

APPLICATION OF LIBS SPECTROSCOPY  
(Laser-Induced Breakdown Spectroscopy)  
FOR DETECTION OF GASEOUS SPECIES

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## I. Introduction

Laser based spectroscopy techniques are in many respects superior to other spectroscopic methods due to the extraordinary properties of laser light which is:

monochromatic - it has a very small frequency width  
coherent - the waves are in phase both in space and in time  
energetic - the energy density can be extremely high.

The spectroscopic methods using lasers are therefore often characterised by:

high spectral resolution  
high time resolution  
high space resolution  
high signal strength  
nonintrusive measurement

For combustion diagnostic purposes these qualities are especially desirable as a flame or a melt constitute a hostile environment with a strong background emission. Essentially three techniques are used:

Laser Induced Fluorescence - LIF  
Raman scattering  
Coherent Anti-Stokes Raman Scattering - CARS

all with different, complementary advantages (1,2).

The aim of this work is to investigate whether Laser Induced Breakdown Spectroscopy (LIBS) might be a good complement to these methods.

## II. Theory.

The principle of LIBS is well known. A laser beam, when focused on a sample, creates a plasma consisting of electrons and excited and ionized atoms. The power necessary for breakdown varies with the sample, which may be a gas, a liquid or in a solid phase. In the first case the laser beam is focused in a continuous flow alternatively inside a closed cell (3,4). In the second case, a paper can be moist with the liquid to avoid splashing (5). If the test is solid, the laser beam is focused on the surface (6-10).

The sample can be molecular as well as atomic. Molecules dissociate into atoms before absorption of energy by inverse bremsstrahlung. This means that an electron absorbs a photon which, from the requirement of conservation of energy and momentum, is possible only when the electron is colliding with an atom or an ion.

When the electric field of the laser radiation exceeds the dielectric strength of the sample, i.e. when the polarizing force is stronger than the atomic binding, dielectric breakdown occurs resulting in avalanche ionization and the creation of a plasma. Thus the laser beam does not have to be tuned to a particular transition of the atom or molecule. A plasma can be achieved with any laser wavelength, but the threshold of the breakdown power varies. It would decrease significantly if the laser wavelength should coincide with a transition.

At atmospheric pressure the power density required is typically  $1-10 \text{ MW} / \text{cm}^2$  corresponding to a temperature of about  $10\ 000 \text{ K}$  and an electron density of  $10^{17} / \text{cm}^3$ . The plasma expands quickly whereby the temperature and the electron density decreases.

If the power density is of the order mentioned above, the plasma is a spark, measuring approximately  $1 \times 4 \text{ mm}$  with its base towards the focusing lens. The characteristics of plasmas in general and a helium plasma in particular, are described in Ref. 11.

During de-excitation energy is lost through bremsstrahlung emission, radiating transitions, electron recombination and

by expanding shock waves (12-16). The LIBS method is based on analysing the emitted UV and visible radiation. This can be done by integration in time or with time resolution. The latter variant is called Time REsolved Laser Induced Breakdown Spectroscopy (TRELIBS) (13, 17).

In a first phase of de-excitation there are ionic as well as free to free and free to bound atomic transitions, resulting in ionic lines superimposed on a continuous spectrum. In a second phase, when the continuum and most ionic lines have disappeared, the atomic lines appear. Possibly the atoms recombine, via excited or ionized states, into molecules that show molecular bands. The duration of the first phase is about 1 us, the second lasts for typically 10-15 us; the last period may remain even longer but with very weak signal strengths (17,18).

The recombination radiation is characteristic for every element and may be used as a means of identifying the constituents of a gas mixture, a solution or an alloy. The relative signal strength, as compared to a well known species at identical circumstances, gives the composition of the test sample.

The light intensity during the first phase after the creation of the plasma is roughly 100 times stronger than during the subsequent phase; hence the spectrum to be analysed using the LIBS method mainly originates from the first us. In TRELIBS the emission is registered only during a short time interval, a time gate. The length of this gate should be small in comparison to the timescale of the events. After the continuum and the ionic lines have disappeared, the signal to noise ratio as a rule increases to a maximum and then decreases along with the weakening of the emission (15,19). For the detection of trace elements, the TRELIBS procedure is often the best to adopt. If LIBS is used, the lines used for identification are added to the strong background continuum, reducing the sensitivity for diagnostic purposes (20).

### III. Experimental.

Three different gases were examined: nitrogen, oxygen and sulphur dioxide. A characterisation of these were made, i.e. some ionic, atomic and molecular transitions were identified and the breakdown power threshold was determined. For given conditions such as the power, the wavelength of the laser, the diameter of the laser beam and the gas pressure, the signal strength and the course of events was asserted.

A small amount of oxygen was added to nitrogen in order to establish whether the signal strength is linear to the partial pressure and to find out what the detection limit would be. The measurements were repeated for sulphur dioxide in nitrogen.

The laser power dependence of the signal strength, the occurrence of the transition lines and the time history of the emitted lines were also investigated.

Furthermore, examinations were made concerning the significance of the laser wavelength with respect to the above mentioned quantities.

### III.1 The set-up.

The experimental set-up is shown in Fig.1. The laser beam passed through an attenuator, which is adjustable from zero to total dampening. By using a prism, the beam was directed to the focusing lens. The focal length of this lens was 10 cm (4") during the first part of the experiments but was then changed to 7.5 cm (3") in order to obtain a smaller plasma and consequently higher brightness.

The scattered light was analysed perpendicular to the laser beam. The plasma was imaged onto the entrance slit of the spectrograph using a lens with a focal length of 7.5 cm (3") and a magnification ratio of one to one.

The apparatus.

The laser. During the main part of the experiments the IR radiation from a Nd:YAG laser (Quanta-Ray DCR 1), wavelength 1.06  $\mu\text{m}$ , repetition rate 10 Hz was used. The outgoing beam was randomly elliptically polarized.

The spectrograph (Jarrell-Ash model 1233/1234) has three different gratings. The first has a dispersion of 24.0 nm/mm, the dispersion of the second one is 6.0 nm/mm and that of the third grating is 1.5 nm/mm.

The diode array detector (Tracor Northern model 6144) consists of 1024 diodes, out of which 720 can be intensified. The spectrum is dispersed onto the detector and consequently displayed on the screen of the multichannel analyser (Tracor Northern TN-1710 ). The spectral sensitivity of this is about the same as the one shown in fig. 2.

The delay unit. For TRELIBS measurements a signal delay unit was needed to give a time gate of optional length with a variable delay. It was triggered by a signal from the laser 5  $\mu\text{s}$  before every laser pulse. In order to assure the timing the pulses were studied on an oscilloscope screen (Fig. 3). The inaccuracy of the time indications was estimated to be

10% of the delay time.

Since the attenuator only works for vertically polarized light, a hard coated polarizer was introduced into the beam path. With constant power from the laser and moderation of the beam by the attenuator, it was assumed that the beam has the same diameter, modal structure and polarization independently of the attenuator setting. (Appendix 1)

Calibration. For the wavelength calibration of LIBS and TRELIBS spectra Cd and Hg lamps were used. After the identification of strong oxygen and nitrogen lines, calibration were made with respect to these.

The beam.

The diameter of the beam emerging from the laser is about 8 mm and at the focusing lens, at a distance of about 1.5 m, the diameter is 9.0 mm. The simplification is made that the beam arriving at the focusing lens is nondivergent. Assuming that

$$\frac{\pi * w^2}{s * l} \text{ is much less than } 1$$

$l$  is the wavelength of the laser  
 $w$  is the diameter of the beam waist in focus and  
 $s$  is the distance from the focusing lens to the plasma  
one arrives at the following expression for  $w$ :

$$w = \frac{4 * l * f}{\pi * d}$$

$d$  is the diameter of the beam at the lens.  
 $f$  is the focal length of the lens

In our case this makes the area of the focal plane about  $10^{-6} \text{ cm}^2$ . A typical pulse energy was 100 mJ, which gave an energy density in the focal plane of  $100 \text{ kJ/cm}^2$ .



General considerations.

The laser power output varied during the measurements due to warming-up effects in the lasersource. The importance of this variation is stated separately for the different measurements.

A maximum gain of the intensifier of the diode array was used at all times in order to avoid possible nonlinearities in the gain. Neutral density filters were placed before the slit when attenuation of the signal was needed.

In order to isolate the plasma from the surrounding air, the beam was focused just above the nozzle from which the pure gas was flowing. With this technique the part of air in the plasma was measured to be less than one percent.

Every spectrum recorded throughout this report was an integration from 100 laser pulses in order to minimize the photon noise. During the LIBS experiments the scan time of the detector was 0.10006 s, set to match the repetition rate of the laser.

The constant dark current of the diode array is subtracted from all spectra. The number of counts per channel minus the underlying continuum background gives a relative estimate of the signal strength.

### III.2 Gas mixing procedure.

The flow meters (Aalborg FM 112-02, FM 092-04, FM 034-39) enables determination of flow rates and proportions of gases in a free flow.

The signal strength fluctuated by 50 % but after 15 - 20 independent TRELIBS measurements it seemed probable that it was proportional to the partial pressure for values of the oxygen content above one percent. Under this value the signal deviated considerably indicating a varying influence of the surrounding air.

An attempt to isolate the gasflow was made by flowing the gasmixture through a cell. The result was unsatisfactory as the signal decreased with increasing flow rate. This is probably due to the turbulence in the cell which makes the plasma move out of focus before it has emitted all the light. During the rest of the experiments a vacuum cell was used.

The total pressure was selected to 600 torr. The significance of the pressure to the signal strength was not further investigated.

The procedure of mixing the gases must be done with great care. This is described in appendix 2.

The lowest pressure that could be achieved was 0.1 torr which is sufficiently small in comparison to the total pressure:

$$0.1 / 600 = 0.017 \%$$

#### IV.1 LIBS measurement of nitrogen, oxygen, air and sulphur dioxide.

The breakdown energy threshold in oxygen was found to be 26 kJ / cm<sup>2</sup> and 15 kJ / cm<sup>2</sup> in nitrogen, using the 75 mm lens. The energy used in these experiments was chosen to 34 kJ / cm<sup>2</sup> , being twice the energy needed to get breakdown in air. The accuracy of the reading was +-1 kJ.

The power of the beam was checked before and after every experiment and was found to vary +-5% during measurement. In view of what was later tested, this proved not to be very critical. Comparison of nitrogen and oxygen spectra indicates that the two gases contributed independently so that the signal strength was proportional to the partial pressure. Apart from one or two exceptions, all identified transitions were ionic ( figs. 4-6 ).

The analysis were made with the grating of second highest dispersion. The precision of this is estimated to +- 3Å and the resolution of the spectrograph was 6 Å. The reproducibility of the adjustment of the grating was +- 2 Å.

All this, together with tabulated values of the position and relative strength of atomic and molecular transitions enables identification of most lines. Nevertheless, some remain that seem to originate from neither oxygen nor nitrogen (fig. 7-8). The wavelengths of all identified lines are marked on the spectra. They are also listed in appendix 3.

Sulphur dioxide is somewhat complicated to handle as it condenses after it has been pumped into the cell. The pressure fell from 600 to 595 torr in a few minutes and thereafter less quickly. This was about the size of the increase of the pressure during the creation of the plasma. The breakdown energy is 5,5 kJ / cm<sup>2</sup> with our experimental configuration. Some S and O transitions were identified but many were not (fig. 9).

#### IV.2 TRELIBS measurement of nitrogen, oxygen and sulphur dioxide.

The time gate could not be made shorter than 400 ns, however, this proved not to be any restriction since this length of time is:

- a. short in comparison to the time evolution of the plasma
- b. a minimum to get sufficient luminous power from the atomic lines at later times after the arrival of the light pulse

All subsequent statements of the time delay indicates the end of the time gate, meaning that the onset of the gate is 400 ns before. It must be specially noted that for time delays less than 400 ns, the effective time gate is consequently equal to the delay. The arrival of the laser pulse is indicated by  $t_0$ .

As stated before each spectrum was achieved by an integration of 100 scans.

#### Results.

During the first us the spectrum changes considerably faster than at later times due to the quick dampening of the ionic lines and the continuum. After about 0.5 us the background has decreased to one tenth of the value at 0.2 us ( fig 10; compare ref. 19 ). The interval between recordings is chosen to be 200 ns during this first phase. Thereafter the continuum has diminished enough for the atomic lines to appear. They are visible another five to ten us before vanishing in noise. Throughout this second phase a time interval of two us is sufficient for the registration of the time events (fig. 11).

## Oxygen and nitrogen

The energy of the laser beam was 110 mJ/ pulse. In general we have an excellent signal-to-noise ratio 1-3 us after the arrival of the laser pulse.

All important peaks are identified but as in the case of the LIBS measurements, the origin of many are unknown even after possible trace elements in air was checked. The H I 6563 Å transition could however also be seen. Although possible molecular bands were registered, certain identification of these could not be made even with the grating with the highest dispersion. The disadvantage using this grating is that the amount of light falling upon the array is reduced by one fourth and since the molecule bands have a small luminous power as it is, the remaining light is not sufficient (figs.12-13).

## Sulphur dioxide.

The major difficulty of the TRELIBS measurements of sulphur dioxide is the continuous reduction of light due to the growth of the opaque film on the windows of the cell. To diminish the influence of this the measurements with a long time delay were made first and the cell is cleaned before registration of a new spectral area. At most 30 % of the light strength was absorbed. The energy of the laser beam in these experiments was 160 mJ / pulse at 1.06 um.

The important S II lines are identified. Unfortunately sulphur have few and weak transitions in the visible part of spectrum with the exception of the triplet at 4695 Å (fig. 14). Most recognizable atomic lines originate from oxygen. Compared to spectra of pure oxygen registered under otherwise identical conditions, these are notably weaker. A possible explanation is that the cross section of absorption is much larger for sulphur than for oxygen. The spectrum of oxygen for  $t_0+(2,0-14,0)$  us is shown for comparison (fig.15). The absolute strength of the strongest oxygen transition is about 30 times stronger in pure oxygen than in sulphur dioxide. Possible S<sub>2</sub> molecule bands are seen.

### IV.3 Energy dependence.

Prior to the TRELIBS measurements were performed an investigation was made concerning the dependence of the laser energy on:

- a. the occurrence of the radiating transitions
- b. the signal strength
- c. the time evolution of the lines

For different energies the location of the focal point moved somewhat in the direction of the laser beam. This meant that for each energy setting the imaging lens had to be adjusted until maximum light intensity was obtained. For each laser energy setting, the spectra were registered and the time delay was changed as usual. When comparing the time evolution for the different energies, the gate position thus varied a little, which was unavoidable using the present equipment.

The spectral area 440-540 nm , containing the strong N II transition at 500,5 nm was chosen as a suitable region of investigation.

TRELIBS studies for three different energies were performed. With maximum power in the beam, the dynamic range was selected as large as permitted by the attenuator.

The pulse energy of the beam, which were originally 175, 120 and 60 mJ, designated A, B and C respectively, dropped during measurement with 20%.

Figs. 16-17 give an illustration of the dependence of energy vs. signal strength at different times after the arrival of the light pulse, designated  $t_0$ .

## Results:

- a. the same peaks for different laser energies
- b. the energy dependence of the signal strength is difficult to evaluate; it does not seem to be linear
- c. The margin of error in time ( $\pm 10\%$  of the time delay) is of decisive influence especially during the decline of the continuum, as this evolution is fast.
- c. the course of events seems to be independent of the energy. With higher laser energy the signal is detectable at later times but no new peaks appear.

## Conclusions.

The choice of laser power is not critical within the margins made possible by this laser. During TRELIBS characterisation of nitrogen and oxygen we use 110 mJ in the beam. As mentioned before the value changed  $\pm 10\%$  depending on the occasion and decreased during the experiments. This result is not in contradiction with what has previously been written: Raising the power increases the signal as well as the noise (3), (Cl and F). The degree of ionization varies with energy (5), (liquids). The relation energy vs. signal strength is not linear (8), (steel). The transmitted part of the laser light varies with the energy (14), (aerosols). For a given energy increase, the strength of the ionic transitions increase more than the atomic (21), (metals).

#### IV.4 The dependence of the excitation frequency.

Possible differences in

- a. the occurrence of lines
- b. the signal strength
- c. the course of events
- d. the breakdown threshold energy
- e. the behaviour of mixed gases

when the laser wavelength was changed were explored.

The 1.06 micron light was doubled and tripled to 532 nm and 355 nm, respectively. The energy output was compensated to get the same energy density in the focal plane. The diameter of the focus is proportional to the wavelength, according to the expression on page 6. When this is halved, the power density per unit area is squared. The diameter of the beam, measured with a temperature sensitive paper, was approximately 9 mm, 8 mm and 6 mm for IR, green and UV radiation respectively. The uncertainty is  $\pm 0.2$  mm. If this is taken into account, given the breakdown threshold energy of  $N_2$  and  $O_2$  for the IR radiation, the same energy density in focus would be obtained with

| wavelength   | $N_2$  | $O_2$  |
|--------------|--------|--------|
| 1.06 $\mu m$ | 15 mJ  | 26 mJ  |
| 532 nm       | 5.0 mJ | 8.7 mJ |
| 335 nm       | 3.8 mJ | 6.6 mJ |

#### Results

- a. the same transitions were visible for all excitation wavelengths
- b. the signal strength was weaker for shorter wavelengths
- c. the same time evolution was observed
- d. the breakdown threshold energy is a varying function of frequency
- e. the relative signal strength in a gasmixture is independent of the wavelength



## Considerations

The focal plane is smaller for shorter wavelengths why less light can enter the spectrometer because of the geometry (Cmp. p. 6).

Some quantities change as the frequency is varied i.e. :

1. the diameter of the beam
2. the modal structure of the beam
3. the polarization of the beam
4. the length and appearance of the pulse
5. the quality of the optical adjustment (lens aberration changes with wavelength; prisms, cut-on and cut-off filters were used to isolate the light from interfering wavelengths after doubling and tripling of the frequency.)
6. the stability of the power output is aggravated for shorter wavelengths (+- 50 % at 355 nm )

The energy threshold for breakdown was found to be

|              | N <sub>2</sub> | O <sub>2</sub> |
|--------------|----------------|----------------|
| 1.06 $\mu$ m | 15 mJ          | 26 mJ          |
| 532 nm       | 2.8 mJ         | 3.7 mJ         |
| 355 nm       | 2.1 mJ         | 6.9 mJ         |

The difference as compared to the previously estimated values are rather large. This is probably due to the very unstable laser power output for the doubled and tripled frequencies.

## Conclusions.

The frequency dependence of the breakdown power is not obvious. In view of all the above mentioned uncertainties, no other statements can be made. Apart from this, the plasma seems to be independent of the excitation frequency. This agrees with what is found in Refs. 19 and 22.

#### IV.5 The Detection Limit of Oxygen in Nitrogen.

In order to estimate the detection limit of a gas it is of primary concern to find a suitable ionic or atomic transition. Points of consideration are:

- a. the signal strength
- b. the mean life time
- c. the vicinity of other atomic lines. They must not be closer than the resolution of the spectrometer. There must not be a nitrogen line of a much larger magnitude too near since this would severely degrade the sensitivity of the system.
- d. the background continuum of nitrogen. This must be comparatively low in the examined spectral area. Getting a sufficient amount of light onto the diode array necessitates the use of the second best resolving grating, making the detected spectral area about 100 nm wide.
- e. the spectral sensitivity of the diode array. The maximum is found at 400nm and drops rapidly at either side (fig.2).

The choice of spectral region may differ depending on whether LIBS or TRELBS is to be used (20). As it happens there is no suitable ionic oxygen line to be applied to LIBS. However, three strong transitions might be applied to the TRELBS technique: 4368 Å, 6157 Å and 7157 Å. At the first wavelength, the detector quantum efficiency is about 0.25 counts/ photon; at the second it has decreased to 0.15, while the value at 7157 Å is 0.08. Unfortunately the nitrogen background around 4368 Å is disturbingly high, eliminating this alternative. Comparison by measurement of the remaining two lines indicated the 6157 Å as the best. Next, the value of the time delay and the length of the time gate was optimized. The time delay must be set so that the background continuum is small compared to the line strength. Since the 6157 Å transition is the most long-lived in the spectral area, the time gate was set as long as possible. With the available equipment this is 12 us, which was quite sufficient.

The signal to noise ratio was measured for different values of the onset of the time gate. It was done directly on the screen by magnification of the peak concerned. The number of counts for a given atomic transition minus the background was compared to the number of counts for what was evaluated as average noise fluctuations. The procedure was repeated several times in order to compensate for the varying sensitivity of the diodes in the diode array.

It is found suitable to select the onset of the gate at 2.0 us after  $t_0$ .

As the output power of the laser varies during the measurement, we had to have a means of eliminating this direct dependency along with other varying quantities. One procedure is to compare the number of counts of the oxygen line with the number of counts of the nearby nitrogen transitions at 6000 Å and 6008 Å. When the oxygen concentration was less than 1 % an inaccuracy of the same order was established if the line strength of the nitrogen peak was considered a relative measure of the laser power. This comparison is necessary as the maximum number of counts may vary up to  $\pm 20\%$  for otherwise identical measurements. The exact reason for this considerable variation was not further investigated.

The signal to noise measurement as well as the evaluation of the relative signal strength have an uncertainty of  $\pm 30\%$  and must be made repeatedly in order to get better statistics.

The total pressure in the cell increased 5-10 torr during the creation of the plasma.

#### Results:

The concentration of oxygen is probably linear to the line strength. With the laser output energy of 110 mJ / pulse and using a STN ratio of 2 as detectable, the detection limit of oxygen in nitrogen is 0.1 % ( fig. 18 ).

#### IV.6 The detection limit of sulphur dioxide in nitrogen

The choice of transition was made with the same considerations as listed for the detection of oxygen in nitrogen. The LIBS detection was found to be very high. Only the triplet 4695 Å is strong enough for the purpose, but is badly positioned at the base of a vigorous nitrogen peak.

The accuracy of the mixing process was checked by comparison with a premixed gas compound and was found to agree with the previously calculated value ( $\pm 5\%$ ).

The onset of the time gate was set to  $t_0 + 1.8 \text{ us}$  and the length is made as long as possible so that all light was collected.

The total pressure in the cell was 600 torr.

#### Results

The signal strength is linear to the concentration of sulphur dioxide ( fig. 19).

The detection limit with the laser energy output 190  $\pm$  10 mJ was found to be 400 ppm.

#### Improvements to the detection limits.

Assuming that the total number of counts is proportional to the laser power ( which is at least not an overestimate ) and that the detected light is Poisson distributed, the STN would increase with the square root of the power.

Compensation for the random noise in the diode array (See next section).

#### IV.7 Signal to noise measurements.

The reasons for the presence of noise are

- a. the shot noise of the dark current
- b. the photon noise (Poisson distribution)
- c. the reset noise of the diodes in the diode array
- d. the noise of the intensifier

In addition, the varying sensitivity of the diodes in the diode array has the same effect on the spectra as ordinary noise. Compensation for this could be done by dividing each spectrum with an image of the diodes made by light which is not spectrally decomposed.

The photon noise makes the smallest contribution and goes as the square root out of the number of counts / channel.

A simple but rough evaluation of the total noise can be made in any of the two following ways:

1. Observation of the noise in a small part of a spectrum of an ordinary lamp, which is assumed to have a continuous wavelength distribution.
2. When observing a certain atomic resonance line, i.e. from a calibration lamp, move the grating back and forth to see how much the maximum count varies for different diodes / channels.

In our case the noise is found to be a little less than 10 % of the total count.

## V. Summary and discussion.

### Properties of LIBS:

- a. simple arrangement and adjustment
- b. independence of laser wavelength
- c. nonintrusive measurement
- d. high signal strength
- e. multi-element technique
- f. gives relative concentration of the elements
- g. detection limit lower than 1000 ppm
- h. the sample does not have to be prepared

### Comments:

- a. The method can be used for inconveniently positioned targets which enables measurement "in field", e.g. outside the laboratory. The Raman scattering arrangement is also simple but it cannot be used when the background light is strong as the signal strength is weak. The LIF arrangement is also quite simple though it requires an extra dye laser as compared to LIBS.
- b. A dye laser tuned to a particular transition is not needed. This also applies for Raman scattering.
- c. When probing of a hostile environment, it is necessary that it is non-intrusive. This a general characteristic of all laser techniques.
- d. When there is a luminous background, as in all melts and flames, the signal strength must be strong. Both LIF and CARS have this property but the adjustment of CARS is extremely critical. The LIF signal is often substantially reduced due to quenching.
- e. The Raman technique is the biggest competitor to LIBS on this point as both LIF and CARS are mainly used for one element at a time. What method is best depends on the examined mixture.

f. This property enables indirect identification of molecular species. However when Raman scattering is applicable, it gives the absolute concentration very accurately. With LIF absolute concentrations can be obtained but a great deal of calculations and assumptions have to be made in order to account for the effects of the quenching.

g. The detection limit depends on what combination of elements is dealt with as one has to find a strong transition without interfering background from any other element. With an optimized experimental set-up the detection limit should be even lower than was achieved here. Among the other techniques LIF has the highest sensitivity with detection limits of 1-10 ppm. It also has the advantage of being an imaging technique. Unfortunately some transitions in i. e. oxygen and nitrogen are difficult to reach as they lie in the UV and VUV range.

Although the CARS signal is strong, it is difficult to detect concentrations lower than 1 % which makes it unsuitable for detection of trace elements.

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#### Appendix 1.

Fig. 20 shows the outcoming energy vs. the scale on the attenuator . The reproducibility was  $\pm 1\%$  of the power output. The adjustment between 13.0 and 14.0 on the attenuator cannot be used in our analysis since the moderation of the beam is here made simply by entering an opaque disc gradually into the beam, making it asymmetric.

#### Appendix 2. Gas mixing in a closed cell.

The system is shown in fig. 21.

Suitable line of actions:

1. Evacuate the system
2. Close to cell
3. Rinse tubes with oxygen
4. Evacuate
5. Put a slight overpressure of oxygen in the tubes
6. Open to cell and fill up to e.g. one tenth of the total pressure
7. Repeat point 1 - 5 with nitrogen instead of oxygen
8. Open to cell and fill with an even flow up to the desired total pressure.
9. Wait 3-4 minutes for the gases to mix properly
10. Repeat point 8 and 9 if necessary.

Comments:

1. The cell must naturally not have a leakage during the time of the mixing process that is of a size that would affect the accuracy of the dilute concentration. This was here  $+ 5\%$
6. First the mixing proportions were 1:9 as stated in the list. The procedure was repeated with the proportions 1:4 to check the pressure meter.
9. The time of the mixing alters with the size of the cell. In our case the volume was approximately  $10^{-5} \text{ cm}^3$  .

Appendix 3. Identified transitions.

LIBS: Oxygen

2972 II

3135 II

3274 II

3377 II

3390 II

3749 II

3947 I

3954 II

3973 II

4076 II

4119 II

4190 II

4317 II

4349 II

4367 II

4417 II

4450 II

4467 II

4591 II

4642 II

4649 II

4676 II

4705 II

4925 II

4943 II

6157 I

6455 I

6654 I

LIBS: Nitrogen

3007 II  
3437 II  
3919 II  
3956 II  
3995 II

4041 II  
4100 I  
4242 II  
4447 II  
4601 II

4607 II  
4631 II  
4788 II  
4803 II  
5005 II

5045 II  
5666 II  
5679 II  
5932 II  
5942 II

6483 II  
6611 II

LIBS: Sulphur dioxide

4142 II, 4145 II, 4153 II, 4163 II  
4694 I  
5433 II, 5454 II, 5474 II  
5606 II  
5640 II

TRELIBS: Oxygen

$t_0 + 0.40 \text{ us}$

3390 II

3407 II

3471 II

3713 II

3727 II

3749 II

3912 II, 3919 II

3947 I

3973 II, 3982 II

4070 II, 4072 II, 4076 II

4119 II

4153 II

4190 II

4317 II

4345 II, 4349 II

4367 II

4415 II, 4417 II

4448 II, 4452 II

4467 II

4591 II, 4596 II

4642 II, 4649 II, 4661 II

4676 II

4699 II, 4705 II

4925 II

4943 II

7157 I

$t_0 + 3.0 \text{ us}$

3823 I

3947 I, 3954 I

4133 II

4368 I

5330 I

5436 I

6106 I

6157 I

6258 I, 6261 I

6366 I, 6374 I

6455 I

6654 I

7002 I

7157 I

7254 I

TRELIBS: Nitrogen

$t_0 + 0.40 \text{ us}$

3437 II

3838 II

3919 II

3955 II

3995 II

4041 II

4237 II, 4242 II

4447 II

4602 II, 4607 II

4613 II, 4621 II, 4631 II

4643 II

4788 II

4803 II

4987 II, 4994 II, 5001 II, 5003 II, 5005 II, 5007 II,  
5010 II, 5016 II  
5025 II  
5046 II  
5535 II

5666 II, 5676 II, 5679 II, 5686 II  
5928 II, 5931 II  
6482 II  
6610 II

$t_0 + 3.0 \text{ us}$

3995 II  
4000 I, 4109 I  
4237 II, 4242 II  
4447 II  
4915 I

4933 I  
5169 I  
5180 I  
5281 I  
5293 I

5752 I, 5765 I  
5829 I  
5854 I  
6000 I, 6008 I  
6481 I, 6482 I, 6483 I, 6485 I

6623 I, 6637 I, 6645 I, 6653 I, 6656 I  
6723 I



TRELIBS: Sulphur dioxide

$t_0 + 0.40 \text{ us}$

O 3390 II

S 3933 II

S 4142 II, 4145 II, 4153 II, 4163 II

O 4368 I

O 4642 II, 4649 II

S 4816 II

S 4924 II, 4925 II

O 4925 II

S 5429 II, 5433 II

S 5454 II

S 5473 II

S 5509 II

S 5564 II

S 5606 II

S 5640 II

S 5660 II

O 5157 I

$t_0 + 2.0-14.0 \text{ us}$

3390 II

S 4142 II, 4145 II, 4153 II, 4163 II

O 4368 I

S 4694 I, 4695 I, 4696 I

S<sub>2</sub> 4747

S 4925 II

S 4994 I

S<sub>2</sub> 5036

S<sub>2</sub> 5090

O<sub>2</sub><sup>+</sup> 5296

O 5436 I  
S 5454 II  
S 6052 I  
O 6157 I  
S 6385 II, 6397 II

O 6454 I  
S 6749 I, 6757 I  
O 7157 I  
O 7254 I

Appendix 4. Literature search and list of references in  
chronological order

The following list of references contains every publication to be found dealing specifically with LIBS and TRELIBS.

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Figure Captions.

1. Experimental set up
2. A typical sensitivity curve of a diode array
3. The timing scheme
4. LIBS: Oxygen 440 - 530 nm
5. LIBS: Nitrogen 440 - 530 nm
6. LIBS: Air 440 - 530 nm
7. LIBS: Oxygen 300 - 650 nm
8. LIBS: Nitrogen 300 - 650 nm
9. LIBS: Sulphur dioxide 350 - 700 nm
10. The relative strength of the background continuum as a function of time measured at a point not in the vicinity of an atomic transition.  
x - oxygen  
o - nitrogen
11. The time development of the spectrum of oxygen, 380 - 480 nm.  $t_0$  designates the arrival of the laser pulse.  
 $t_1 = t_0 + 0.20$  us  
 $t_2 \quad + 0.40$  us  
 $t_3 \quad + 0.60$  us  
 $t_4 \quad + 1.0$  us  
 $t_5 \quad + 3.0$  us  
 $t_6 \quad + 5.0$  us  
The relative strength of the spectra are not comparable.
12. TRELIBS: Oxygen 350 - 700 nm
13. TRELIBS: Nitrogen 350 - 700 nm
14. TRELIBS: Sulphur dioxide 350 - 700 nm
15. TRELIBS: Oxygen 350 - 700 nm,  $t_0 + (2.0 - 14.0)$  us
16. The relative signal strength as a function of pulse energy  
o - total line strength ( including continuum background),  
at  $t_0 + 0.16$  us  
v - line strength  $t_0 + 0.16$  us  
x - total line strength  $t_0 + 0.40$  us  
w - line strength  $t_0 + 0.40$  us
17. Relative signal strength as a function of pulse energy  
x - total signal strength  $t_0 + 3.0$  us  
v - line strength  $t_0 + 3.0$  us

- o - tot sign. str.  $t_0 + 5.0$  us
- - line str.  $t_0 + 5.0$  us
- 18. Signal to noise ratio vs. concentration of  $O_2$ . Each dot represents a different measurement.
- 19. Signal to noise ratio vs. concentration of  $SO_2$ . Each dot represents a different measurement.
- 20. See app. 2
- 21. See app. 3

FIG 1

EXPERIMENTAL SET - UP

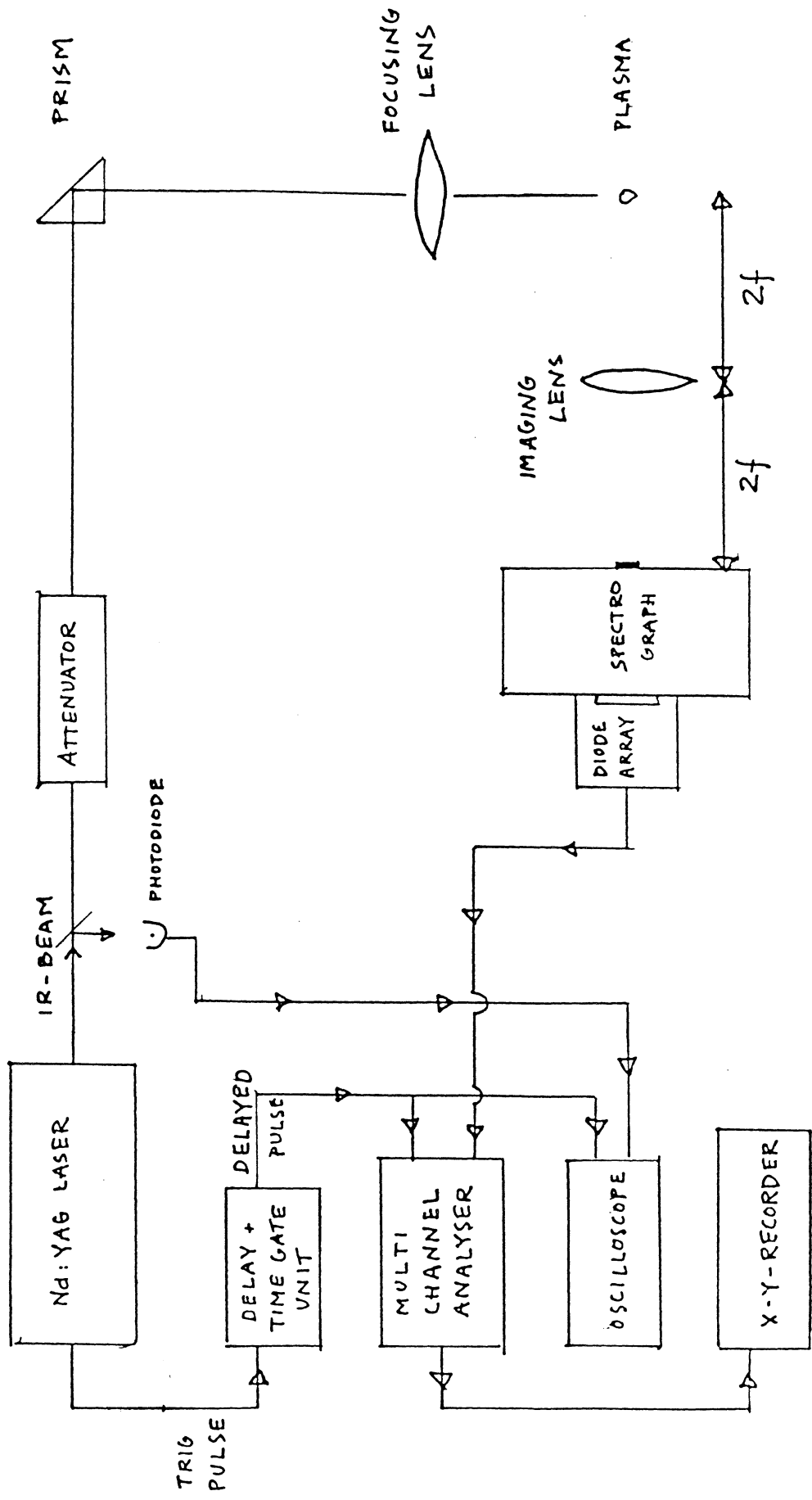




FIG 2

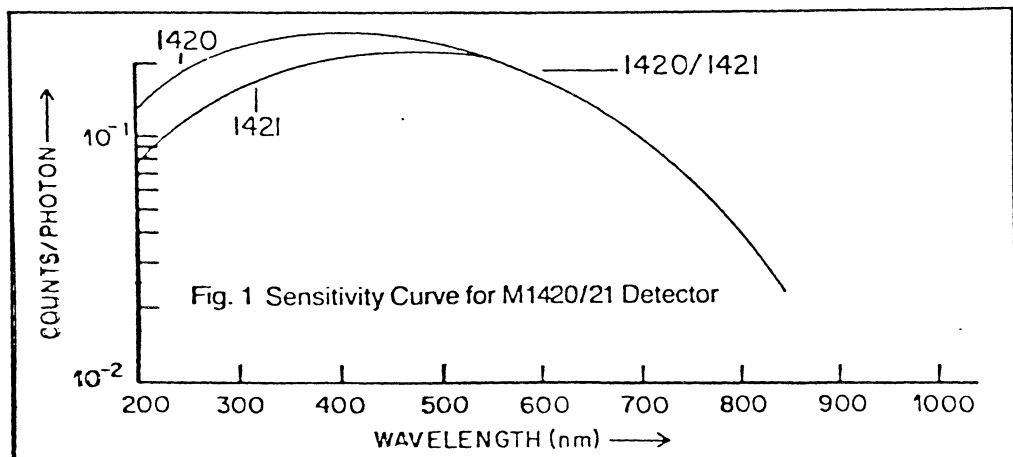


FIG 3

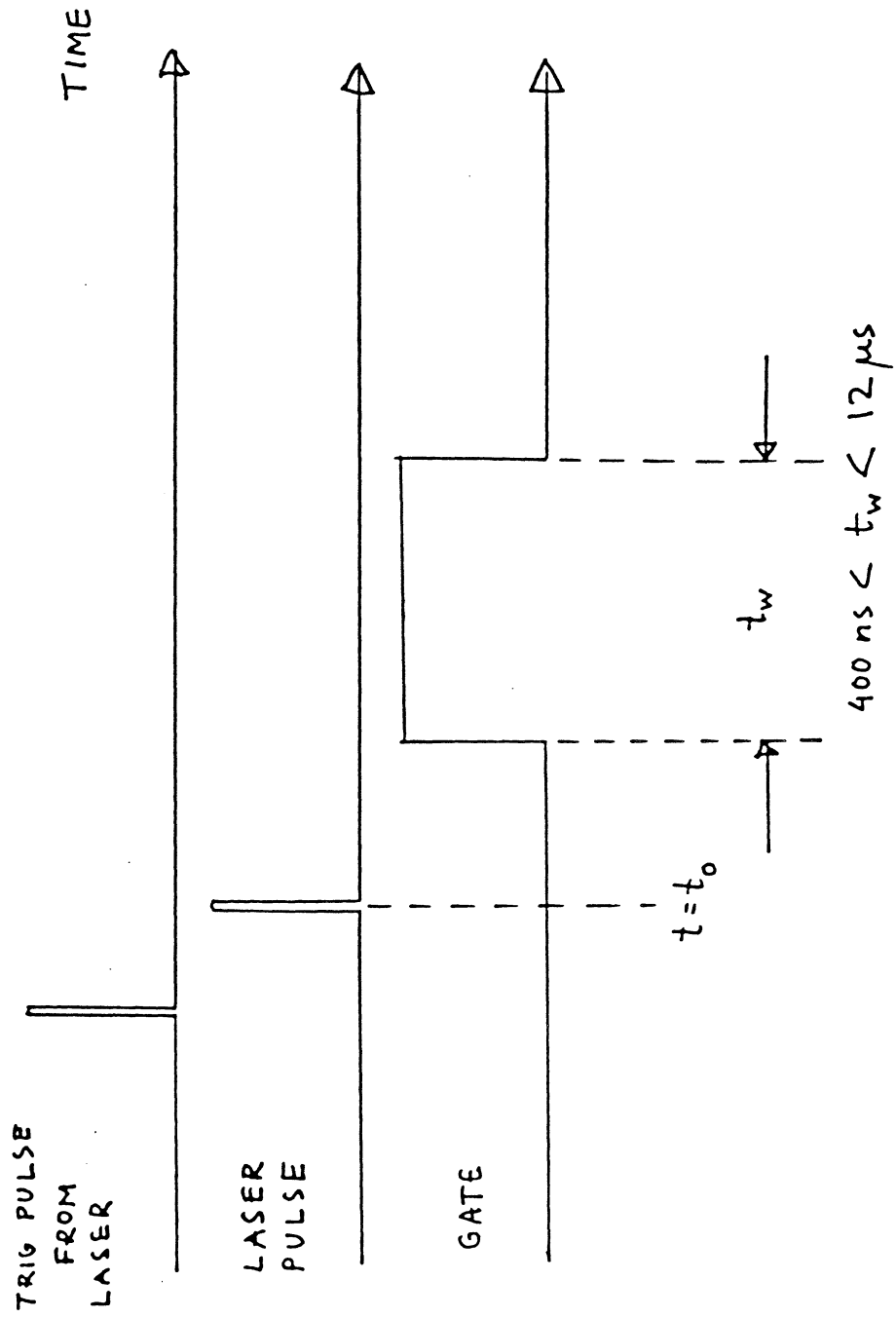


FIG 4

O<sub>2</sub>

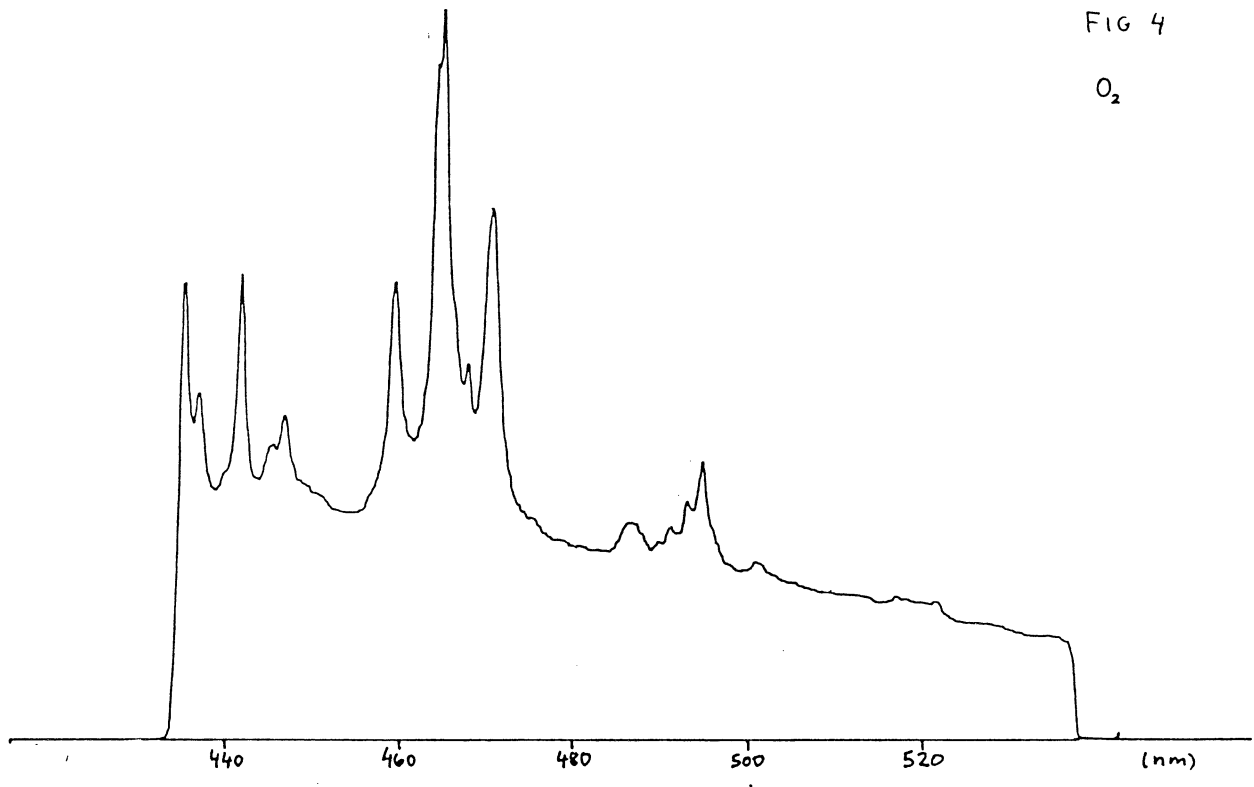


FIG 5

N<sub>2</sub>

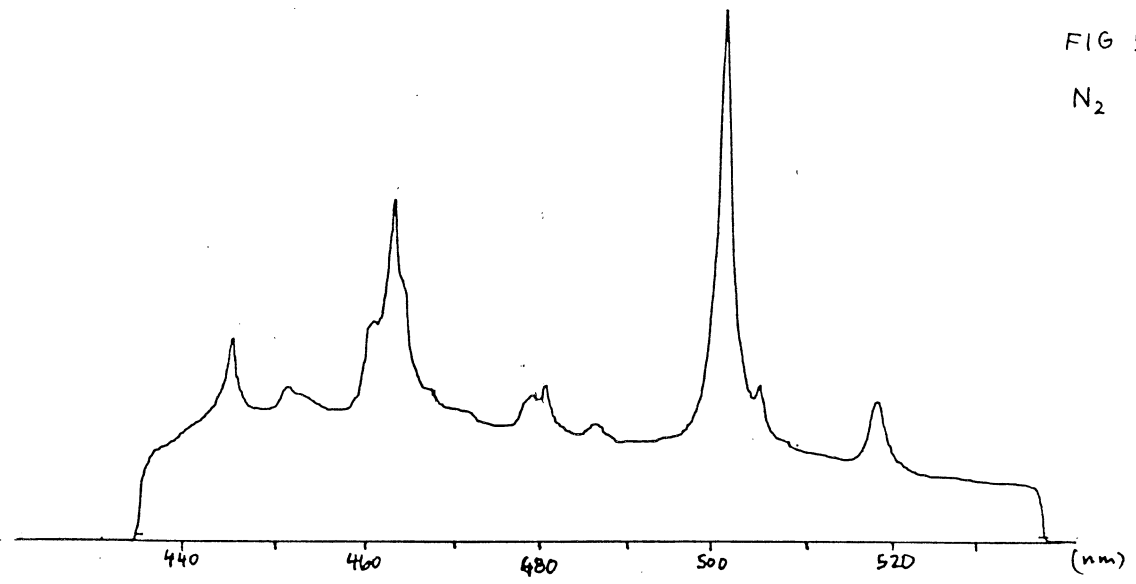
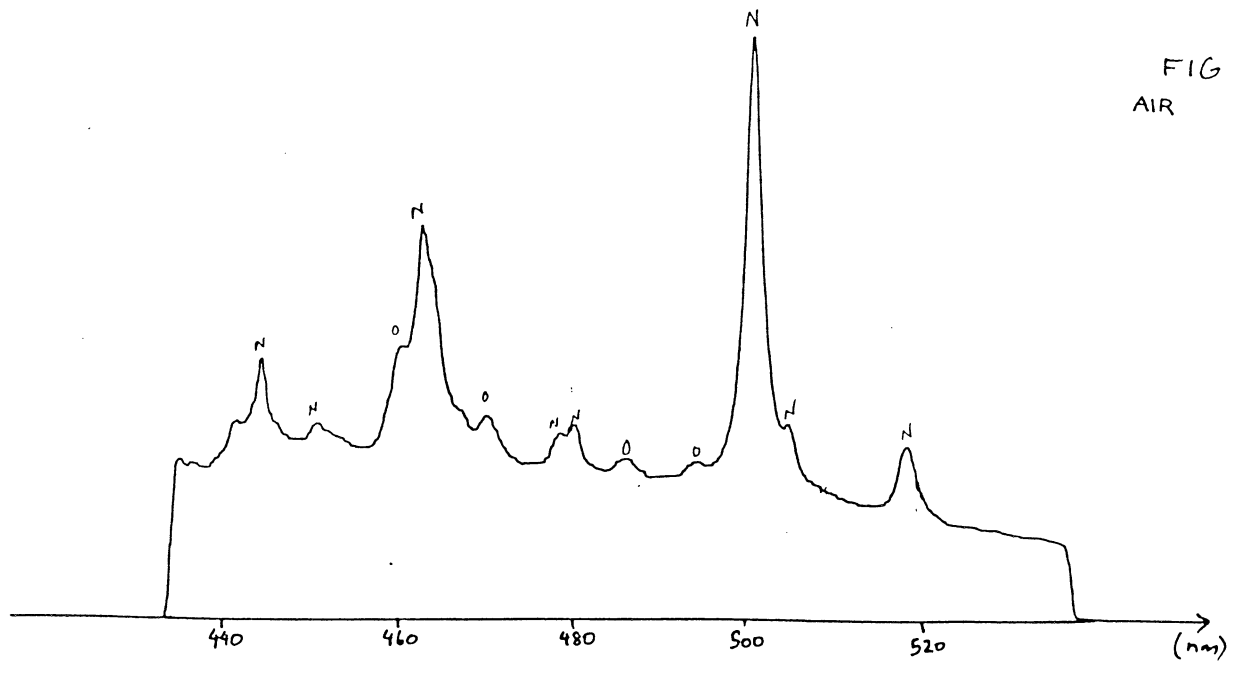
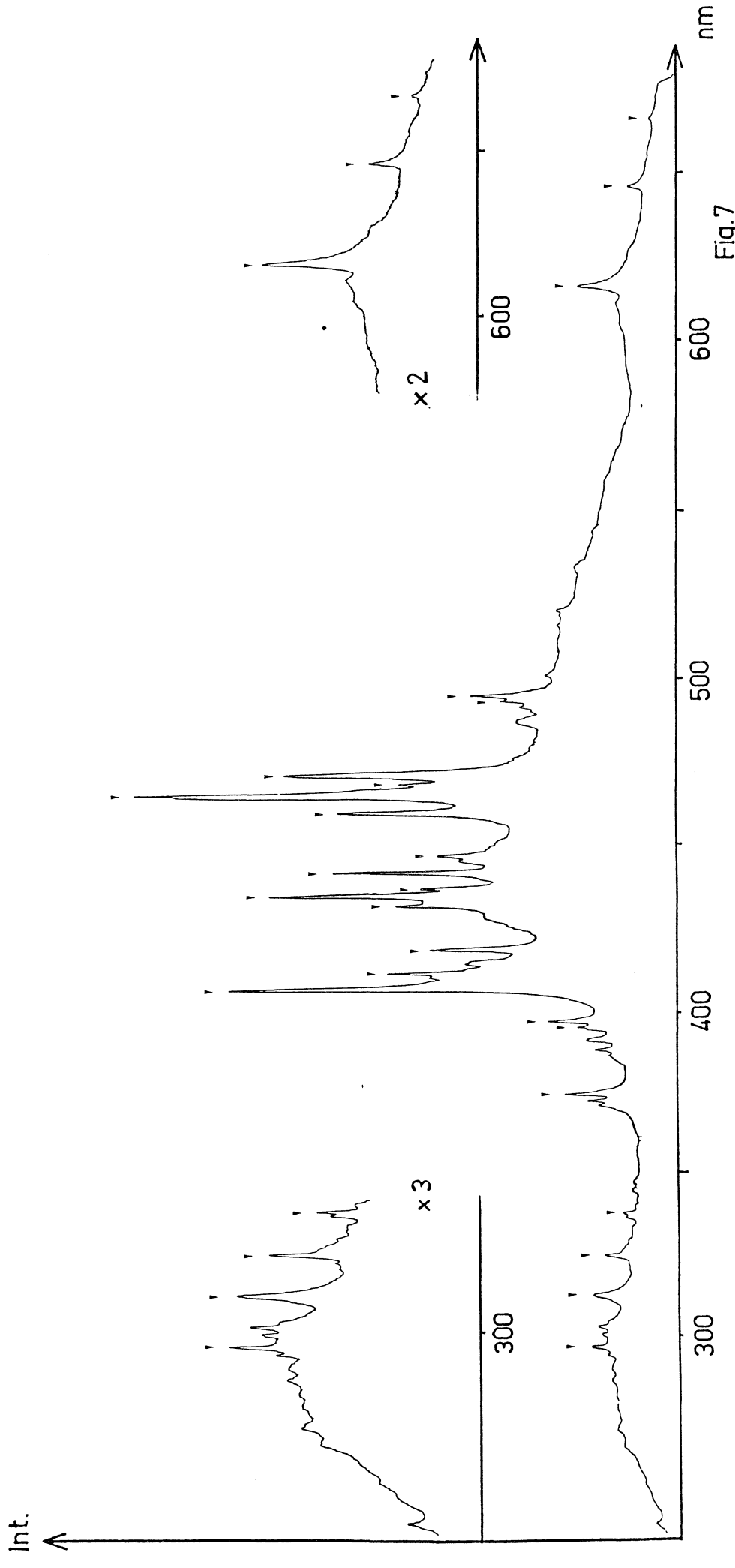
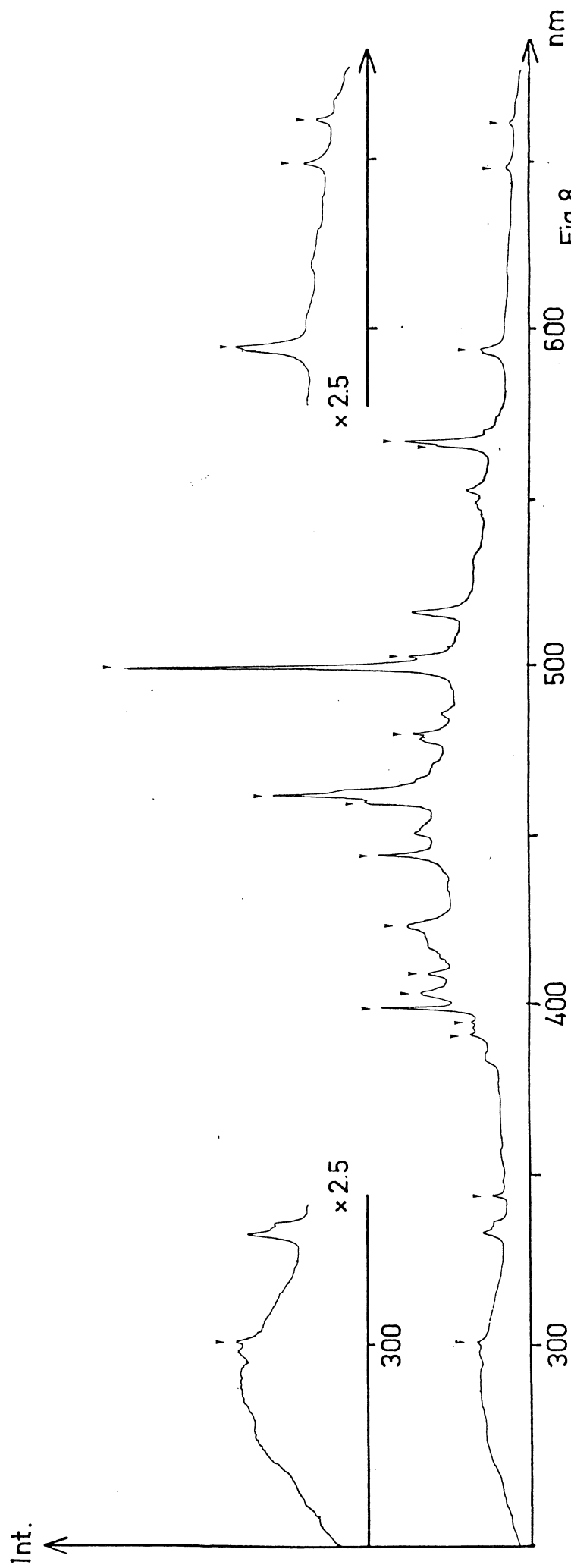


FIG 6  
AIR







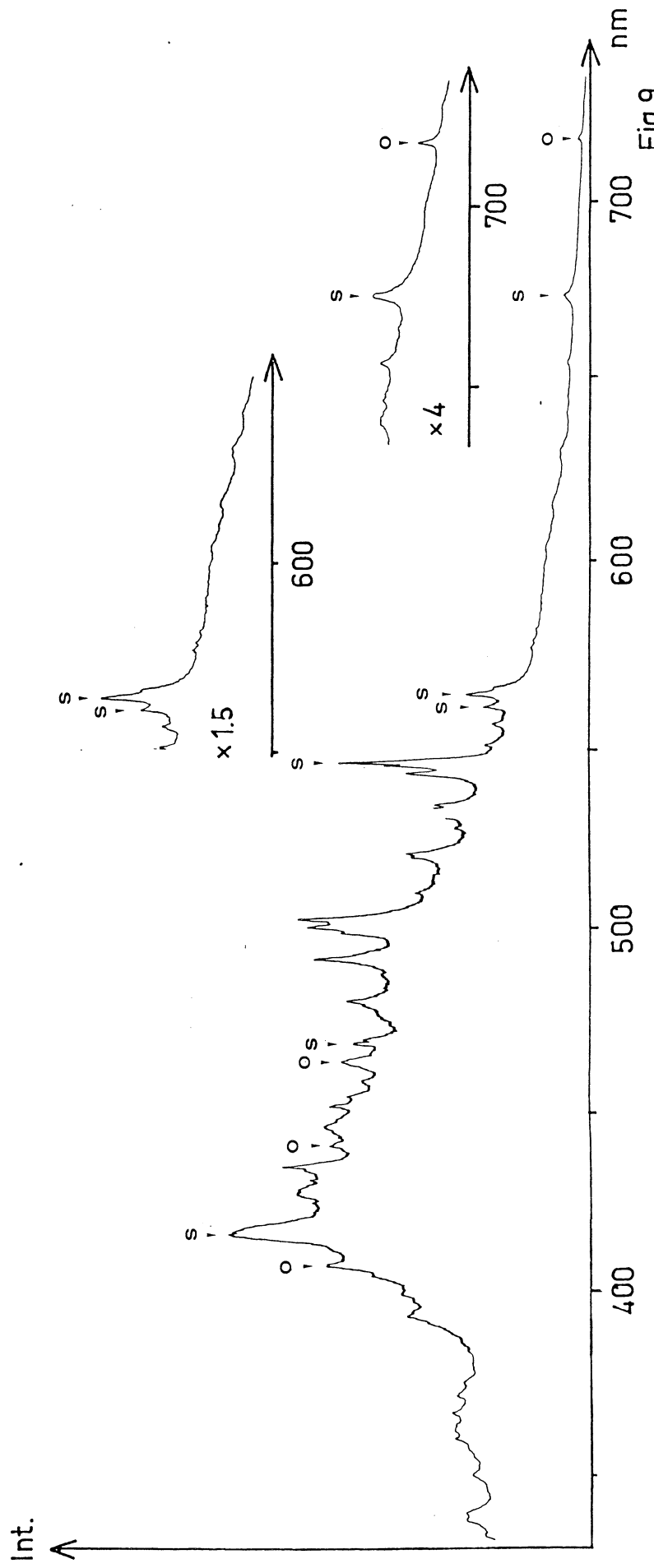
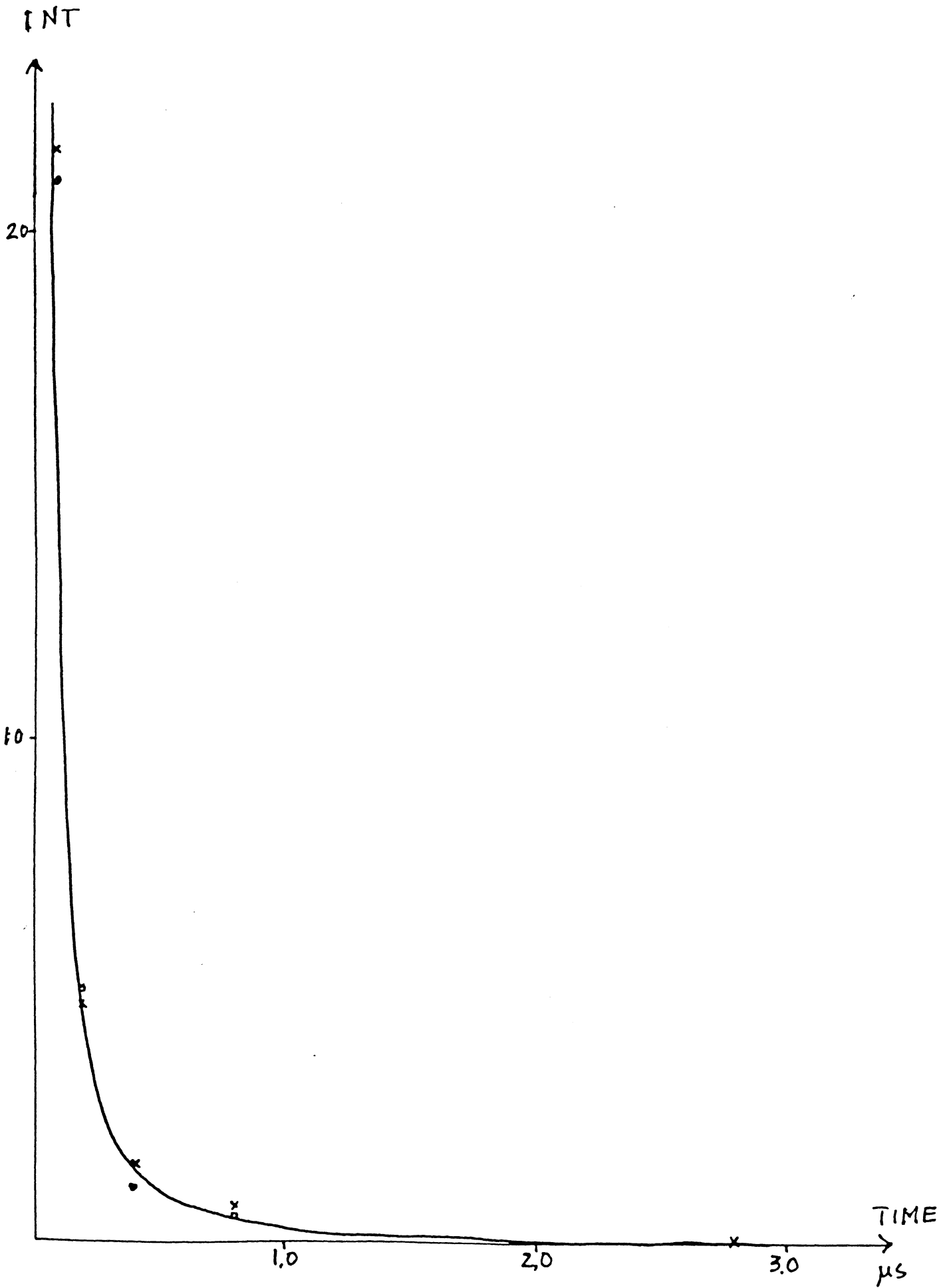


Fig.9

FIG 10



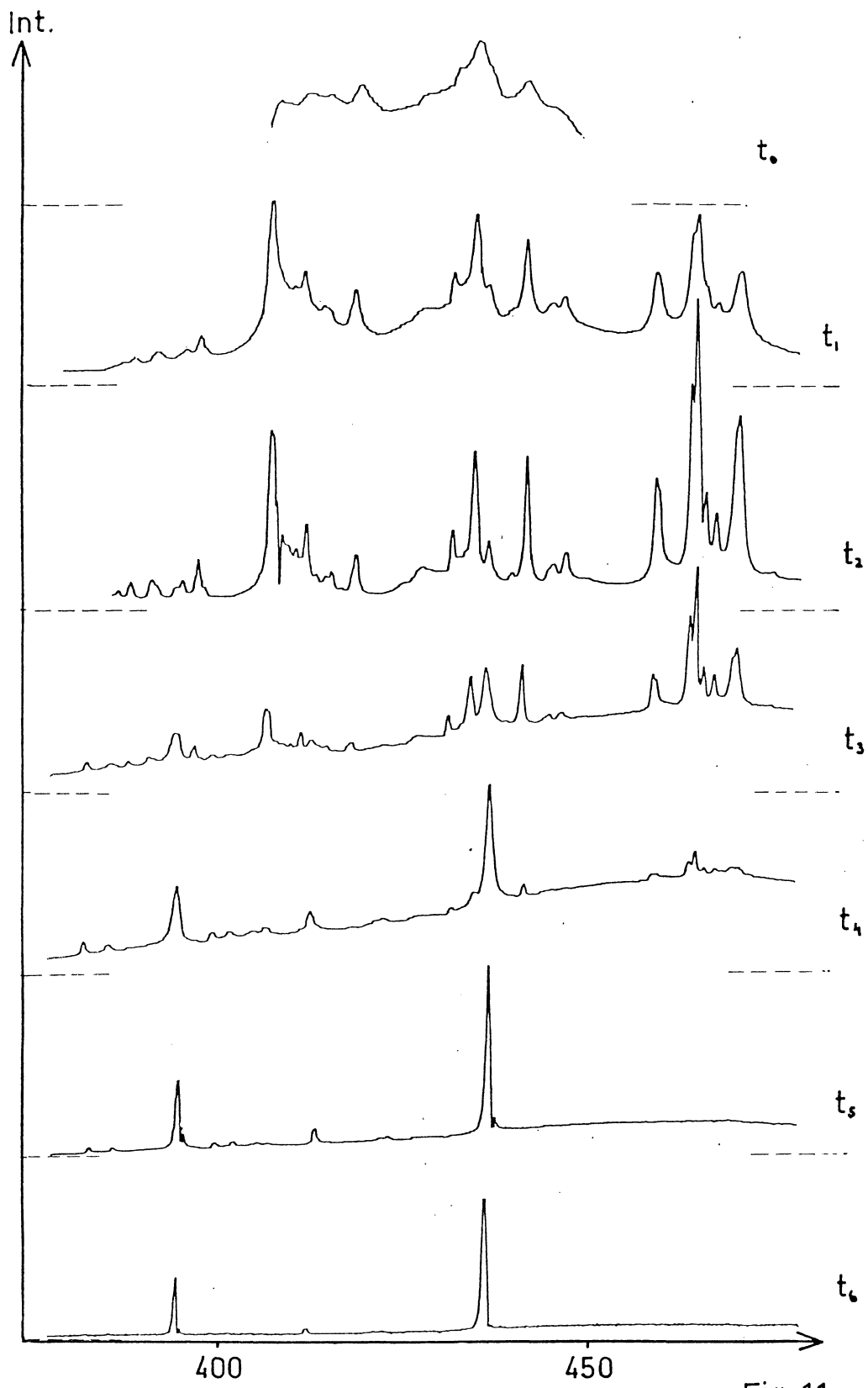


Fig. 11



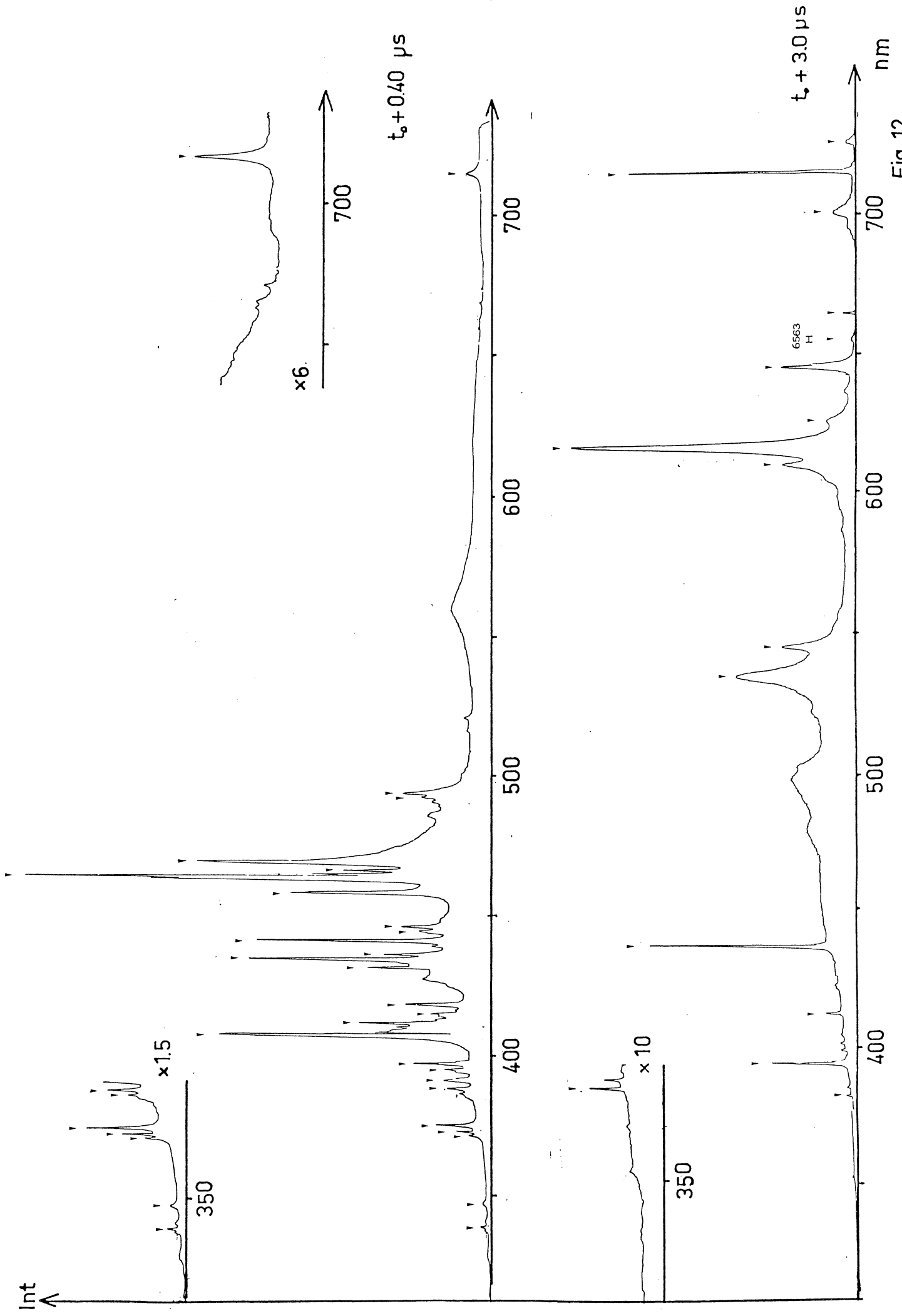


Fig. 12

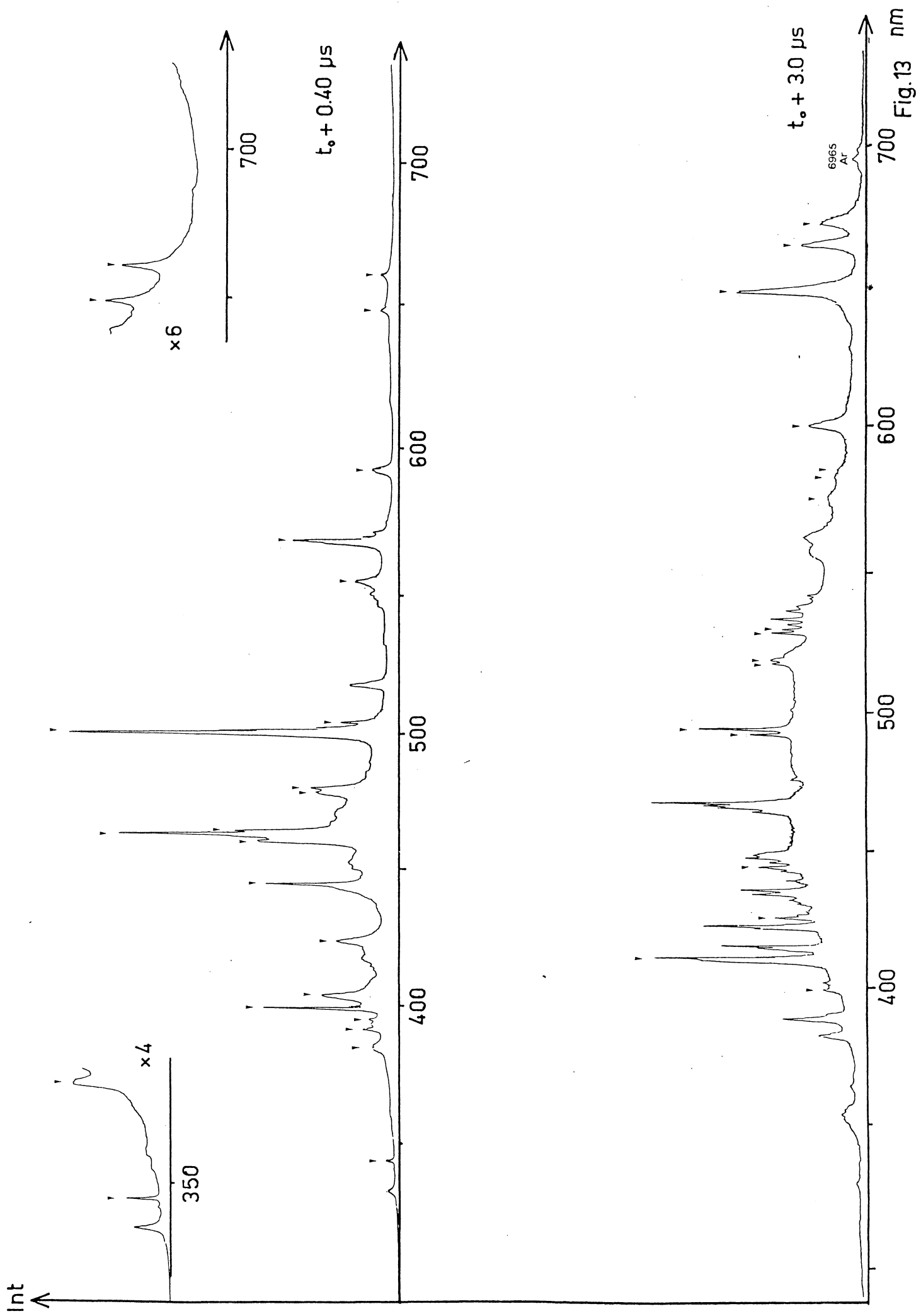


Fig. 13 nm

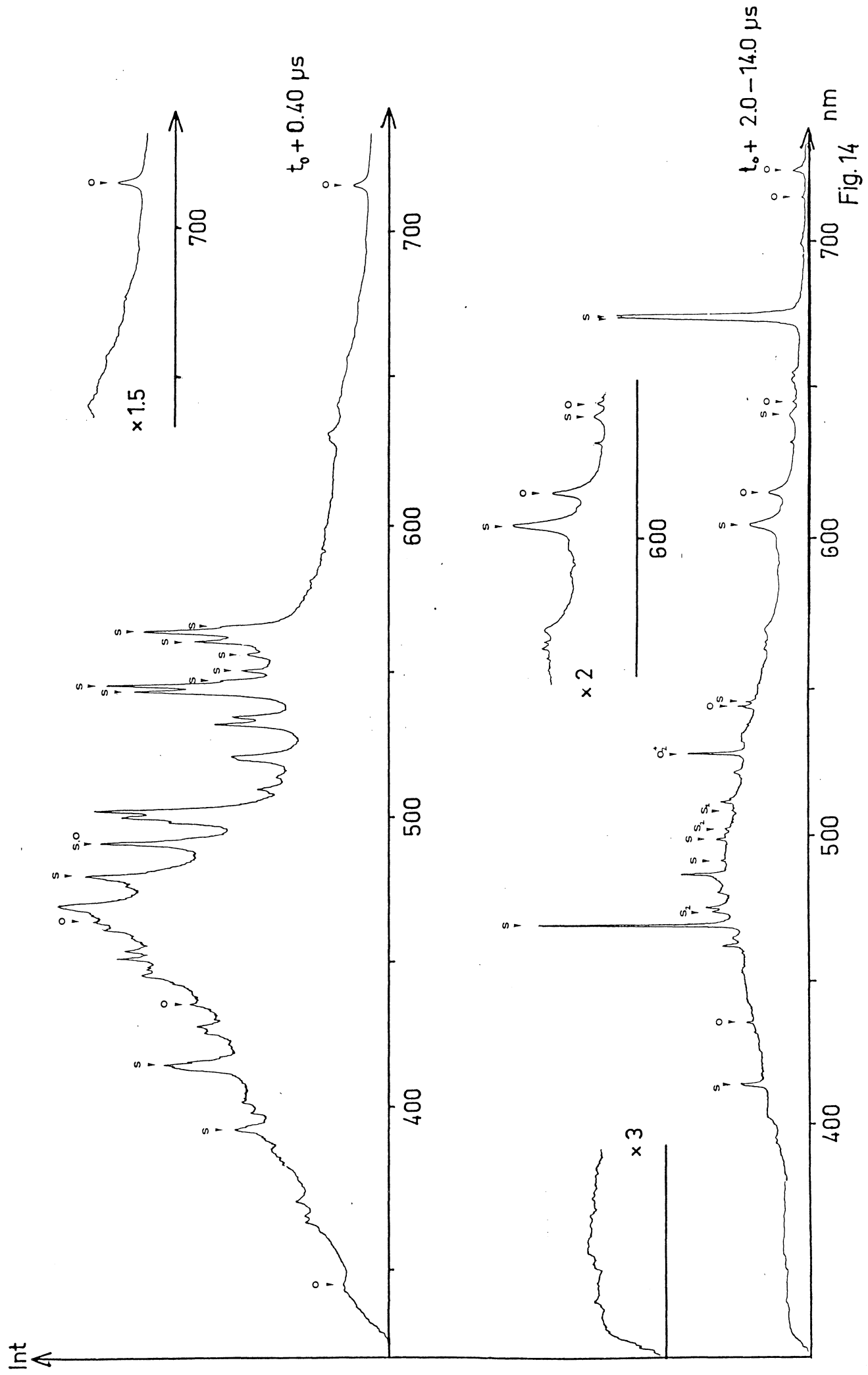


Fig. 14

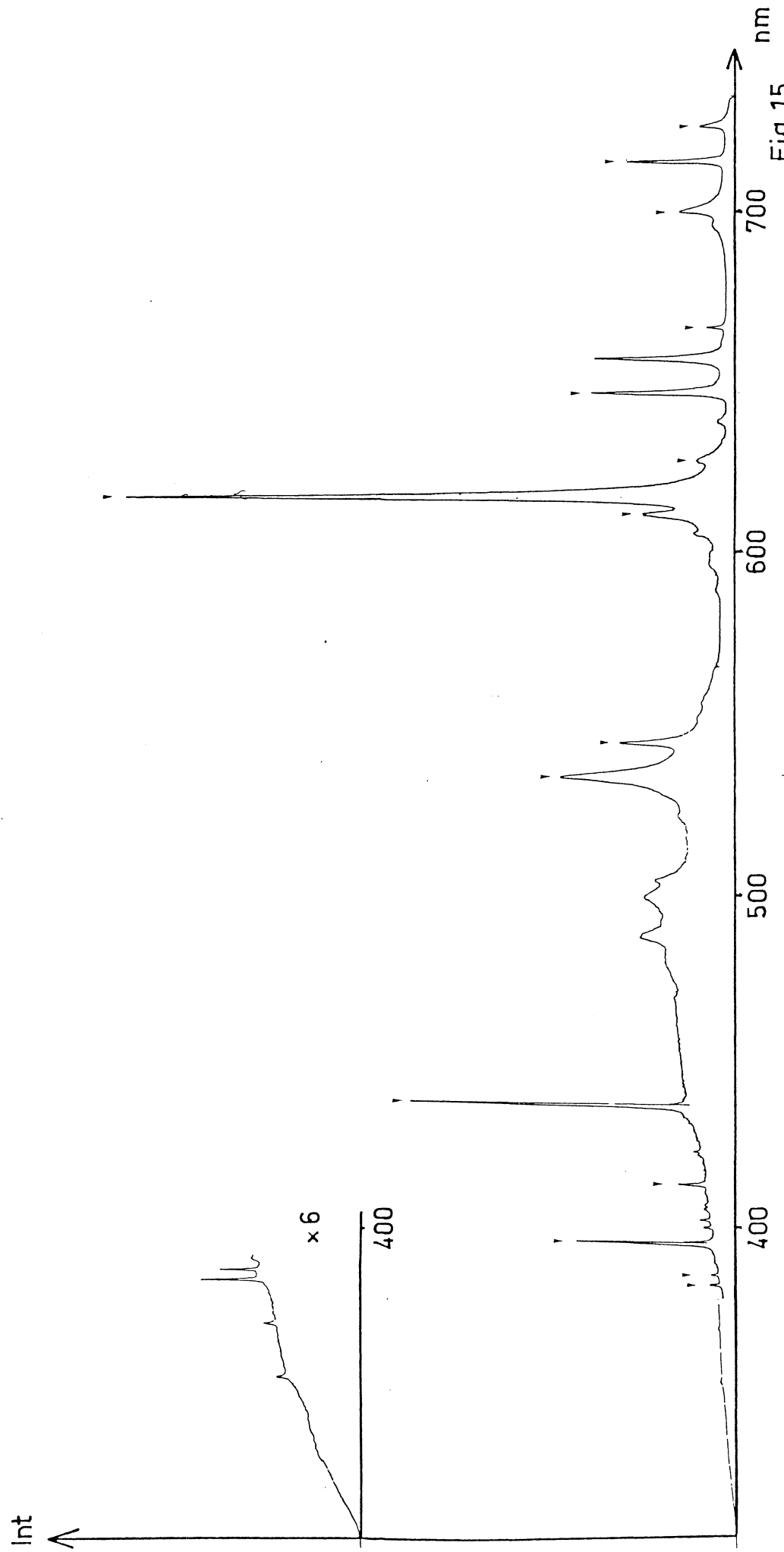
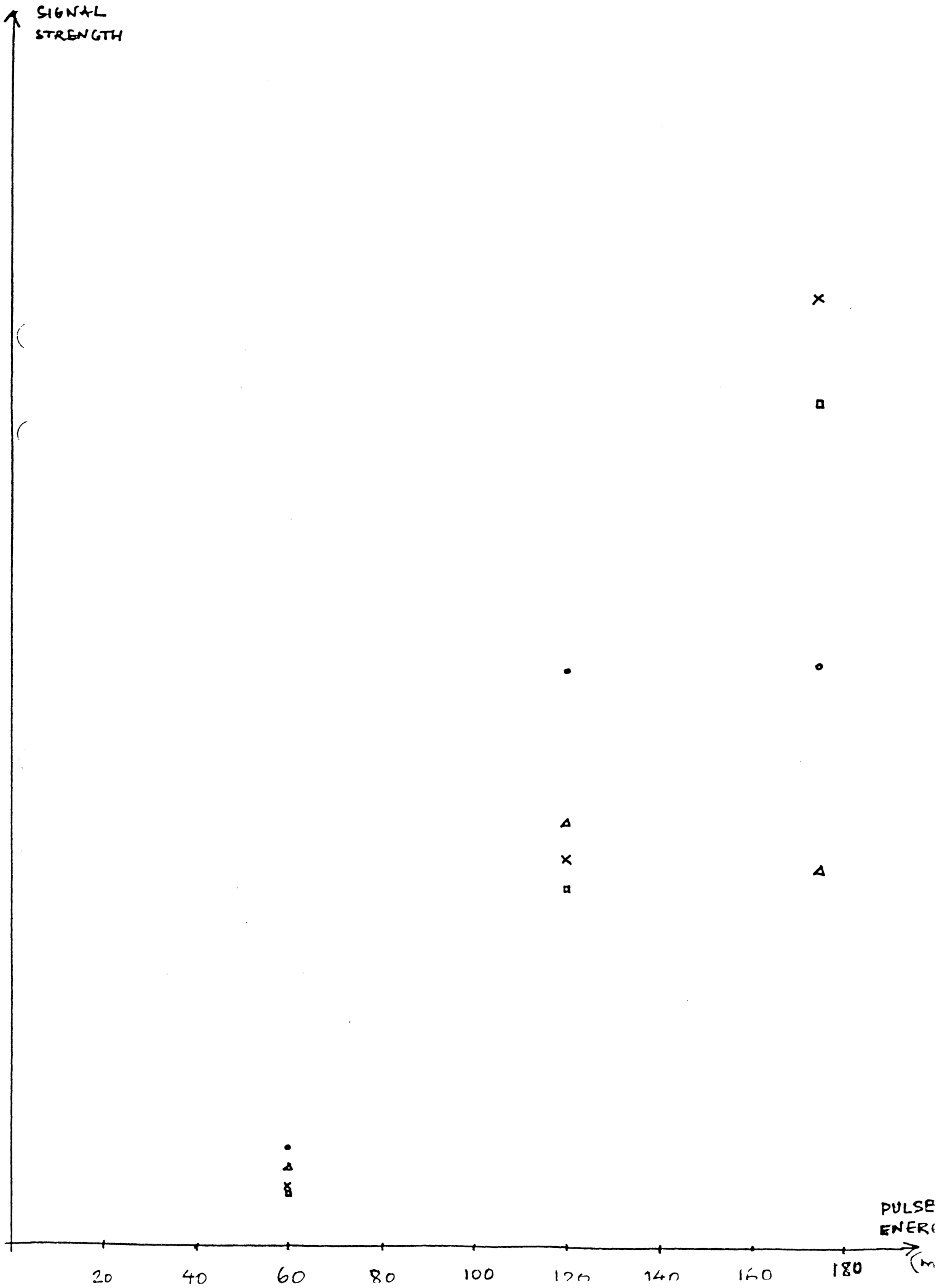


FIG 16

SIGNAL  
STRENGTH

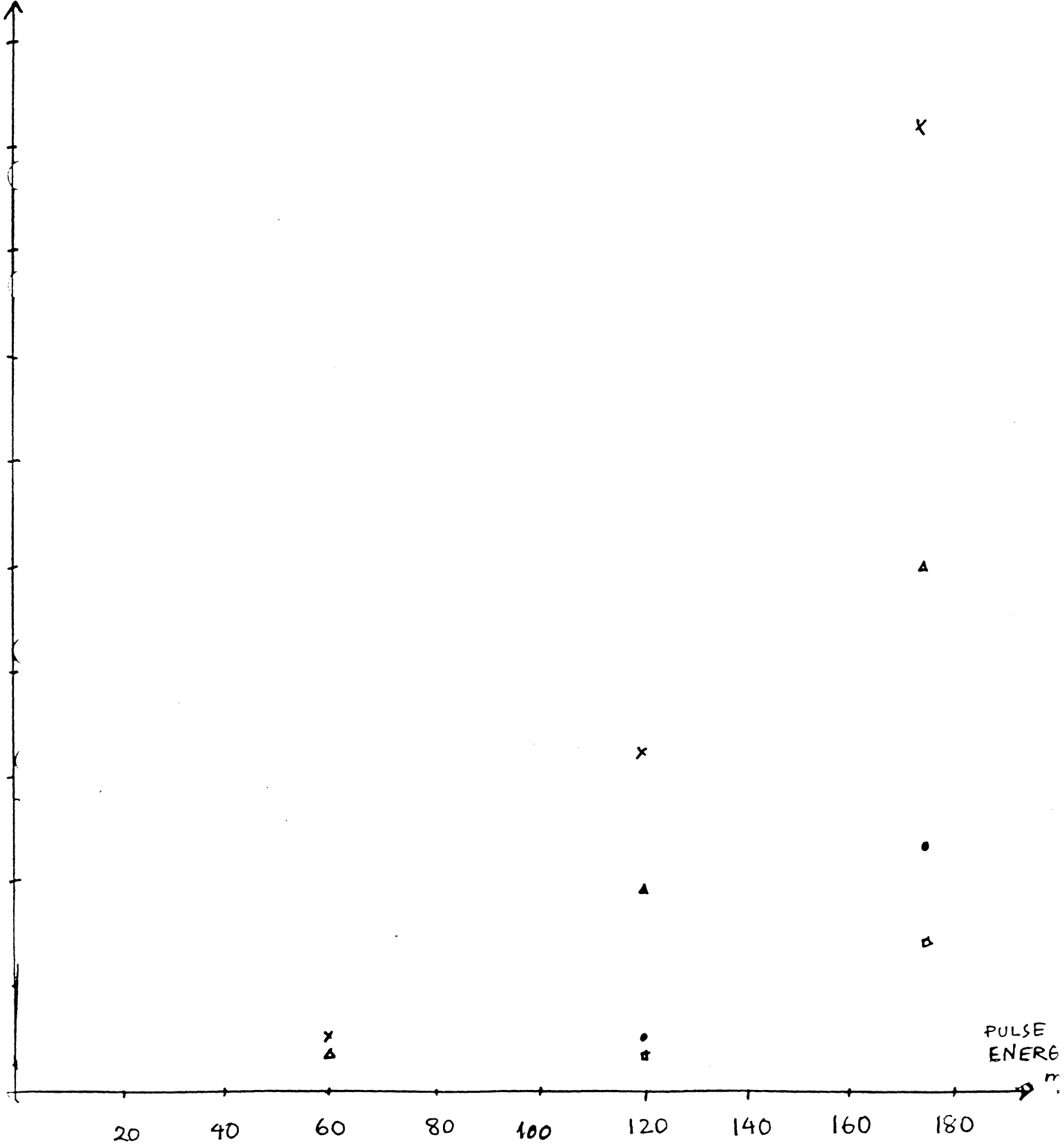


PULSE  
ENERGY

(m)

SIGNAL  
STRENGTH

FIG 17



PULSE  
ENERG

FIG 18

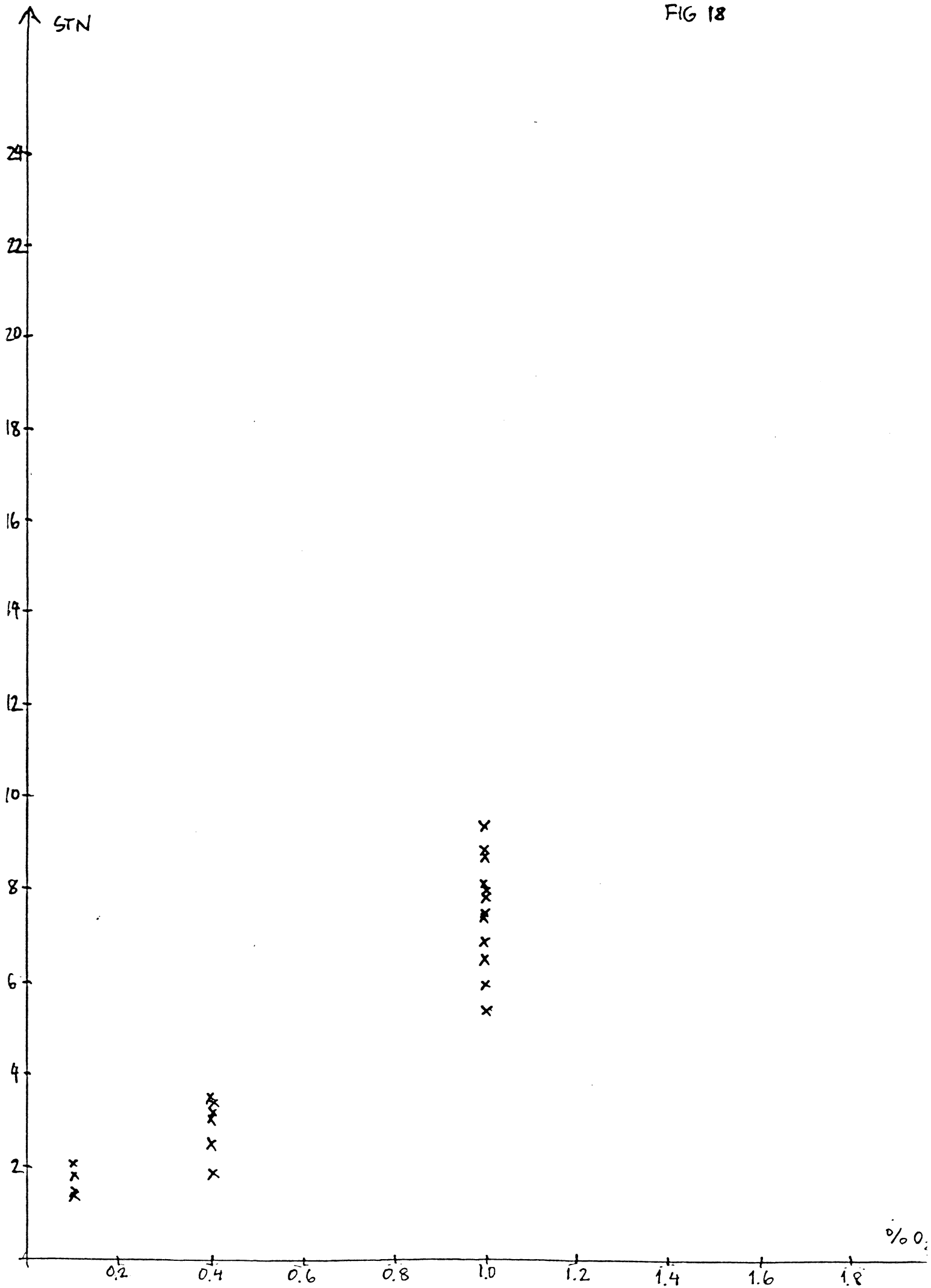


FIG 19

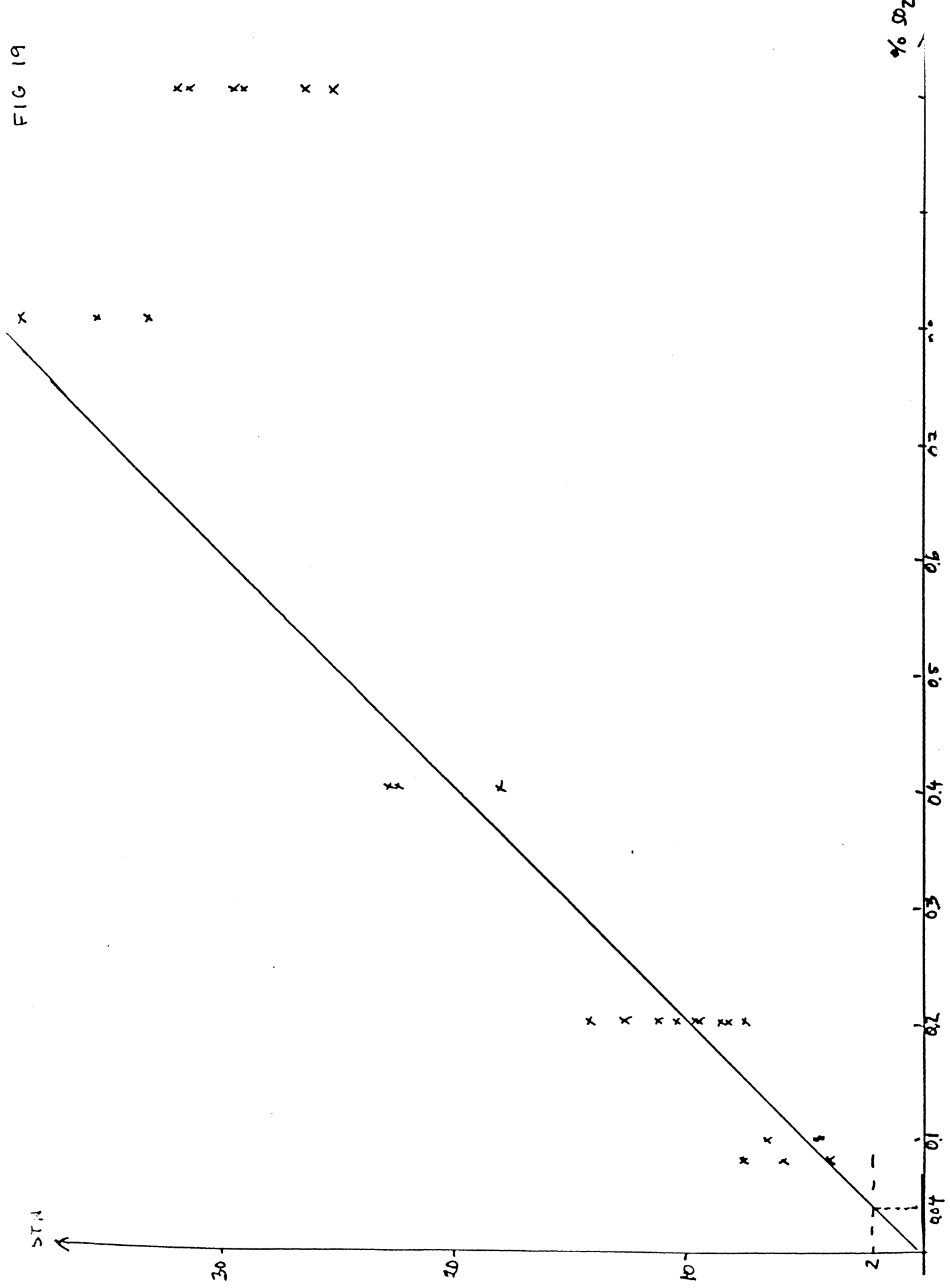




FIG 20

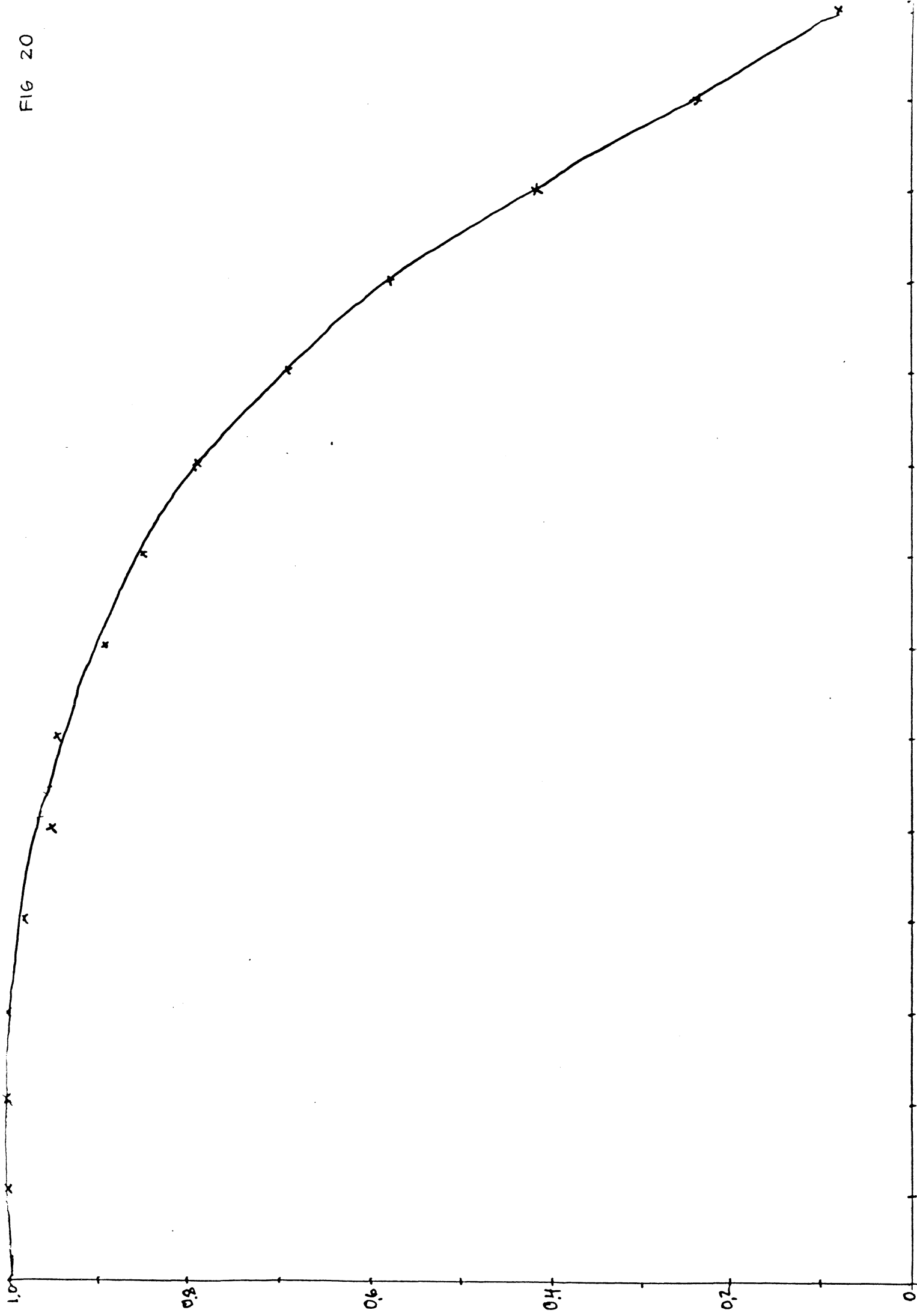
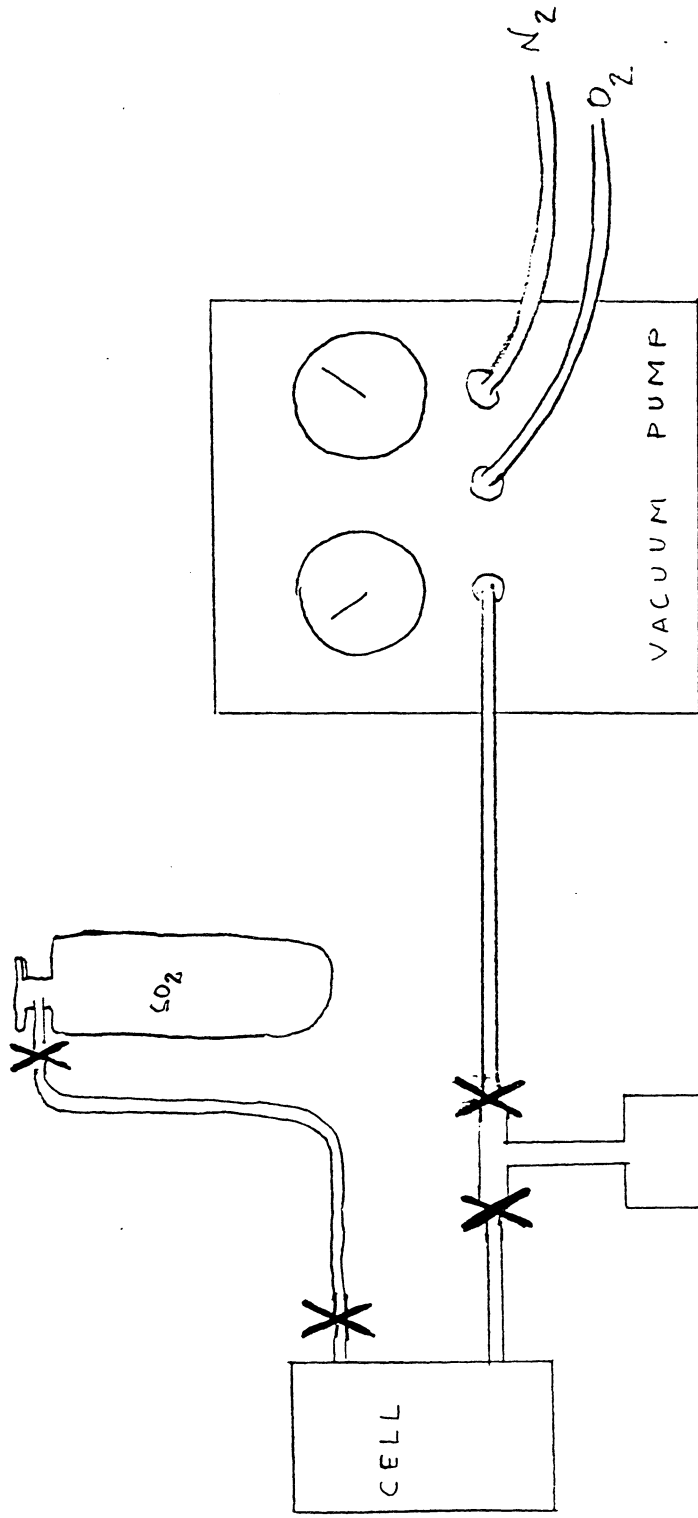


FIG 21



THE GAS MIXING SYSTEM