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ATOMIC AND MOLECULAR GAS PHASE SPECTROMETRY.(U)
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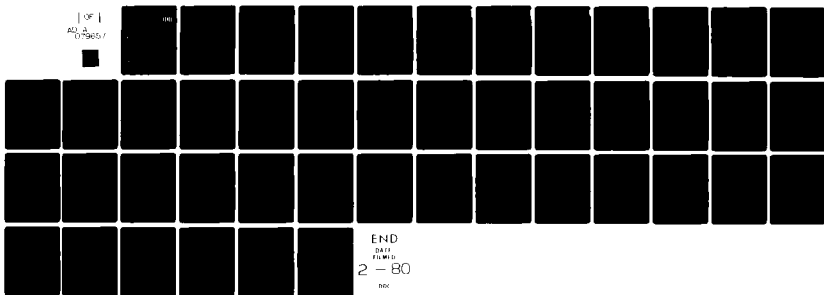
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Combustion Fluorescence Plasmas Nebulized Diagnostics Flame Temperature Multislement Analysis Analytical Quantum Efficiencies Pulsed Tunable Dye Laser Atomic Spectroscopy Molecular Spectroscopy Spatial Profiles		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The research is divided into combustion diagnostics and analytical gas phase atomic and molecular spectrometry. New and improved techniques to spatially and temporally measure flame gas temperatures and species have been and are being developed. These techniques are all based upon fluorescence detection. By measuring the ratio of two fluorescence transitions (in a probe, such as indium) excited with two different wavelengths, the flame temperature can be measured with a precision and accuracy better than 50 K. The two main temperature techniques developed depend upon either the linear relationship between		

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fluorescence and the excitation flux on the approach to saturation of the fluorescence with high excitation fluxes. The measurement of total species concentrations in flames and fluorescence quantum efficiencies is readily performed by measurement of the absolute fluorescence flux reaching a calibrated detector as a function of absolute laser flux. A rather simple graphical method allows both species concentration and species fluorescence quantum efficiencies to be measured. Using these approaches, both flame temperature and species concentration spatial profiles in a variety of laboratory flames (acetylene/air, acetylene/N₂O, H₂/air, H₂/O₂/Ar, etc.) have been measured. Experimental analytical gas phase spectrometric studies have involved; the development and refinement of pulsed (and cw) tunable dye laser excitation of atoms produced by spraying aerosols into combustion flames, furnaces, and inductively coupled plasmas; the development and refinement of an EIMAC xenon arc source-flame-slew scan atomic fluorescence spectrometer for multielement analysis in real samples, such as engine oils, biological materials, etc.; the development and refinement of an innovative source for atomic fluorescence flame spectrometry, namely the use of an ICP source which has the benefits of both a continuum source in terms of wavelength selectivity and line sources in terms of intense narrow line output; and development of chemiluminescence produced above a furnace (into which samples are nebulized) as an analytical method.

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63. "APPLICATION OF LASER-EXCITED ATOMIC FLUORESCENCE SPECTROMETRY TO THE DETERMINATION OF IRON", M.S. Epstein, S. Bayer, J. Bradshaw, E. Voigtman, and J.D. Winefordner, Spectrochim. Acta B., submitted.
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67. "FURTHER IMPROVEMENTS IN DETECTION LIMITS IN LASER EXCITED ATOMIC FLUORESCENCE SPECTROMETRY", J.N. Bower, J. Bradshaw, J.J. Horvath, and J.D. Winefordner,
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72. "A REVIEW AND TUTORIAL DISCUSSION OF NOISE AND SIGNAL-TO-NOISE RATIOS IN ANALYTICAL SPECTROMETRY-III. MULTIPLICATIVE NOISES", C.Th.J. Alkemade, W. Snelleman, G.D. Boutilier, and J.D. Winefordner, Spectrochim. Acta B., submitted

"DETERMINATION OF FLAME AND PLASMA TEMPERATURES AND DENSITY PROFILES BY MEANS OF LASER EXCITED FLUORESCENCE", J. Bradshaw, S. Nikdel, R. Reeves, J. Bower, N. Omenetto, and J.D. Winefordner, ACS Symposium Monograph on "Laser Probes of Combustion Chemistry".

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The research completed during the past four years can be generally divided into combustion diagnostics and analytical gas phase atomic and molecular spectrometry. Significant advances have been made in both areas. New and improved techniques to spatially and temporally measure flame gas temperatures and species have been and are being developed. These techniques are all based upon fluorescence detection. Earlier studies involved the use of a conventional xenon arc lamp source, whereas recent studies involve the use of a pulsed, high peak power tunable dye lasers. By measuring the ratio of two fluorescence transitions (in a probe, such as indium) excited with two different wavelengths, the flame temperature can be measured with a precision and accuracy better than 50 K. The two main temperature techniques developed depend upon either the linear relationship between fluorescence and the excitation flux on the approach to saturation of the fluorescence with high excitation fluxes. The measurement of total species concentrations in flames and fluorescence quantum efficiencies is readily performed by measurement of the absolute fluorescence flux reaching a calibrated detector as a function of absolute laser flux. A rather simple graphical method allows both species concentration and species fluorescence quantum efficiencies to be measured. Using these approaches, both flame temperature and species concentration spatial profiles in a variety of laboratory flames (acetylene/air, acetylene/N₂O, H₂/air, H₂/O₂/Ar, etc.) have been measured.

Analytical gas phase spectrometric studies have spanned a considerable breadth. Theoretical calculations of signal-to-noise ratio have been made to obtain: approaches to the optimization of spectral measurement systems (linear spectral scan spectrometers vs sequential slow scan spectrometers vs multiple detector spectrometers vs multiplex spectrometers, such as Hadamard Transform and Fourier Transform); approaches to the optimization of conventional and time resolution of luminescent components (cw source-cw detection, pulsed source-gated detection with no time resolution, and pulsed source-gated detection with time resolution); approaches to the optimization of atomic and molecular analytical methods (absorption vs emission vs fluorescence vs Raman and the use of optogalvanic and optoacoustic detection as well as the use of non-linear methods involving more than one photon processes); and finally approaches to the optimization and use of image detectors (vidicons, SIT, ISIT, diode arrays, etc.) over photomultiplier detectors for optical spectroscopy.

Experimental analytical gas phase spectrometric studies have involved: the development and refinement of pulsed (and cw) tunable dye laser excitation of atoms produced by spraying aerosols

into combustion flames, furnaces, and inductively coupled plasmas; the development and refinement of an EIMAC xenon arc source-flame-slew scan atomic fluorescence spectrometer for multielement analysis in real samples, such as engine oils, biological materials, etc.; the development and refinement of an innovative source for atomic fluorescence flame spectrometry, namely the use of an ICP source which has the benefits of both a continuum source in terms of wavelength selectivity and line sources in terms of intense narrow line output; and development of chemiluminescence produced above a furnace (into which samples are nebulized) as an analytical method. By means of these approaches, considerable selectivity (near specificity in several cases) is obtained with detection limits in the picograms per milliliter in most cases and with precisions (%RSD) of the order of 5% or better. The above techniques have been applied to the selective measurement of ultratrace elements in real samples, such as elements in river water and the selective measurement of trace elements in samples with complex matrices, such as zinc in copper alloys, trace elements in orange juice, and trace elements in fly ash.

Other analytical and diagnostical studies performed include: a comparison of wavelength vs amplitude modulation in optical spectroscopy; use of a continuum source, resonance monochromator for atomic absorption flame spectrometry; identification of the molecular fluorescence components of unseeded and seeded flames; identification of the major spectral noise peaks in flame emission and fluorescence spectrometry; a tutorial and definitive report on additive and multiplicative noises in optical emission and fluorescence spectrometry; an evaluation of commercial RF-electrodeless discharge lamps and the design of an experimental approach to prepare and evaluate microwave electrodeless discharge lamps for atomic fluorescence flame spectrometry; and an evaluation of several multiplex (including the Hadamard spectrometer) approaches and image devices for multiple element measurements in atomic emission and fluorescence spectrometry.

In summary, the past 4 years have been fruitful in the development of combustion diagnostical approaches which will have considerable use in evaluating large flames (as in combustors) and in developing selective, sensitive approaches to trace element measurements.

10. REVIEW OF PROGRESS IN PAST FOUR YEARS

Fundamental and Diagnostical Studies

Flame Temperature Measurements. Two basic approaches have been developed and have been or are being evaluated. These approaches involve either the measurement of the fluorescence intensity ratio of direct line fluorescences (with excitation of the resonance level via the ground state or via the metastable state and measuring the resulting direct line fluorescence) in an indium type atom (In, Ga, Tl, Pb, etc.) or the measurement of the ratio of resonance fluorescence intensity resulting when excitation is via the resonance absorption process or via the metastable state [refer to the APPENDIX]. In the former case, the excitation must be on the linear portion of the fluorescence intensity vs source intensity curve and in the latter case; saturation must be approached. In the former case, conventional xenon arc sources can be used whereas in the latter, a high peak power laser must be used since the saturation spectral irradiances of transitions of atoms in hydrocarbon flames are very large. In both cases, steady state conditions must be met and the sources must not cause disequilibrium to occur. By means of these approaches, temperature spatial profiles in a number of laboratory flames have been determined. The spatial resolution of the former method with an EIMAC xenon arc source is $\sim 5 \text{ mm}^3$ whereas for the latter with a pulsed tunable dye laser is $\sim 0.2 \text{ mm}^3$. The former technique could, of course, be done with a pulsed tunable or cw tunable dye laser using neutral density filters to minimize saturation and to obtain $\sim 0.2 \text{ mm}^3$ spatial resolution. By means of pulsed tunable dye lasers, it is possible also to obtain temporal resolution, e.g., temperature values within a 20-30 ns period 100 times a second.

Species Concentration and Quantum Efficiency Measurements. For a 2-level atom (or molecule), it can be shown that the fluorescence radiance, B_F is related to the laser excitation flux, Φ , by

$$\frac{1}{B_F} = \frac{1}{\Phi} \left[\frac{K_1}{n_T Y} \right] + \frac{K_2}{n_T}$$

where K_1 is a constant containing the laser excitation bandpass and area and K_1 and K_2 are constants containing known parameters as the transition probability, statistical weight, gas path length over which fluorescence is measured, and energy of the emitted photon. By measuring the absolute laser flux, area, and bandpass, the fluorescence radiance, and the fluorescence path length, it is possible to determine both absolute values n_T (the total concentration of species) and Y (the quantum efficiency of the fluorescence process) from the intercept and slope. The former is valuable in combustor modelling and in absolute analysis and the latter is valuable in understanding the deactivation processes in gases and plasmas.

For a three level (or greater number of levels), the relationship

between B_F , ϕ , n_T , and Y is quite similar to the 2 level case but more complex in that now radiationless rate constants must be known (or negligible) to evaluate n_T and Y from the intercept and slope of the $\frac{1}{B_F}$ vs $\frac{1}{\phi}$. Under certain experimental conditions, it

is possible to approximate the terms containing the radiationless rate constants. Work is currently in progress demonstrating the potential use of this approach for evaluation of atomic and molecular species concentrations in laboratory type flames. This approach should also be useful for evaluating the species concentrations in combustors; obviously here extremely high peak power lasers will be needed. Also it is feasible to obtain both spatial and temporal profiles by using high peak power pulsed, tunable dye lasers.

During the past 2 years, we have verified the validity of the above theoretical approach with accurate experimental measurements.

During the past year, we have used the pulsed tunable dye laser approach to spatially profile seeds (Ba, Sr, In, etc.) sprayed into laboratory flames (H_2 and C_2H_2 -based flames). Although the possibility of temporal profiles exists, only initial measurements have so far been performed.

Signal-to-Noise Ratio Calculations

Signal-to-noise is perhaps the most important of all spectrometric figures of merit. The signal-to-noise ratio influences the precision (%RSD) and the detection limit (LOD) of an analytical measurement. A tutorial approach was recently published in which additive noises were considered in both emission and luminescence studies. More recently, a similar approach has been prepared on multiplicative noises which unfortunately are also intimately related to the signal level. In these studies, the influence of sampling time (related to measurement time), instrument response time or integration time, and modulation with ac detection were considered with respect to their effects on the SNR. Some rather apparent but basic conclusions are that all methods are affected by white noise, that modulation and ac detection is useful only if the noise source is not modulated, that additive flicker noises can be minimized by proper choice of response and sampling times, that multiplicative flicker noise can be minimized only by use of an ideal internal standard, and that proportional (whistle)-noises can be avoided by proper choice of modulation frequency.

In a separate report, wavelength, amplitude, and sample modulation were compared. Theoretically sample-blank-standard modulation is an ideal analytical approach but experimentally it is difficult to perform with a sufficient modulation frequency to minimize flicker noises. Therefore, the best, current experimental approach is to wavelength modulate to minimize drift (flicker) in the background (in emission or luminescence studies.) Amplitude modulation is the simplest to perform but more susceptible to drift problems. If white noise is dominant, then the best approach is

to use dc detection.

In other separate studies, multiplex (Hadamard and Fourier Transform Spectrometers) systems, multiple photodetector systems (direct readers), sequential slow scan spectrometers, and sequential linear scan methods were compared for optical (UV-VIS) spectroscopy with the following general conclusions: based on SNR calculations, the multiplex systems will have little use in high or even moderate background cases, such as flame emission, or in molecular absorption with a continuum background source; the multiple photodetector spectrometer is the best if one knows which spectral transitions to measure and if there is little need to even change to other transitions; the sequential slow scan (computer programmed) spectrometer is the most versatile and best if 10 or fewer transitions are to be measured or if initial cost is the most critical factor; the linear sequential scan spectrometer is of little quantitative use but is a reliable qualitative analysis tool. Experimental studies by us and others have verified these theoretical predications.

In another study, it was shown that (based on SNR) the image detectors are at best poorer than photomultiplier detectors for atomic spectrometry. For molecular spectrometry, particularly when absorption or luminescence detection of gas or liquid chromatographic effluents is used, the image devices are generally superior to photomultipliers in terms of SNR for a given measurement time and for a large range of spectral components. Experimental verification of these theoretical concepts have also been carried out.

Finally, it was shown that a pulsed source-gated detector with time resolution has considerable advantage for luminescence spectrometry (compared with pulsed-source-gated detection with no time resolution, modulated source with averaging detection, and cw source with cw detection) if the spectral interferent has a shorter lifetime than the analyte. If this is not the case then the more conventional approaches (modulation or cw) are simpler and at least as good (based on SNR). Experimental verification of these theoretical concepts have also been carried.

Analytical Gas Phase Spectrometric Studies

Laser Excited Atomic Fluorescence Spectrometry. At this point in time, it is apparent that laser excited atomic fluorescence spectrometry (LEAFS) has very specific and specialized uses, i.e., it is not yet a routine analytical tool primarily because of the high initial cost, the complexity and cost of operating many lasers, and the applicability of tunable dye lasers to only a single excitation transition within a short time period (say 5 min), i.e., tunable dye lasers can not yet be slow scanned reliably to a wide range of wavelengths. Nevertheless, we have shown that LEAFS (see Figure 1) has tremendous potential for certain applications, namely where extremely low detection limits are needed and where high spectral selectivity is needed. It should be mentioned that despite the inert atmosphere of the inductively coupled plasma,

relatively poor limits of detection (see Table I) were obtained with pulsed dye or cw dye laser excitation; the high plasma background noise prevented improvements compared to the flame atomizer system. In Table IA, we have given detection limits (LODs) obtained by LEAFS in the past 4 years. These values rival or exceed the best LODs reported by others by similar and different methods. We have also applied LEAFS to the measurement of trace elements in a variety of samples, difficult or impossible to measure by any other method (see Tables II and III for typical examples). In addition to the excellent LODs, the linear dynamic ranges of most elements is 10^5X to 10^7X and the %RSD $\sim 5\%$.

Inductively Coupled Plasma Atomic Flame Fluorescence Spectrometry. In this study, high concentrations of a given element are sprayed into the inductively coupled plasma (ICP) which is the source of excitation for atoms produced via spraying samples into the flame; atomic fluorescence is measured (see Figure 2). It was shown theoretically and verified experimentally that because the ICP has little self absorption even at concentrations of 20,000 ppm and rare self-reversal (except at high heights), it is an ideal source for FAFS. The ICP source is intense and the spectral lines of atoms in the ICP are narrower than for atoms in the flame, and so by simply varying the elemental content of the solution sprayed into the ICP, one can have a narrow line source for virtually any element. The major advantage of using an ICP as a source for FAFS rather than spraying the analyte into the flame and using the emission of the ICP for analysis is that in the ICP-FAFS case, the flame acts as a resonance monochromator, minimizing or eliminating complex spectral interferences arising in an ICP used for emission analysis. In our case, using 20,000 ppm of elements in the ICP, the detection limits shown in Table IV resulted. These values could be improved substantially (by 100X) by (1) increasing the concentration of element in the ICP, (2) increasing the time constants on the measurement system, and (3) increasing the solid angle of collection of ICP radiation spraying on the flame. This approach also has 2 other unique advantages, namely: (1) scatter can be corrected by use of a nearly ICP line, such as Ar, or by making use of self absorption in the ICP which results in a plateauing of fluorescence intensities but in a corresponding increase in the scatter; and (2) measurement of high concentrations of (>1000 ppm) by spraying the sample into the ICP and a low fixed concentration of analyte into the flame which now acts as a resonance monochromator. In Table V, typical application results of the ICP-FAFS system is given. Detection limits obtained with the ICP-FAFS system were superior to emission ICP values obtained with our experimental system and estimated LOD, for the same line. However, the LODs in our case were generally 3 to 10X poorer than the best previously given in the literature for emission ICP.

Multielement EIMAC Atomic Fluorescence Spectrometry (MEAFS). This system consisting of an EIMAC xenon arc lamp, a flame, a photomultiplier detector, a synchronous photon counter, and a programmed computer for wavelength slewing and for data processing. Both

amplitude and wavelength moderation have been used. Although the detection limits (see Table I) are not as good as other techniques (those mentioned above or atomic absorption), the system provided reliable results for real sample analyses for 20 or fewer elements. The MEAFS system (worth less than \$50,000) is easy to use, reliable, and versatile. Limits of detection in the sub ppm range were obtained for a large number of elements and applications were made to trace elements in biological samples, jet engine oils, standard reference materials, and metals (see Tables VI, VII, VIII).

Atomic Spectrometry in Furnances. During the past 4 years, both cw and discrete sampling furnaces were studied. The presence of and difficulty of interpretation of the effects of matrix materials on the emission, absorption, or fluorescence signals has led us to the following conclusion: furnaces should only be used for analysis if the sample can not be done by a flame, an ICP, etc., i.e., if one is sample limited or sensitivity limited. Atomic fluorescence detection with tunable dye laser excitation results in sub-picogram LODs but real sample analyses are plagued with interferences difficult to interpret.

More recently, we have evaluated the potential use of chemiluminescence of species produced in a cw furnace and reacting with an oxidant, such as N_2O , Cl_2 , etc. Molecular chemiluminescence spectra result which can be used for trace measurements of species such as As and Sb in our case. We intend to go to the use of F_2 which is a stronger oxidant and should be a useful "source" of excitation for a wide variety of elements.

Other Studies

By means of a continuum source of excitation, a flame for the sample introduction, and a cw furnace with analyte being continuously introduced and a photomultiplier detector, a highly spectral selective resonance monochromator system was evaluated for atomic absorption flame spectrometry. The system performed as expected but was somewhat inferior to a conventional line source atomic absorption flame spectrometer. Further studies are warranted.

By means of pulsed and cw tunable dye laser excitation, molecular fluorescence of native species (C_2 , CH, OH, NH, CN) and introduced species PO, SrOH, CaOH, CrO, MnO, BaCl, BaOH, BaO) have been observed and identified. Because of the low fluorescence intensities of the latter species, few analytical capabilities exist; however, the fluorescence of the native and introduced species can lead to spectral interferences in a few specialized cases. The contributions of shot and flicker emission and fluorescence noises to the total noise as a function of wavelength (200-800 nm) were also evaluated for a variety of laboratory flames; the source of excitation for fluorescence was an EIMAC xenon arc lamp. The noise sources in pulsed laser excited atomic fluorescence spectrometry are currently being measured.

A theoretical and experimental comparison of optoacoustic and optogalvanic detection with fluorescence detection is currently in progress; initial results indicate that optoacoustic detection is very specialized and has few uses for UV-Visible optical spectrometry of gases. Optogalvanic detection does not seem to be as sensitive and certainly not as selective as fluorescence detection.

By means of signal-to-noise ratio expressions, derived for limiting noise cases, estimated detection limits for atomic absorption (with line and continuum sources), atomic emission (flame vs ICP), and atomic fluorescence (flame and ICP atomizers and line vs continuum sources operating on the linear and saturated regime) was obtained. These calculated detection limits indicate that atomic emission with an ICP is excellent but has nearly reached its ultimate sensitivity whereas atomic fluorescence with laser sources can theoretically be improved by several orders of magnitude and ultimately exceed the detection power of the ICP-emission method by several orders of magnitude. To estimate solution concentrational detection limits from the gaseous atom detection limits (in terms of atoms cm^{-3} in Table IX), one needs to divide the n -values by $\approx 10^{11} \beta_a$ where β_a is the free atom fraction in the hot gas for the analyte atom ($\beta_a = 1$ if the species is 100% atomized). Actually, if the efficiency and rate of introduction of sample solution into the flame varies significantly from the values used to estimate the 10^{11} factor, then the "constant" (10^{11}) must be charged. During the past 4 years, Hadamard spectrometry and a modified Michelson spectrometer (interferometer) have been evaluated experimentally and theoretically and have been shown to have little use for the UV-Visible Spectral region, especially for emission, fluorescence, and absorption spectrometry where either the cell emission and/or the source emission is intense and spectrally broad. Calculations (SNR) have similarly shown that the conventional Michelson interferometer, the SISAM system, or any other modifications will also be of little use in the UV-Visible region because of a great reduction on SNR compared to more conventional approaches.

Other studies have included: the use of information theory to evaluate analytical methods; particularly with respect to resolving power, the measurement of the detection limits of rare earths by ICP emission; a study of the factors affecting aerosol production in nebulizer-burners; an evaluation of a selectivity concept based upon H. Kaiser's approach; a deviation of radiance expressions for atomic fluorescence assuming continuum excitation and for molecular fluorescence and phosphorescence assuming narrow line excitation, a definitive report on why the ratio of the sodium D_1 and D_2 fluorescence varies with excitation via the D_1 or D_2 transition; the use of an atomic absorption inhibition release titration for studying the chemical equilibria and kinetics in flames; the measurement of phosphorous via molecular fluorescence of PO in flames; and several application papers involving the measurement of lead in confection wrappers and trace elements in orange juice.

TABLE IA

DETECTION LIMITS (AQUEOUS SOLUTION) OBTAINED BY LASER EXCITED
ATOMIC FLUORESCENCE SPECTROMETRY LEAFS AND BY SEVERAL OTHER METHODS

Element	Detection Limit (ng/ml)					Optogalvanic ⁶ Laser
	Line Source ¹	Continuum Source ² MEAFS	LEAFS ³	AAS ⁴	AEICP ⁵	
Ag	0.1	1.	4.	2.	0.2(4)	-
Al	100.	200.	0.6	20.	0.4	-
As	100.	-	-	400.	2.	-
Au	1,000.	150.	-	200.	-	-
Ba	-	-	8.	20.	0.01(0.2)	-
Be	10.	15.	-	2.	~(0.3)	-
Bi	10.	-	3.	30.	~(50)	-
Ca	20.	-	(0.01) ⁷ 0.08	2.	0.0001(4)	-
Cd	0.001	6.	8.	1.5	0.07**(1)	-
Ce	-	-	500.*	-	0.4(20)	-
Co	5.	15.	(19) ⁷ 200.*	15.	0.1**(2)	-
Cr	50.	1.5	1.	3.	0.2(4)	2.
Cu	1.	1.5	1.	2.	0.04**(2)	100.
Dy	-	-	300.*	-	~(2)	-
Er	-	-	500.*	-	~(-)	-
Eu	-	-	20.*	-	~(1)	-
Fe	8.	10.	30.	10.	0.09(2)	2.
Ga	10.	-	0.9	-	0.6(40)	0.07
Gd	-	-	800.*	-	0.5(8)	-
Ge	15,000.	-	-	-	~(50)	-
Hf	-	-	-	200.	~(-)	-
Hg	80.	-	-	-	~(50)	-
Ho	-	-	100.*	-	~(-)	-
In	100.	25.	0.2	-	~(40)	0.008
Li	-	-	0.5	1.	~(3)	-
Lu	-	-	3,000.*	-	~(-)	-
Mg	1.	0.1	(0.009) ⁷ 0.2	0.1	0.003(20)	0.1
Mn	6.	2.	0.4	3.	0.02(0.5)	0.3
Mo	500.	100.	12.	20.	0.4(5)	-
Na	100,000.	-	<0.1	0.5	0.02(10)	0.05

TABLE IA - cont.

Element	Detection Limit (ng/ml)					Optogalvanic ⁶ Laser
	Line Source ¹	Continuum Source ² MEAFS	LEAFS ³	AAS ⁴	AEICP ⁵	
Nb	-	-	1,500.*	-	0.2(20)	-
Nd	-	-	2,000.*	10.	-(10)	-
Ni	3.	25.	2.	-	0.2(6)	8.
Os	-	-	150,000.*	15.	-(200)	-
Pb	10.	50.	(1,3) ⁷ 13.	-	1.** (20)	0.6
Pd	1,000.	100.	-	-	2.(40)	-
Pr	-	-	1,000.*	-	-(30)	-
Pt	50,000.	700.	-	-	-(30)	-
Rh	3,000.	0	100.*	-	-(30)	-
Ru	-	-	500.*	-	-(60)	-
Sb	-	-	50.*	30.	-(30)	-
Sc	-	-	10.*	-	-(1)	-
Se	40.	-	-	250.	1.** (20)	-
Si	600.	-	-	100.	-(10)	-
Sm	-	-	100.*	-	-(10)	-
Sn	30.	150.	-	70.	3.(6)	6.
Sr	30.	0.9	(0.1) ⁷ 0.3	1.	0.003(0.2)	-
Tb	-	-	500.*	-	-(-)	-
Te	5.	-	-	70.	-(20)	-
Ti	-	200.	2.	80.	0.03(1)	0.2
Tl	8.	6.	4.	30.	-(75)	0.09
Tm	-	-	100.*	-	-	-
V	70.	30.	30.	50.	0.06(2)	-
Yb	-	-	10.*	-	-	-
Zn	0.02	15.	-	1.	0.1(2)	-

1. The values come from references within J.D. Winefordner, J. Chem. Ed., 55, 72(1978).
2. The values come from D.J. Johnson, F.W. Plankey, and J.D. Winefordner, Anal. Chem., 46, 1858(1974).
3. Values from S.J. Weeks, H. Haraguchi, and J.D. Winefordner, Anal. Chem., 50, 360(1978), except those with * which were taken from references listed in Winefordner, J. Chem. Ed., 55, 72(1978).

TABLE IA - cont.

4. All values come from Perkin Elmer atomic absorption commercial literature on the Model 460.
5. All values from P.W.J.M. Boumans and F.J. de Boer, Spectrochim. Acta, 30B, 309(1975), except for those with ** and those in (). All values in () come from commercial literatures from Jarrell-Ash Division, Fisher Scientific Co., Wlatham, MA for their 3rd generation ICP plasma Atom Comp. All values with ** come from K.W. Olson, W.J. Haas, and V.A. Fassel, Anal. Chem., 49, 632(1977).
6. Values taken from J.C. Travis, G.C. Turk, and R.B. Green, Chapter in New Applications of Laser to Chemistry, ACS Monograph, Vol. 85.
7. J.N. Bower, J. Bradshaw, J.J. Horvath, and J.D. Winefordner, Anal. Chem., submitted.

TABLE IB. DETECTION LIMITS (ng/ml)

Element	Fluorescence Wavelength(nm) ($\lambda_{\text{excitation}}/\lambda_{\text{fluorescence}}$)	LICPAFS		LFAPS		ICPAES
		Pulsed ^c	CW ^d	Pulsed		
Iron ^a	FeI 296.7/373.5	50	-	0.06 ^e		26(4.3) ^h , 0.2 ⁱ
Tin ^a	SnI 300.9/317.5	500	-	3 ^f		200(111) ^h , 6 ⁱ
Barium ^b	BaII 455.4/455.4	2	-	-		1(1.3) ^h , 0.06 ⁱ
Indium ^b	BaII 614.2/455.4	30	6	-		-
	InI 410.2/410.2	300	-	0.88 ^g		400(187) ^h , 30 ⁱ

^a Flashlamp-pumped dye laser

^b Nitrogen laser-pumped dye laser

^c This work, with detection limit defined as 3 x std. deviation of the noise using an observed time constant of 1 s

^d Continuous wave dye laser detection limit, from B.D. Pollard, M.S. Blackburn, S. Nikdel, A. Massoumi, and J.D. Winefordner, Appl. Spectrosc., **33**, 5(1975).

^e LFAPS detection limit using the same transition as LICPAFS with a 10 s time constant and multipass cell from M.S. Epstein, S. Bayer, J. Bradshaw, E. Voigtman, and J.D. Winefordner, Spectrochim. Acta, submitted.

^f LFAPS detection limit using the same transitions as LICPAFS with a 1 s time constant and single pass cell from M.S. Epstein, J. Bradshaw, S. Bayer, J. Bower, E. Voigtman, and J.D. Winefordner, Appl. Spectrosc., submitted.

^g LFAPS detection limit using the same transitions as LICPAFS with a time constant from 0.5 to 5 s and a single pass cell from S.J. Weeks, H. Haraguchi, and J.D. Winefordner, Anal Chem., **50**, 360(1978).

^h Best ICPAES detection limits using our monochromator/detection system for a 0.3 s time constant; estimated ICPAES detection limits for same lines in parenthesis from R.K. Winge, V.J. Peterson, and V.A. Fassel, Appl. Spectrosc., **33**, 206(1979).

TABLE IB - cont.

- i State-of-the-art ICPAES detection limits using pneumatic nebulization from P.W.J.M. Boumans, and R.M. Barnes, ICP Newsletter, 3, 445(1978).

TABLE II

Determination of Iron in Standard Reference Materials
using Laser-Excited Atomic Fluorescence Spectrometry

<u>SAMPLE</u>	<u>LEAFS ANALYSIS^a</u>	<u>CERTIFIED VALUE^b</u>
Trace Elements in Water (SRM-1643)	78 ng/g	75 ± 1 ng/g
Unalloyed Copper (SRM-394)	145 ± 6 µg/g	147 ± 8 µg/g
Fly Ash (XRM-1633)	6.2 ± 0.2%	6.2 ± 0.3% ^c

^a ± one standard deviation of analytical results, where multiple samples were analyzed

^b Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234

^c Not certified by NBS.

TABLE III

Determination of Nickel and Tin by Laser-Excited Atomic Fluorescence Spectrometry

<u>ELEMENT</u>	<u>SAMPLE</u>	<u>CERTIFIED CONCENTRATION^a</u>	<u>Fe/Ni CONCENTRATION RATIO</u>	<u>LEAFS ANALYSIS RESULTS^{b,c}</u>
Nickel	SRM 1643 (water)	49 ± 1 ng/g	2	50 ± 2 ng/g (300.249 nm)
	SRM 396 (unalloyed copper)	4.2 ± 0.1 µg/g	34	4.1 ± 0.1 µg/g (300.249 nm) 5.4 ± 0.4 µg/g (299.446 nm)
	SRM 1633 (fly ash)	98 ± 3 µg/g	633	99 ± 3 µg/g (300.249 nm) 99 ± 4 µg/g (299.260 nm) 150 ± 12 µg/g (299.260 nm) ^d 623 µg/g (299.446 nm)
Tin	SRM 394 (unalloyed copper)	65 ± 5 µg/g	-	66 ± 3 µg/g (317.505 nm)
	SRM 396	0.8 ± 0.3 µg/g	-	0.7 ± 0.2 µg/g (317.505 nm) ^e

^a Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.

^b Wavelength of excitation for nickel; wavelength of fluorescence for tin in parenthesis ().

^c Using high finesse etalon (laser bandwidth 0.002 nm), except where noted.

^d Without etalon (laser bandwidth 0.05 nm).

^e Using multipass cell.

TABLE IV

LIMITS OF DETECTION (ng/ml)

ELEMENT	λ (nm) ^a	FLAME ^b	ICAP-excited AFS ^{c,d}		ICAP-emission		best ^g	AFS line ^h	
			this work	literature	same line ^e	commercial ^f		120	30
Al	308.2 309.3	S-NOA	1000	-	23	15	1	120	30
As	235.0	S-AA	5000	-	142	25	25	70	100
Ca	422.6	S-AA	4	100	10	4 ^j	0.0005	0.3	1
Cd	228.8	S-AA	0.8	80	2.7	1	0.3	0.2	1
Co	240.7 241.1 241.4 242.5	S-AA	11	-	>23	2	0.4	1.5	10
Cr	357.8 359.3 360.5	S-AA	2	-	23	4	1	0.3	3
Cu	324.7 327.4	S-AA	2	50	5.4	2	0.3	0.3	2
Fe	248.3 248.8 249.0	S-AA	6	-	>20	2	0.2	0.6	10
Mg	285.2	S-AA(fr)	0.09	5	1.6	20 ^j	0.01	0.09	0.9
Mn	279.5 279.8 280.1	S-AA	2	100	12	0.5	0.06	0.5	2
Mo	313.3 315.8	S-NOA	400	-	>37	5	0.5	750	30
Pb	283.3	S-AA	800	-	142	20	10	10	20

TABLE IV - cont.

ELEMENT	λ (nm) ^a	FLAME ^b	ICAP-excited AFS ^{c,d}		ICAP-emission		best ^g	AFS line ^h
			this work	literature	same line ^e	commercial ^f		
V	318.5	S-NOA	400	-	>17	2	0.2	88
	318.4							
	318.3							
Zn	213.9	S-AA	0.5	80	1.8	2	0.3	0.2

^a Wavelengths of major fluorescence line(s) contributing to the fluorescence spectral intensity. Since the spectral bandpass of the monochromator is 16 nm, other lines may contribute some intensity.

^b Flame type: S-AA = nitrogen-separated air/acetylene; (fr) - fuel-rich; S-NOA = nitrogen-separated nitrous-oxide/acetylene.

^c Detection limits from this work correspond to an analyte fluorescence signal equal to 3 times the standard deviation of the baseline (SNR=3) calculated from either 16 one-second integrations or from 3/5 the peak-to-peak noise on the baseline using a three second time constant.

^d From C. Hussein and G. Nickless, ICAAS Conference Sheffield, England, 1969.
V. Sychra, V. Sooboda, and I. Rubeska, Atomic Fluorescence Spectroscopy, VanNostrand, London, 1979.

^e Predicted ICAP-emission limits of detection for the same line(s) used to excite AFS using data from R.K. Winge, V.J. Peterson, and V.A. Fassel, Appl. Spectrosc., 32, 206(1979).

^f Commercial multielement limits of detection based on SNR = 2 for ICAP-emission using Jarrel Ash data.

^g State-of-the-art limits of detection for ICAP-emission using pneumatic nebulization (SNR=2) using data from P.W.J.M. Boumans and R.M. Barnes, ICP Newsletter, 3, 445(1978).

^h Line source atomic fluorescence detection limits in a similar flame (SNR=2) from V. Sychra, et al (see item d).

ⁱ Atomic absorption detection limits (SNR=2) from G. Kirkbright and M. Sargent, Atomic Absorption and Atomic Fluorescence Spectroscopy, Academic Press, London, 1974.

^j Limit of detection based on the normal analytical line, not the most sensitive line for Jarrel Ash data.

TABLE V

SAMPLE ANALYSIS USING ICAP-EXCITED AFS AND ICAP-EMISSION

SAMPLE	ELEMENT	CERTIFIED VALUE ($\mu\text{g/g}$) ^a	ANALYZED VALUES ($\mu\text{g/g}$)	
			ICAP-excited AFS	ICAP-emission
Unalloyed copper (SRM-394)	Zn	375 $\pm$ 38	376 $\pm$ 3	325 $\pm$ 25
Unalloyed copper (SRM-396)	Zn	4.7 $\pm$ 0.3	4.8 $\pm$ 0.1	c
Fresh water (SRM-1643)	Zn	0.065 $\pm$ 0.003	0.0656 $\pm$ 0.0008	d
	Cd	0.008 $\pm$ 0.001	0.0079	d
Fly ash (SRM-1633)	Zn	210 $\pm$ 20	219 $\pm$ 4	d
Orange juice	Cu	e	0.57	0.60
	Zn	e	0.45	0.46

^a Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.

^b $\pm$ one standard deviation of analytical results where multiple samples were analyzed.

^c Cannot be analyzed by ICAP-emission with out experimental setup.

^d Analysis capability of ICAP-emission for this element in this matrix already established.

^e not a standard reference material.

TABLE VI

MEAFS ANALYSIS OF DIGESTED NBS BOVINE LIVER-SRM 1577 BY MEAFS

<u>ELEMENT</u>	<u>WAVELENGTH</u>	<u>NBS VALUE</u>	<u>MEAFS VALUE</u>
Zn	213.856 (nm)	133 ± 2 (μg/g)	135 (μg/g)
Fe	248.327	265 ± 8	1395
Mn	279.482	11.1 ± .4	13
Mg	285.213	605 ± 8	609
Cu	324.754	193 ± 8	195
Ca	422.673	123 ± 6	30

TABLE VI

MEAFS ANALYSIS OF DIGESTED NBS ORCHARD LEAVES-SRM 1571 BY MEAFS

<u>ELEMENT</u>	<u>WAVELENGTH</u>	<u>NBS VALUE</u>	<u>MEAFS VALUE</u>
An	213.856(nm)	25 ± 3 (µg/g)	23 (µg/g)
Cd	228.802	0.11 ± .02	2
Ni	232.003	1.3 ± 2	4
Fe	248.327	300 ± 20	500
Mn	279.482	91 ± 4	95
Pb	283.306	45 ± 3	50
Cu	324.754	12 ± 1	11

TABLE VIII
COMPARISON OF CONCENTRATIONS FOUND FOR FIVE METALS (BY MEAFS)
IN SEVERAL JET ENGINE LUBRICATING OILS WITH S.O.A.P.^a RESULTS

Sample No.	<u>Fe, ppm</u>		<u>Mg, ppm</u>		<u>Cu, ppm</u>		<u>Ag, ppm</u>		<u>Cr, ppm</u>	
	Reported ^a	Found	Reported ^a	Found	Reported ^a	Found	Reported	Found	Reported ^a	Found
185	22	21	36	34	22	22	34	37	27	29
186	19	20	32	32	19	20	30	32	24	32
190	82	80	25	30	36	35	13	9	16	16
191	8	6	2	2	1	1	1	1	1	1
192	7	5	2	2	1	2	1	1	0.8	1

^aS.O.A.P. (Spectrographic Oil Analysis Program) values are average of 50 laboratories using atomic absorption. Sample numbers are those designated in the S.O.A.P. studies.

^bValues found in present work with air/acetylene flame and MEAFS.

^cWavelengths used: Fe, 248.327; Mg, 285.213 nm; Cu, 324.754 nm; Ag, 328.068 nm; Cr, 357.869 nm.

TABLE IX

COMPARISON OF CALCULATED DETECTION LIMITS FOR SEVERAL FLAME/PLASMA SPECTROSCOPIC METHODS

METHOD	LIMIT OF DETECTION, atom cm ⁻³			
	C ₂ H ₂ -Air	C ₂ H ₂ -N ₂ O	H ₂ -O ₂ -Ar	ICP
ATOMIC FLUORESCENCE				
<u>Xenon Arc Source ($\lambda_o = 300$ nm)</u>				
Detector noise limit: $\bar{R}_D = 10^2 s^{-1}$	3x10 ⁵	3x10 ⁵	3x10 ⁵	3x10 ⁵
Detector noise limit: $\bar{R}_D = 10^4 s^{-1}$	3x10 ⁶	3x10 ⁶	3x10 ⁶	3x10 ⁶
Background noise limit	10 ⁹	3x10 ⁹	3x10 ⁸	3x10 ⁸
<u>Electrodeless Discharge Lamp ($\lambda_o = 300$ nm)</u>				
Detector noise limit: $\bar{R}_D = 10^2 s^{-1}$	7x10 ⁴	7x10 ⁴	7x10 ⁴	7x10 ⁴
Detector noise limit: $\bar{R}_D = 10^4 s^{-1}$	7x10 ⁵	7x10 ⁵	7x10 ⁵	7x10 ⁵
Background noise limit	2x10 ⁸	5x10 ⁸	3x10 ⁶	10 ⁷
<u>Laser, typical operating values ($\lambda_o = 300$ nm)</u>				
Detector noise limit: $\bar{R}_D = 10^2 s^{-1}$	10 ²	10 ²	10 ²	10 ²
Detector noise limit: $\bar{R}_D = 10^4 s^{-1}$	10 ³	10 ³	10 ³	10 ³
Background noise limit	10 ⁵	3x10 ⁵	3x10 ⁴	3x10 ⁴
<u>Laser, saturation ($\lambda_o = 300$ nm)</u>				
Detector noise limit: $\bar{R}_D = 10^2 s^{-1}$	2x10 ⁻¹	2x10 ⁻¹	2x10 ⁻¹	2x10 ⁻¹
Detector noise limit: $\bar{R}_D = 10^4 s^{-1}$	2x10 ⁰	2x10 ⁰	2x10 ⁰	2x10 ⁰
Background noise limit	10 ²	3x10 ²	3x10 ¹	3x10 ¹

TABLE IX, continued
COMPARISON OF CALCULATED DETECTION LIMITS FOR SEVERAL FLAME/PLASMA SPECTROSCOPIC METHODS

METHOD	LIMIT OF DETECTION, atom cm ⁻³			
	C ₂ H ₂ -Air	C ₂ H ₂ -N ₂ O	H ₂ -O ₂ -Ar	ICP
ATOMIC ABSORPTION (Source noise limited - λ _o = 300 nm)	10 ²	3x10 ²	3x10 ¹	3x10 ¹
Xenon Arc Source	4x10 ⁸	8x10 ⁸	8x10 ⁸	4x10 ⁹
Hollow Cathode Discharge	7x10 ⁷	1x10 ⁸	1x10 ⁸	7x10 ⁸
ATOMIC EMISSION (Background noise limited)				
λ _o = 300 nm	10 ⁹	10 ⁸	10 ⁹	10 ⁴
λ _o = 600 nm	10 ⁵	5x10 ⁴	10 ⁴	3x10 ³

Figure 1A

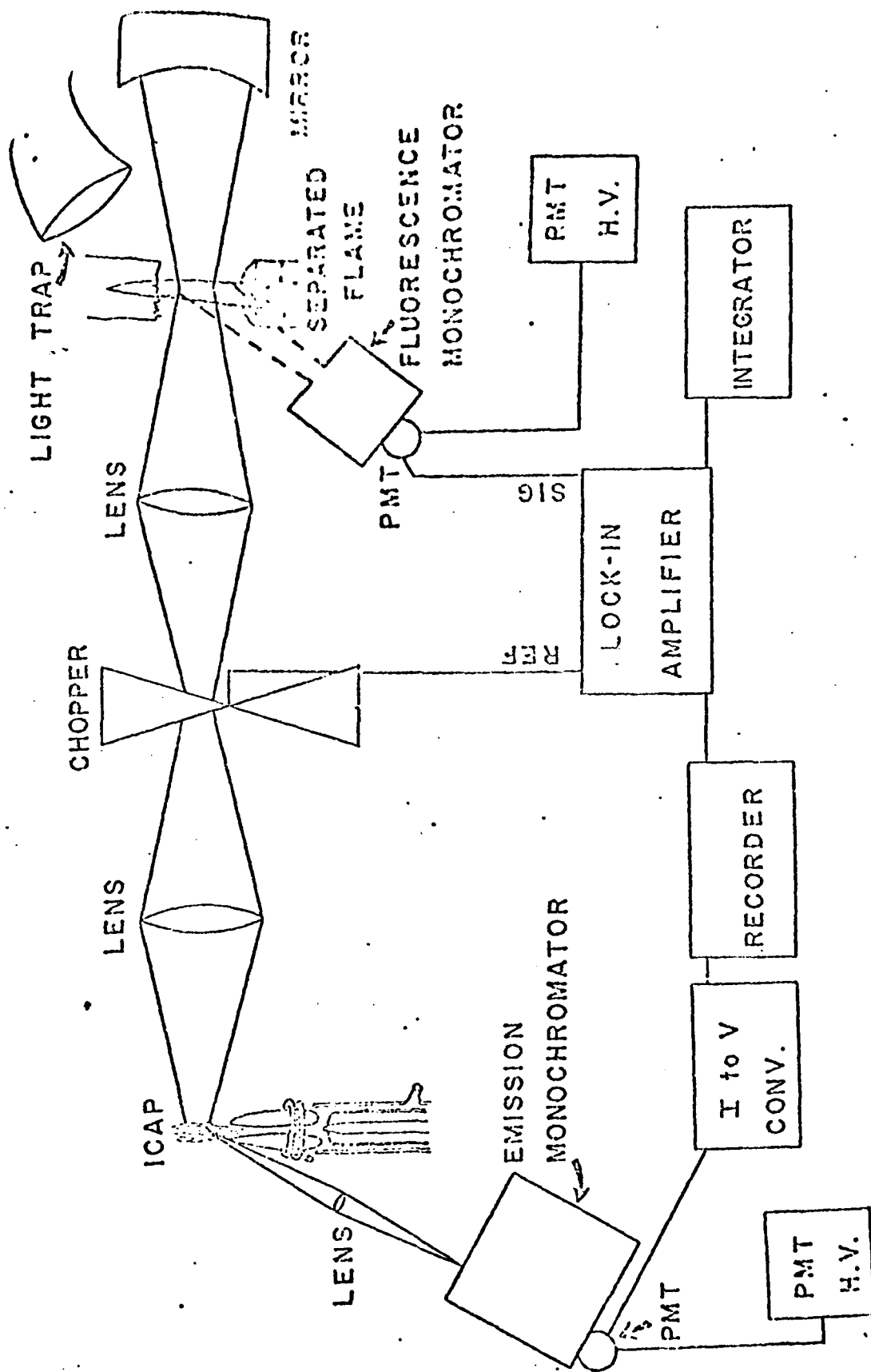


Figure 1B

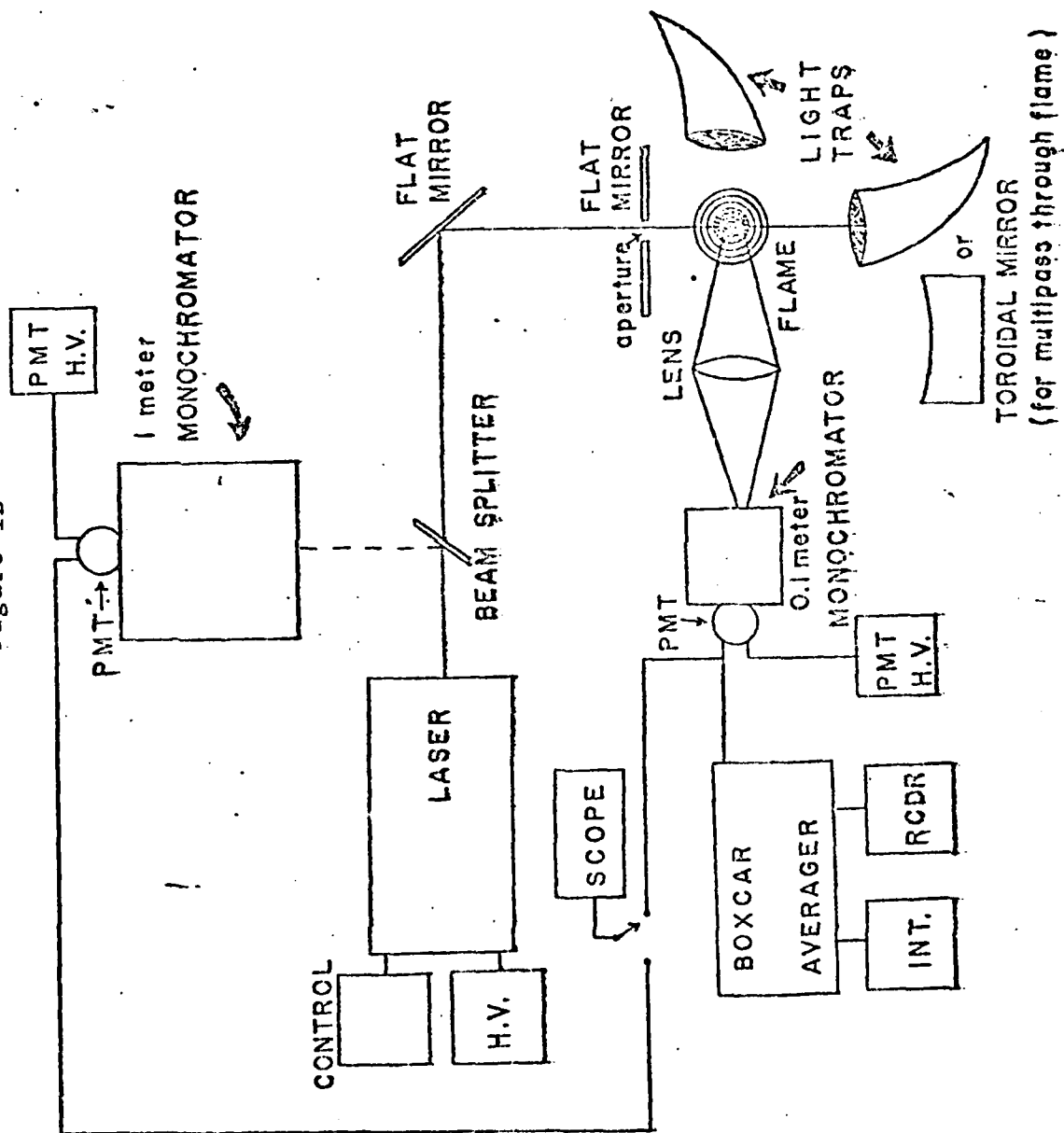
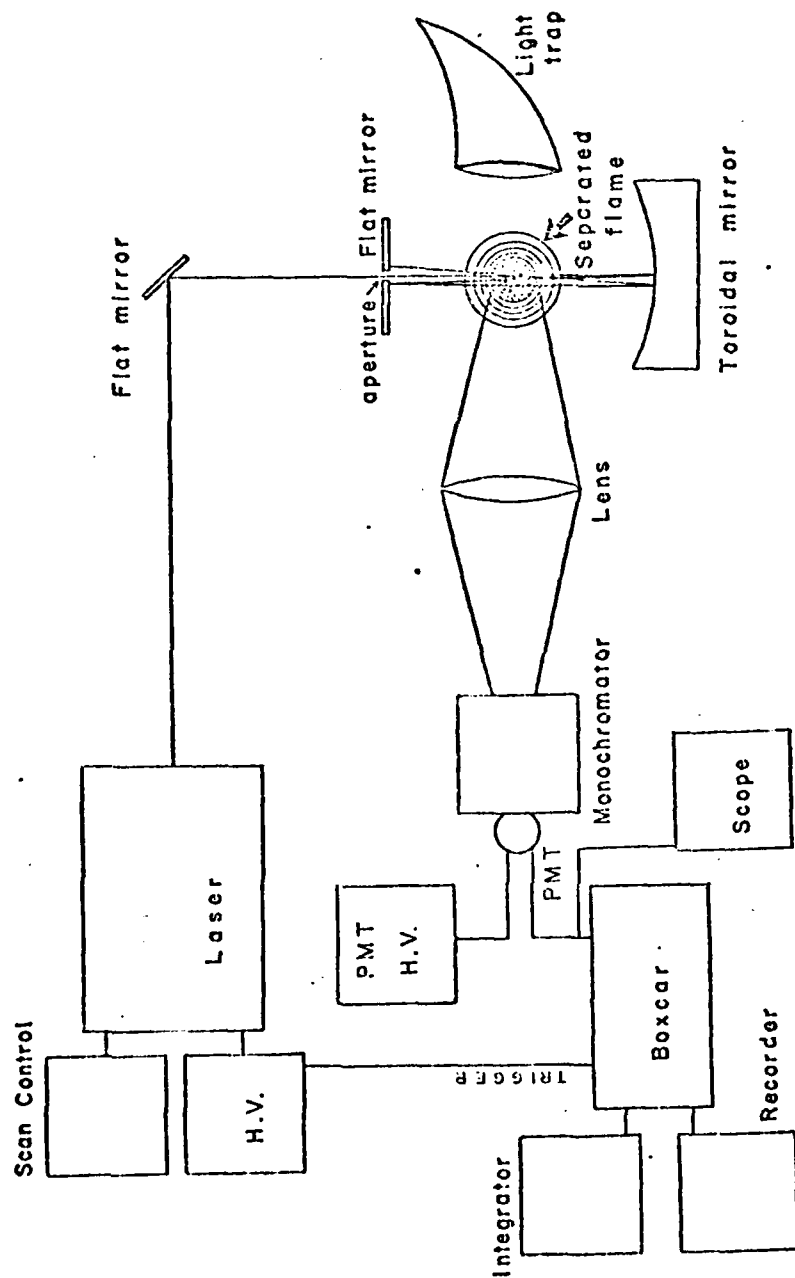


Figure 2



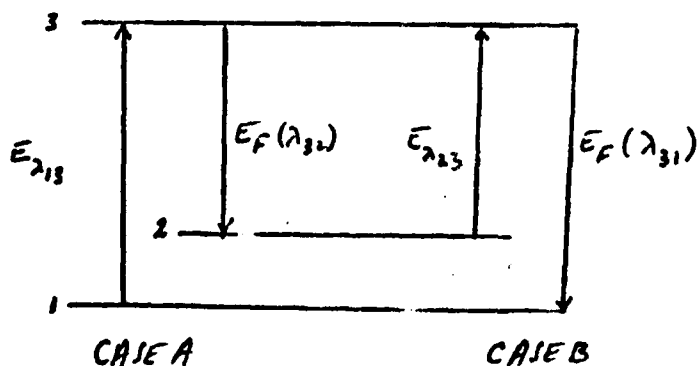
APPENDIX

REPORT

Two flame temperature measurement methods have been developed and used for several small laboratory flames. The methods are called Two Line Linear Fluorescence Method (TLLF) and Two Line Saturation Fluorescence Method (TLSF). In TLLF, the ratio of two direct line fluorescence signals under the linear fluorescence - source flux condition are measured, i.e., the irradiance ratio $E_F(\lambda_{32})/E_F(\lambda_{31})$ is measured (E_F is the fluorescence irradiance for the wavelength λ_{32} and λ_{31}) and the flame temperature T_f is calculated from

$$T = \frac{5040 V_2}{\log\left(\frac{E_{\lambda_{23}}}{E_{\lambda_{13}}}\right) + 6 \log\left(\frac{\lambda_{23}}{\lambda_{13}}\right) + \log\left(\frac{E_F(\lambda_{32})}{E_F(\lambda_{31})}\right)}$$

where E_{λ} is the source (laser) spectral irradiance at the 2 excitation lines λ_{23} and λ_{13} . A diagram of the transitions are shown below



The major assumptions are that the two cases be done close together (within 1 μ s) that steady state, linear operation occurs for each case, and that state 2 is thermally populated at the flame temperature. In our case, CASE B and CASE A occurs repetitively but with an ≈ 30 ns delay between them. The major assumptions have been shown to be valid. Calibration of the spectrometric system is essential here.

In TLSF, the fluorescence irradiance at λ_{32} is measured following excitation first at $\lambda_{13}(E_{\lambda_{13}})$ and then at $\lambda_{23}(E_{\lambda_{23}})$ delayed by ≈ 30 ns. In this case, saturation must occur and so the spatial-temporal characteristics of the laser beam must be monitored so that measurements only occur in the saturation domain. In addition, the laser spot size for $E_{\lambda_{13}}$ and $E_{\lambda_{23}}$ excitation must be the same. The flame temperature, T_f , is then calculated from

$$T_f = \frac{4868}{\log \left(\frac{E_{F_{3+1}}^{1+3}}{E_{F_{3+1}}^{2+3}} \right) + 0.125}$$

here $E_{F_{3+1}}^{1+3}$ is the fluorescence irradiance at λ_{31} with excitation at λ_{13} and $E_{F_{3+1}}^{2+3}$ is the fluorescence irradiance at λ_{31} with excitation at λ_{23} . Here it is not necessary to calibrate in the spectrometer but only to know the relative fluorescence signal levels.

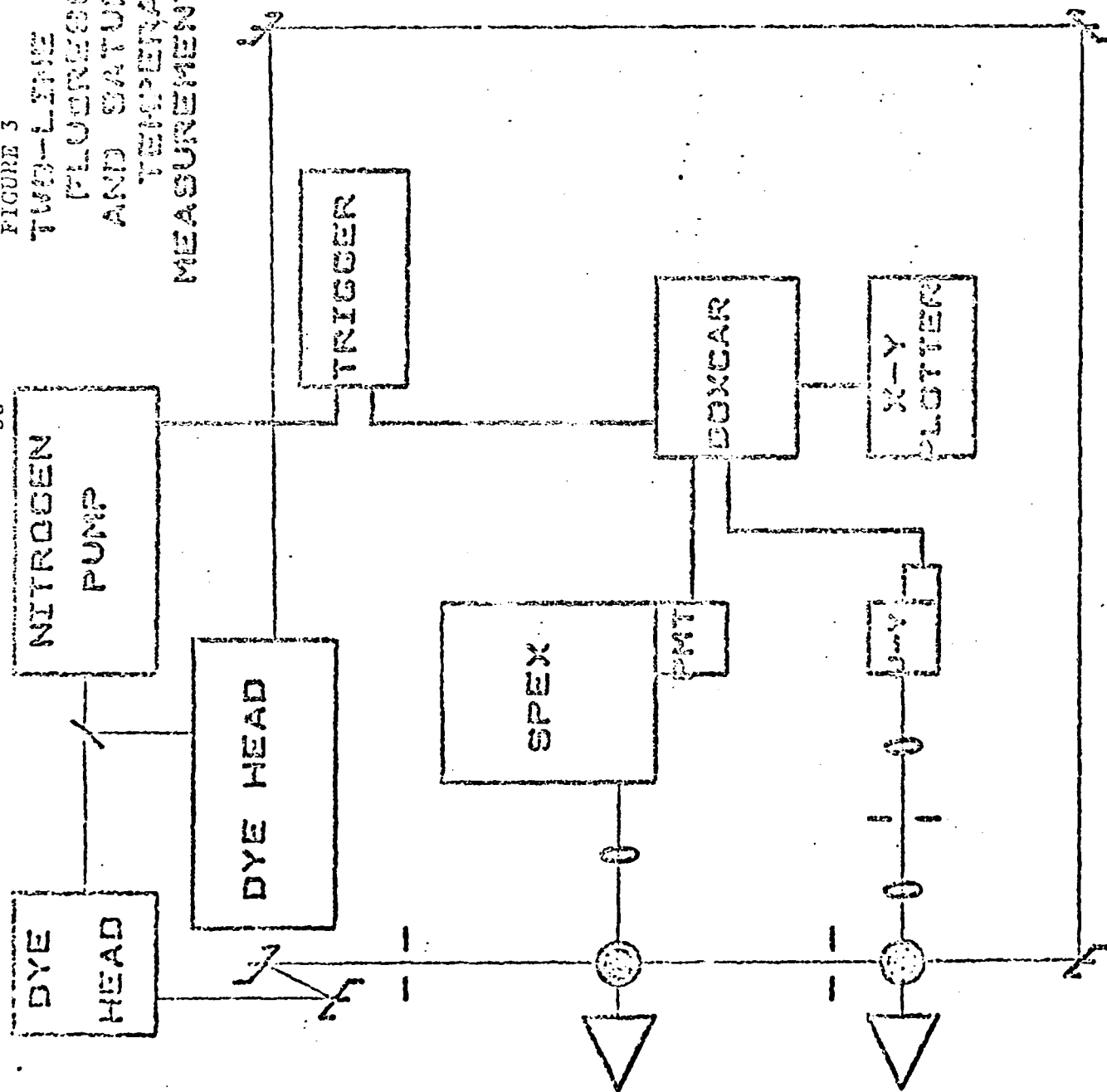
The experimental system for these measurements is shown in a schematic fashion in Figure 3. Several experimental flame temperatures as measured by the TLSF and TLLF methods are given in Table I; in Table X, literature values are also given for the same flames. The spatial and temporal resolution of the TLSF and TLLF temperature values is 1.5 mm x 0.5 mm x 3 mm and 30 ns respectively, which falls within the required resolution for flame modeling.

The experimental system is currently being interfaced via CAMAC units to our PDP 11/34 minicomputer to allow spatial flame temperature measurements of a variety of flames and plasmas. A manual horizontal temperature profile of our ICP is shown in Figure 4. The major limitations to flame temperature measurements by the much simpler and more precise (better SNR) method is the dye laser source spectral irradiance. Currently, the TLSF method can be used with non-quenching flames (H_2 -based) and plasmas (inductively coupled Ar plasma), but with quenching flames (hydrocarbon based) because of the low quantum efficiencies of the probes (In, Ga, Tl, Pb, etc.), the saturation spectral irradiance is so large as to prevent saturation with our Molelectron UV-14-DL-14 Dye Laser system. Calculations show that the Lambda Physik excimer laser-Lambda Physik dye laser system will "saturate" In, Ga, Tl, Pb, etc., in hydrocarbon based flames. We hope sufficient funds will be available in the near future to purchase the Lambda Physik excimer laser (~\$35,000.); the other laser items are already available in our laboratory.

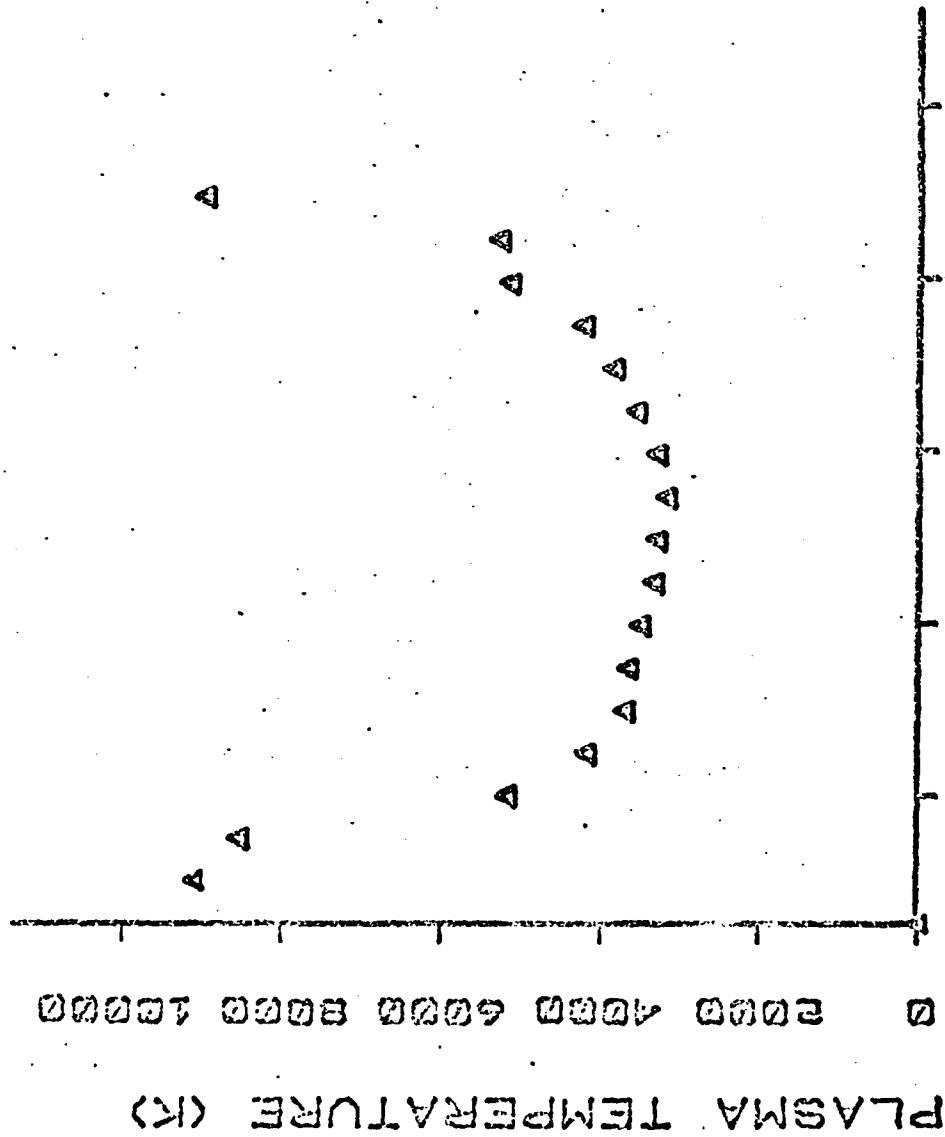
Other related studies in progress include the measurement of atom quantum efficiencies and total concentrations (m^{-3}) of atoms and molecules in flames (see Table II). The experimental equipment for these studies is shown in Figure 5. Some typical results via

several methods are shown in Table XI and Table XII (papers describing these approaches will be forwarded to AFOSR within a month). In addition to the flame temperature measurement methods, TLLF and TLSF with elemental probes (In, Ga, Tl, Pb, etc.). We are also developing similar TLLF and particularly TLSF methods with native flame species (e.g., OH, CH, C₂, etc.). Flame fluorescence (laser induced) background spectra have been measured; these results indicate the potential use of TLSF and TLLF for temperature measurements (several papers concerning flame fluorescence spectra will be sent to AFOSR within a month).

FIGURE 3
TWO-LINE ATOMIC
FLUORESCENCE
AND SATURATION
TEMPERATURE
MEASUREMENT SYSTEM



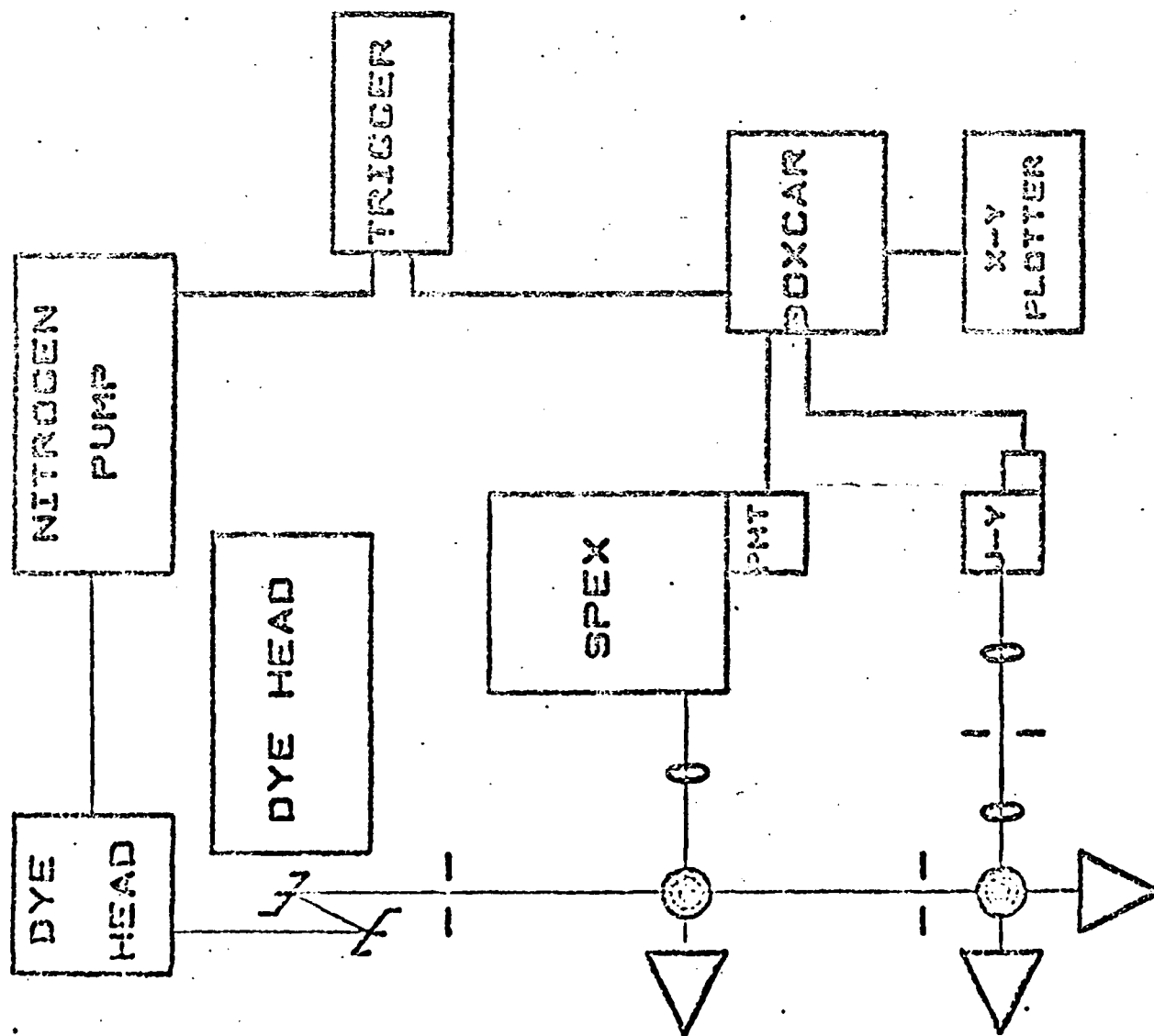
ICAP TEMPERATURE PROFILE



DISTANCE ACROSS TORCH

(1 DIVISION = 1 MILLIMETER)

FIGURE 5
 NITROGEN PUMPED
 DYE LASER SYSTEM
 FOR INVESTIGATION
 OF QUANTUM
 EFFICIENCIES
 AND NUMBER
 DENSITIES VIA
 SATURATION



TEMPERATURE MEASURED BY TWO-LINE

TABLE X

ATOMIC/IONIC FLUORESCENCE

PLASMA/FLAME	METHOD	SPATIAL VOLUME	SPECIES	TEMPERATURE MEASURED (K)	LITERATURE VALUE (K)
HYDROGEN 4.0 ARGON 8.0 OXYGEN 8.0 ARGON SEPARATED	TIME AVERAGED SATURATION FLUOR.	3.4M ³	INDIUM I	2400. ± 25.	2400.
SAME AS ABOVE	SINGLE PULSE SATURATION FLUORESCENCE	3.4M ³	INDIUM I	2450. ± 200.	2400.
ACETYLENE 1.8 AIR 10.0 ARGON SEPARATED	TIME AVERAGED TWO-LINE ATOMIC FLUORESCENCE	3.4M ³	THALLIUM I	2400. ± 25.	2430.
INDUCTION COUPLED PLASMA 750 W 87 MHZ ARGON	TIME AVERAGED SATURATION IONIC FLUORESCENCE	3.4M ³	SARIUM II	2500. ± 100.	2500.

SATURATION POWER AND QUANTUM EFFICIENCY RATIOS

TABLE XI

ELEMENT	SATURATION POWER (W)		QUANTUM EFFICIENCY RATIO (POWER)	QUANTUM EFFICIENCY RATIO (SLOPE)
	ARGON	NITRO-GEN		
SODIUM	850	2600	5.06	5.70
CALCIUM	150	220	1.70	1.01
STRONTIUM	110	120	1.10	1.20
INDIUM	2400	7000	2.92	5.64

ARGON VS NITROGEN FLAME

75 PICOSECOND SAMPLING

ELEMENT	SLOPE RATIO (X) ARGON/NITROGEN	NUMBER DENSITY (SIGNAL)				INTERCEPT RATIO SIGNAL- RATIO	INTERCEPT DENSITY
		ARGON OXYGEN HYDROGEN	NITROGEN OXYGEN HYDROGEN	RATIO ARGON NITROGEN	RATIO SIGNAL- RATIO		
NA	5.7	46	42	1.10	0.94	1.16	
IN	5.6	60	58	1.59	1.15	1.37	
CA	1.8	57.5	71	0.81	0.98	0.83	
SR	1.2	42	49	0.87	0.96	0.91	