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McMAHON, B.B. and SIMMONS, E.L.

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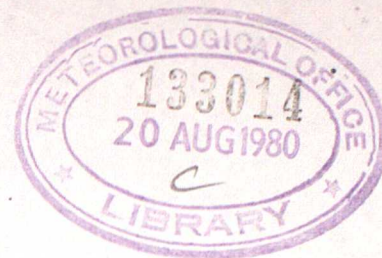
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MET O 19 BRANCH MEMORANDUM No 59



GROUND-BASED MEASUREMENTS OF ATMOSPHERIC
NO₂ BY DIFFERENTIAL OPTICAL ABSORPTION

by

B B McMAHON & E L SIMMONS

Met O 19
(High Atmosphere Branch)
Meteorological Office
London Road
BRACKNELL
Berks RG12 2SZ

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Introduction

Nitrogen dioxide (NO_2) is important to stratospheric ozone chemistry and has been studied using a variety of techniques since this was first recognised by Crutzen (1970). Balloon-and aircraft-based measurements of the vertical distribution of the gas are reviewed in Drummond and Jarnot (1978). Ground-based measurements of direct solar absorption by NO_2 , though only providing information on total column abundances, have the advantage of being relatively cheap and easy to perform.

During 1979/80 a ground-based grating monochromator system was developed at Beaufort Park to measure NO_2 absorption of the direct solar beam on clear mornings. The technique employed exploits characteristic structure in the absorption cross-section of NO_2 in the spectral range 435-450 nm.

This report describes the technique used and presents values for atmospheric NO_2 that have been obtained. The values were found to lie in the range $0.6 - 7.7 \times 10^{16}$ molecules cm^{-2} . A comparison is made with values reported by other workers who used similar techniques; it is concluded that the total column values of a few $\times 10^{17}$ molecules cm^{-2} reported by Pommereau and Hauchecorne (1979) were anomalously high.

A shortened version of this paper has been submitted for publication (McMahon and Simmons, 1980).

The Monochromator System

A one-metre f 11 'McPherson' grating monochromator was employed for the task of making repetitive spectral measurements of direct sunlight in the wavelength range 435-450 nm. The grating position was determined by a sine bar and leadscrew, so that one revolution of the leadscrew corresponded to 5 nm change in wavelength. The leadscrew was driven, through gearing, by a reversible synchronous motor, and a disc with 16 radial slots was attached to the leadscrew drive. A sensor detected the passage of each slot and initiated the integration of the signal from a photomultiplier at the exit slit of the monochromator. Integration lasted 360 ms, and was thus completed before the passage of the next slot after 375 ms. Small changes in the wavelength range covered by each integration could be achieved by displacing the slot sensor. Three revolutions of the disc provided measurements in 48 spectral channels across the above range and at a resolution, determined by the slit widths, of 0.5 nm. The time taken to scan up and then down in wavelength was 40 s. The sun was tracked using a clockwork heliostat with a servo-controlled fine adjustment. A lens brought the sun's rays, after passage through a copper sulphate solution absorption filter, to a defocussed image on a ground glass plate fitted in front of the monochromator entrance slit. A silicon photodiode was mounted behind the plate, set to one side, but angled to view the rear of the illuminated area. The combined effect of photodiode spectral response and copper sulphate absorption was that the photodiode signal gave a measure of solar intensity in a fairly broad band roughly centred on the spectral region of interest. Solar spectra were recorded digitally on cassette tape using a ratiometric A/D converter which had the effect of normalising each channel intensity with respect to the simultaneous broad-band signal; in addition to increasing dynamic range this provided partial compensation for rapid atmospheric turbidity changes which can lead to spurious spectral features during scanning. The broad-band signal was integrated over each scan and logged together with Greenwich Mean Time, at the start of each scan, for use in the subsequent analysis. An analogue presentation of the above data on a two-channel chart recorder was found useful for assessing the quality of the data. The system was on occasions left to run automatically without supervision; the broad-band signal provided an indication of whether or not cloud obscuration of the solar disc occurred at these times. In order to minimize tape changes the control logic reduced the frequency with which pairs of up/down scans were made after the first hour. Up to five hours of data could then be recorded on a single C 60 cassette tape. The formatting of the cassette data was amenable to computer checking for possible errors due to instrumental malfunctions.

Fig 1 illustrates the optical arrangement in front of the monochromator entrance slit. A simplified diagram of the system's electronics is provided in Fig 2.

Theory

In the spectral range 435 to 450 nm the principle causes of attenuation of the solar beam in the atmosphere are Rayleigh scattering by air molecules, particulate scattering and absorption by NO_2 , water vapour (H_2O) and ozone (O_3). The NO_2 absorption coefficient reaches a broad maximum and exhibits considerable structure in the above range. This behaviour was exploited to deduce the total amount of NO_2 in the absorbing path from complete spectral measurements of the direct solar beam across the range, after making corrections for the other sources of attenuation.

The direct solar monochromatic intensity, I_λ , within the above range, received at the Earth's surface at time t is given by

$$I_\lambda = I_\lambda^0 \exp - [\delta_\lambda + m\gamma_\lambda + n\sigma_\lambda + x\beta_\lambda + cK_\lambda] \quad (1)$$

where: I_λ^0 is the extraterrestrial solar intensity at wavelength λ
 γ_λ is the Rayleigh scattering optical depth of the vertical atmospheric column at wavelength λ
 $\sigma_\lambda, \beta_\lambda, K_\lambda$ are the NO_2 , O_3 , and H_2O absorption coefficients, respectively, at wavelength λ
 m is the mass of the atmospheric path traversed by the solar beam expressed as a multiple of the vertical atmospheric mass
 n, x and c are the total quantities of NO_2 , O_3 and H_2O , respectively, in the slant path
 δ_λ is the particulate scattering optical depth of the slant path.

The difference between the logarithms of the monochromatic intensities measured at a fixed location on the Earth's surface at times t and t^* is given by

$$\log_e \left(\frac{I_\lambda}{I_\lambda^*} \right) = (\delta_\lambda^* - \delta_\lambda) + \gamma_\lambda (m^* - m) + \sigma_\lambda (n^* - n) + \beta_\lambda (x^* - x) + K_\lambda (c^* - c) \quad (2)$$

where all quantities marked with an asterisk refer to time t^* . The solar zenith angles (χ, χ^*) were calculated from the equation of time, knowing the times of measurement and the positional coordinates of the measurement site. The mass numbers m, m^* appropriate to Rayleigh scattering are complicated functions of χ and χ^* because of atmospheric curvature and

refraction. Kasten's approximation to m (Kasten, 1964) was used for angles less than 60° , Lambert's expression (Sivkov, 1967) used for angles between 60° and 80° and interpolation between tabulated values of the Bemporad function (Kondratyev, 1969) used for angles greater than 80° . The particulate scattering optical depth, δ_λ , will vary slowly with wavelength over the narrow spectral range considered (Kuznetsov & Nigmatullina, 1977; Eldridge, 1966; Ahlquist & Charlson, 1969), and to a good approximation was assumed to take the form

$$\delta_\lambda = \delta_0 + \epsilon\lambda \quad (3)$$

Atmospheric O_3 absorbs relatively weakly, and with little structure, in this range; in general, atmospheric NO_2 absorption will be much stronger. O_3 amounts (x, x^*) routinely determined from a Dobson spectrophotometer at the same site were used when available, otherwise a 'climatological' value was used. Robinson's expression for γ_λ (McCartney, 1969) together with the values for σ_λ and β_λ determined, respectively, by Wilkerson et al (1974) and Johnston & Graham (1977) were used in the analysis.

If complete spectral measurements are made at the times t and t^* in the 435-450 nm range and corrections are applied for Rayleigh scattering and O_3 absorption, then the spectrum formed by taking the difference between the logarithms of the two spectra will only contain information about NO_2 and H_2O absorption and particulate scattering. An advantage of considering the complete spectrum is that atmospheric NO_2 absorption may then be unambiguously identified by its characteristic structure.

H_2O absorbs very weakly in isolated parts of this spectral range (Curcio et al, 1955), but the absorption coefficients K_λ are unknown. This problem is avoided by omitting possible H_2O absorption wavelength channels from the analysis. Assuming equation 3 to hold for δ_λ , the effect of particulate scattering is removed by subtracting the best-fit straight line from the difference spectra, using the least squares method, after making the above corrections. This also has the effect of removing any overall linear variation due to absorption by atmospheric NO_2 as well as the effect of any difference in the gain of the measurement system between the two times. If the resulting (differential absorption) spectrum is regressed against a spectrum of NO_2 absorption also expressed as a deviation from the best-fit line, the regression coefficient τ will correspond to the difference in slant-path NO_2 between t and t^* . It would therefore be possible to determine the slant-path abundance at a time t given the abundance at t^* , but in practice

a 'reference' abundance is not known. An alternative approach was adopted; each member of a set of spectra recorded at a time of increasing solar elevation was processed, in the above manner, with a reference spectrum. Whenever possible, the reference spectrum was obtained at a high solar elevation on the same day as the rising-sun spectra in order to maximise the difference in slant-path NO_2 between the spectra and the reference. Assuming that NO_2 is horizontally uniform and constant during the rising-sun period, a value for the vertical column over the period was derived from the variation of τ with time. Denoting the ratio of slant-to-vertical NO_2 by $\mu(\chi)$ the vertical column is given by the slope of the 'quasi-Langley' plot of τ against μ .

The requirement of constant NO_2 over the rising-sun period was examined in the light of the present understanding of its atmospheric chemistry, neglecting possible advective changes. Rapid photolysis of stratospheric NO_2 is believed to occur at sunrise, followed by a gradual increase in the daytime abundance due to slow N_2O_5 photolysis. Photochemical changes in tropospheric NO_2 are understood to be very small. A study of the photochemical model results of Clough & Hinds (1978) showed that, by surface sunrise, the effect on slant-path NO_2 due to chemical changes in the vertical abundance should be small compared with that of decreasing slant-path (most of the slant-path changes having taken place), justifying the assumption of constant NO_2 at this time. However, since the above effects are predicted to become comparable near midday, rising-sun spectra obtained within an hour of midday were ignored.

The function $\mu(\chi)$ is given by the secant of the solar zenith angle at an assumed height of 26 km for the centre-of-mass of the NO_2 distribution, which is consistent with the stratospheric profiles determined from aircraft and balloon (Drummond & Jarnot, 1978; Noxon et al, 1979(a)). During episodes of high boundary-layer NO_2 the height would be lower, leading to an under-estimate of μ and consequently an over-estimate of total vertical NO_2 given by the slope of the quasi-Langley plot. In the absence of knowledge of the boundary-layer contribution, this possible source of error was minimised by ignoring solar spectra obtained at μ greater than 7. The maximum possible over-estimate of the vertical column that could arise from this cause is consequently only around 20%.

Observational Procedure

Solar spectra were recorded at Beaufort Park using the monochromator system described above on clear mornings from sunrise onwards. Measurements were made repetitively until noon unless viewing conditions deteriorated to the extent that useful spectra could no longer be obtained. The site position was such that measurements could not be continued through to sunset.

Cumulus cloud mornings were avoided because occasional obscurations of the sun's disc caused servoing difficulties as well as unacceptably large and rapid variations in the received solar intensity. The effect of rapid changes in the broad-band signal on the recorded spectra is illustrated in the example of Fig 3. Useful results were obtained when there was only a thin veil of weakly structured cirrus cloud present, since variations in the broad-band signal were then less marked.

Small reductions in the E.H.T. supply to the exit slit photomultiplier were sometimes necessary to keep the output of the A/D converter within the desired range.

Spectral measurements at a relatively high solar elevation were made after each morning set of spectra, if viewing conditions permitted, for use as a reference in the analysis. The development of cumulus convection sometimes prevented reference spectra from being obtained.

It was clear, from the spiky appearance of the difference spectra derived initially, that there was incomplete removal of the solar Fraunhofer structure (which is very pronounced in this spectral region), and therefore some instrumental wavelength drift occurring. Precise observations of suitable mercury and cadmium emission lines revealed a steady drift with time during the morning towards longer wavelengths, the total drift amounting to nearly 0.08 nm. A drift in the opposite direction was observed when the instrument was left scanning in the afternoon. A possible explanation for the drift is differential expansion of the monochromator casing in response to solar heating. In order to obtain good spectral alignment between each spectrum and a reference spectrum, spectral shifting was deliberately introduced into a set of consecutive reference spectra. This was achieved by moving the slot sensor mentioned earlier. A set of cams and microswitches was used to generate a 3-bit slot-sensor position indicator which was logged with the data. It was possible to record eight reference spectra in quick succession at spectral positions progressively shifted so as to span the region of known instrumental drift. When viewing conditions permitted, more than one such spectrum was recorded at each shift position in order that signal-to-noise could be improved by averaging. By recording eight increasingly shifted spectra followed by eight decreasingly shifted spectra, it was possible to ensure that the mean

time at which each averaged spectrum was recorded, was the same. This minimised the effect of any overall change in slant-path NO_2 , during the time of observation, on the resultant set of eight averaged reference spectra.

A carefully purified sample of NO_2 was used to determine, again with 0.5 nm resolution, the shape of the spectrum of NO_2 absorption as observed by the monochromator. The sample was introduced into a glass cell and the spectrum of a white light source recorded with the sample in the optical path. A second spectrum was recorded, using an empty cell, to provide the reference spectrum required to derive the absorption spectrum. Since a means of determining the quantity of NO_2 in the cell was not available, the absorption spectrum was quantified using the published coefficients of Wilkerson et al (1974).

Computer Analysis

After each set of morning observations, cassette data was transcribed to computer tape using a PDP 11/40 mini-computer. A program was then run to read the computer tape, which translated the binary-coded-decimal data into Fortran integers and checked for possible errors in the data format. Adjacent up/down spectra were averaged to compensate for a slight displacement in the spectral range caused by electronic and mechanical backlash in the system. The mass numbers m and μ were computed for each averaged spectrum from the equation of time, making use of the time information logged with each spectrum.

It was found that variations in the integrated broad-band signal of greater than 10% between adjacent up/down scans were usually associated with spurious spectral features; this was therefore made a criterion for rejection of up/down pairs of spectra in the program. Error-free spectra were automatically written to an on-line disc, after up/down averaging, together with their respective times, mass numbers and slot-sensor position indicators (numbered from 1 to 8).

A second program analysed the disc data for NO_2 absorption. The associated J.C.L. specified the rising-sun, and reference data sets to be analysed. Whenever rising-sun and reference spectra were not available for the same day, another day's reference spectra were specified. Reference spectra could be identified by the program from the pattern of successive shift positions.

Analysis of the data began with the maximising of the wavelength alignment between each rising-sun spectrum and the reference. Since misalignment gives rise to many sharp features in the difference spectra, the appropriate reference spectrum (using interpolation between adjacent spectra) was selected from the set of eight so as to minimise the mean square curvature of the difference formed. This method of achieving alignment made full use of the available wavelength channels. Instrumental drift is more difficult to spot and correct for if only a few selected channels are used. Brewer et al (1974) only measured solar intensities at three wavelengths, a maximum and two minima in NO₂ absorption, using a spectrometer. Other authors such as Noxon (1979(a)) and Harrison (1979) chose to record solar intensities only at Fraunhofer maxima and minima to reduce the effect of instrumental drift.

Corrections, described earlier, for the sources of attenuation other than NO₂ absorption were applied to the difference spectra, and quasi-Langley plots produced (neglecting a total of nine possible H₂O absorption channels in the regression computations). Corrected difference spectra were also plotted for visual comparison with the spectrum of NO₂ absorption.

Discussion of Results

Rising-sun spectra were recorded on 18 mornings from September 1979 to May 1980. Values for the slopes of quasi-Langley plots are presented in Table 1 together with the μ -ranges and corresponding time intervals over which they were evaluated. Slopes were calculated for μ -ranges over which overall linearity prevailed, which on occasions required calculating two slopes for adjacent μ -ranges on the same day. The reference spectra used in the analysis on each occasion are also indicated in Table 1. Slopes are in the range $0.6 - 7.7 \times 10^{-6}$ molecules cm⁻².

Quasi-Langley plots, together with the corrected spectra from which they were derived, are presented in the Appendix. Successive spectra have had their origin shifted obliquely with respect to the first by an amount proportional to the time difference, in order to illustrate developments with time; the lowest curve in each case is the NO₂ absorption spectrum. In most cases there is a strong resemblance between this spectrum and the corrected spectra, but there are cases of mornings for which the corrected spectra are rather spiky. Most of these latter cases are due to slight wavelength misalignment between the rising-sun and reference spectra, usually because reference spectra were used from different days and the imposed spectral shifts didn't quite cover the required range. One (24 January 1980) was caused by inadequacies in the

heliostat servo and the remainder possibly caused by thin structured cirrus cloud passing in front of the solar disc during scanning. The existence of high-altitude cloud, invisible to the eye, was sometimes implied by variations in the broad-band solar luminance signal seen on the chart recorder trace. Instrumental noise will, of course, be more noticeable in the corrected spectra in cases where the slant-path NO_2 , relative to the reference, is very small.

It was found that, despite the appearance of the corrected spectra, the resulting quasi-Langley plots were almost unaffected by small misalignments in wavelength. The correlation between corrected spectra and the spectrum of NO_2 absorption, however, is much more sensitive to the appearance of corrected spectra. Correlation coefficients varied from about 0.1, at worst, to values in excess of 0.95 on 21 December 1979 for example. Some corrected spectra indicated slight additional absorption in the H_2O regions identified by Curcio et al (1955), but the quasi-Langley plots were unaffected because of the omission of these regions from the analysis.

On most days the slope obtained at μ -values greater than about 7 was steeper than at lower values. This could have been due to a significant tropospheric contribution to the vertical NO_2 column, leading to a centre-of-mass altitude well below the 26 km assumed in the evaluation of μ . Photochemical changes in the vertical abundance are certainly not expected to be responsible, and it seems unlikely that purely advective changes should so often have led to a steeper, rather than a shallower slope, at high μ -values. Further evidence for a significant tropospheric component came from the erratic behaviour of the quasi-Langley plots on some mornings, for which advection of low level NO_2 was probably responsible. Although the uncertainty in μ due to tropospheric NO_2 was minimised by neglecting points corresponding to μ greater than 7, a changing vertical NO_2 column complicates the interpretation of the slopes. The effect of gradually increasing vertical NO_2 , for example, is to reduce the rate at which the slant-path NO_2 appears to change with decreasing μ . Thus an apparent reduction in the vertical NO_2 may be due to an actual increase. The most reliable values for vertical NO_2 in Table 1 will be those derived from quasi-Langley plots which were essentially linear over the largest μ -ranges, since it becomes increasingly improbable that advective changes will mimic the markedly non-linear temporal variation of μ the larger the μ -range used. If slopes evaluated over a μ -range of less than 3, say, were omitted from Table 1, then days for which two slopes were reported would not arise.

An obvious occasion when a parcel of tropospheric NO_2 (probably in the boundary layer) passed through the slant-path was 18 October 1979 (see Appendix),

when there was a marked positive excursion of the regression coefficients, lasting about 10 minutes. The cause of the observed peak may have been the passage of NO_2 from a middle-distance source through the site. Harrison & Holman (1979), using an in-situ surface measurement technique, observed NO_2 peaks of similar magnitude and duration at a rural site in N-W England, and attributed them to meandering plumes from middle-distance urban areas passing through their sample site. In the present case, a study of anemograph traces from Beaufort Park on the days when tropospheric influences were apparent revealed no significant dependence upon wind direction. The study was complicated by the fact that winds were usually light and variable, and therefore difficult to determine from anemograph traces, in the anticyclonic conditions often associated with cloudless skies. A further complication was that winds from a fairly wide range of directions could have transported NO_2 from a local source into the slant-path between the monochromator and the sun. Probably the most important local sources were morning rush-hour car exhaust fumes from the nearby A3095 or even the M3, M4 or A329(M) motorways.

In general, there is a tendency for the scatter of the points in the quasi-Langley plots to increase towards midday, which may be due to increased vertical convection of boundary-layer NO_2 . The smooth appearance of some of the plots (for example 10 May 1980) implies that the contribution to the scatter from instrumental noise is probably quite small, in most cases, compared with the scatter caused by actual changes in slant-path NO_2 . When comparing the slopes and scatter of the quasi-Langley plots in the Appendix, the differing horizontal and vertical scales used should be noted.

Comparison with other Measurements

Noxon (1975) reported a mean total daytime NO_2 column of 0.5×10^{16} molecules cm^{-2} above Fritz Peak Observatory (3000 metres a.m.s.l.) whereas Pommereau and Hauchecorne (1979), using a similar ground-based spectral scanning technique, reported much higher values of a few $\times 10^{17}$ molecules cm^{-2} above Haute-Provence Observatory (651 metres a.m.s.l.). Their values compare with a mean Beaufort Park (70 metres a.m.s.l.) value of around 2.5×10^{16} molecules cm^{-2} . Noxon's smaller values are understandable in view of the smaller tropospheric contribution to the NO_2 column expected at his high-altitude site, but the French results are more difficult to explain.

In order to determine an absolute value for total NO_2 from each spectrum, the French workers recorded a lunar spectrum at the same local time on two consecutive nights (3/4 April 1977) at largely differing lunar zenith angles.

Assuming the vertical NO_2 was the same at both times, and using one of the spectra as a reference, they deduced the total NO_2 present at the time of the reference spectrum by extrapolating a two-point quasi-Langley plot to zero atmospheric mass number. Use of this reference spectrum throughout their analysis enabled a total NO_2 column to be calculated for every spectrum, whether solar or lunar. However, a synoptic study revealed that the low-level atmospheric circulation over S-E France changed quite considerably over the 24 hour period concerned. On the night of 3 April 1977, low-level air from the Bay of Biscay and western France passed over Haute-Provence, but on the following night the air had probably traversed a much longer land track, possibly including the more industrialised north of France. Thus the assumption of the same vertical NO_2 at the same local time made by the French workers may not have been valid; if there was a greater tropospheric contribution to the total NO_2 on the second night, all their reported values would be too large. Currently understood seasonal, diurnal and latitudinal (Noxon, 1979(b)) stratospheric NO_2 variations can not account for differences of up to two orders of magnitude in the total column amount.

Noxon et al (1979, 1979(a)) have presented evidence of response to stratospheric warmings, reporting stratospheric column values in the range 1.5×10^{15} molecules cm^{-2} . Harrison (1979) reported similar stratospheric values. The above workers used a ground-based technique, deducing stratospheric NO_2 abundances from spectral measurements, in the range 435-450 nm, of the scattered light from the zenith sky in the period around sunrise and sunset. Despite some debatable assumptions made about scattering geometries, crepuscular changes in NO_2 ; and, in Noxon's case, the importance of stratospheric O_3 absorption, stratospheric NO_2 columns were consistently found to lie in the above range. This implies that tropospheric contamination was probably present to varying degrees on all of the occasions when total column measurements were made at Beaufort Park. Pommereau & Hauchecorne's total column values appear to be even less representative of the stratospheric column.

Concluding Remarks

The present apparatus and method of analysis have demonstrated the possibility of measuring the NO_2 total column at a site not enjoying the best of viewing conditions. On occasions there may have been complicating influences due to advective changes in tropospheric NO_2 , but the results do lend some support to the relatively low values of NO_2 column reported by Noxon. The values reported by Pommereau & Hauchecorne appear to be anomalously high.

Consideration is being given to the design of a spectrophotometer system optimized for this type of measurement which could be used at a site well removed from tropospheric NO₂ sources. Provision may be made for mounting it on an aircraft, so as to offer the possibility of measuring NO₂ above the most frequent cloud layers and the polluted boundary layer. The use of a diode-array detector of the diffracted spectrum could extend the range of possible ground-based viewing conditions, since a simultaneous measurement across the spectrum would preclude spurious spectral features caused by cloud structure crossing the sun's disc during scanning.

References

- Ahlquist, N.C. & Charlson, R.J. Measurement of the Wavelength Dependence of Atmospheric Extinction due to Scatter. *Atmos. Env.* 3, 551-564 (1969).
- Brewer, A.W., McElroy, C.T. & Kerr, J.B. Spectrophotometric Nitrogen Dioxide Measurements. *Proc. III Conference on C.I.A.P.*, Feb. 1974, 257-263.
- Clough, S.A. & Hinds, M.K. Model Studies of the Role of the Chlorine Species and the Possible Effects of Chlorofluorocarbon Releases on Stratospheric Composition. *Meteorological Research Committee Publication* 449, October 1978.
- Crutzen, P.J. The Influence of Nitrogen Oxides on the Atmospheric Ozone Content. *Quart. J. R. Met. Soc.* 96, 320 (1970).
- Curcio, J.A., Drummeter, L.F. & Cosden, T.E. The Absorption Spectrum of the Atmosphere from 4400-5500 Å. *Nav. Res. Lab. Report* 4669 (1955).
- Drummond, J.R. & Jarnot, R.F. Infrared Measurements of Stratospheric Composition II. Simultaneous NO and NO₂ Measurements. *Proc. Roy. Soc. Lond. A.* 364, 237-254 (1978).
- Eldridge, R.G. Haze and Fog Aerosol Distributions. *J. Atmos. Sci.* 23, 605-613 (1966).
- Harrison, A.W. Midsummer Stratospheric NO₂ at 45°S. *Can. J. Phys.* 57, 1110-1117 (1979).
- Harrison, R.M. & Holman, C.D. The Contribution of Middle- and Long-Range Transport of Tropospheric Photochemical Ozone to Pollution at a Rural Site in North-West England. *Atmos. Env.* 13, 1535-1545 (1979).
- Johnston, H.S. & Graham, P. Unpublished Absorption Coefficients of NO₂ and O₃. *Dept. of Chemistry, Univ. of California, Berkely, CA.* (1977).
- Kasten, F. A New Table and Approximation Formula for the Relative Optical Air Mass. *U.S. Army Materiel Command C.R.R.E.L. Technical Report* 136, Hanover, New Hampshire. Nov. 1964.
- Kondratyev, K.Y., Radiation Characteristics of the Atmosphere and the Earth's Surface. *Pub: Amerind Pub. Co. Pvt. Ltd., New Dehli.* pp. 129-132 (1973).
- Kuznetsov, G.I. & Nigmatullina, K.S. Determination of Nitrogen Dioxide Content in the Atmosphere by an Optical Method. *Moscow, Acad. Nauk SSSR, Izv., Fiz. Atmos. Okean.* 13, 886-889 (1977).
- McCartney, E.J. Optics of the Atmosphere: Scattering by Molecules and Particles. *Pub: John Wiley & Sons Inc., New York.* (1976).
- McMahon, B.B. & Simmons, E.L. Ground-Based Measurements of Atmospheric NO₂ by Differential Optical Absorption. *Submitted for publication in Nature* (1980).
- Noxon, J.F. Nitrogen Dioxide in the Stratosphere and Troposphere Measured by Ground-Based Absorption Spectroscopy. *Science* 189, 547-549 (1975).
- Noxon, J.F., Whipple, E.C. & Hyde, R.S. Stratospheric NO₂ 1. Observational Method and Behaviour at Mid-Latitude. *J. Geophys. Res.* 84, 5047-5065 (1979(a)).
- Noxon, J.F. Stratospheric NO₂ 2. Global Behaviour. *J. Geophys. Res.* 84, 5067-5076 (1979(b)).
- Noxon, J.F., Marovich, E. & Norton, R.B. Effect of a Major Warming upon Stratospheric NO₂. *J. Geophys. Res.* 84, 7883-7888 (1979).

Pommereau, J.P. & Hauchecorne, A. Observations Spectroscopiques Depuis le sol du Dioxyde d'Azote Atmosphérique. C.R.Acad.Sci.Paris.B.288, 135-138 (1979).

Sivkov, S.I. Computation of Solar Radiation Characteristics. Pub: Israel Program for Scientific Translations Ltd., Jerusalem. (1971).

Wilkerson, T.D. et al. Absorption Spectra of Atmospheric Gases. Tech. Note BN-784, Inst. for Fluid Dynamics & Applied Mathematics, Univ. of Maryland, College Park, MD. (1974).

Table 1

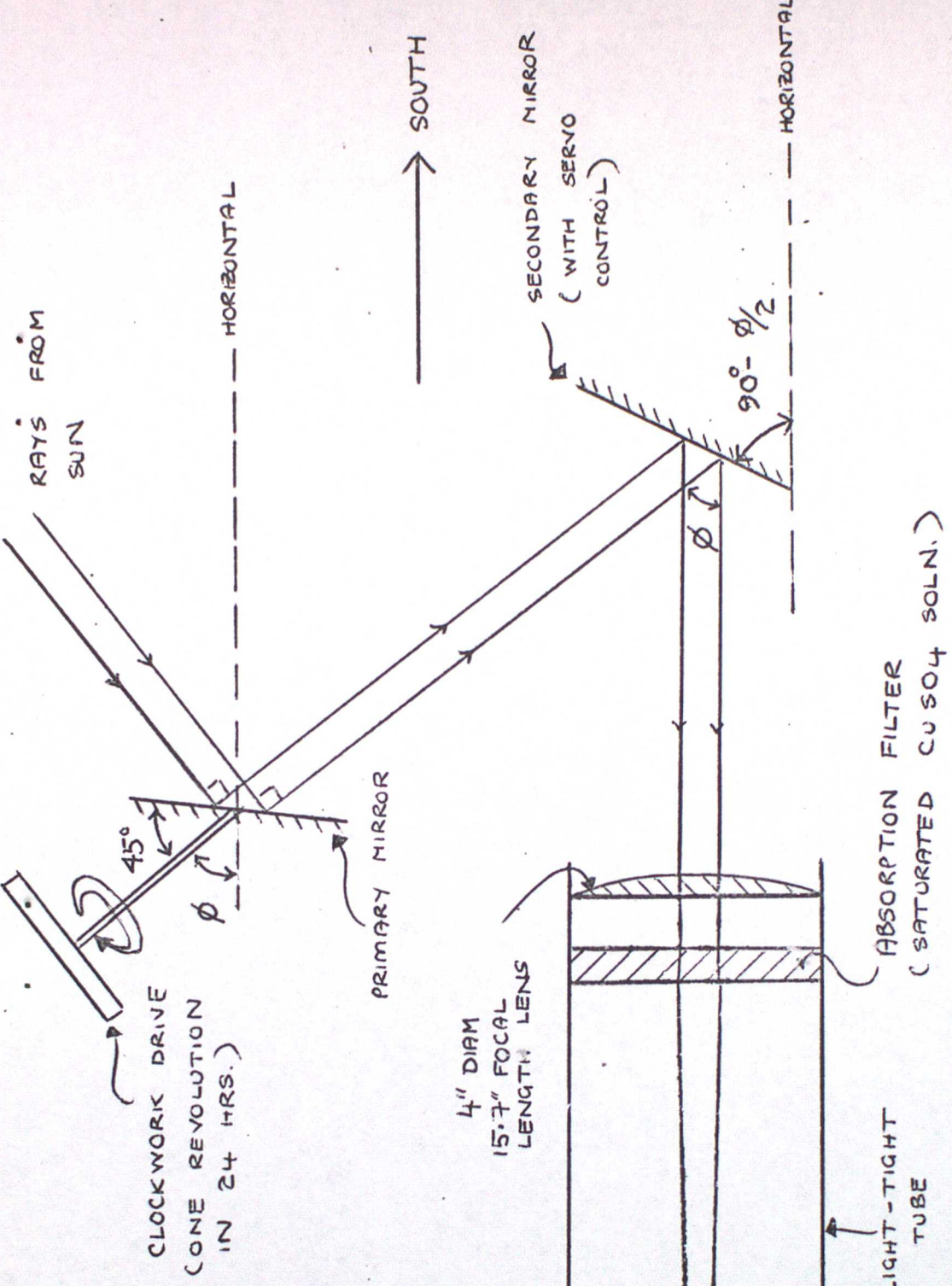
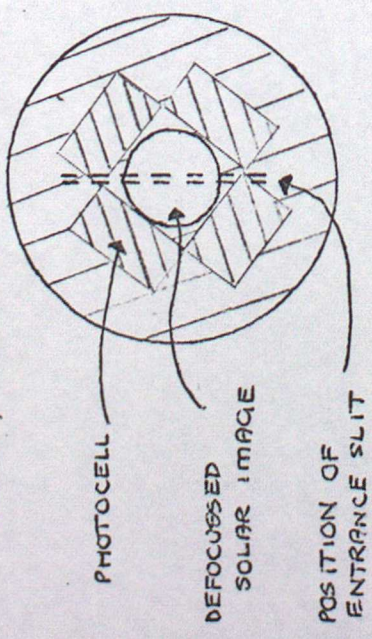
Values of the total vertical NO₂ column at Beaufort Park,
Bracknell, Berkshire (51°23'N, 0°47'W, 70 metres a.m.s.l.)

Date	Time interval (GMT)	μ -range [†]	Reference spectra used	Total NO ₂ estimated from slope, (10 ¹⁶ molecules cm ⁻²)
6 September 1979	0610-0839	1.9-7.0	14 December 1979	0.9±0.2
18 October 1979	0802-0938	2.5-4.4	4 January 1980	3.4±0.3
2 November 1979	0832-0922	3.3-4.6	4 January 1980	1.3±0.6
5 November 1979	0756-0857	4.0-7.0	14 December 1979	0.9±0.3
9 November 1979	0807-1044	2.8-6.8	14 December 1979	0.9±0.2
13 November 1979	0813-0842	5.2-7.0	4 January 1980	4.1±0.3
	0846-1044	2.9-5.2		0.7±0.4
21 December 1979	0911-1058	3.9-7.0	14 December 1979	3.0±0.6
31 December 1979	0916-0935	5.8-6.8	4 January 1980	4.1±0.8-0.4
	0935-1103	3.8-5.8		0.6±0.4
2 January 1980	0913-1003	4.0-7.0	4 January 1980	1.9±0.8
24 January 1980	0901-1112	3.1-6.4	4 January 1980	1.7±0.9
4 March 1980	0729-0840	3.4-7.0	4 January 1980	5.6±0.8
22 March 1980	0647-0701	5.8-7.0	22 March 1980	2.7±0.5
	0701-0831	2.6-5.8		0.9±0.1
30 March 1980	0747-1000	2.1-5.5	4 May 1980	0.8±0.8-0.2
20 April 1980	0544-0656	3.0-7.0	1 May 1980	1.9±0.4
10 May 1980	0520-0741	2.0-6.2	4 May 1980	2.4±0.5
11 May 1980	0509-0529	5.4-7.0	4 May 1980	7.7±0.1
	0529-0838	1.6-5.4		4.3±0.5
16 May 1980	0502-0541	4.4-7.0	4 May 1980	1.2±0.7
19 May 1980	0503-0642	2.6-6.6	4 May 1980	5.8±0.4

[†] Values of μ greater than 7, or corresponding to times within one hour of midday, are not included.

NB: Greater weighting should be given to NO₂ values derived from plots which were essentially linear over a wide range in μ ² (eg. 6 September 1979). Advective changes in tropospheric NO₂ may be responsible for the changes in slope observed on four of the above dates, complicating the estimation of the total column amount.

PLAN VIEW OF GROUND-GLASS PLATE



NB: THE HELIOSTAT IS DRAWN FOR EQUINOX AT LOCAL NOON.
 ϕ = LATITUDE
 THE SIGNAL FROM THE FOUR PHOTOCELLS IS USED TO DRIVE THE SECONDARY MIRROR IF A FINE ADJUSTMENT IS NECESSARY.

APPROX 15"

OPTICAL ARRANGEMENT IN FRONT OF MONOCHROMATOR ENTRANCE SLIT

FIG 1 :

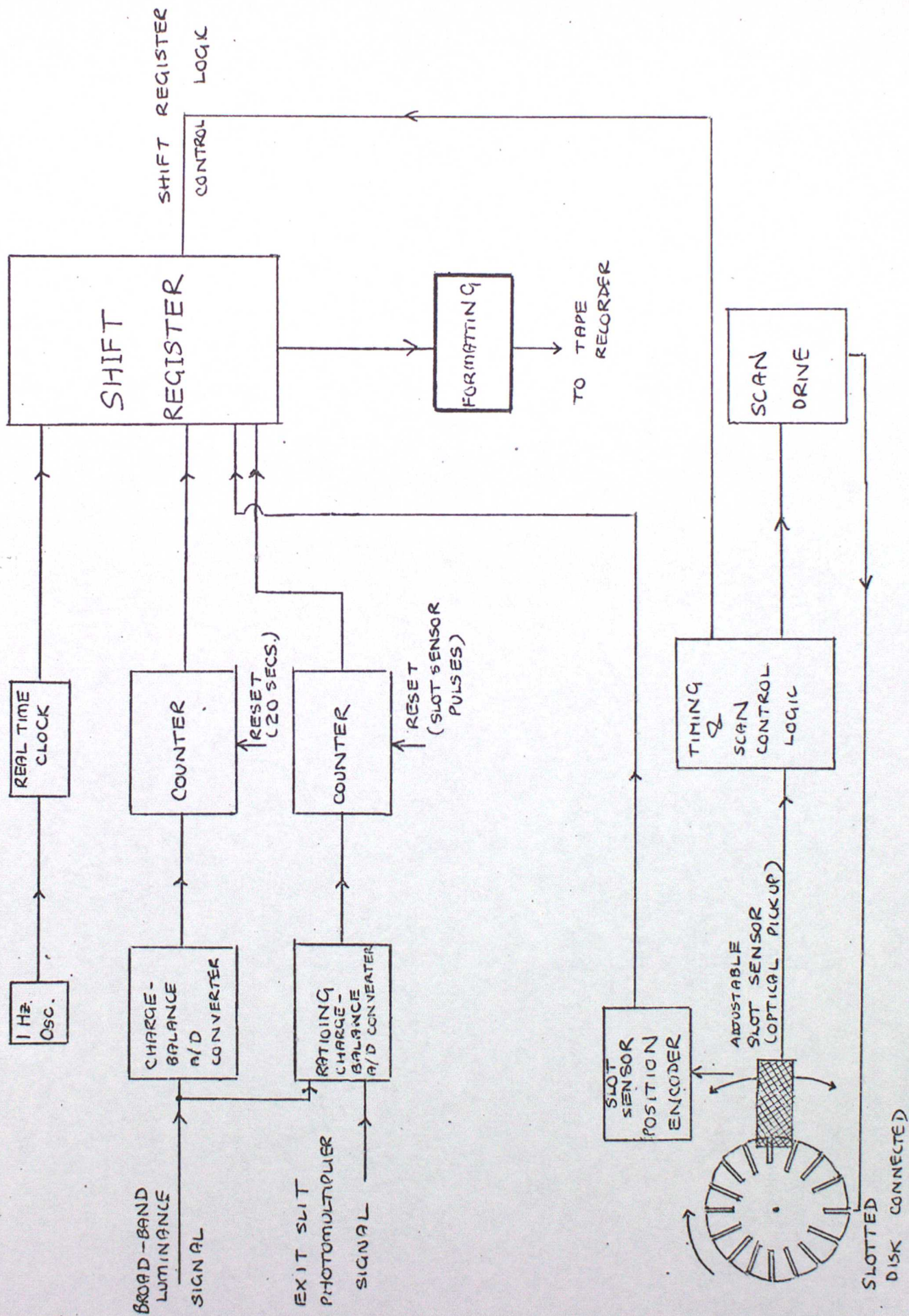
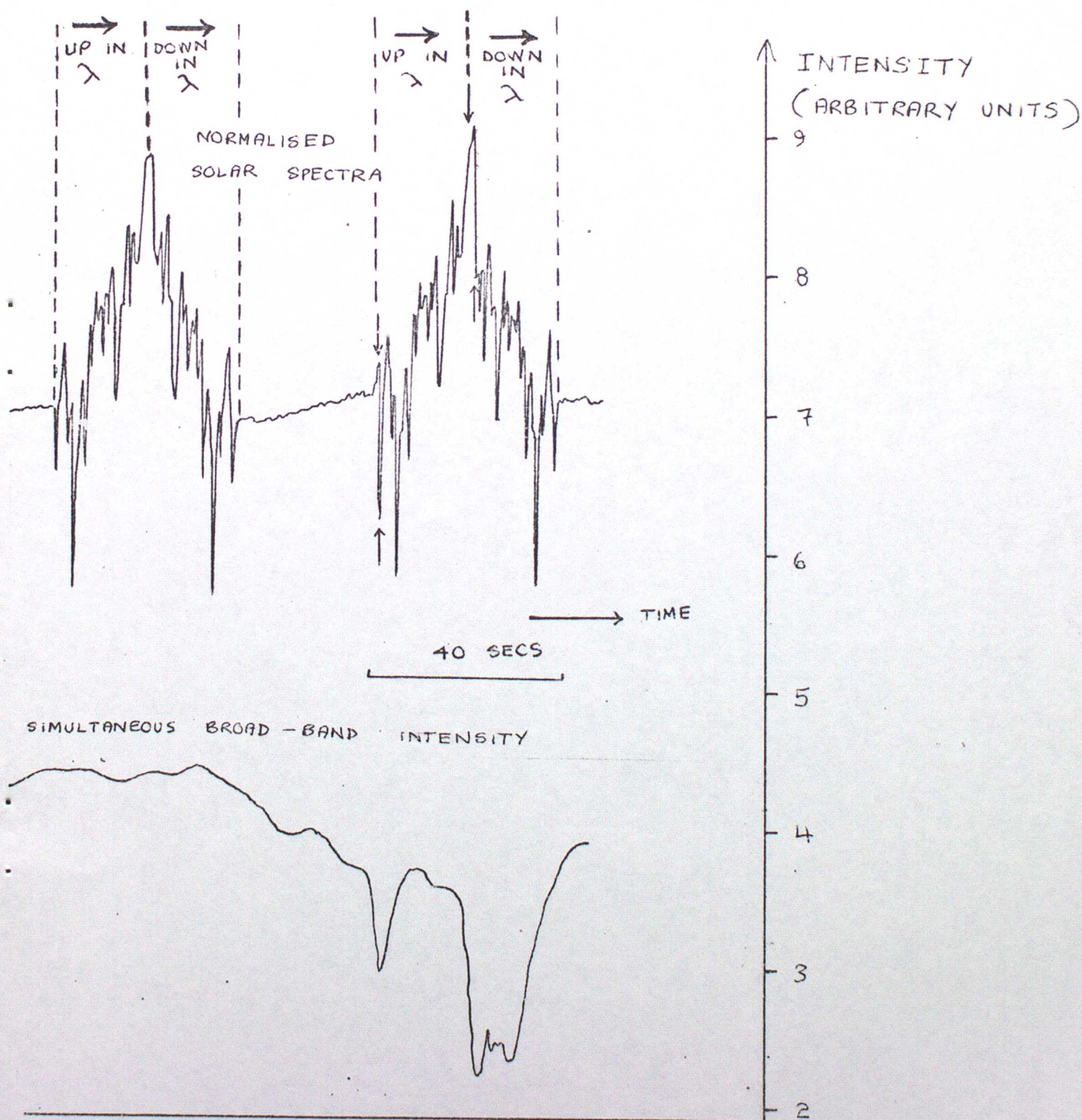


FIG 2 : SIMPLIFIED BLOCK DIAGRAM OF MONOCHROMATOR SYSTEM ELECTRONICS

Fig 3: EXAMPLE OF THE EFFECT OF CUMULUS ON SPECTRA

The above chart recorder traces were obtained at a high solar elevation on 1 May 1980 when occasional cumulus cloud obscurations of the solar disc occurred. Arrows indicate some of the spurious features in the normalised up/down spectra associated with these obscurations. It may be seen that the first up/down spectrum displays greater symmetry than the second.



APPENDIX

QUASI-LANGLEY PLOTS AND ASSOCIATED CORRECTED SPECTRA (PRESENTED IN CHRONOLOGICAL ORDER)

NOTE:

CORRECTED SPECTRA

The bottom curve represents the NO_2 absorption spectrum used in the regression calculations, after suitable scaling to assist visual comparison with the corrected spectra. Arrows mark the H_2O channels omitted from the analysis. An optical depth of 0.1, relative to the reference, is given by the length of the vertical bar shown. The time of observation of rising-sun spectra (in GMT) is also indicated.

QUASI-LANGLEY PLOTS

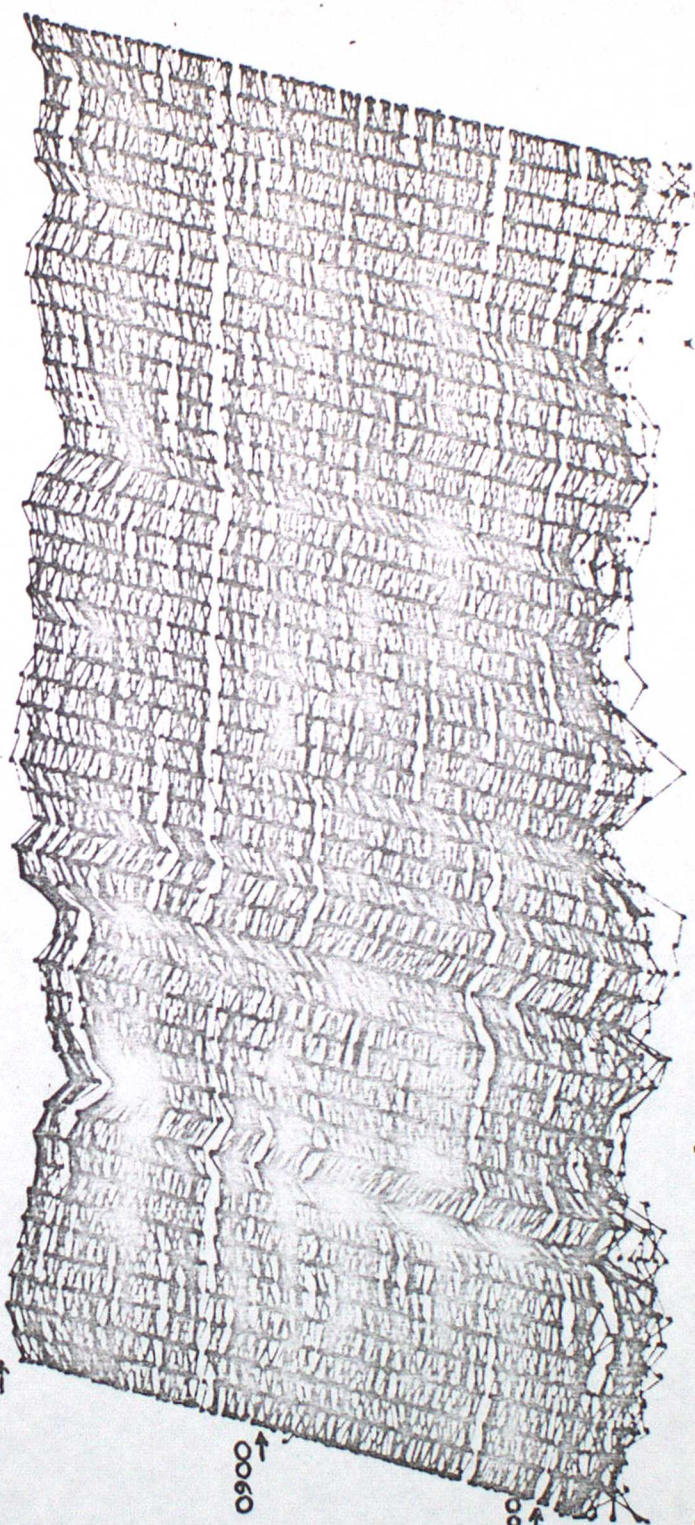
The limits of the ranges in atmospheric mass number, μ , over which slopes were calculated are indicated by the vertical marks above the μ axis. If slopes are to be compared by eye, the differing horizontal and vertical scales used in these plots should be carefully noted.

6 SEP '79

GMT
1200 →

0900 →

0800 →



435

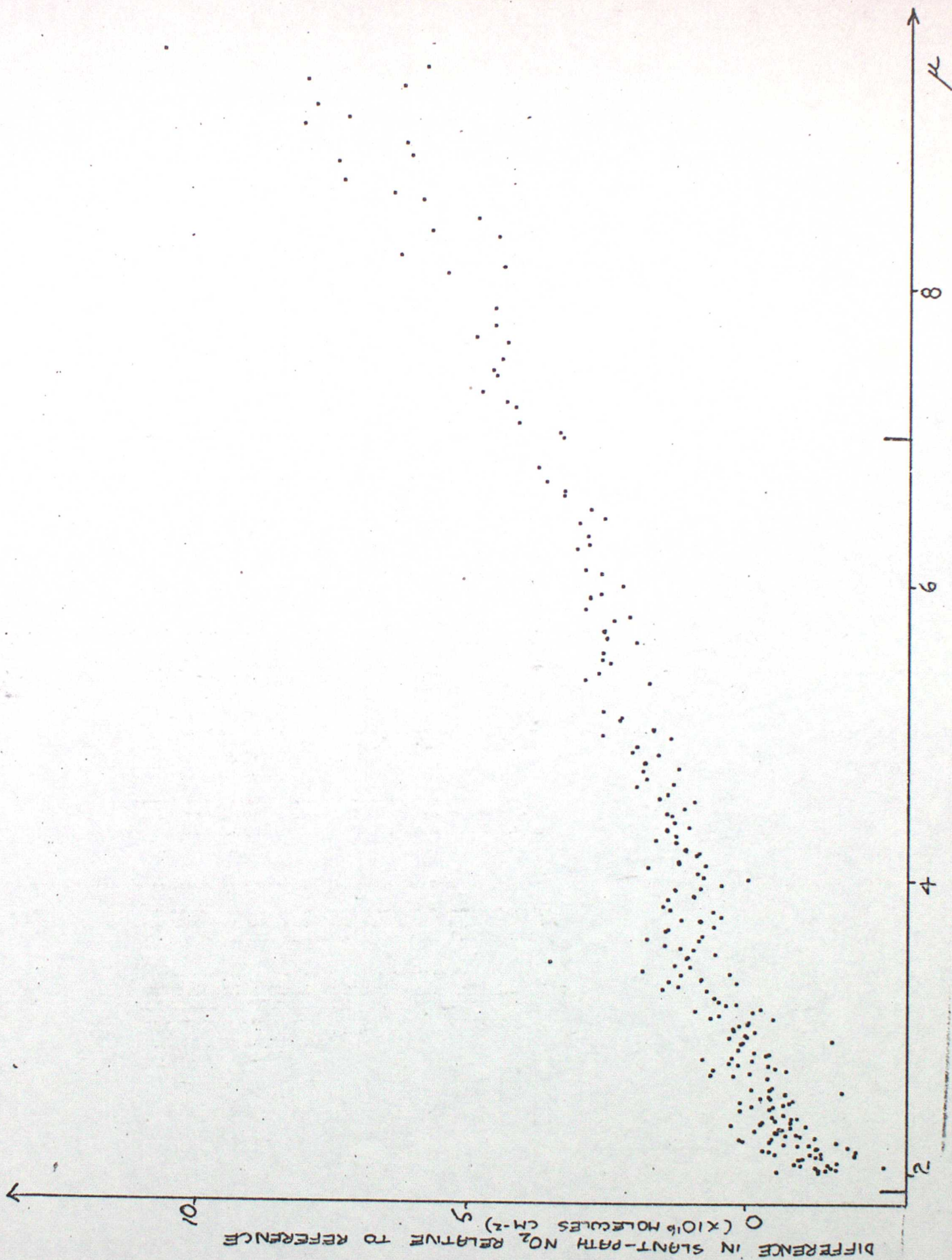
440

445

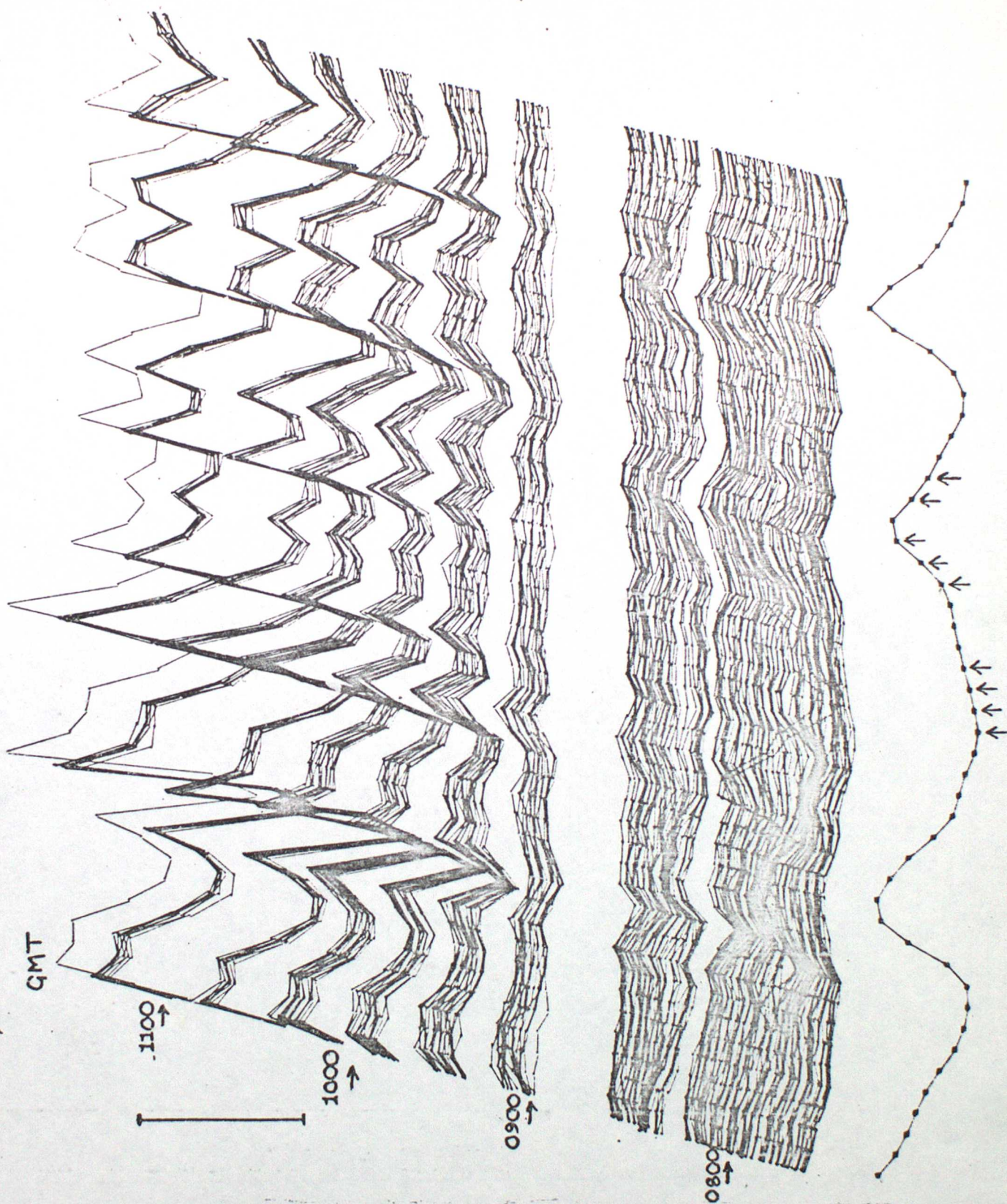
450

455

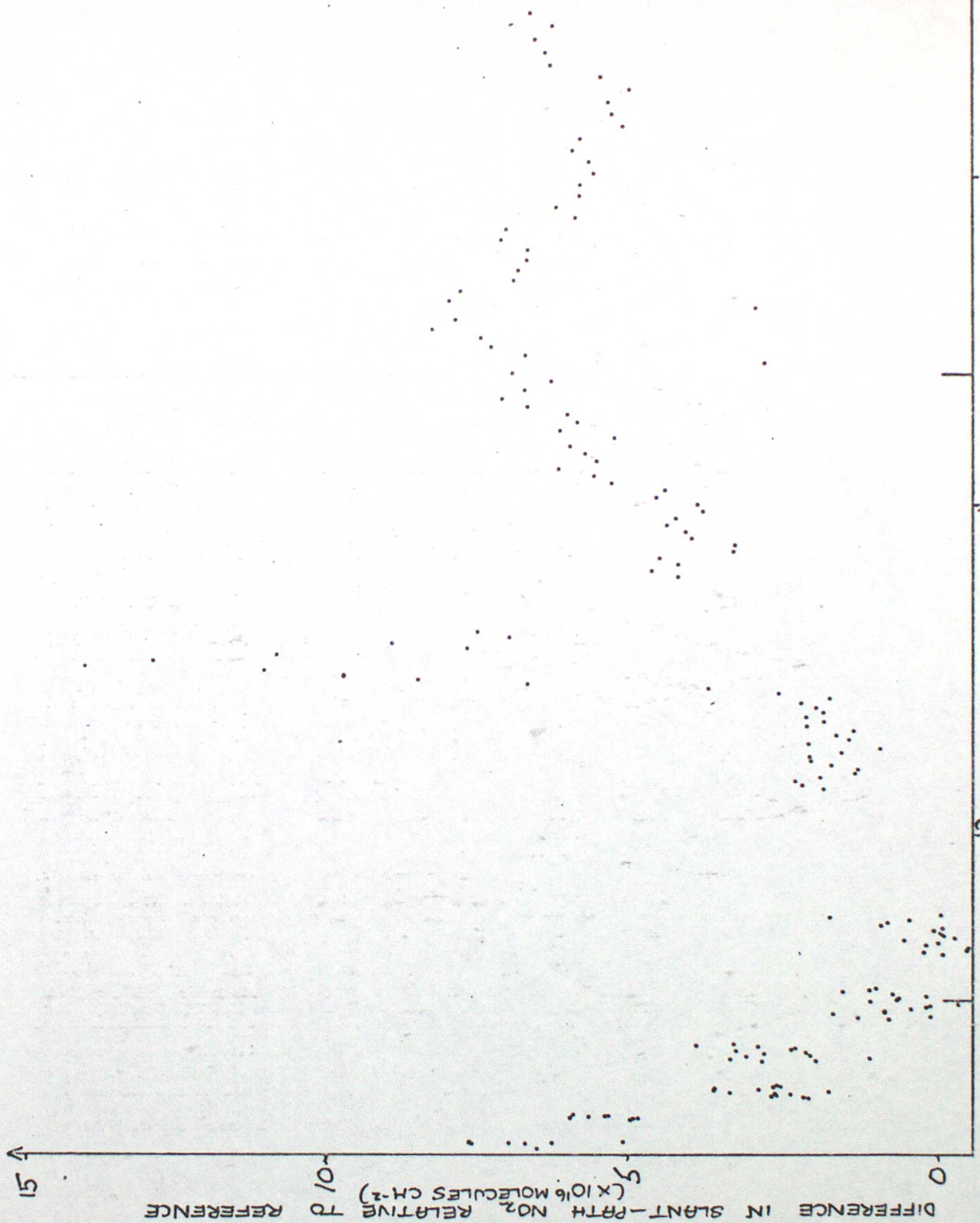
6 SEP '79



18 OCT '79

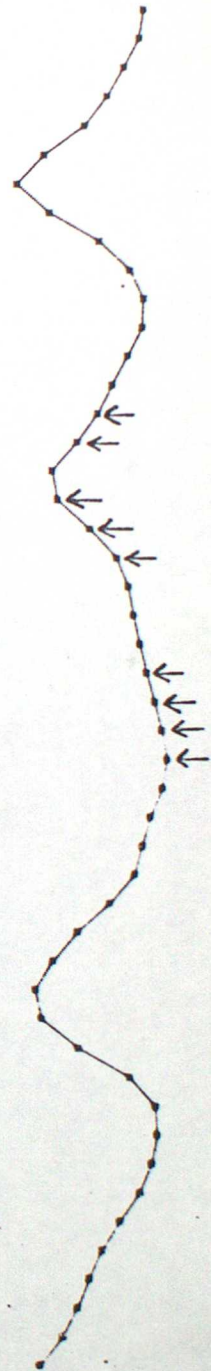
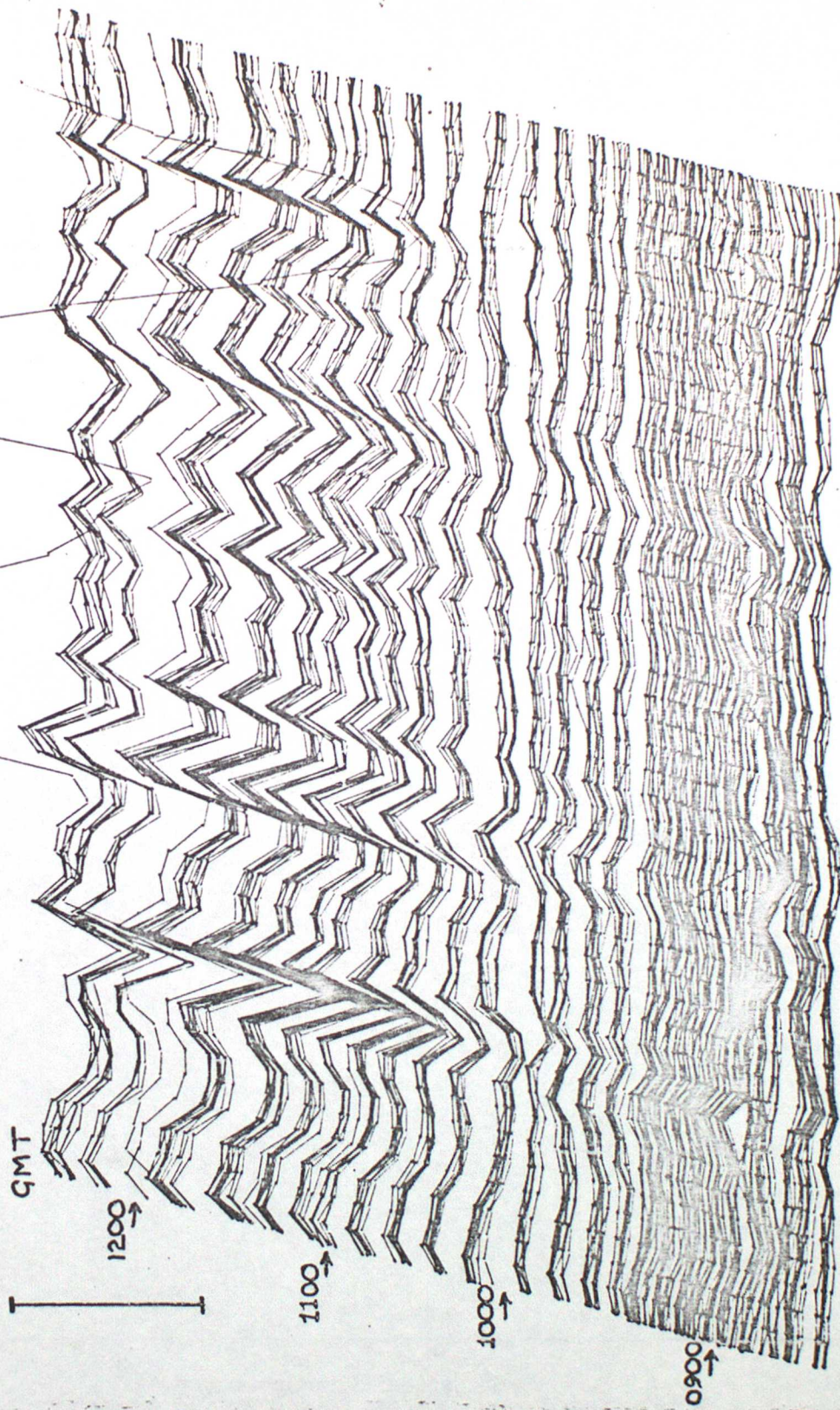


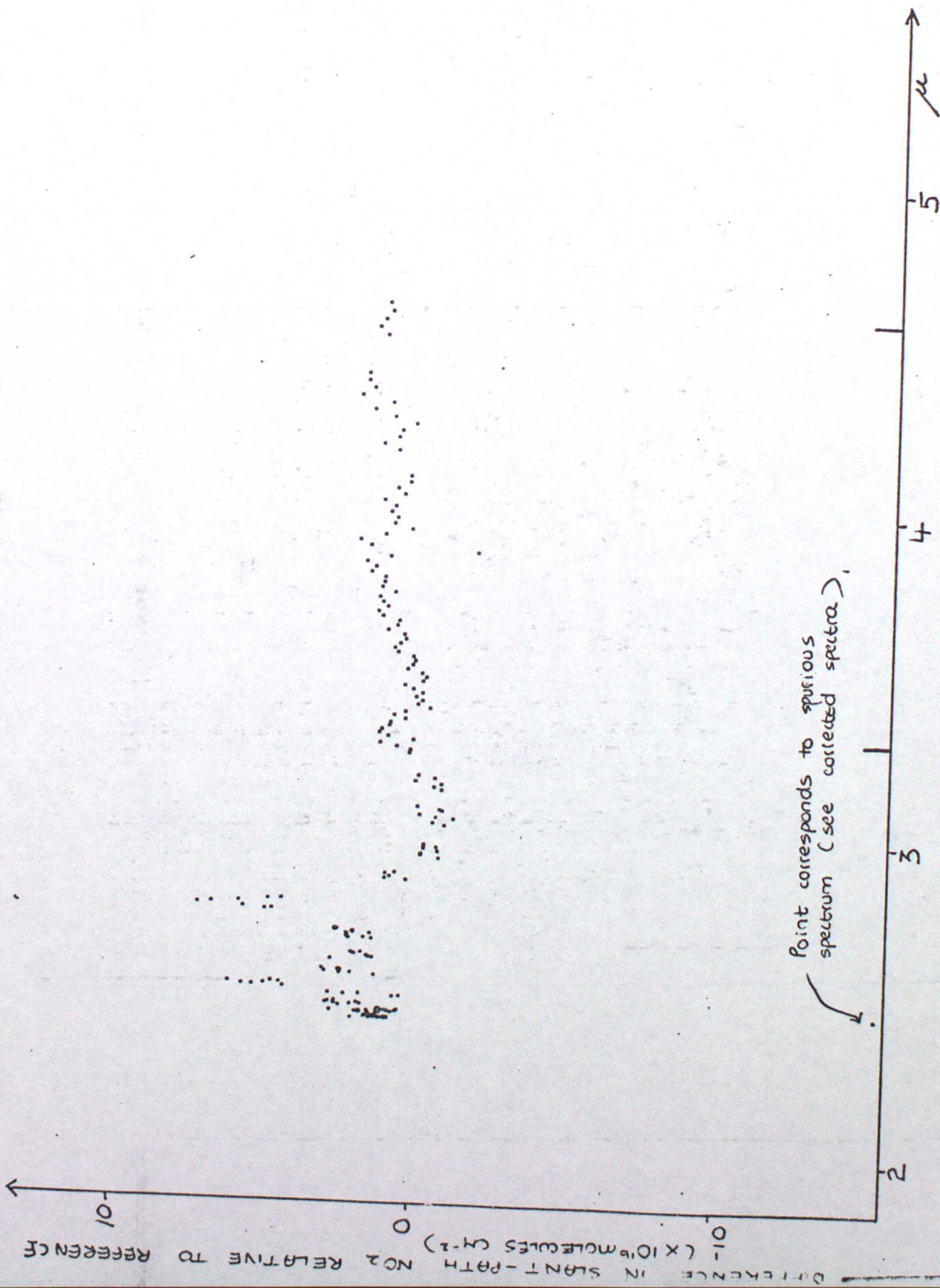
18 OCT '79



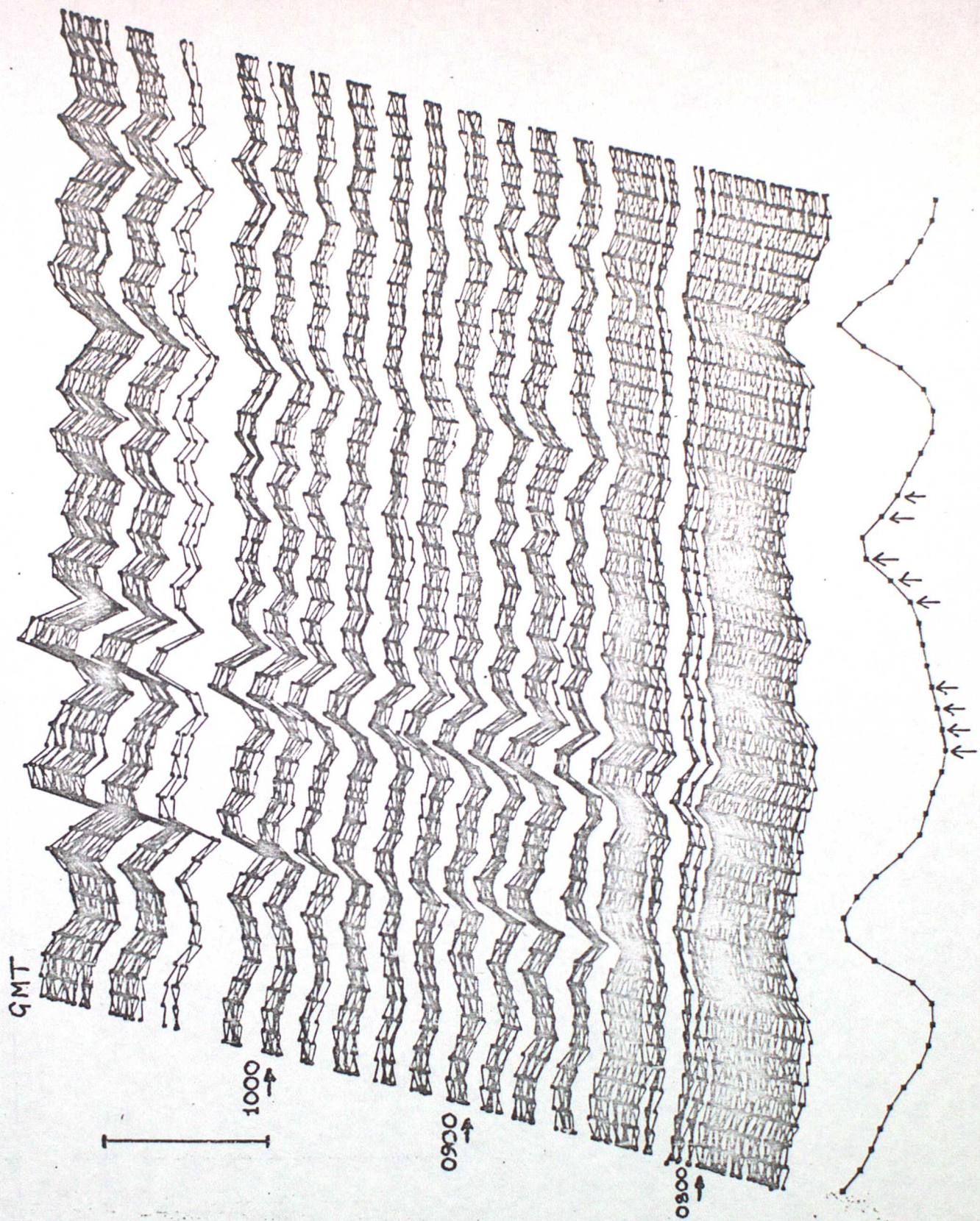
2 NOV '79

Spurious spectrum
caused by sudden
heliostat adjustment





5 NOV '79



435

440

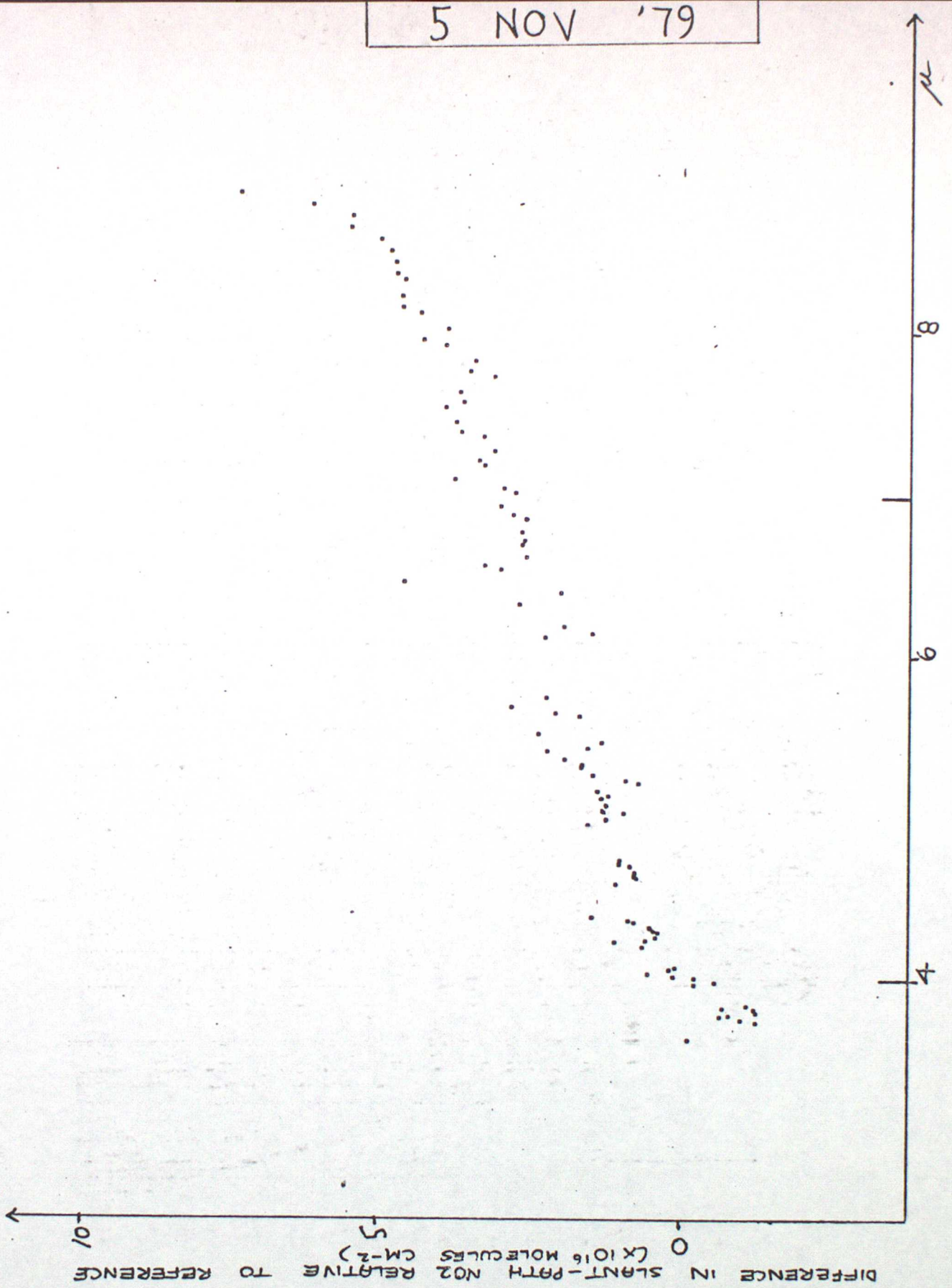
445

450

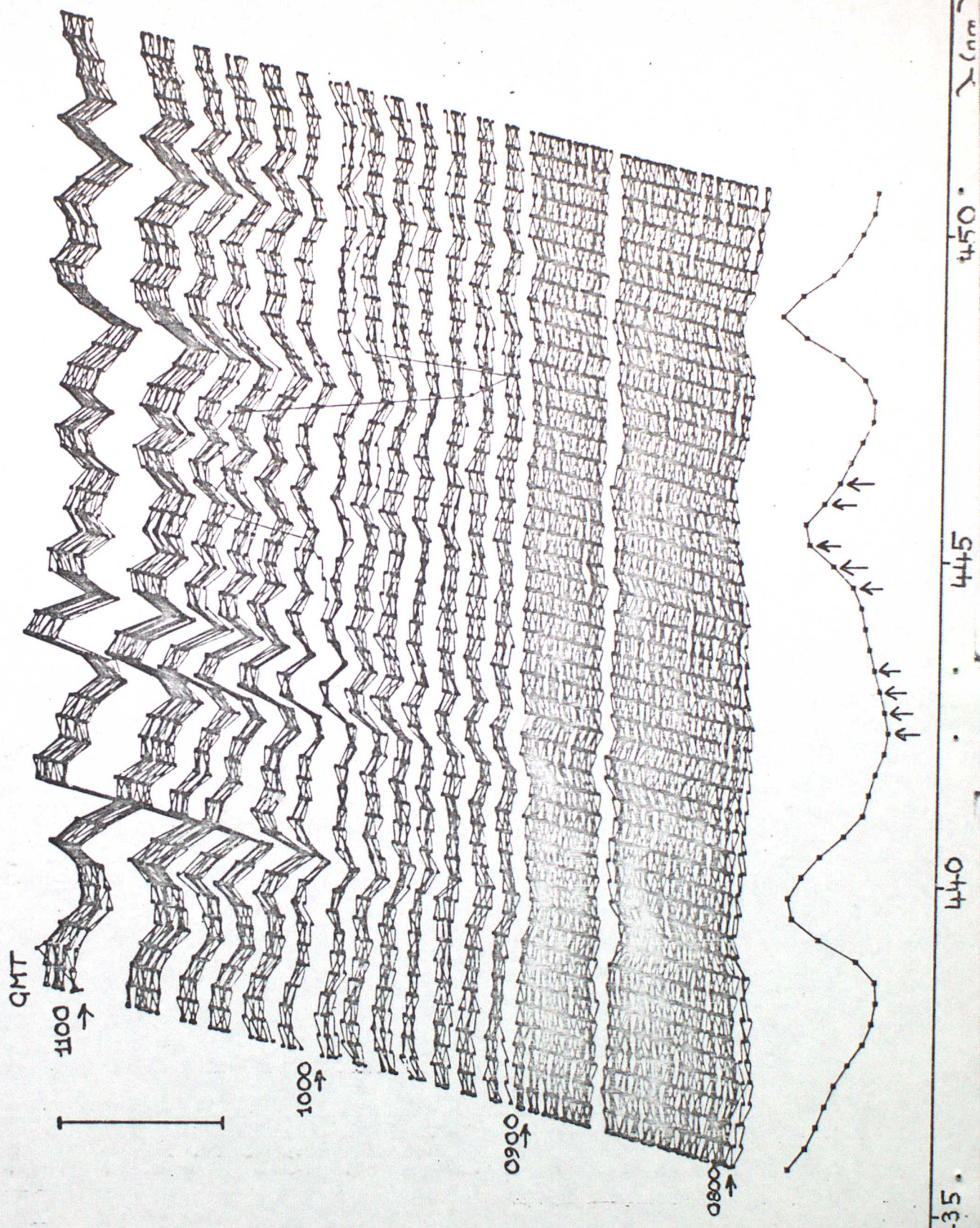
455

460

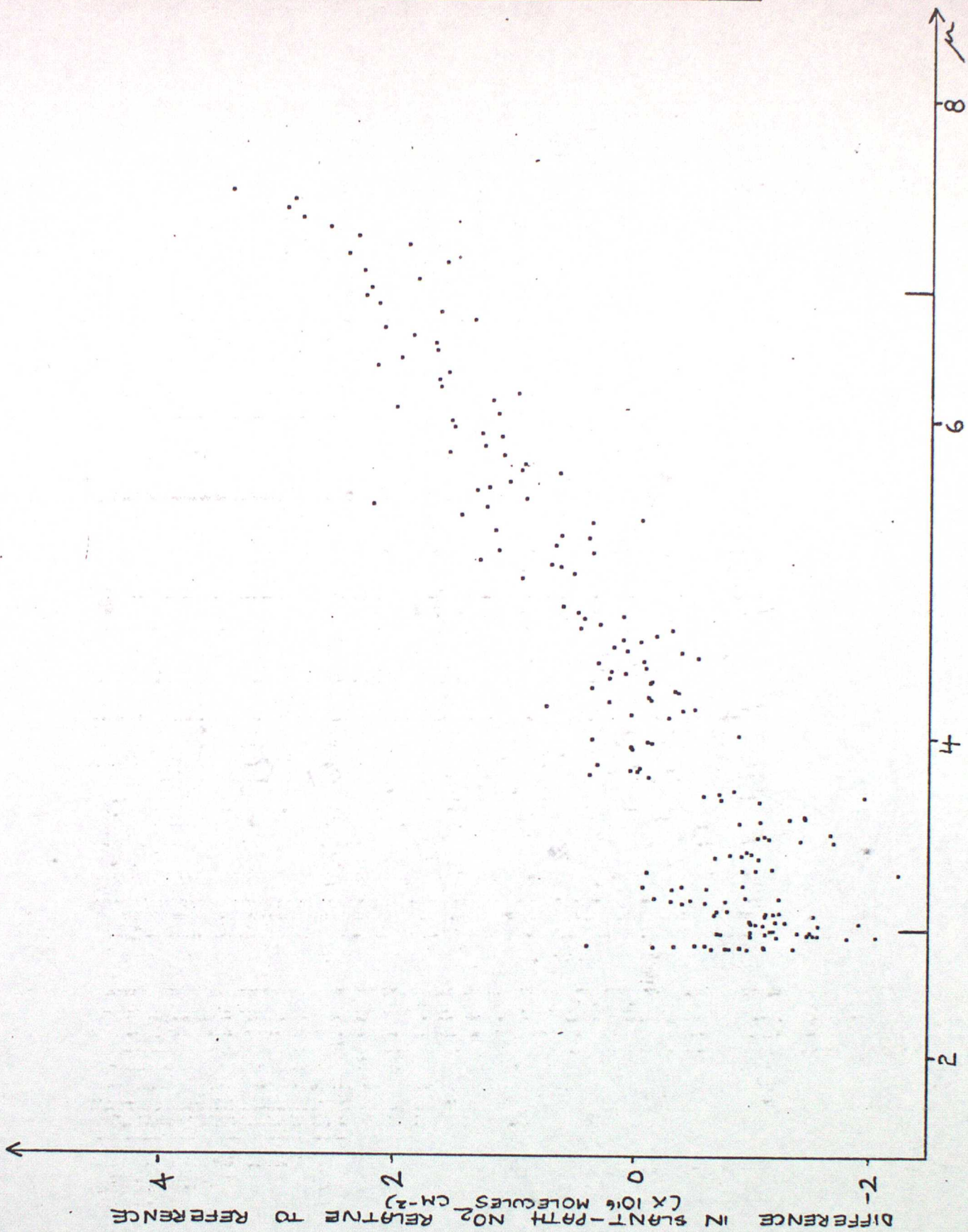
5 NOV '79



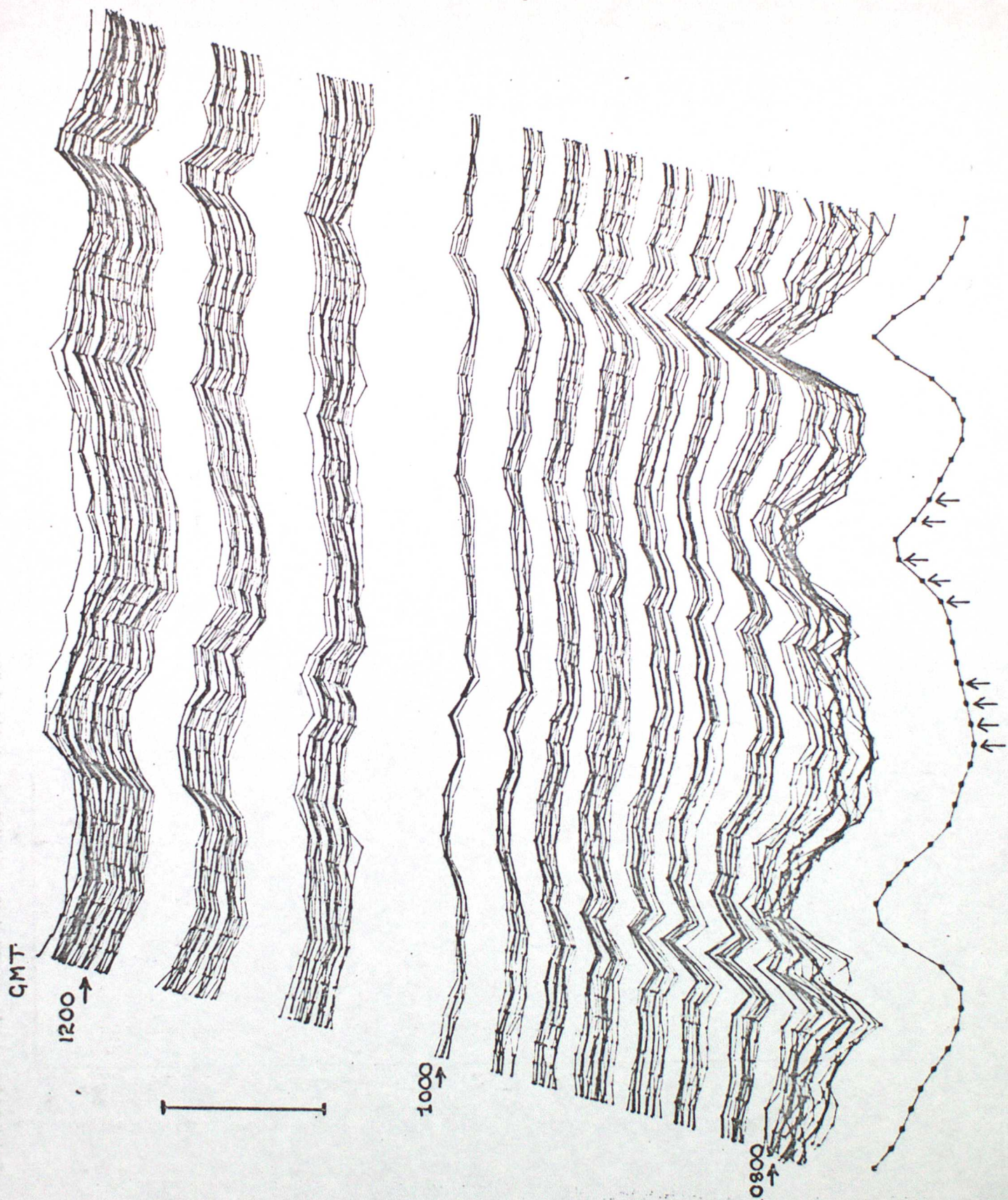
9 NOV '79



9 NOV '79



13 NOV '79



λ(m)

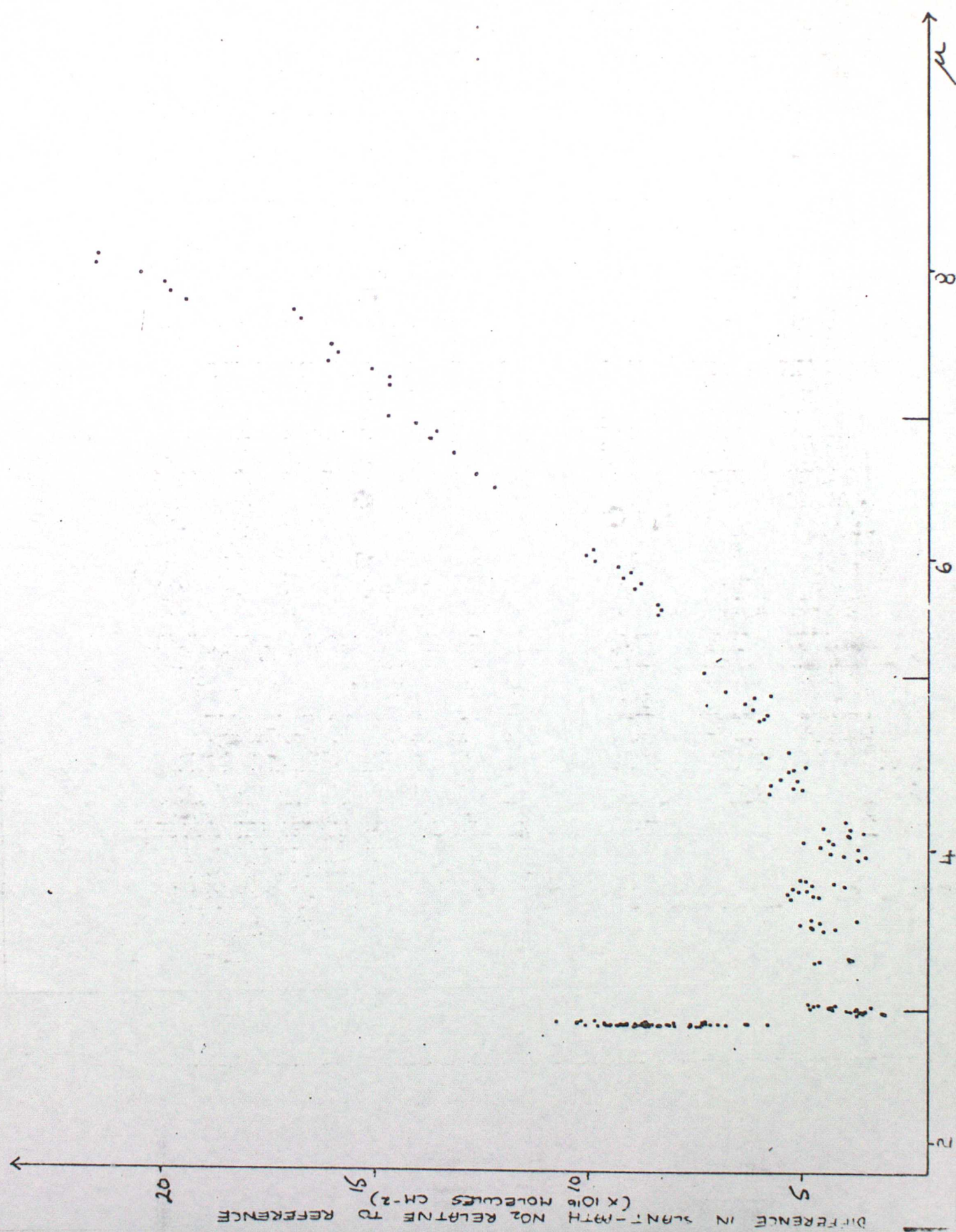
450

445

440

435

13 NOV '79



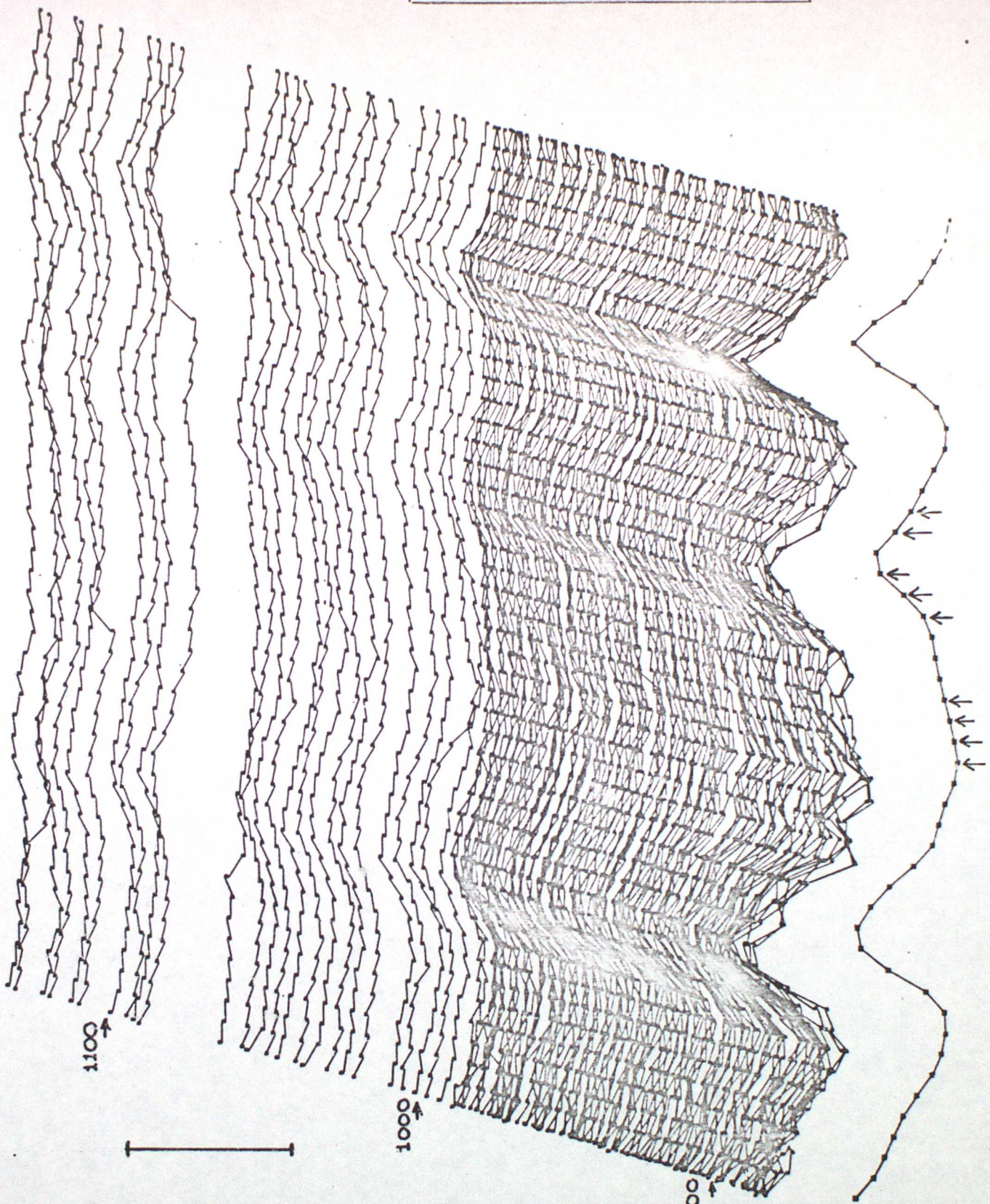
21 DEC '79

GMT

1100

1000

0900



435

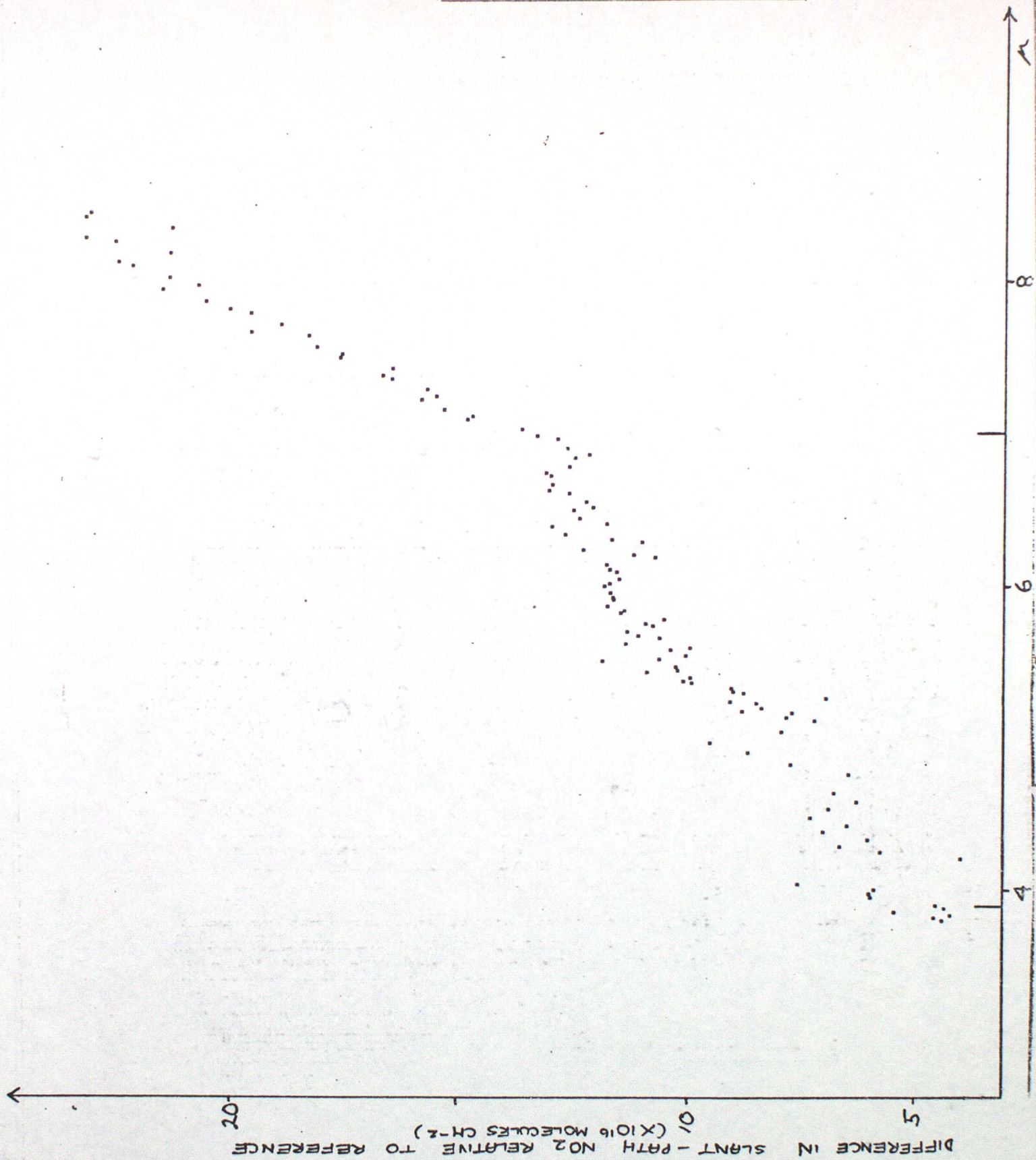
444

444

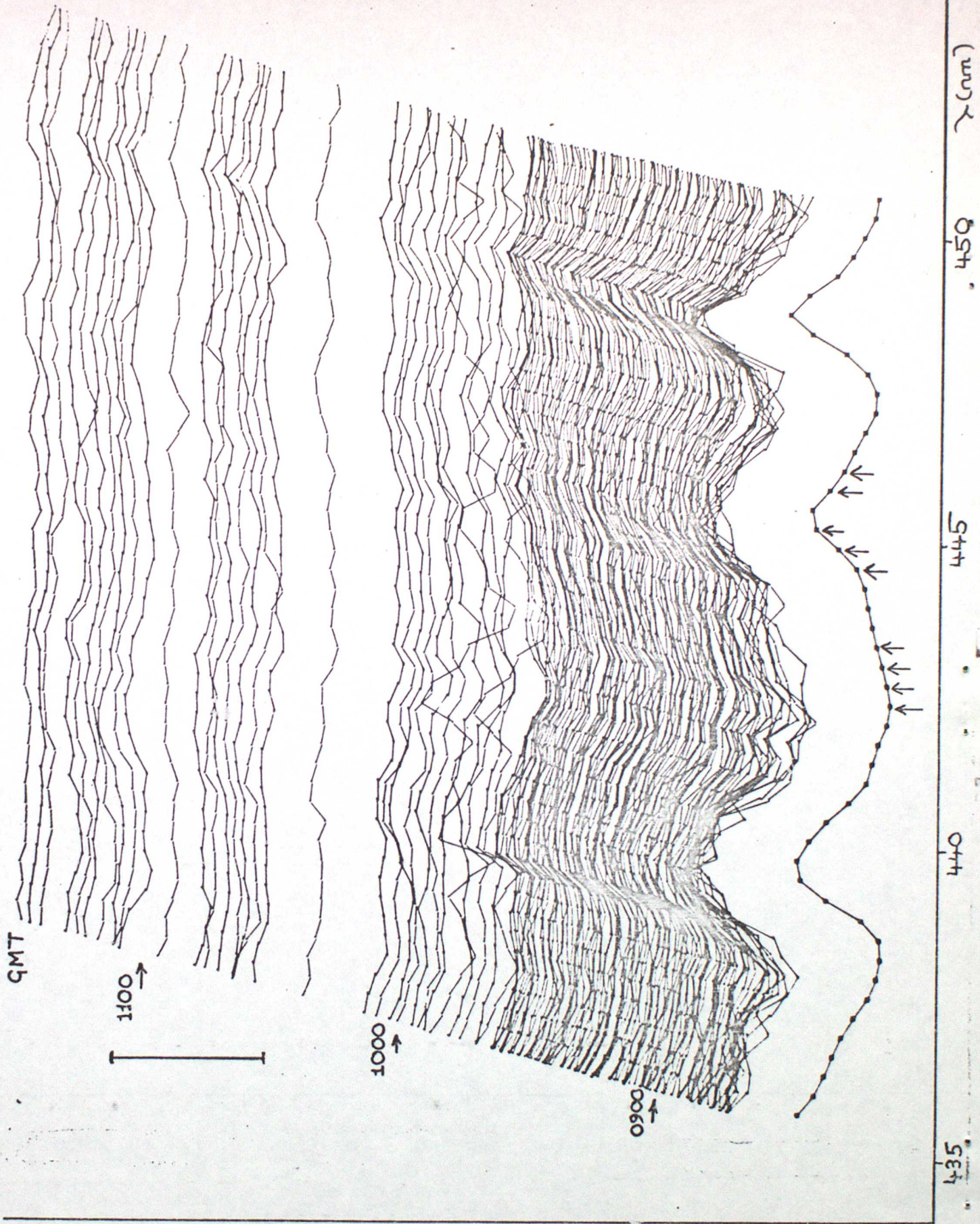
450

(mm)

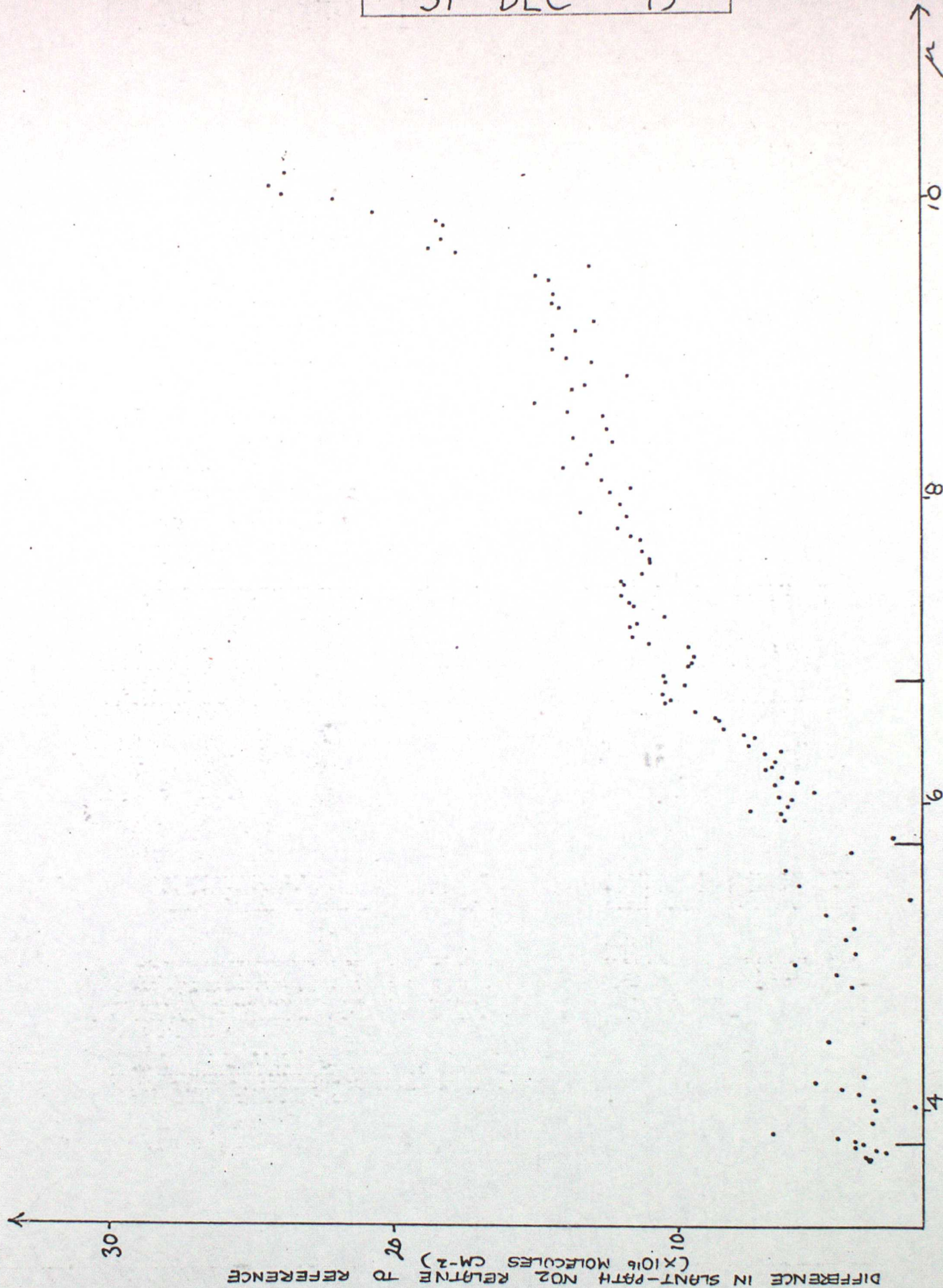
21 DEC '79



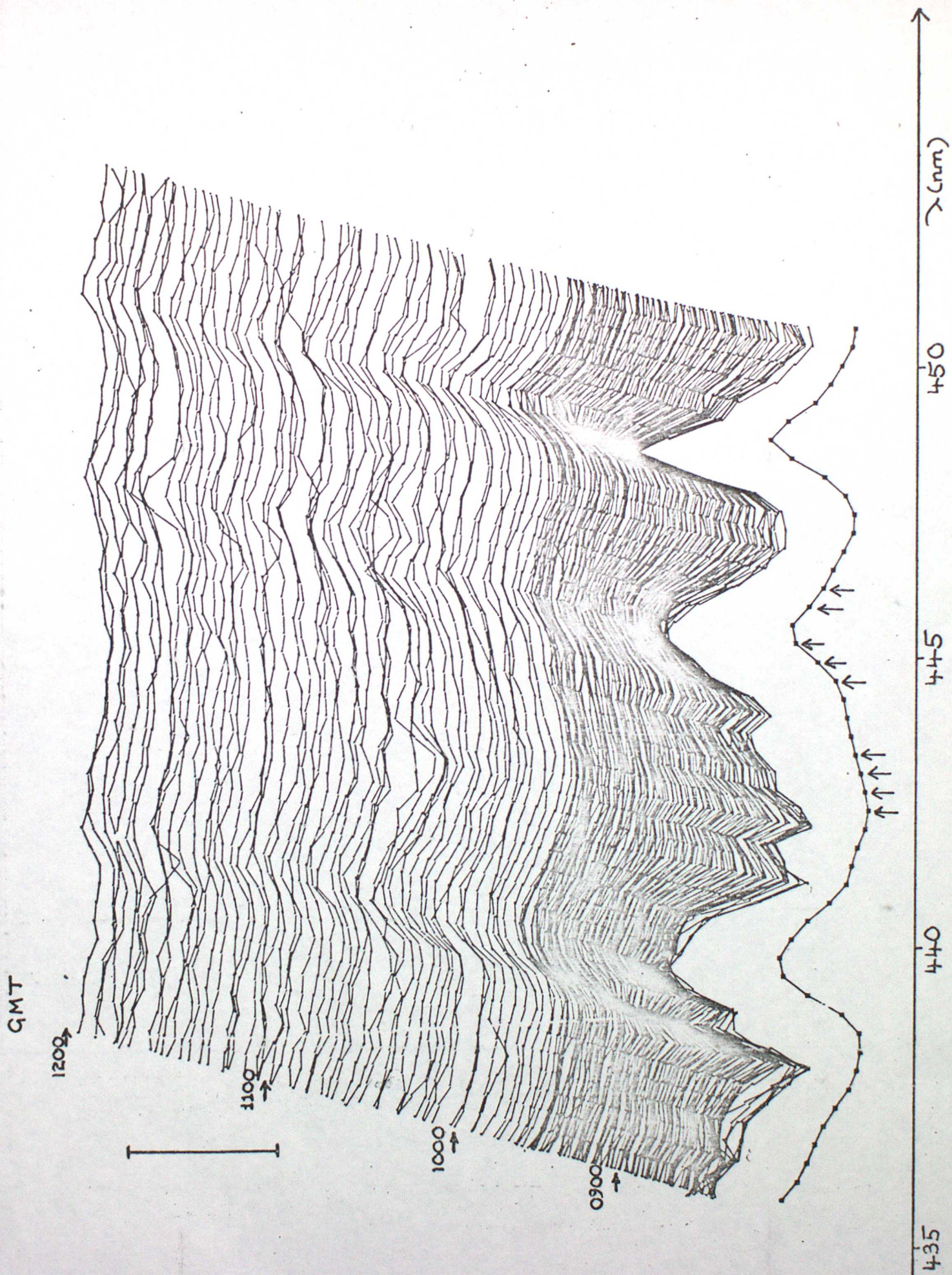
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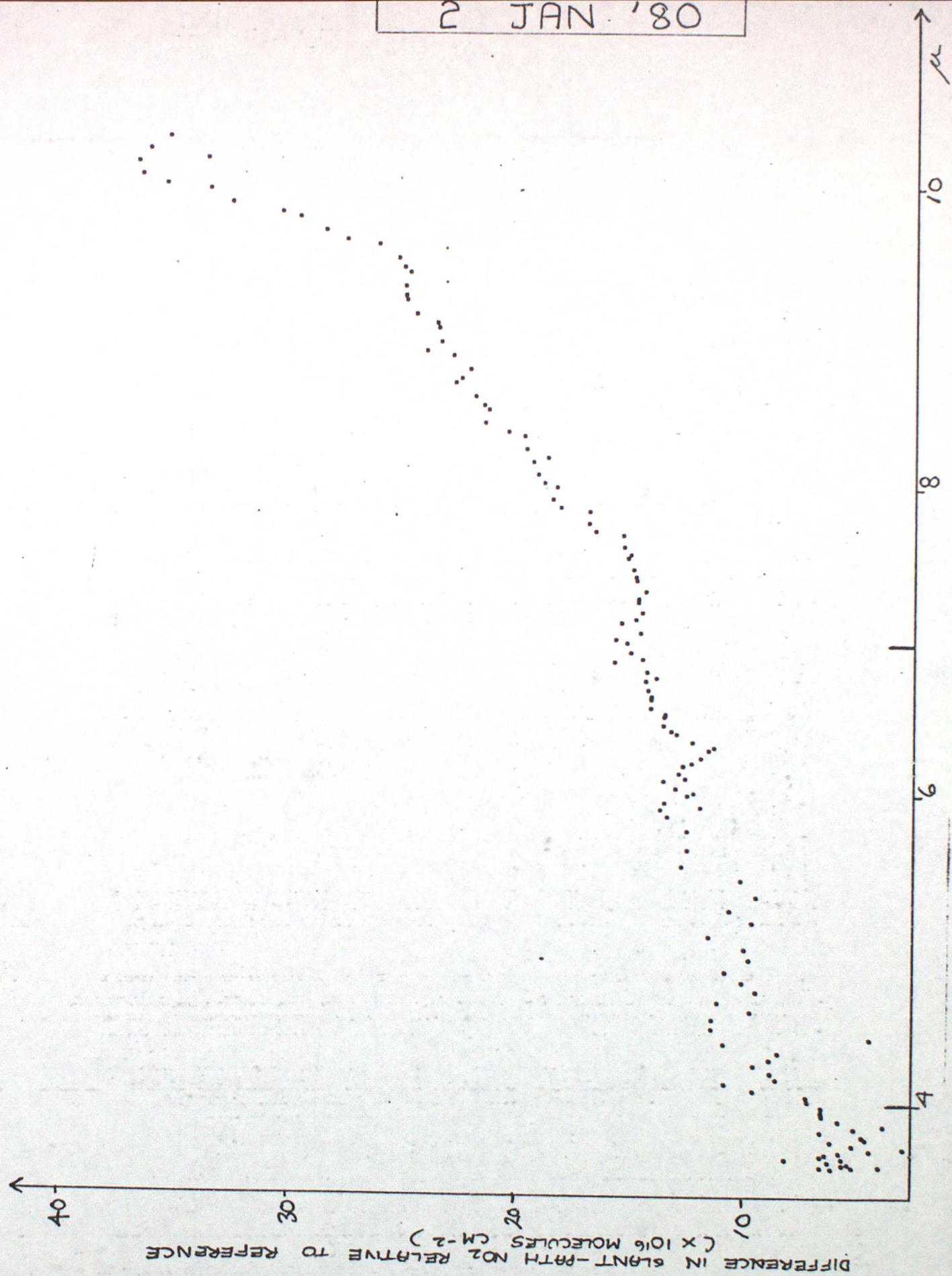
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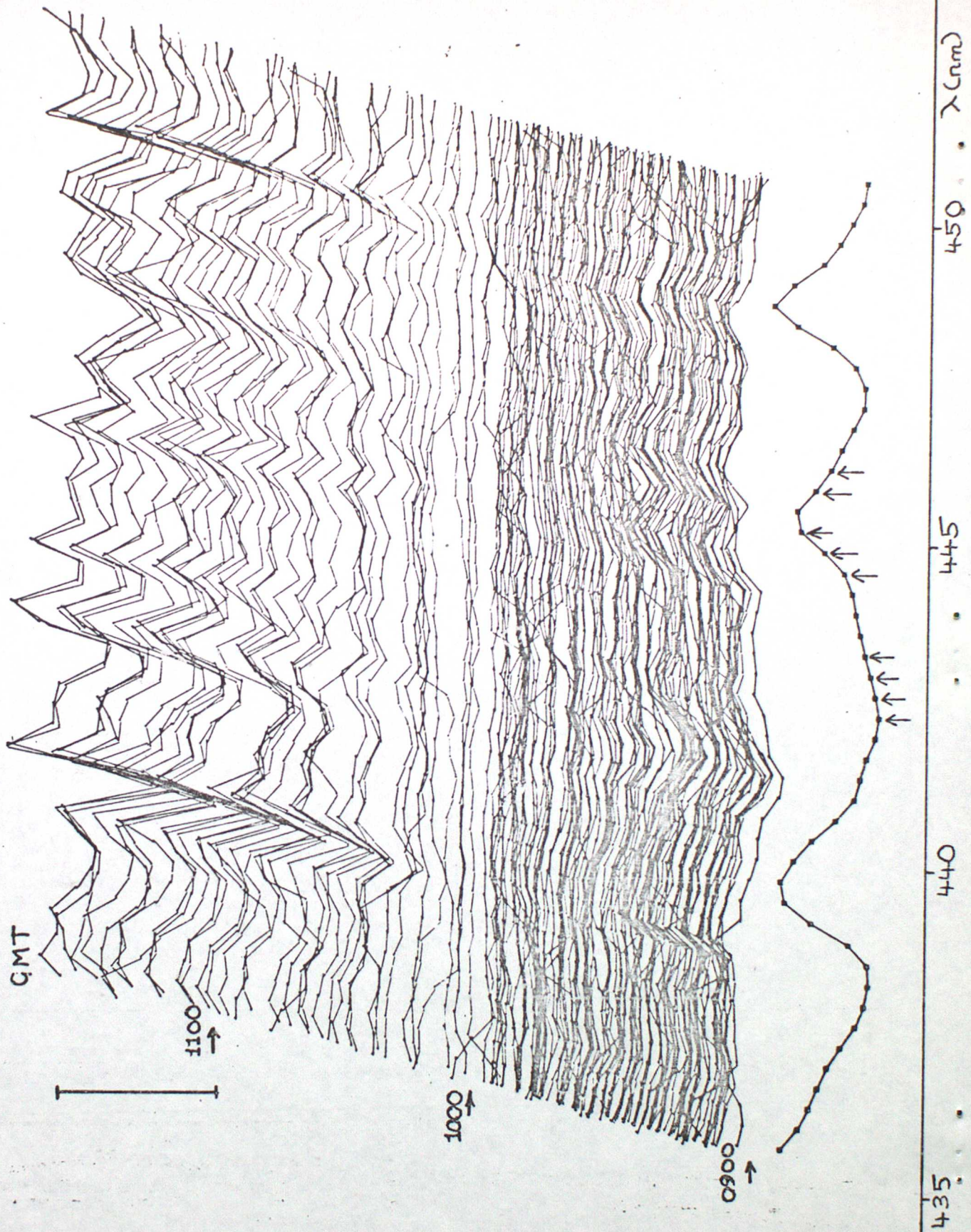
2 JAN '80



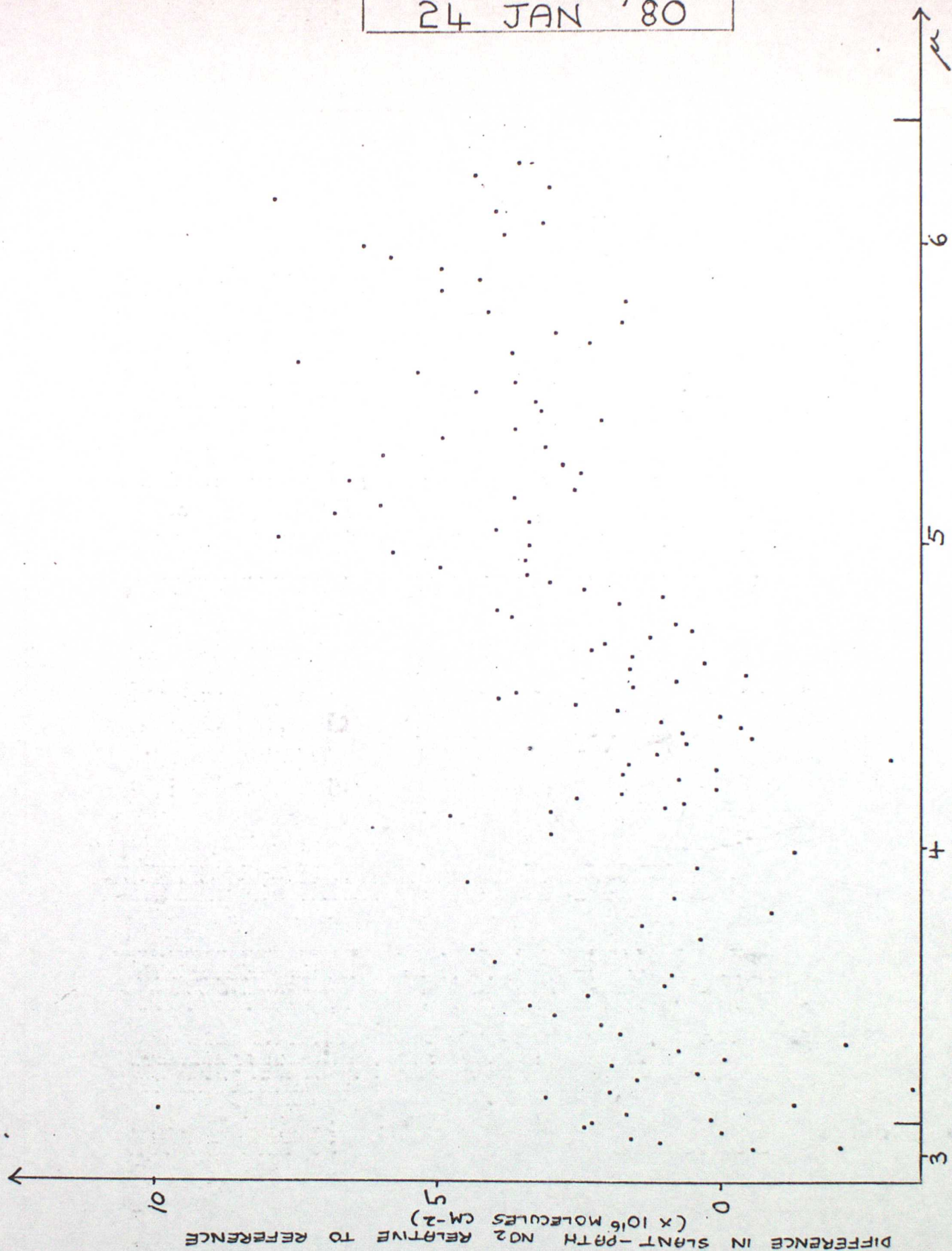
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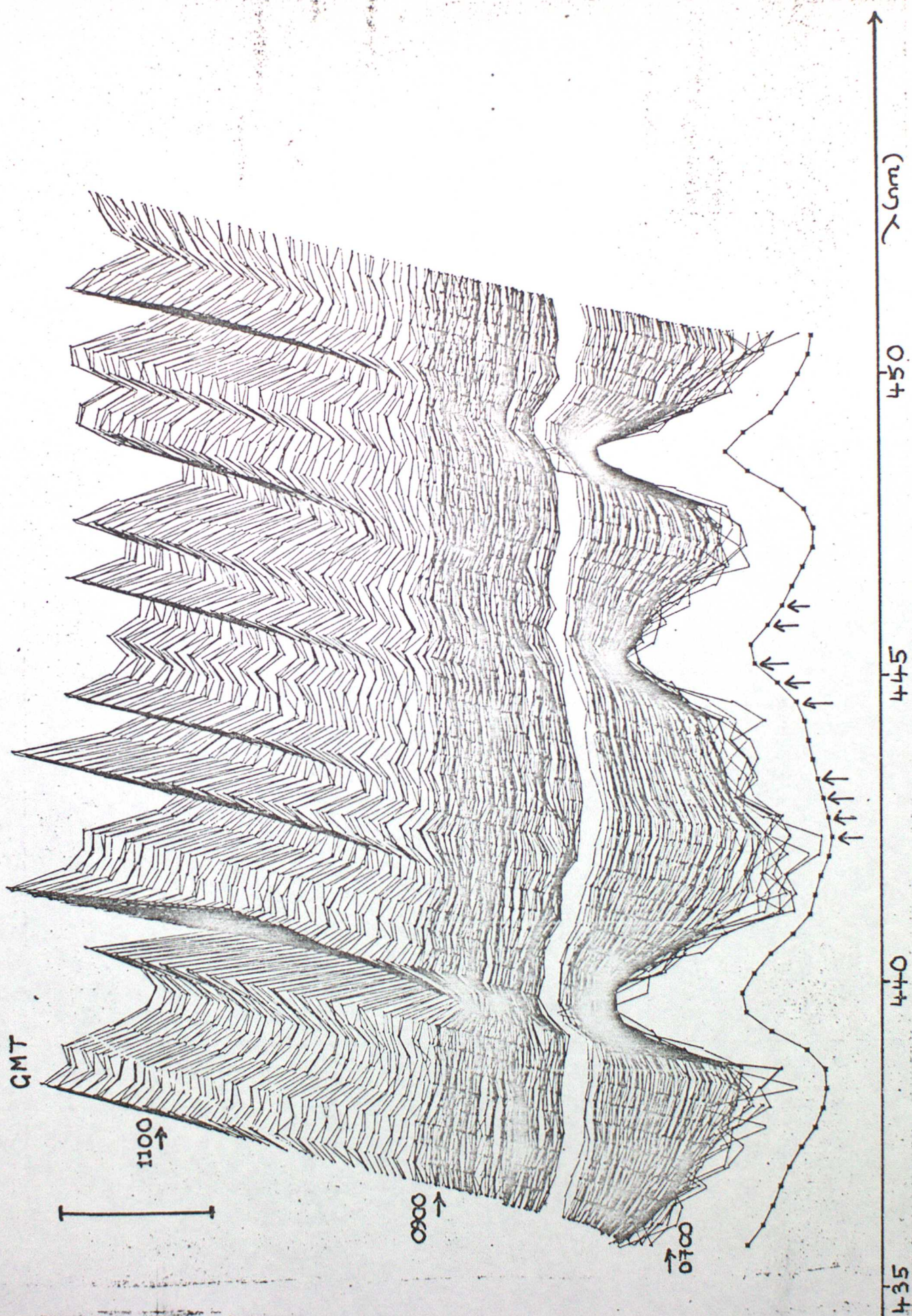
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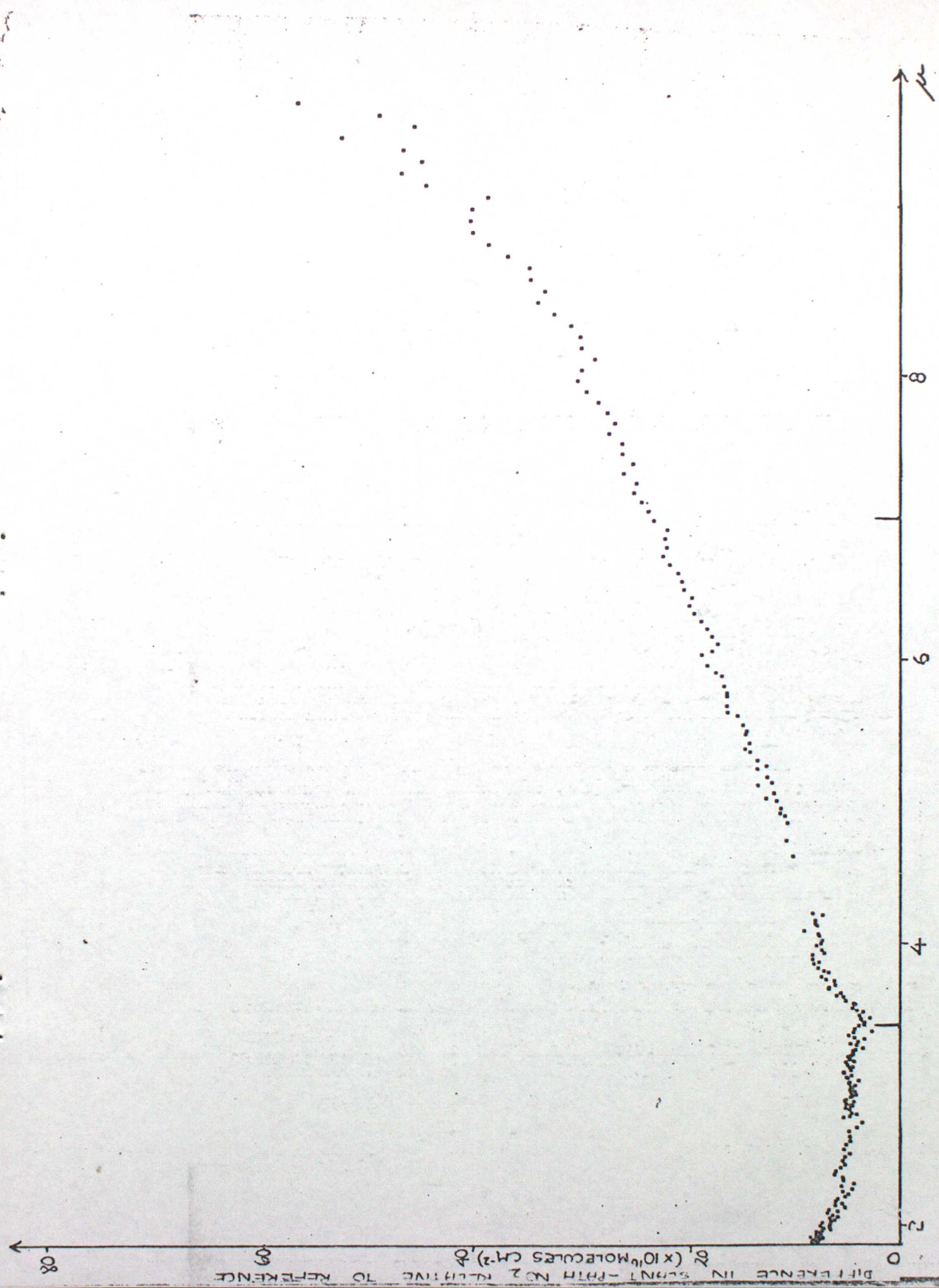
24 JAN '80



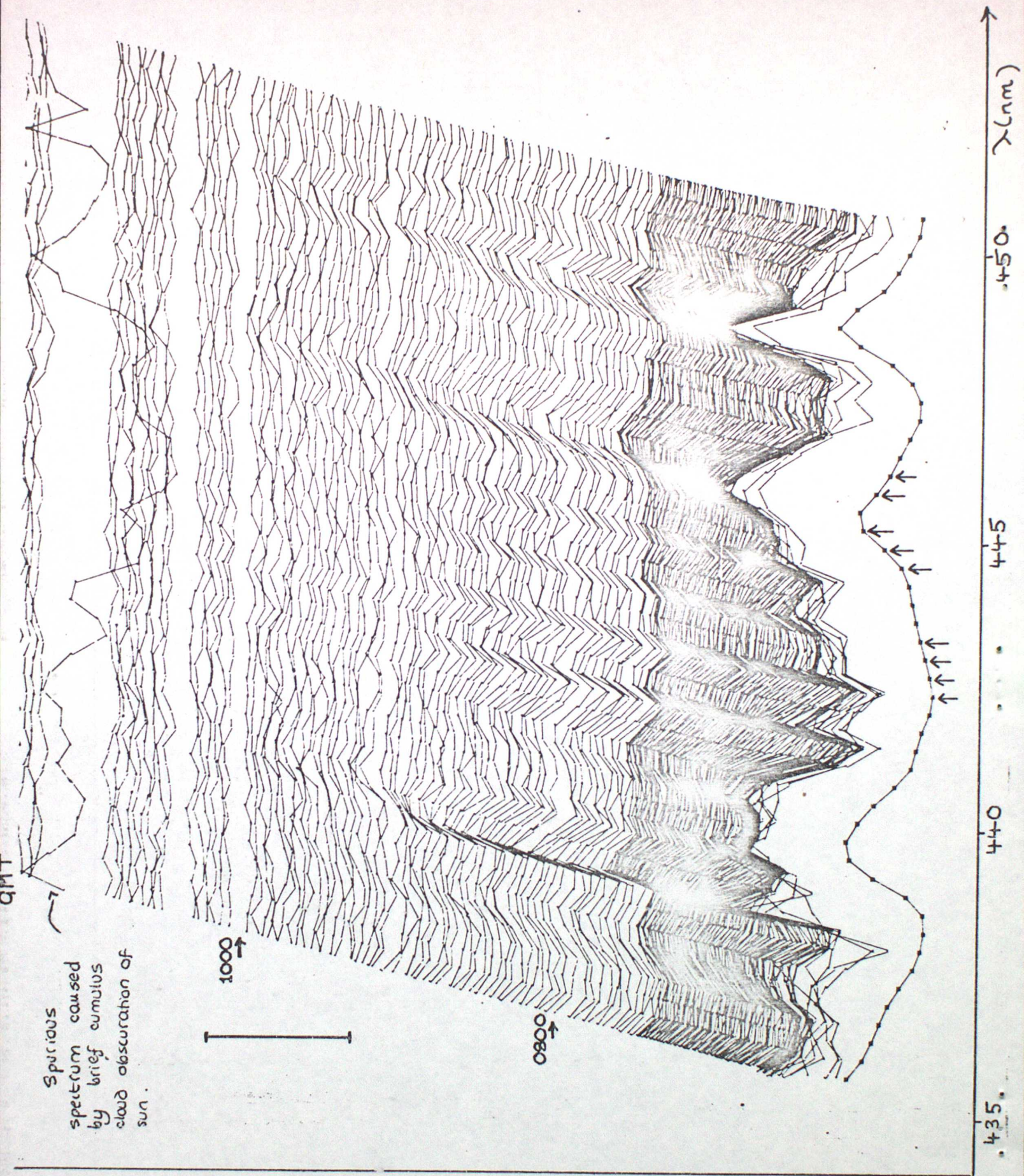
4 MAR '80



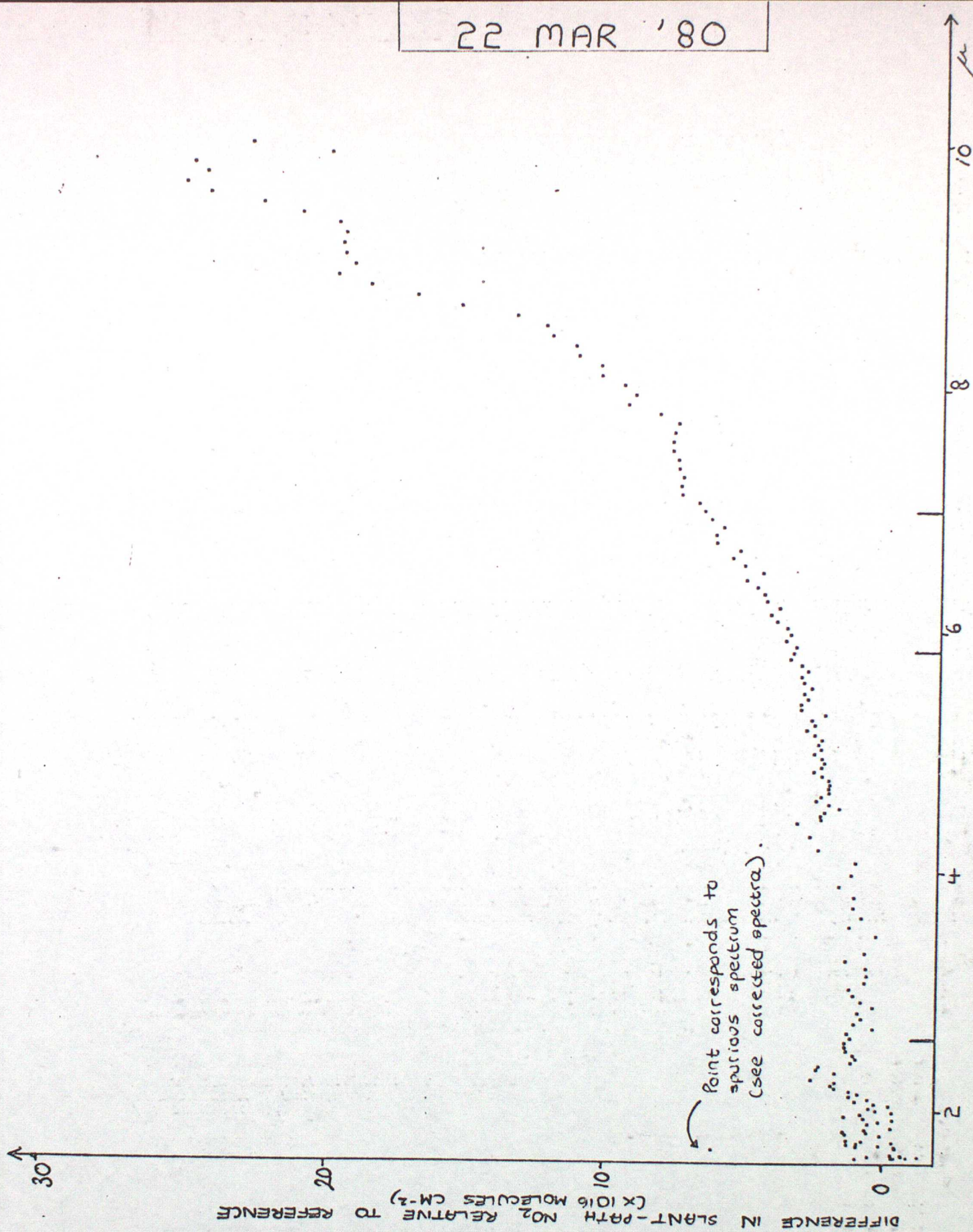
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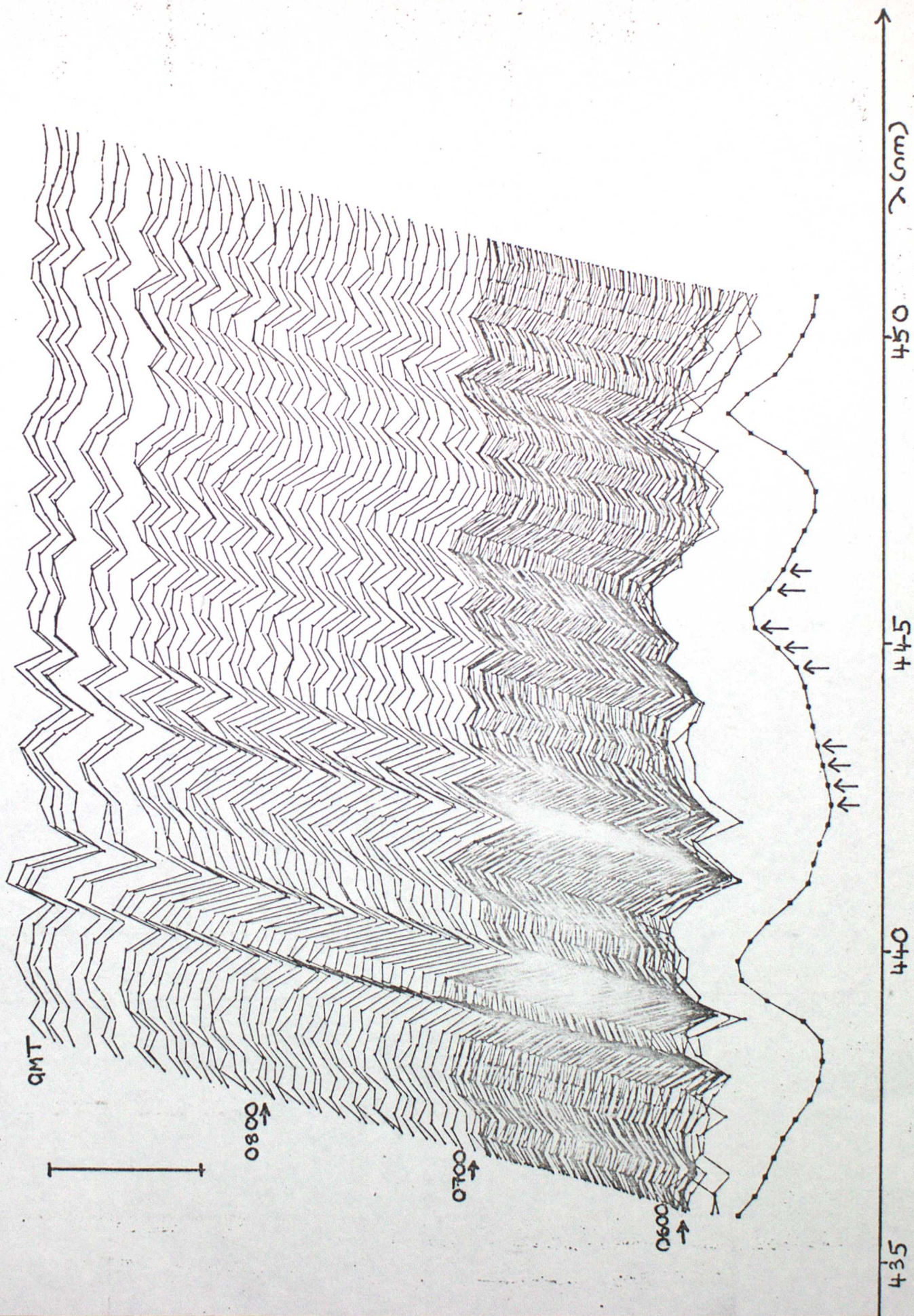
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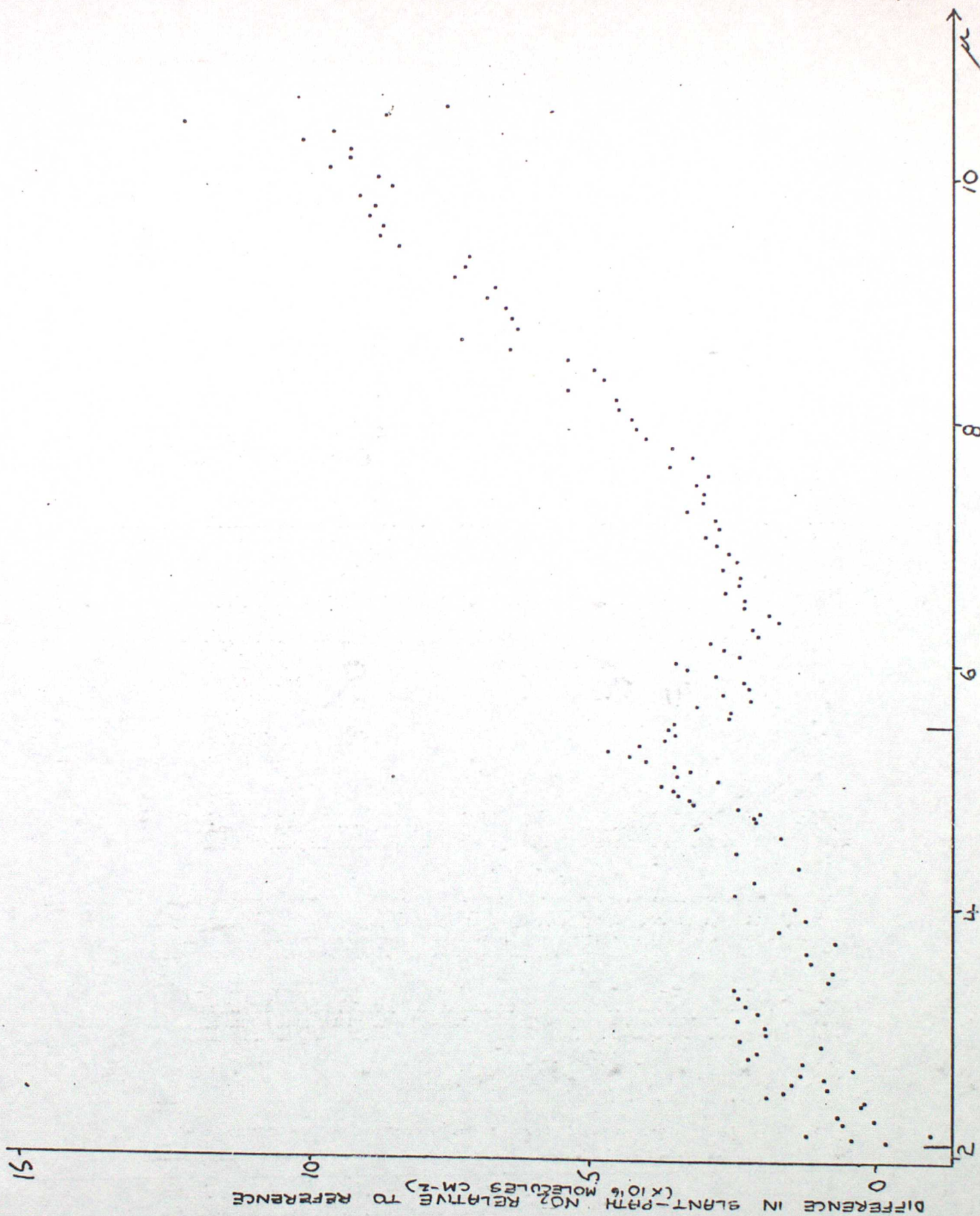
22 MAR '80



30 MAR '80



30 MAR '80



20 APR '80

(m)

430

445

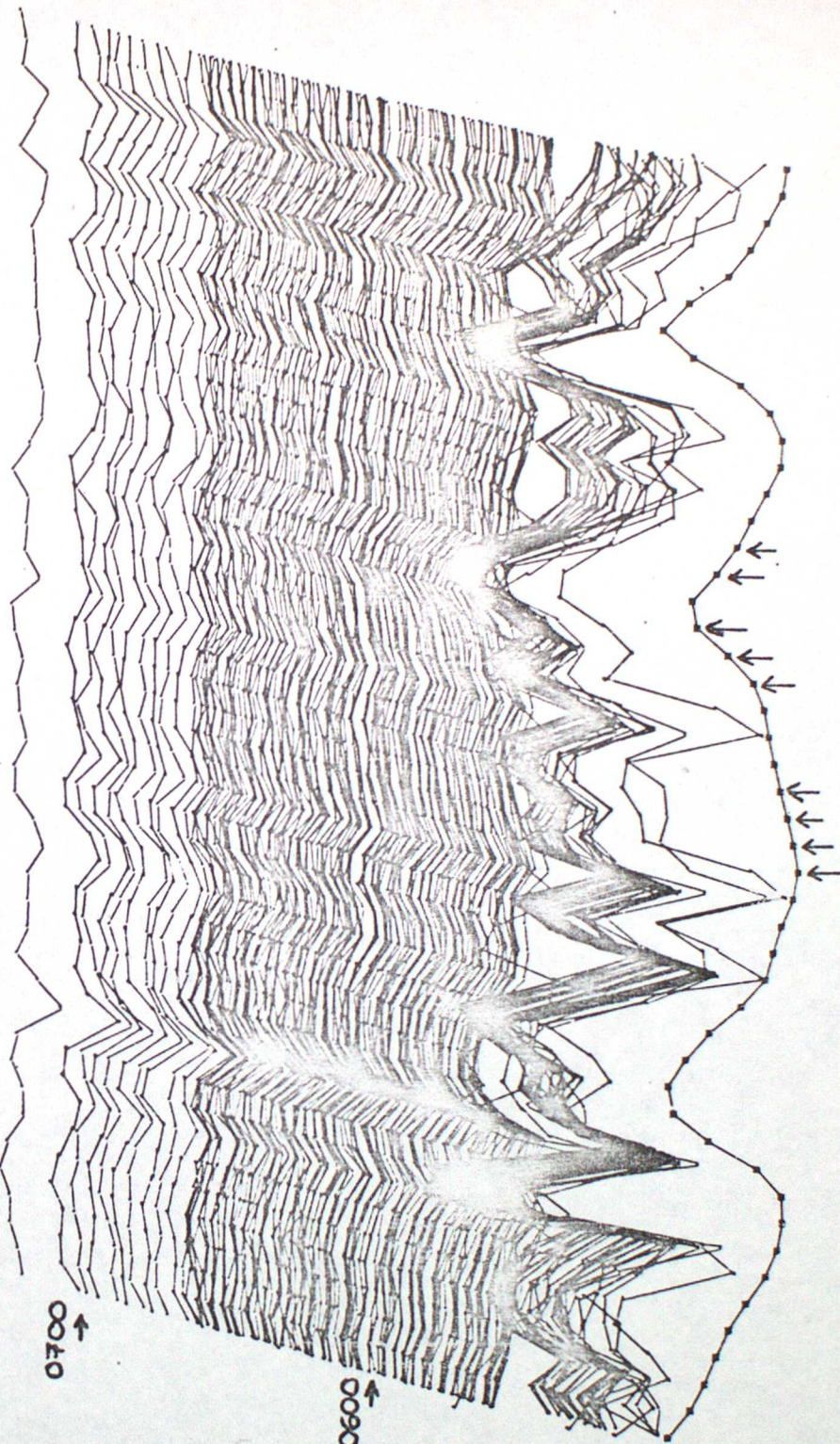
440

435

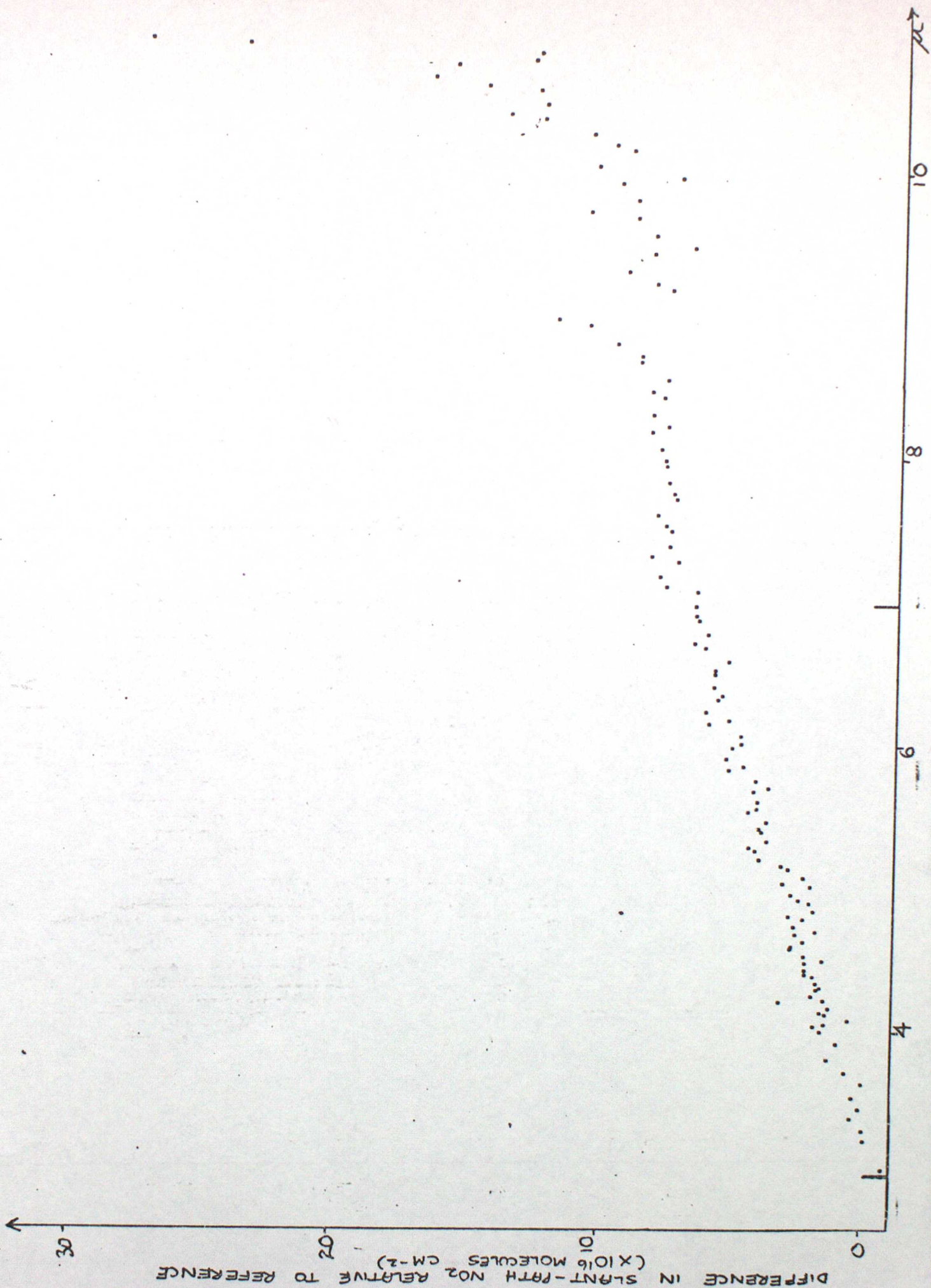
GMT

0700 ↑

0600 ↑

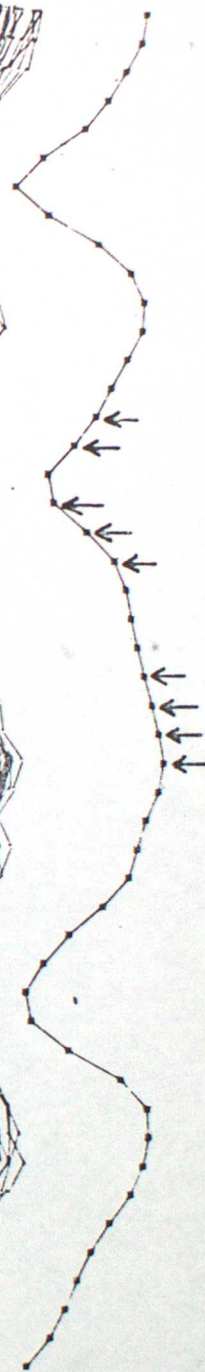
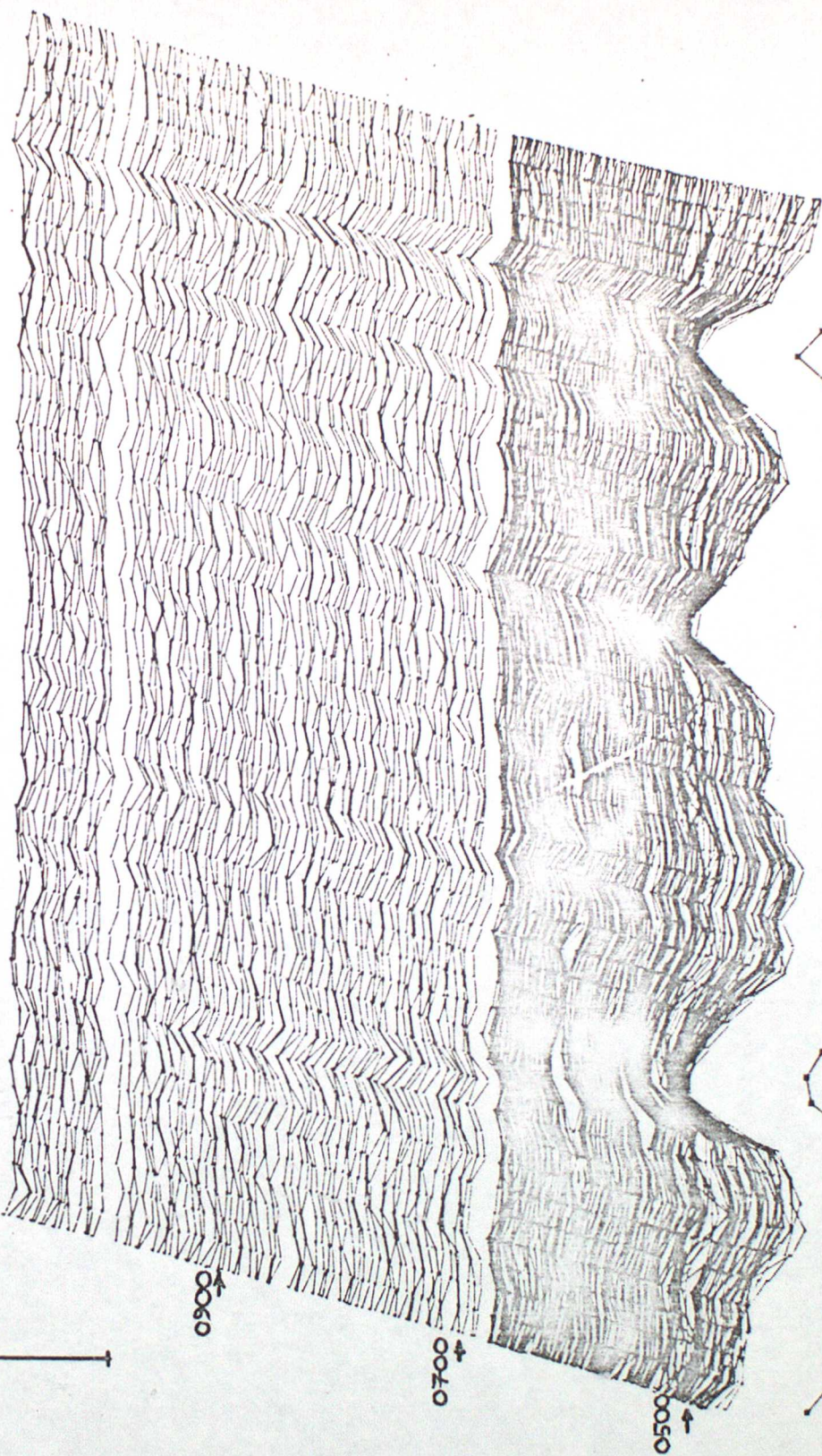


20 APR '80



10 MAY '80

GMT



435

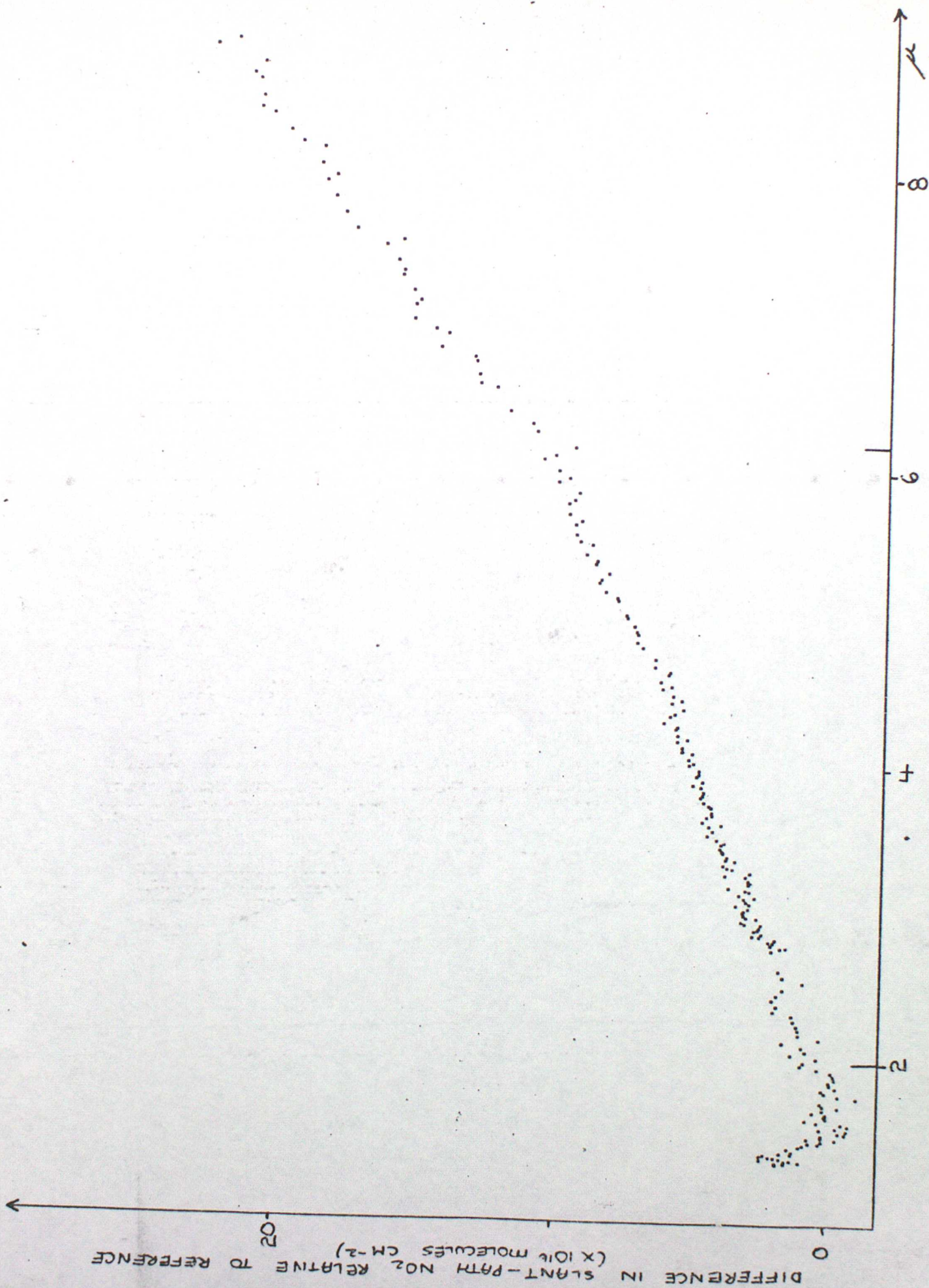
440

445

450

λ (nm)

10 MAY '80

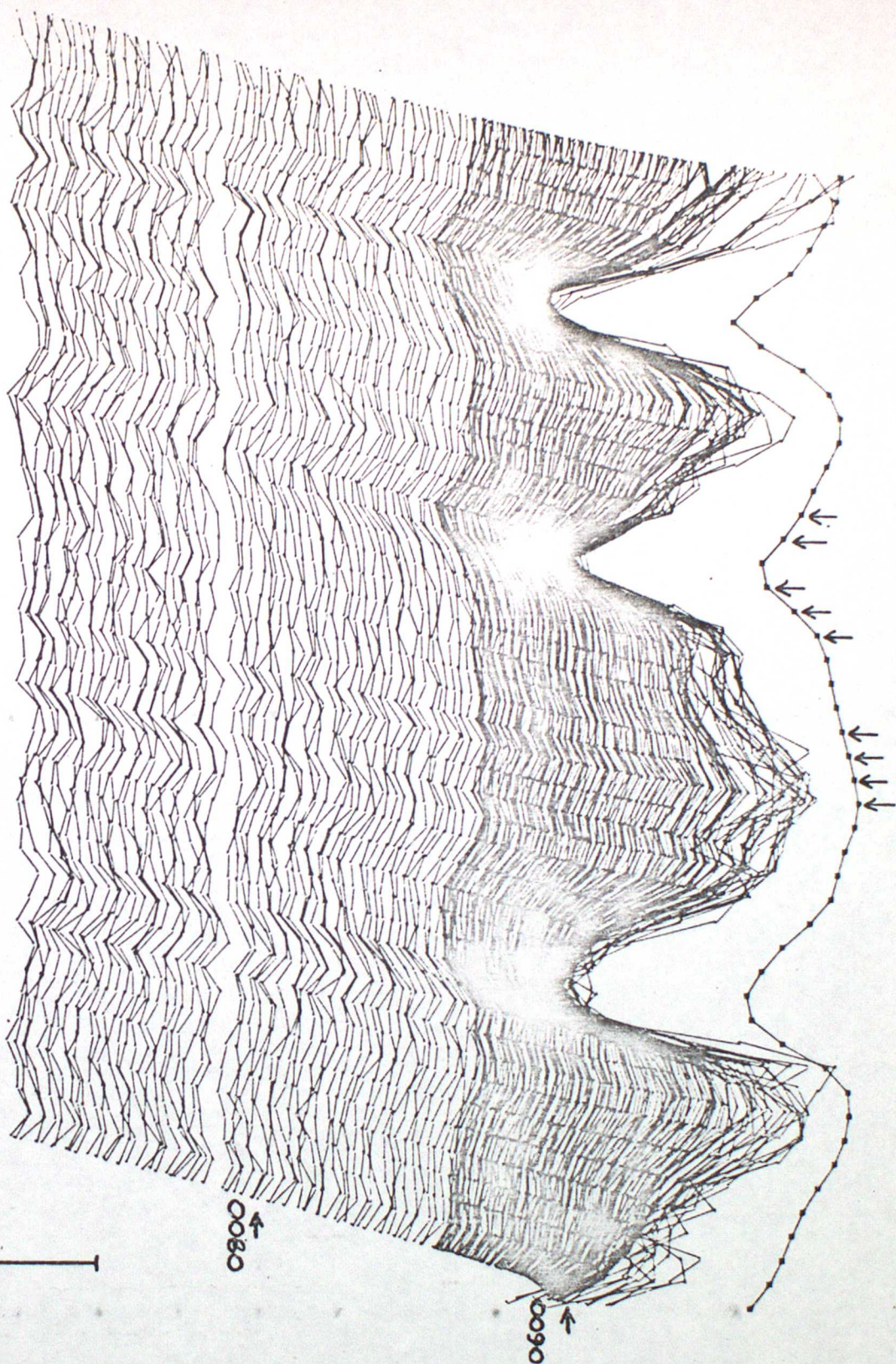


11 MAY '80

GMT

0600

0600



435

440

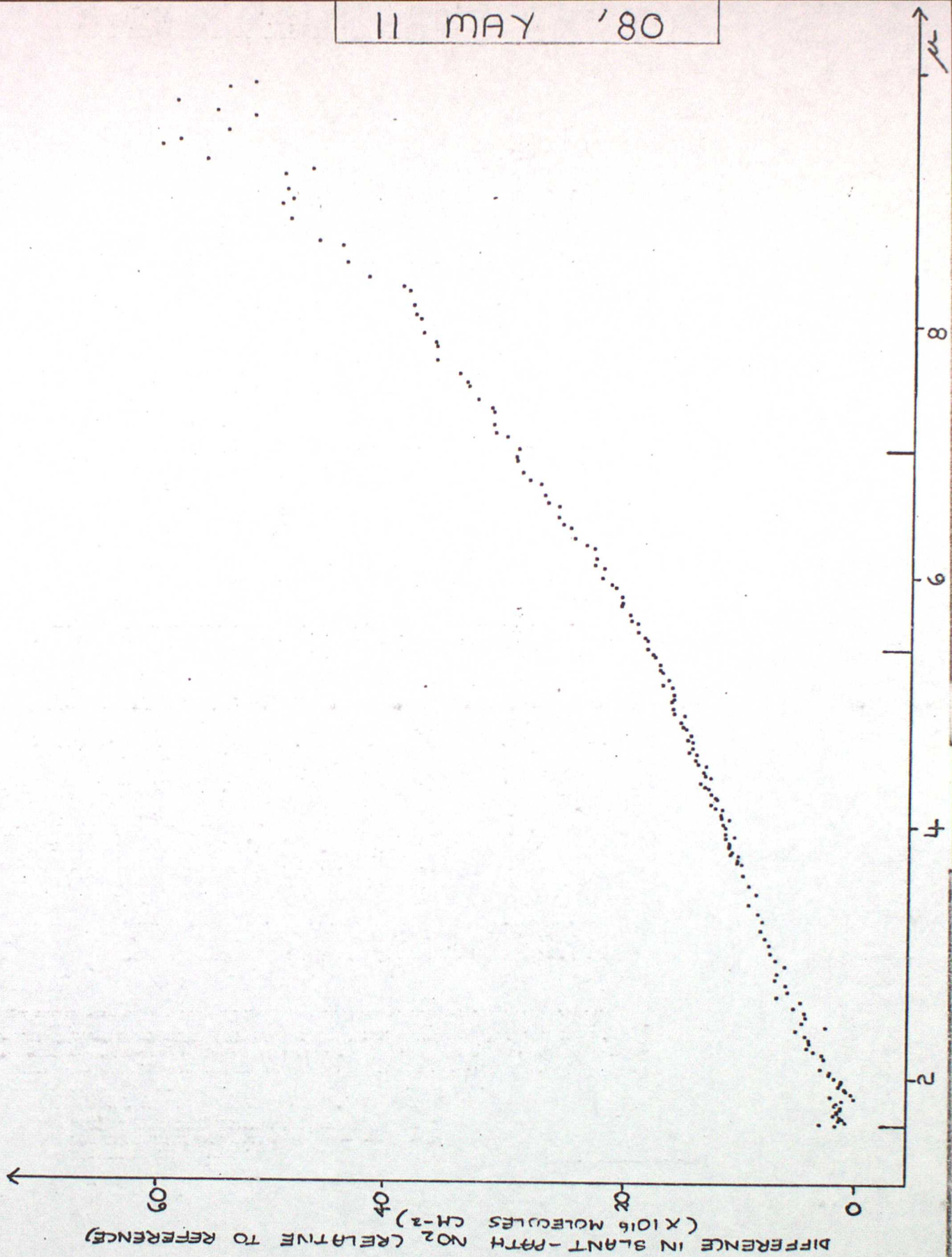
445

450

455

460

11 MAY '80



16 MAY '80

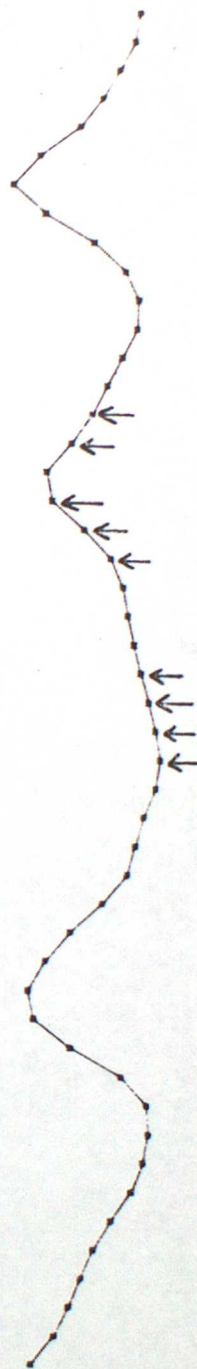
GMT

1100

0000

0010

0050



54 435

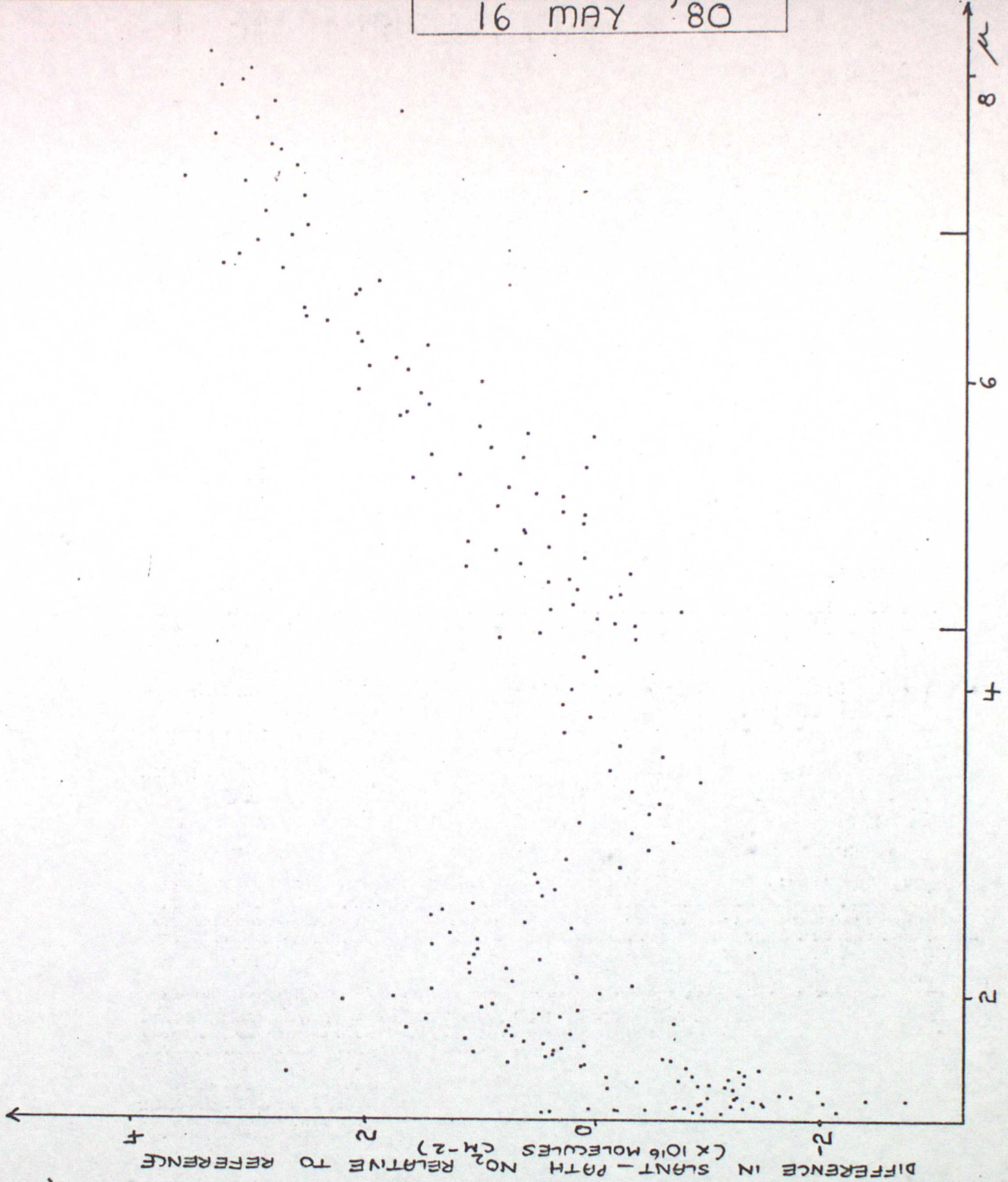
044

445

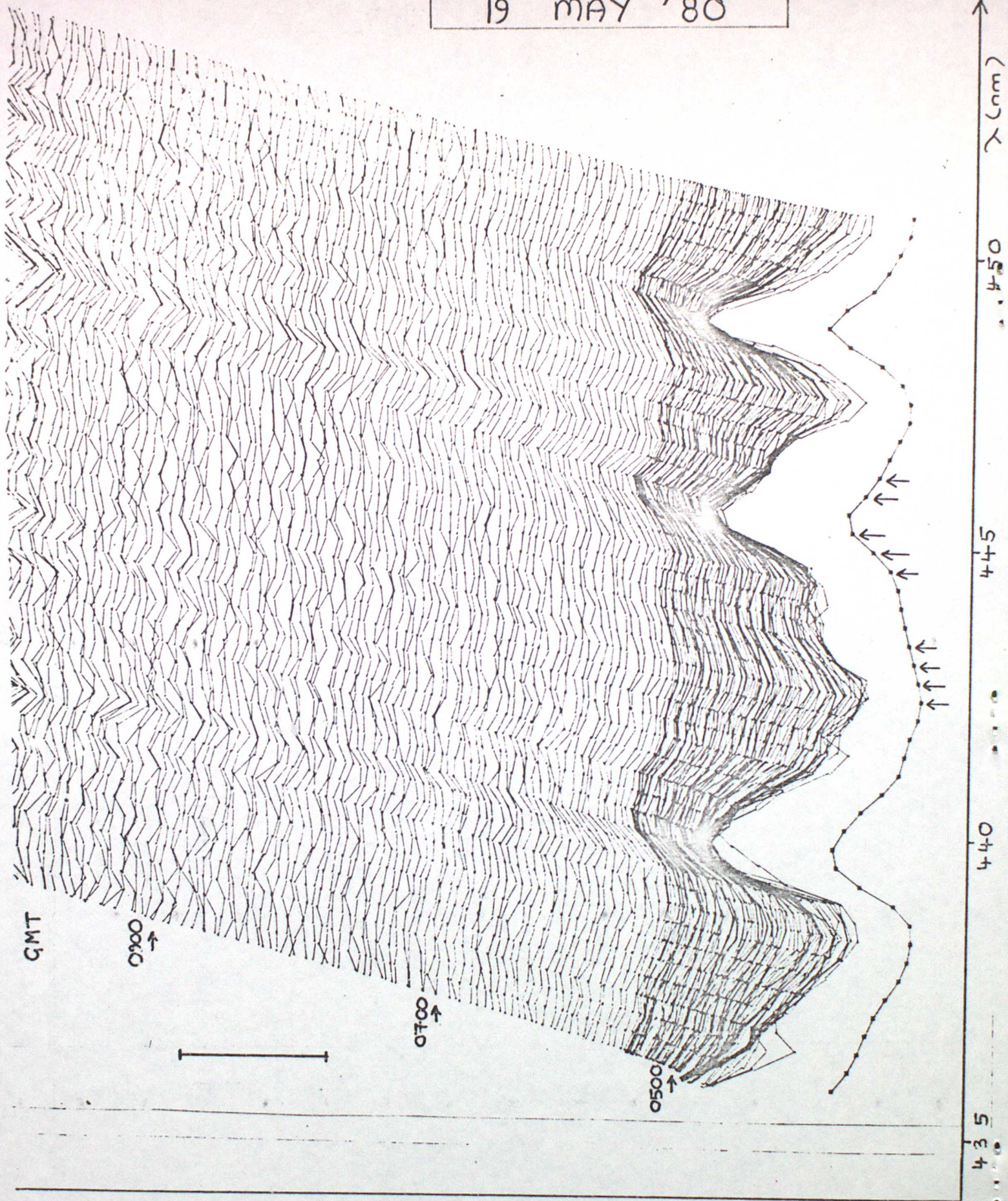
450

50

16 MAY '80



19 MAY '80



19 MAY '80

