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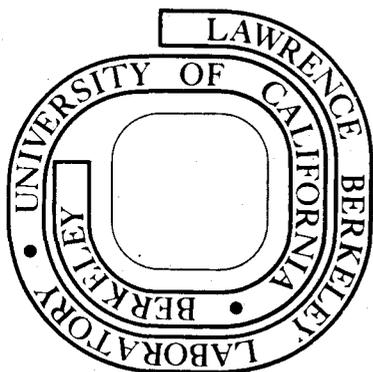
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MEASUREMENT OF NO<sub>2</sub> CONCENTRATION IN COMBUSTION  
USING FLUORESCENCE EXCITED BY AN ARGON-ION LASER<sup>†</sup>

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Abstract

Preliminary results on the measurement of NO<sub>2</sub> in a premixed hydrogen-air flame are reported. A laser-excited fluorescence detector was constructed for the purpose. Measurements of the effective broadband fluorescence (6700 Å - 7500 Å) emission cross-sections excited by five Ar<sup>+</sup> laser lines were carried out using NO<sub>2</sub>-air mixtures in the 1-1000 ppm range of concentrations, under atmospheric pressure and temperature conditions. These yielded values on the order of 10<sup>-25</sup> cm<sup>2</sup>/sr. Fluorescence intensity was linear with NO<sub>2</sub> concentration in the range 1-500 ppm at total pressure of 1 atm and room temperature. Measurement of fluorescence at atmospheric pressure but elevated temperatures up to 700°K indicated almost no change in effective emission cross-section when a 1000 ppm NO<sub>2</sub>-air mixture was studied. At higher temperatures, thermal decomposition was observed. The instrument sensitivity under room temperature conditions was about 1 ppm, and under flame conditions was about 7 ppm. When measurement of NO<sub>2</sub> in a 1.1 equivalence (fuel rich) ratio flame was attempted, no NO<sub>2</sub> (> 20 ppm) was found. Even when 1000 ppm NO<sub>2</sub>-in-air mixture was used to oxidize hydrogen, NO<sub>2</sub> concentration greater than 20 ppm could not be detected in the combustion region. This sensitivity could be obtained only somewhat behind the flame front due to NO<sub>2</sub> chemi-luminescence radiation generated at the flame front. Improved spatial discrimination should allow more extensive and sensitive measurements which would help towards resolving the questions of existence and mechanisms for NO<sub>2</sub> formation in combustion.

I. Introduction

The measurement of gaseous species in combustion has usually been carried out by extraction using sampling probes and subsequently analyzing the extracted gas. This procedure has suffered from several inherent difficulties involving disturbances of flow near the tip of the probe, catalytic effects near and inside the probe and limitations on probe physical size. The study of chemical reactions caused within the sampling probes is a subject of continued interest as evidenced by the recent works of Siewert<sup>(1)</sup> and England & Houseman<sup>(2)</sup>. Also since the process of sample extraction involves long times in comparison with characteristic times for chemical or fluid dynamic processes, such systems are neither capable of measuring instantaneous phenomena needed to study turbulence, nor can transient or short-lived species such as radicals be measured. Optical probing offers possibilities of both spatial and temporal resolution without disturbing the flow and has recently received attention for

studying microscopic scale combustion phenomena. In this paper a relatively simple fluorescence technique to measure point concentration of NO<sub>2</sub> is described and some preliminary results are reported on a search for NO<sub>2</sub> in a premixed hydrogen-air flame. Fluorescence spectra of NO<sub>2</sub> excited by five Ar<sup>+</sup> laser lines have been measured when mixed with air in the 1-1000 ppm range of concentrations under atmospheric pressure and temperature conditions. Effective broadband fluorescence (6700 Å - 7500 Å) emission cross sections are obtained for the five Ar<sup>+</sup> lines. The linearity of fluorescence intensity with NO<sub>2</sub> and the effect of temperature were investigated.

NO<sub>2</sub> is known to absorb light in a wide part of the visible spectrum. Considerable effort has gone into understanding and characterizing the absorption and fluorescence spectra of NO<sub>2</sub>, and also into the development of highly sensitive detectors. Several papers<sup>(3-6)</sup> have reported fluorescence spectra excited by Ar<sup>+</sup> and Kr<sup>+</sup> laser lines under low pressure (10<sup>-3</sup> - 10 Torr) conditions, made vibrational assignments, determined vibrational constants and provided life-time information on the excited NO<sub>2</sub> molecule. Also, development of a sensitive fluorescence based NO<sub>2</sub> monitor has been carried out at the Aerospace Corp.<sup>(7-10)</sup>. Their effort was motivated by the need to monitor atmospheric NO<sub>2</sub> content and has resulted in the development of equipment with good sensitivity (ppb), although it involves sampling and long integration times. Considerable improvement in reducing background noise in their photon-counting device was achieved by use of special non-fluorescent liquid filters for blocking the laser light. The work reported here, while focussing on achieving good space and time resolution, simply applied the same basic principles, although the present work was carried out with relatively simple and inexpensive equipment in the combustion region of a hydrogen-air flame.

II. Experimental Details

A schematic of the experimental equipment is shown in Fig. 1. The laser beam from a Spectra Physics model 164 Ar<sup>+</sup> laser was focussed in the flame region using a 100 mm focal length lens, giving a diffraction limited waist diameter of ~ 61λ. Two aperture stops were used subsequent to this lens to cut down unwanted scattered light. The laser beam was chopped with a rotating wheel and synchronous detection was employed to reject room background light. The chopping wheel, focusing lens and aperture stops were enclosed to further reduce scattered laser light. The focal point of the beam lay directly over the flame source, which was simply a nozzle mounted on an X-Y

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traverse. The beam was then absorbed in a light trap. Scattered light from the focal point of the beam was detected normal to the beam direction using  $f/3.3$  collection optics. The viewing background was also a light trap which reduced the scattered room and laser light to a negligible value. Fluorescence spectra were determined using a  $1/4$ -meter Jarell-Ash monochromator. The photodetector was an extended S-20 spectral response (RCA 4526) uncooled PMT. The fluorescence signal was extracted with a Princeton Applied Research model HR-8 lock-in amplifier.

All measurements were carried out in a flowing gas jet emerging from the nozzle placed under the laser beam. The gas mixture ( $\text{NO}_2$  in air) was obtained in 0.1% nominal concentration from Matheson Gas Co. Flow-metering was carried out by standard Fisher-Porter flow-rators. Dilution of the  $\text{NO}_2$  mixture to obtain lower concentrations was carried out using bottled air. Two separate nozzles were used to produce jets of  $\text{NO}_2$  mixtures. One was made of quartz and provided with a nichrome wire heater wrapped around it. The second nozzle, used with the flame, was made of brass, and had an exit diameter of 6.3 mm.

By varying the jet speed over a wide range and observing that the fluorescence intensity did not vary, it was ascertained that no significant absorption occurred on the walls of the nozzle or the connecting tubing. Fluorescence intensity as obtained using the quartz nozzle was compared with that obtained with the brass nozzle and was found to agree. Similar tests also ensured that dilution of the  $\text{NO}_2$ -air jet with room air did not occur in the region of measurement in the jet.

All cross-sections reported here were computed using the Rayleigh scattered intensity from air as reference. In order to ensure that stray scattered laser light did not contribute to the measured Rayleigh scattering by air (called  $\text{Ray}_{\text{air}}$  hereafter) the Rayleigh scattering was measured for He. This was approximately 62 times smaller than for air, indicating that background light could not possibly exceed 1.6% of  $\text{Ray}_{\text{air}}$ . It was found that bottled air had no measurable particulate contamination. The absence of particulate scattering was verified by comparing the ratio of the Rayleigh and the Raman scattering for  $\text{N}_2$  with the measurements of Penney et al. (11).  $\text{Ray}_{\text{air}}$  was found to be the same as  $\text{Ray}_{\text{N}_2}$  within the accuracy of measurement and the result was interpreted as additional verification that no particulates were present.

For the determination of the variation of emission cross-section with temperature for  $\text{NO}_2$  the temperature was measured using a Chromel-Alumel thermocouple. In the flame studies the temperature was determined from the Rayleigh scattered intensity according to the relation

$$\frac{T}{300^\circ\text{K}} = \frac{I_{300}}{I_T} \times \frac{\sigma_{300}}{\sigma_T}$$

where

$$\sigma_T = \sum \sigma_1 C_1$$

$I$  = intensity at temperature indicated by subscript

$\sigma_T$  = effective Rayleigh scattering cross-section

$\sigma_1$  = Rayleigh scattering cross-section of specie 1

$C_1$  = fractional concentration of specie 1.

In the computation of temperature in this manner, it was assumed that before the flamefront the composition consisted of the unburnt gases, and after the flamefront, of the products of complete combustion. The various  $\sigma_1$  were computed from (12)

$$\sigma_1 = \frac{4\pi^2}{\lambda^4} \left[ \frac{n_1 - 1}{N_1} \right]^2$$

where

$n_1$  = refractive index of specie 1 at molecular number density  $N_1$ .

The hydrogen-air flame studied was of 1.1 equivalence ratio. The flame was studied when air was the oxidizer and also when the 0.1%  $\text{NO}_2$ -air mixture was used as oxidizer to deliberately introduce  $\text{NO}_2$  into the flame and follow its history through the flame front.

### III. Results and Discussion

Fig. 2 shows a typical spectrum of the continuum excited by 1 watt power of the 4880 Å  $\text{Ar}^+$  line. This trace was obtained using a Corning 3-68 filter with cutoff at 5400 Å to suppress the Rayleigh scattered light. The slit used was 1 mm wide corresponding to 30 Å bandpass. The spectrum is a broad continuum extending from the laser line to 7500 Å - the observation limit given by the limit of the PMT sensitivity. No strong features are observed and, due to the broad bandpass used and the large collisional quenching at atmospheric pressure, the various vibrational lines of  $\text{NO}_2$ ,  $\text{N}_2$  and  $\text{O}_2$  are too weak to be seen. No qualitative change in the spectrum appears when the  $\text{NO}_2$  is excited by the other  $\text{Ar}^+$  lines.

Table 1 gives the effective fluorescence cross-sections for  $\text{NO}_2$  for the five  $\text{Ar}^+$  lines investigated. These values were obtained using only a Corning 2-64 sharp cut red filter, so that the effective bandpass for the fluorescence was approximately 6700 Å to 7500 Å, with the upper limit given by the photomultiplier response. These values are only approximate, were obtained by using the Rayleigh scattering intensity as reference, and are corrected for the photomultiplier quantum efficiency. Although the 4579 Å line has the largest cross section, the differences are not large and the 4880 Å line, which is more intense, was used for the measurements to be described below.

A graph of the fluorescence intensity versus  $\text{NO}_2$  concentration in air at atmospheric pressure is shown in Fig. 3. This appears linear in the 1-500 ppm, and we note that at much lower concentrations Gelbwachs et al. (7) have reported linear behavior. In the range from 500-1000 ppm the fluorescence increases somewhat less than linearly with  $\text{NO}_2$  concentration, which may be due to self-quenching of the  $\text{NO}_2$ . If this is so the effective self-quenching cross section of  $\text{NO}_2$  is much larger (100-1000 times) than the quenching cross section of nitrogen and oxygen.

It is most likely that the fluorescence quenching in the red region is due to vibrational and rotational de-excitation caused by quenching collisions with air molecules<sup>(3)</sup>, and thus the intensity will be dependent on the density and temperature of the quenching species as well as on the NO<sub>2</sub> concentration. Birnbaum<sup>(13)</sup> has shown results indicating that the fluorescence intensity is independent of total pressure, for a given fractional concentration of NO<sub>2</sub>. This means that the effective fluorescence cross-section is inversely proportional to air density at room temperature.

We have compared the quenching effects of N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub> with air, at atmospheric pressure, by diluting the 0.1% NO<sub>2</sub>-air mixture with these gases and measuring the fluorescence intensity at atmospheric pressure. The effective fluorescence cross-section remained constant, to within 10% for 50% dilution, indicating that all these gases have similar quenching properties. This is somewhat surprising in the case of H<sub>2</sub>, because of its small mass.

We have also investigated the effect of temperature on the effective fluorescence cross-section, at 1 atm pressure. Fluorescence intensity measurements were made using the heated quartz tube and the 0.1% NO<sub>2</sub>-air mixture, and the results are shown in Fig. 4. If there is no thermal decomposition of the NO<sub>2</sub>, the effective fluorescence cross-section would be proportional to the fluorescence intensity divided by the gas density. The sharp drop in this quantity above 700°K is attributed to thermal dissociation of NO<sub>2</sub>, in general agreement with the known rate of decomposition<sup>(14)</sup>. Below 700°K the extent of dissociation is small, and the data indicates that the effective cross-section is approximately independent of temperature. This indicates a strong temperature effect on the quenching process since the density is inversely proportional to the temperature and Birnbaum's results<sup>(13)</sup> indicated that the effective fluorescence cross-section was inversely proportional to density.

On the basis of these results, we assert that the effective fluorescence cross-section will be approximately the same in the hydrogen-air flame at 2100°K as it is at room temperature. This really involves extrapolation of the results given in Fig. 4 to 3 times greater temperature. Although there are many uncertainties, this extrapolation should be good to within a factor of 3.

The ultimate sensitivity of the system for detection of NO<sub>2</sub> is set by the noise background. For room temperature conditions this corresponded to about 0.25 ppm in 1 atm, as determined by feeding the jet with bottled air. The noise was somewhat smaller than this, but there was a positive signal of this magnitude which may be due to fluorescence of the filter, or to some residual NO<sub>2</sub> which had been absorbed on the tubing feeding to the jet.

A search for NO<sub>2</sub> fluorescence in a 1.1 equivalence ratio (fuel rich) hydrogen-air flame was carried out. Measurements were made in the cold gas prior to the flame front, in the flame front, and in the hot gases 2-3 mm downstream from the

flame front. No detectable signal could be measured. Radiation from the combustion zone resulted in an increased background signal, which increased the noise level to the equivalent of  $\pm 1$  ppm peak-to-peak at room temperature. A 100 sec time constant was used to filter the output of the lock-in detector. If, as previously discussed, the effective fluorescence cross-section is independent of temperature and composition, then this indicates an NO<sub>2</sub> concentration less than 7 ppm in the hot gases, where the temperature is about 2100°K. If we further allow for a possible factor of 3 error in the extrapolation of the calibration from 600°K to 2100°K, then it can be asserted that the NO<sub>2</sub> concentration in this particular flame is certainly less than 20 ppm.

The intensity of the Rayleigh scattered light was used to measure the spatial variation of temperature in the flame. The spatial resolution was not adequate to resolve the rise in temperature near the flame front, but downstream of the flame front the measured temperature of 2100°K is in good agreement with the adiabatic flame temperature.

The flame experiments were also carried out using a 0.1% NO<sub>2</sub>-air mixture. Measurements on the centerline of the jet are shown as a function of distance from the orifice in Fig. 5. These start in the cold, unburned gas and proceed towards the tip of the conical flame front. As the flame front is approached, the NO<sub>2</sub> fluorescence decreases towards zero from the 0.1% value. Unfortunately, the spatial resolution was not as good as it could have been, and thus some part of the decrease may be due to a portion of the measurement volume lying in the flame front. In any event, it is obvious that the NO<sub>2</sub> is rapidly destroyed at the flame front. No detectable NO<sub>2</sub> could be measured downstream of the flame front, again with an upper limit of about 20 ppm.

The bright greenish emission characteristic of the chemi luminescent reaction<sup>(15)</sup>  $\text{NO} + \text{O} \rightarrow \text{NO}_2^*$  was clearly visible in the region of the flame front. It is evident that significant quantities of NO are formed in the dissociation of NO<sub>2</sub>. This emission produced a large background radiation which raised the noise level of the NO<sub>2</sub> fluorescence detection signal in the vicinity of the flame front. Thus the 20 ppm detection limit on NO<sub>2</sub> was achieved only somewhat downstream of the flame front.

In the case where there is no NO<sub>2</sub> added to the air, a proposed mechanism of formation of NO<sub>2</sub> is through oxidation of NO by O, OH and HO<sub>2</sub> radicals<sup>(16)</sup>. The NO is formed principally by means of the well-known Zeldovich mechanisms. As a result of such reactions superequilibrium concentrations of NO<sub>2</sub> are in principle possible and have been reported, for example, by Merryman and Levy<sup>(16)</sup>. Their experimental measurements were based on probe sampling. Unfortunately the 20 ppm limit on NO<sub>2</sub> concentration in the present in-situ measurement is not low enough to invalidate the sampling probe measurements of NO<sub>2</sub>. It will be necessary to lower the detection limit and carry out more extensive measurements with different equivalence ratios and other parameters in order to arrive at definitive results on the possible presence of superequilibrium concentrations of NO<sub>2</sub> in the combustion region. Based on our present understanding of the problems,

this should be possible.

In the case where 0.1% NO<sub>2</sub> was added to the flame, rapid reduction of NO<sub>2</sub> to NO by H has been reported by Sawyer and Glassman<sup>(17)</sup>. One might expect an NO<sub>2</sub> concentration downstream of the flame front which would be higher than 20 ppm; such does not appear to be the case. Unfortunately the combination of rather poor spatial resolution and the large signal background prevented a careful study of the rate of disappearance of NO<sub>2</sub> in the vicinity of the flame front; however, this can be rectified.

#### IV. Summary

The use of NO<sub>2</sub> fluorescence as excited by Ar<sup>+</sup> laser for NO<sub>2</sub> concentration measurements in flames was described. The NO<sub>2</sub> concentration in a premixed hydrogen-air flame issuing from a 6.3 mm orifice was found to be less than 20 ppm. Even when 0.1% NO<sub>2</sub> was added to the air, the concentration of NO<sub>2</sub> somewhat downstream of the flame front was less than 20 ppm. When compared with sampling probe measurements of NO<sub>2</sub> concentrations, the data are not sufficiently extensive, nor is the concentration limit sufficiently low to invalidate the probe measurements.

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TABLE I

Effective Emission Cross-Section  $\sigma$

Exciting Wavelength $\lambda_L$ A	$\sigma_{\lambda_L}$ cm <sup>2</sup> /sr	$\sigma_{\lambda_L}/\sigma_{4880}$
4880 A	$1.06 \times 10^{-25}$	1
4765	$1.43 \times 10^{-25}$	1.35
4579	$2.67 \times 10^{-25}$	2.52
4658	$1.32 \times 10^{-25}$	1.25
4727	$1.11 \times 10^{-25}$	1.05

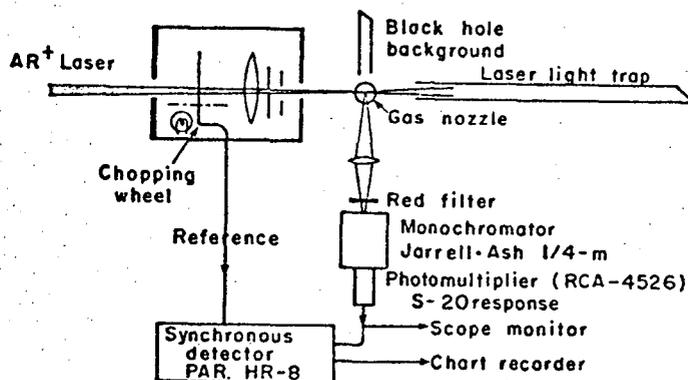


Fig. 1 Schematic of the Experimental Apparatus

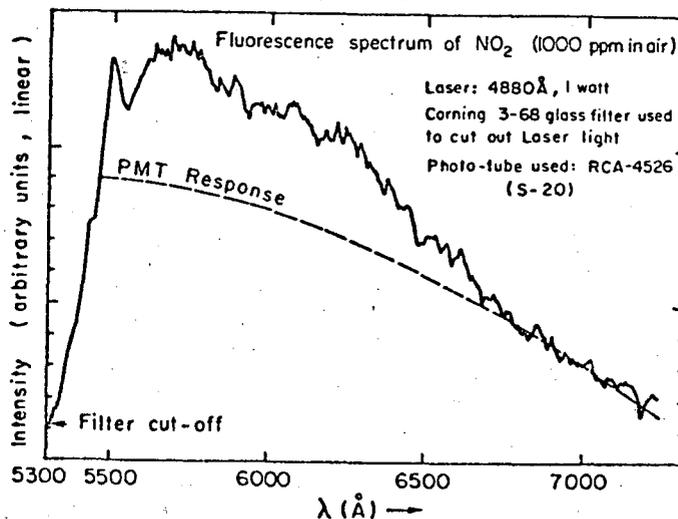


Fig. 2

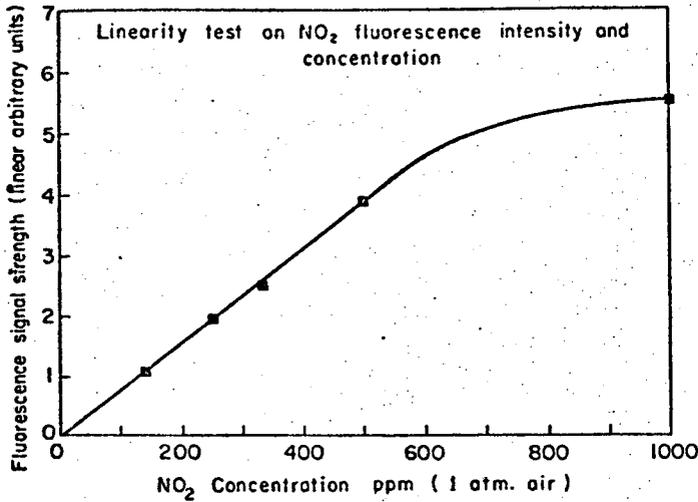


Fig. 3

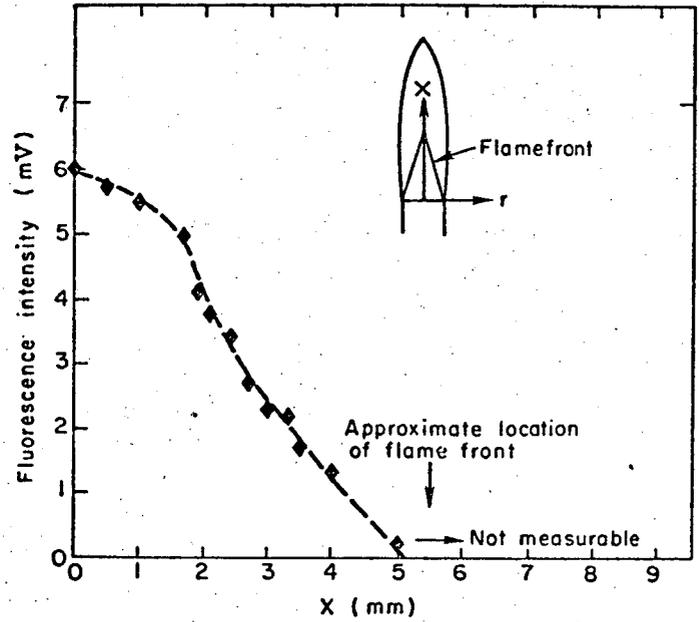


Fig. 5 Measurement of fluorescence intensity when 1000 ppm NO<sub>2</sub>-air mixture was used as oxidiser. The apparent drop prior to the flamefront is due to poor spatial resolution.

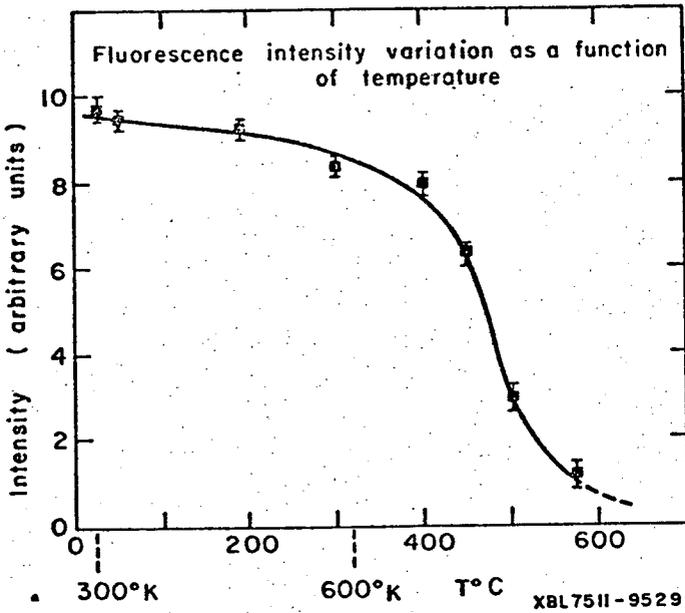


Fig. 4

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