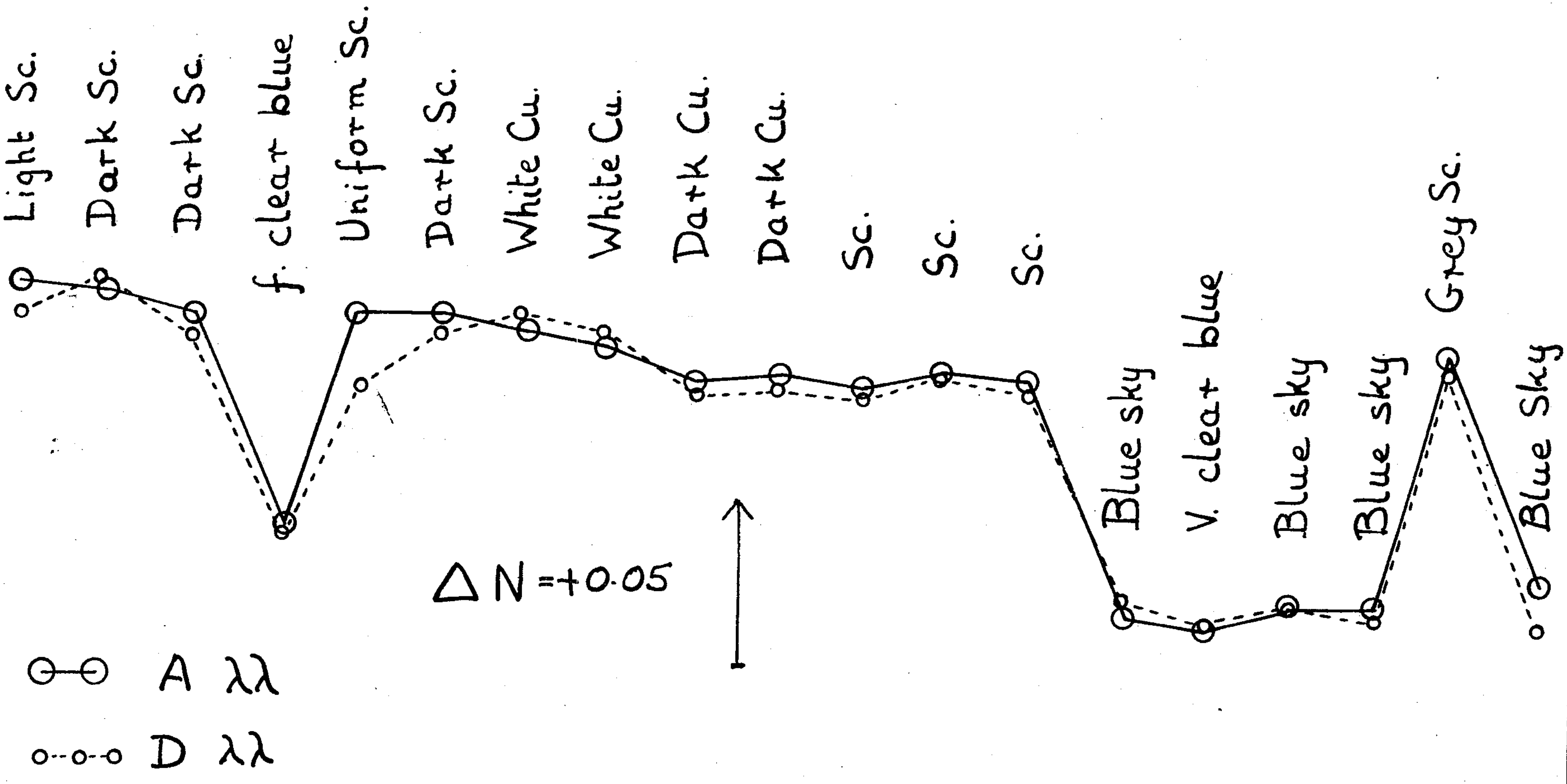


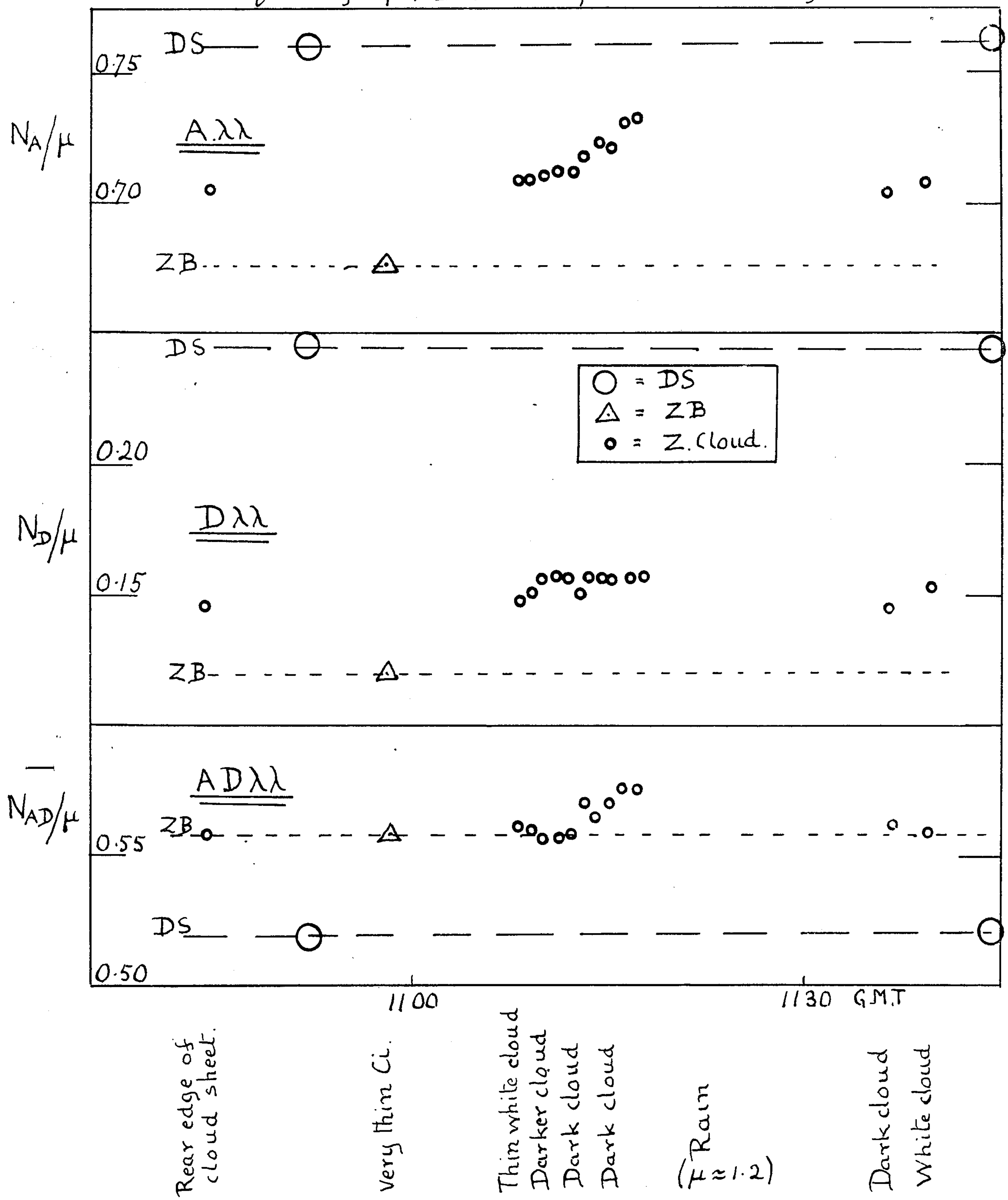
Fig. 4·11 (a)



SIMULTANEOUS OBSERVATIONS WITH TWO INSTRUMENTS

Fig. 4·11(b) Curves made to coincide for Blue Sky.

Fig: 4·11(c). Observations on Sun and Clear & Cloudy Zenith.
Note equality of AD values for Clear & Cloudy Zenith.



EXTENDED SERIES OF OBSERVATIONS ON STRATOCUMULUS CLOUD WITH 'A' AND 'D' WAVELENGTHS SHOWING TYPICAL VARIABILITY OF MEASUREMENTS.

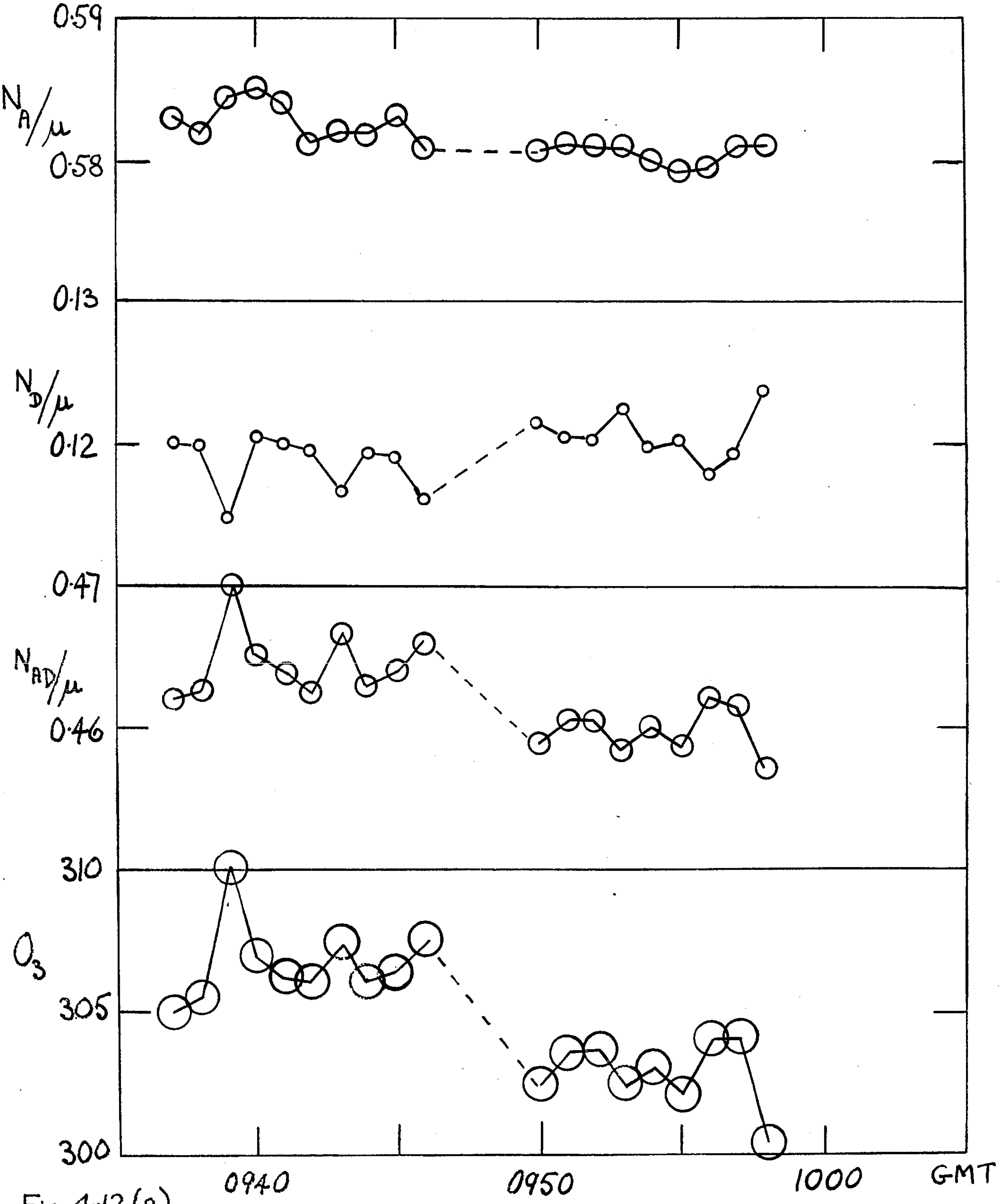


Fig. 4·12 (a)

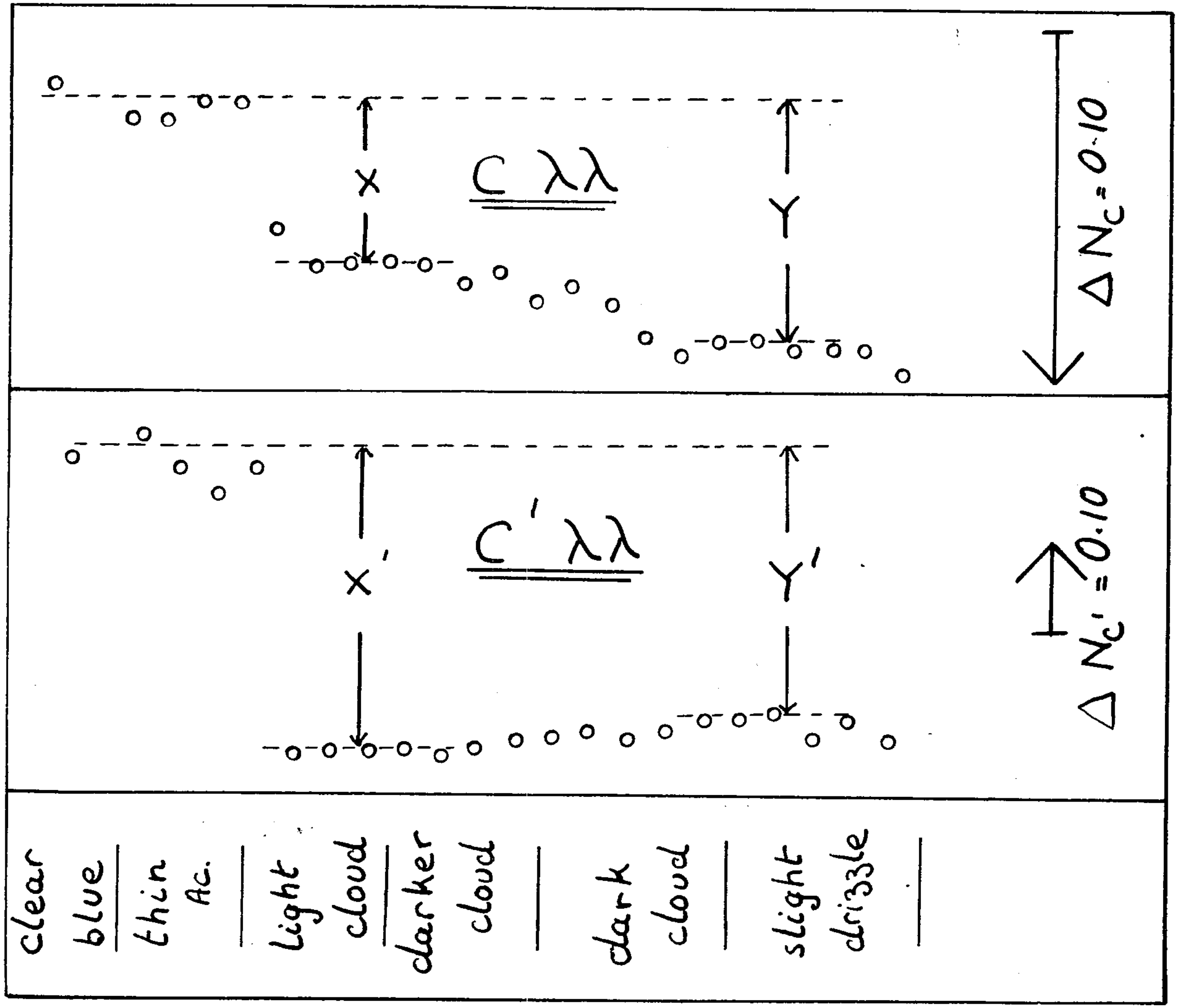


Fig. 4·21 (a).

OBSERVATIONS SHOWING THE EFFECT OF CLOUD ON ZENITH VALUES WITH C & C' WAVELENGTHS.

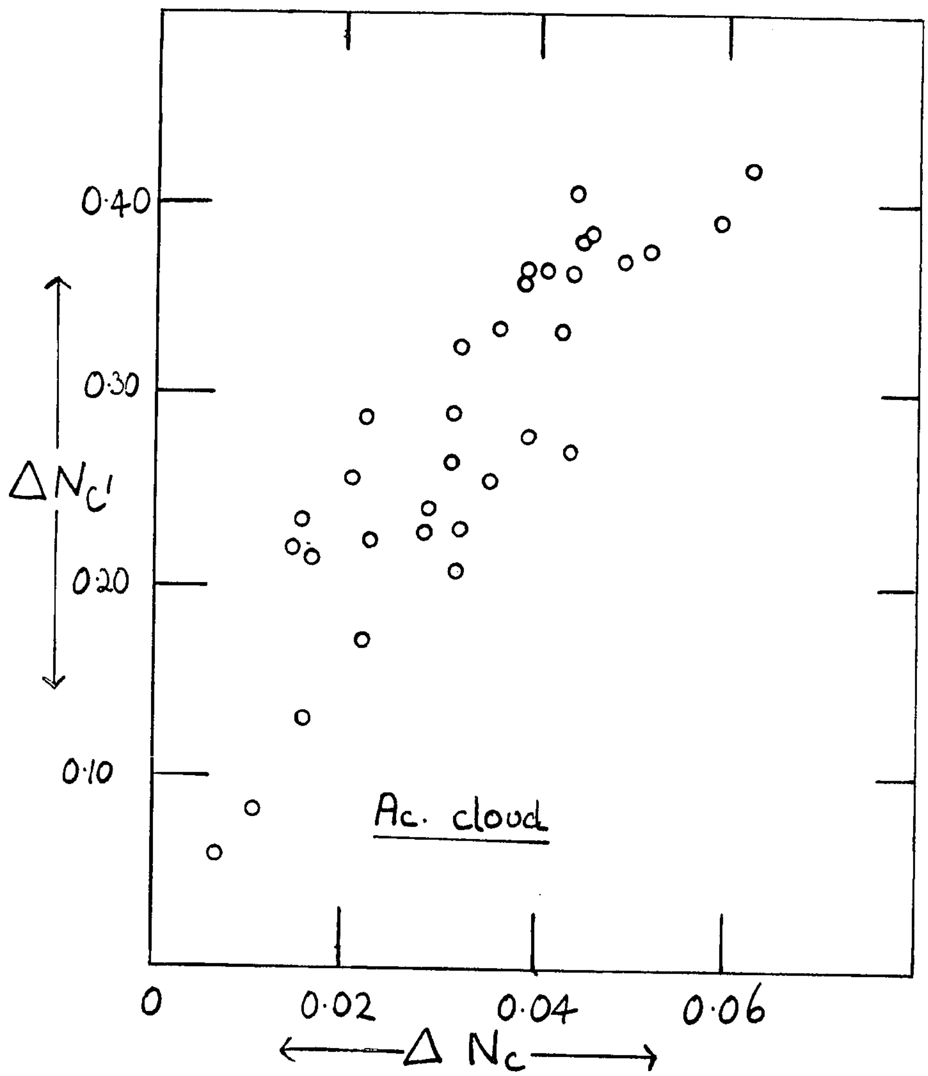
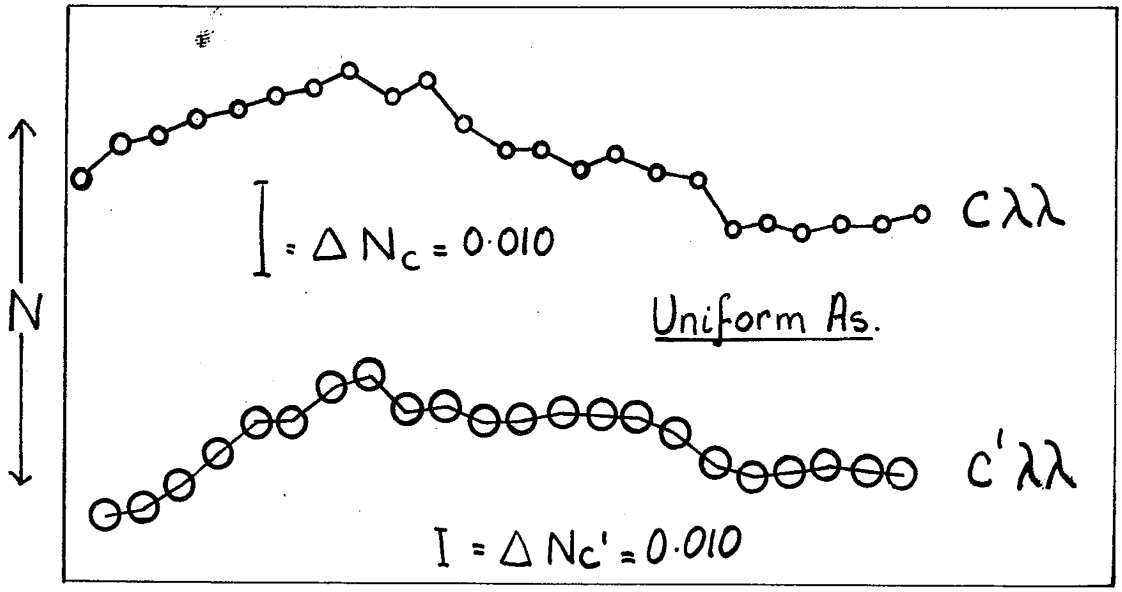


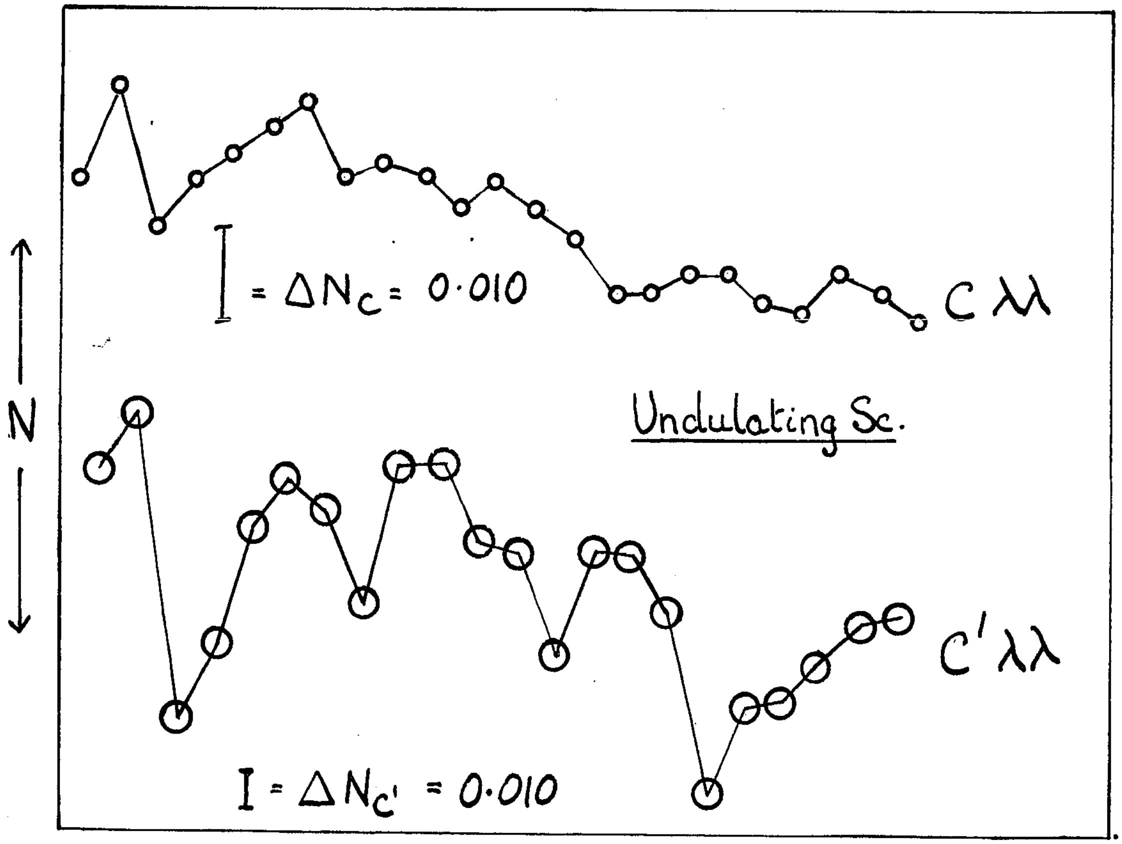
Fig. 4·21(b)

TYPICAL SET OF OBSERVATIONS MADE TO DEDUCE "CLOUD CORRECTION" CURVES.

ΔN IS THE DIFFERENCE BETWEEN THE CLOUD VALUE AND THAT OF CLEAR BLUE SKY.

CLOUDY ZENITH SKY. C & C′ λλ.





10 SECOND OBSERVATIONS ALTERNATE C & C′ λλ

Fig. 4·22( ) EXTENDED SERIES OF OBSERVATIONS WITH C & C′ WAVELENGTHS ON CLOUDY ZENITH SKY SHOWING VARIABILITY WITH UNIFORM & VARIABLE CLOUD.