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LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

AND

ITS APPLICATION TO SOLUTION SAMPLES

By

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ABSTRACT

LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) AND ITS APPLICATION TO SOLUTION SAMPLES

By

Helen Antony Archontaki

Laser-Induced Breakdown Spectroscopy (LIBS) is a new analytical technique, which is a variation of atomic emission spectroscopy. The unique feature of this approach is the atomization and the excitation of the sample by the dielectric breakdown of the medium, which occurs at the focal point of a high-powered laser beam. A brightly emitting, long-lived plasma is created by the breakdown with a temperature on the order 10^4 to 10^5 K and an electron density of 10^{16} to 10^{19} cm^{-3} . Emission from the plasma is gathered, resolved spectrally and detected by time-resolved methods.

The LIBS source differs from other spectrochemical plasmas in being pulsed, high-temperature and electrodeless at the same time. Workers at the Los Alamos National Laboratories were the first to use LIBS for analytical purposes; they have primarily employed the technique with gaseous and solid samples.

In this work, LIBS has been employed for the analysis of solution samples. Two different sample introduction approaches have been taken. First, solutions were converted to dry aerosols by nebulization into a heated spray chamber with an attached condenser. Second, an Isolated Droplet Generator (IDG) was used to break the solution sample into a stream of isolated nanoliter droplets. In both cases, the sample was

directed through the focal point of a high-powered pulsed laser (Nd:YAG), in the form of an aerosol or a liquid stream and analyzed.

In this dissertation, the principles, the instrumentation and the application of LIBS to the determination of several elements are presented. The importance of time-resolution is demonstrated. Plasma characterization, based on the electron density, temperature and background emission was performed. Several experimental conditions were optimized. The linear dynamic range and detection limits are reported for both the aerosol and droplet stream approaches. In the case of liquid streams, a Flow Injection (FI) system has been used to introduce samples to the IDG. Performance characteristics of the FI-IDG-LIBS method in terms of the effect of sample injection volume on sensitivity are given. Interelement studies as well as the feasibility of real sample analyses are discussed. Finally, the potential of the LIBS technique is illustrated.

To my parents

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CHAPTER I

INTRODUCTION

From its early stages of development in the 1930s until the middle 1960s, atomic emission spectroscopy (AES) was often the method of choice for the simultaneous determination of major, minor, and trace constituents in all sample types. Flame emission is the oldest and the simplest atomic spectrochemical method which rapidly grew to become an important analytical technique, particularly after the introduction of Gilbert's total consumption burner by Beckman Instruments in 1951. In the 1940s interest developed in materials that were difficult to analyze by flame emission methods. The war years provided great impetus for the development of more energetic excitation sources than common flames. Hence, arc and spark discharges became important sources particularly for the analysis of solids and refractory materials.

For many years, the high-voltage spark, free-burning dc arc and the combustion flame were the only widely used excitation sources in AES (1). Today, this situation has changed dramatically. The low precision, complex chemical environment and frequent matrix effects associated with dc arc excitation have resulted in diminished application of this source. Although flame and spark sources are still viable and will continue to find applications in the future, their use in AES has gone through a period of decline during the past 25 years.

The wide acceptance of atomic absorption spectroscopy (AAS) during this period was primarily responsible for this decline. But decline in usage does not mean lack of scientific development. There is now abundant evidence that AES has regained its appeal.

One reason for this sharp upturn in the use of AES is that analytical chemists have been increasingly faced with the necessity of determining multiple elements simultaneously at various concentration levels and particularly at low concentrations. Because of these needs "one element at a time" procedures, such as classical chemical approaches or the various AAS methods, have lost some of their attractiveness. The increased emphasis on high-precision, multielement determinations at trace and ultratrace levels, together with the increased importance of micro samples, has led to widespread application of gas stabilized arcs and high-frequency and dc plasma devices. Another factor is a major advance in the heart of any AES analytical system, namely the component that has to vaporize the sample, dissociate the vapor, and excite the free atoms. This advance was the development of the inductively coupled plasma (ICP) source, which is an electrodeless argon plasma formed at atmospheric pressure and sustained by inductive coupling to high-frequency magnetic fields (2).

Because plasma sources are much more energetic than common flames, they can provide higher atomization efficiencies, high degrees of excitation and lower detection limits for many elements. Following the introduction of commercial inductively-coupled and dc plasmas in the mid 1970s, these sources became rapidly accepted as analytical tools. Plasma sources now dominate the sales of emission spectrometers; most of the research on emission sources deals with plasma devices.

Several other types of excitation sources have also been developed or more widely exploited in recent years. These include lasers, hollow-cathode and glow discharge lamps and exploding conductors (3).

This dissertation presents a new analytical technique, which is a variation of atomic emission spectroscopy, named "Laser-Induced Breakdown Spectroscopy" (LIBS). The unique feature of this approach is the excitation of the sample by the dielectric breakdown of the medium, which occurs at the focal point of a high-powered laser beam. A brightly emitting plasma is created by the breakdown with a temperature on the order of 10^4 to 10^5 K and an electron density of 10^{16} to 10^{19} cm^{-3} . The emission from the plasma is gathered, spectrally resolved and converted into an electrical signal by an appropriate radiation transducer. Signal processing by a gated integrator or a boxcar integrator, triggered properly, is used to improve signal-to-noise ratios.

The LIBS source differs from other spectrochemical plasmas in being pulsed, high-temperature and electrodeless at the same time. It can be used for gaseous, liquid and solid samples. Detection can take place directly in ambient air. The technique is noninvasive in the sense that only optical access to and from the sampled medium is required.

In this work, we have used LIBS mainly for the analysis of solution samples. Two different sample introduction approaches have been taken. First, solutions were converted to dry aerosols by nebulization into a heated spray chamber with an attached condenser. Second, an Isolated Droplet Generator (IDG) constructed in our lab (4) has been used to break the solution sample into a stream of isolated nanoliter droplets. In both cases, the sample is then directed through

the focal point of a high-powered pulsed laser (Nd:YAG), in the form of an aerosol or a liquid stream, and analyzed.

In the following chapters, the principles, the instrumentation, and the application of this method to the determination of several elements are presented. Characterization of the laser-induced plasma is described; the importance of time-resolution is pointed out. Optimization of experimental parameters as well as qualitative and quantitative work are shown. Interelement studies and the feasibility of real sample analyses are discussed. Finally, the potential of the LIBS technique is illustrated.

CHAPTER II

HISTORICAL BACKGROUND

In atomic emission spectroscopy, the light from an excited sample is spectrally analyzed to yield qualitative and quantitative information about the elemental constituents. The traditional emission techniques employ arc or spark excitation (5,6) requiring electrodes. Recently, atomic flame fluorescence (7) and the inductively coupled plasma (8) have become accepted sources. None of the latter techniques are particularly useful for direct detection of gas-phase samples in ambient air or usable outside of the analytical laboratory.

Laser-Induced Breakdown Spectroscopy is a field-deployable variation of electrodeless spark spectroscopy where a repetitive spark discharge is formed in air or a carrier gas by a focused laser beam. LIBS is a new technique for spectrochemical analysis, although none of its elements are new; both laser-induced breakdown (9) and atomic emission spectroscopy from plasmas (10) are well established subjects.

The first observations of breakdown in gases induced by pulsed laser radiation were reported by Maker et al. (11) and by Meyerand and Haught in 1963 (12). The latter used a Q-switched ruby-laser system capable of generating giant pulses of optical energy with a peak power of the order of tens of megawatts.

The laser spark phenomenon immediately captured the attention of physicists. After the first reports of the effect, which appeared in

1963, the new phenomenon became the subject of detailed investigations and very lively discussions in physics journals and at conferences in many countries. The discovery of the laser spark stimulated the development of new directions in the physics of discharges and plasma. They included the avalanche breakdown of gases at optical frequencies, generation of plasmas by optical radiation, general theory of propagation of discharges maintained by electromagnetic fields, and so on. There was an urgent need for a theory of multiphoton processes, which is essentially a new branch of quantum mechanics that had seemed to be, until then, of purely academic interest.

Laser-induced gas breakdown and spark phenomena have been studied extensively, both experimentally and theoretically in different gases, over a wide range of pressures, irradiation wavelengths and laser pulse durations. The only requirement of the laser is that it produce the power density required to cause breakdown in the material of interest. This implies pulsed operation and good beam quality; the wavelength has very little effect on the plasma spectrum. Several workers have used pulsed CO₂, ruby and Nd:YAG lasers for LIBS.

According to the classical method for generating a laser spark, when the output of a high power laser is focused in a gas and the intensity in the focal region reaches a critical threshold value, electrical breakdown of the gas occurs (13,14) because the electric field at the focus exceeds the dielectric strength of the gas, not because of selective absorption by an atom or molecule. However, selective absorption can reduce the breakdown threshold (15), which is otherwise a slowly varying function of wavelength.

The elementary processes are very complex and numerous: (i) creation of the first electrons; (ii) heating of these electrons by inverse bremsstrahlung (electron-neutral or electron-ion); (iii) emission of light by bremsstrahlung; (iv) diffusion out of the focal zone; (v) ionizing collisions; (vi) recombination of ions and electrons; (vii) elastic and inelastic collisions; (viii) expansion of the plasma and shock waves: macroscopic movements of the plasma. Because these events occur on the nanosecond and microsecond time scale, such a rapidly evolving system (16) is very difficult to analyze.

There are two generally accepted mechanisms that can lead to optical frequency breakdown of gases. These are the multiphoton absorption process and the cascade- or collision-induced ionization (17). The first process is the simultaneous absorption of a number of photons such that sufficient energy is gained to ionize an atom. The second is analogous to the classical microwave breakdown mechanism, where free electrons gain energy from the electric field and generate more electrons and ions through collisions with atoms; this energy is enough to ionize an atom.

For visible laser radiation the multiphoton absorption can dominate over the cascade mechanism at low gas pressures and short-duration (ps) laser pulses. At atmospheric pressure and longer laser pulse durations (>1 ns), a cascade collision ionization develops when a few seed electrons absorb energy from the laser beam by inverse bremsstrahlung. In the latter case, the laser-induced breakdown of a gas is initiated by the multiphoton absorption producing the first few free electrons, followed by an exponential growth of free electrons through the cascade mechanism. The threshold intensity required for

breakdown is found to be dependent on pressure, specific gas used (its ionization energy), pulse length, laser beam size, frequency of radiation, and focal spot size (14, 17-20). By studying the dependence of threshold on the various experimental parameters, the mechanism responsible for the ionization of the gas can be identified (20-23).

When the breakdown occurs, the gas, which is initially electrically neutral and optically transparent, suddenly becomes ionized and opaque. It absorbs and reflects the laser energy and grows toward the focusing lens during the laser pulse. The result is a luminous plasma, that appears as a bluish-white spark, conical in shape, with a temperature of 10^4 to 10^5 K and an electron density of 10^{18} to 10^{19} cm⁻³. After that, the plasma decays by bremsstrahlung emission, radiative de-excitation and electron-ion recombination.

The time history of the laser spark can be divided into the stages of initiation, growth, and decay (9). The breakdown occurs during the first stage; i.e., ionization develops in a cold gas and an initial plasma appears. The second stage is characterized by the interaction of the rest of the laser pulse with the plasma already formed. It includes the motion of a plasma front maintained by the laser radiation, heating of the plasma to very high temperatures, and absorption and reflection of the laser light by the plasma. Finally, "detonation-like" phenomena are observed in the third stage, and these continue well after the end of the laser pulse. A gradually decaying shock wave appears due to the evolution of the laser pulse energy in the gas; a "detonation" wave emits light resembling the fireball of a nuclear explosion (on a miniature scale). For laser pulses of tens of nanoseconds and in the energy range 0.1-10 J, initiation takes a few nanoseconds, growth lasts for the

duration of the pulse, and the decay can last for tens of microseconds. The classic method for generating a laser spark in a gas is to focus a 0.1-10 J laser pulse to a fluence greater than 10 MW/cm². The current understanding of laser-induced breakdown of gases is well summarized in a review by Raizer (9).

After the discovery of laser-induced breakdown of gases, many studies discussed the mechanisms of breakdown and energy deposition. The physics of laser sparks in gases was investigated as early as 1964 (24). One of the principal experimental tools was time-resolved spectroscopy (25). These first studies were concentrated for the most part on sparks in simple atmospheres such as hydrogen, helium and other pure gases, including analyses of laser-induced plasmas in helium initiated by ruby (26) and CO₂ (27,28) lasers and a detailed examination of a hydrogen plasma (25). The focus of these studies was on the temporal and spatial variation of temperature and electron density, determined through classical plasma spectroscopy. Numerous measurements have been carried out in air and nitrogen (29-31); however, limited data are available in the case of oxygen (32). Tomlinson et al. (33) noted that breakdown in molecular gases is considerably more erratic than in monatomic gases.

With the development of laser-induced breakdown in gases, interest arose in the spark produced by the focusing of an intense laser pulse into a liquid. Studies of this spark have concentrated on the mechanism of optical dielectric breakdown (34,35), the intense short duration light from the spark, the shock wave emanating from the focal volume, cavitation phenomena, and measurements of the spark temperature (36) and electron density (34,36).

Another aspect that is under extensive investigation is the effect of spherical particles on laser-induced breakdown of gases (37-42). It has been recognized that the presence of small liquid or solid particles decreases the breakdown threshold intensities by factors of up to the order of 10^3 (43,44). This decrease can be attributed to several effects occurring simultaneously: (a) Due to the focusing effect of small particles (45), the intensity of the electromagnetic field is amplified several hundred-fold just outside the particle in the forward direction. Similar amplification, however, slightly smaller, occurs also inside the particle. (b) Due to evaporation of the particle, a thin layer of vapor is formed around the particle which modifies the breakdown threshold intensity of the original gas. (c) Due to different properties of the particle's material and the surrounding gas, it may be the particle instead of gas that suffers the breakdown (46). Recently, time-resolved spectra of plasmas initiated on single, levitated aerosol droplets were reported (47).

Spectrochemical applications of laser-induced breakdown took also the direction of the laser microprobe technique, in which the laser was the atomizing source (48-50). Spectra from vaporized surface material were generated by following the laser pulse with a conventional spark excitation. These spectra were sharper and stronger than those produced by the laser alone. Although commercially available, this technique is not considered sufficiently accurate. Another hybrid technique used for solids is the laser-induced spark/inductively coupled plasma (51-54), where the laser spark produces the fine powder and atomic dust for re-excitation in an ICP. Lasers have been used as sample vaporization devices for ICP (55-57) and microwave-induced

plasma (58,59), with ruby lasers being used exclusively in these systems. Recently, a laser ablation/direct-current argon plasma system was developed for direct determination of copper in pelletized ore and solid samples (60-62).

Radziemski and coworkers at Los Alamos National Laboratories were the first to use LIBS for analytical purposes. They developed this technique when called upon to monitor beryllium directly in air and to analyze the effluent stream of a coal gasifier. At the beginning, they applied the time-integrated technique LIBS to the detection of sodium and potassium in a coal gasifier product stream, of airborne beryllium, and of phosphorus, sulfur and chlorine in various organic molecules (63). Then, they used the Time-REsolved Laser-Induced Breakdown Spectroscopy (TRELBS) to get time-resolved oxygen spectra and to detect phosphorus, beryllium, chlorine and fluorine in air (64-66). Time resolution is used to discriminate against background and interfering ionic lines. However, ionic lines may be monitored if they are the strongest characteristic lines of an element. Molecular spectra are observed at late times; proper choice of observation times minimizes interference from molecular emission.

Later, they extended their method to solution samples, brought to the laser focal point by a flowing stream of air, in the form of aerosols (67). The solutions were converted to dry aerosols by nebulization into a heated spray chamber with an attached condenser (68).

Recently, they applied the method to the direct sampling of liquid media (69), particularly aqueous solutions. They discuss characteristics of the laser spark in water, detection limits for several elements in

aqueous solutions, and the enhancement of emission signals by repetitive pairs of laser sparks.

The laser-induced spark has also been studied extensively for direct analysis of solid surfaces (70-75). Among them, the long spark technique (LST) was developed for direct detection of beryllium on filters using the laser spark (74). The LST differs from the laser microprobe with or without crossed excitation, both in the type of lens used for spark formation and in the way the spark is incident on the surface. With the LST, one can rapidly sample a significant area of a surface by moving the surface under the spark.

In addition to the methods reported above, which involve the use of Nd:YAG lasers for the creation of the spark, the same workers evaluated the properties of pulsed CO₂ laser-induced air-plasma by double floating probe (DFP) (76), as well as the continuous optical discharge (COD) generated by focusing a 45-W cw CO₂ laser beam in Xe gas (77).

In general, LIBS is a promising technique for obtaining spectrochemical information from sample locations where it is difficult to place electrodes or extract samples. Since it is electrodeless, all perturbations of the plasma and all interfering lines from electrode materials are eliminated. It can sample species directly in air or in a carrier gas; thus it is very versatile and can be used in the field. LIBS allows monitoring of species in environments where conventional electrode or plasma sources cannot be placed.

CHAPTER III

INSTRUMENTATION

We have performed a variety of LIBS experiments, differing in detail, but identical in principle. The basic apparatus with time resolution is shown schematically in Figure 3-1 as being representative of a general LIBS experiment. Its components are: the laser source, the optics and the sample introduction, detection and signal processing systems.

In operation, the laser beam is focused to a point, where the sample is brought by an appropriate means. At the focal point, breakdown of the carrier gas takes place, and a brightly emitting plasma is created. The plasma consists of electrons, ions and atoms. Radiation from the plasma is collected and imaged on the slit of a scanning spectrometer. A photomultiplier tube is used as a detector. The resultant signal can be observed on an oscilloscope or processed by a boxcar integrator for time resolution and signal averaging. The spectra are recorded on a chart recorder.

In the following sections of this chapter, a description of each component of the LIBS apparatus is given. Especially, the different sample introduction systems used for gases and solutions will be discussed in detail.

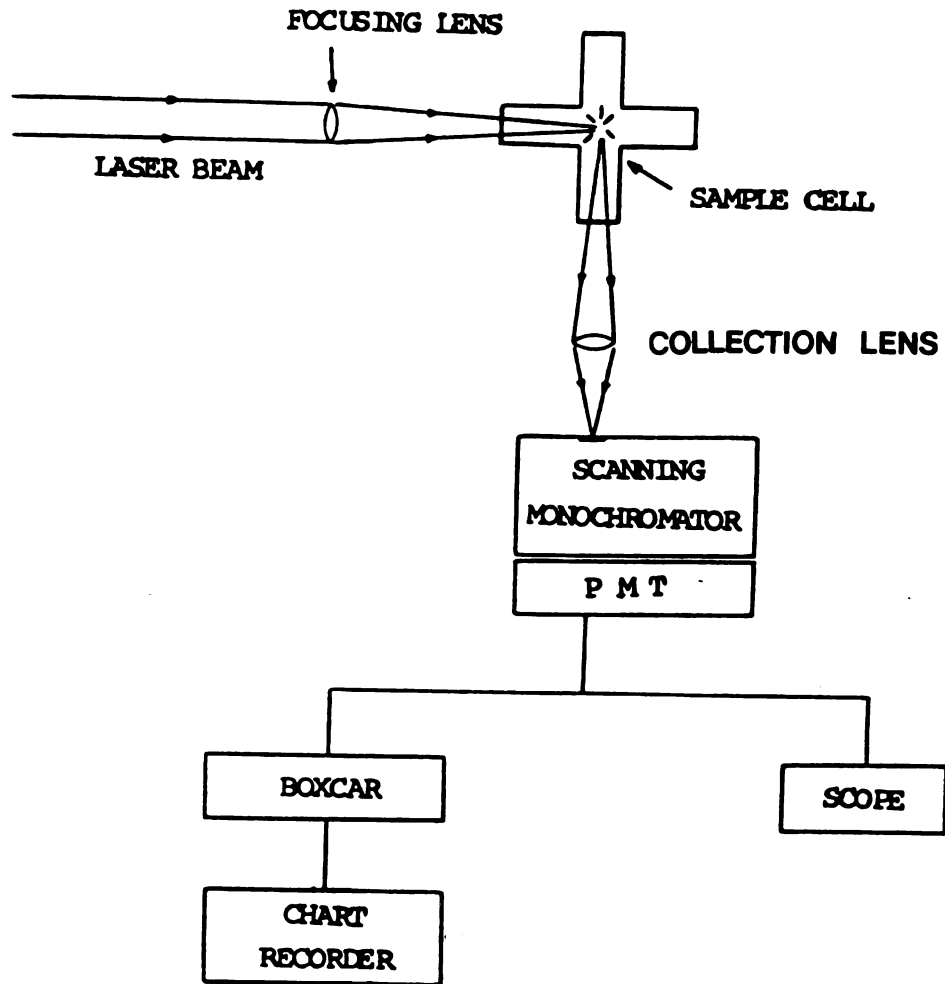


Figure 3-1. Schematic representation of a general LIBS apparatus for time-resolved spectroscopy.

A. Laser Source

The laser source is a Q-switched Quanta Ray DCR Nd:YAG laser operated at 1064 nm. The fundamental frequency has been used to obtain irradiances sufficient (typically 10^8 to 10^9 W / cm²) to break down the various gases. The only requirement of the laser is that it produce the power density required to cause breakdown in the material of interest. This requirement implies the use of a Q-switched pulsed mode. The repetition rate of the laser is 10 Hz and the pulse duration is 10 ns. The energy of the laser beam used should be greater than the threshold for breakdown of the carrier gas since atomization, ionization and excitation of the analyte should occur as well.

B. Optical System

The optical system consists of two lenses with 5-15 cm focal length. One of them is a simple glass lens, which is used to focus the IR laser beam to fluences sufficient for breakdown of the medium. The second lens is quartz and is used to collect and image the light from the plasma on the slit of a scanning monochromator.

C. Sample Introduction Systems.

Different introduction systems have been used for gases and solutions. In addition, as mentioned in Chapter I, solutions have been treated either in the form of aerosols or liquid streams. Because of this complexity, the sample introduction approaches are reviewed separately here for each category.

1. Gases

When the sample is in gaseous form, the sample introduction system is very simple. It consists of the gas container, a sample chamber and a tube connecting them (Figure 3-2a).

The sample cell that we constructed is a six-armed Pyrex glass cross (Figure 3-3), with the laser beam directed at right angles to the flowing sample and the direction of observation perpendicular to both. The cell is made to be symmetrical, although this is not a required configuration. It can be used for gases, vapors, and aerosols. The unabsorbed part of the laser beam is allowed to exit freely from the cell and is blocked afterwards. If it hits a surface close to the plasma, material ablated into the chamber will introduce unwanted spectra and cause spark instability. The "arms" through which the sample flows contain stop-cocks; in this way, the cell can be used for flowing or static samples. Three of the cell windows are glass, while the fourth is made from quartz to allow UV-radiation emitted from elements of interest to pass through to the detection system. The active volume of the plasma is approximately 5 mm long and 2 mm in diameter, so the length of the cell axis traversed by the laser beam is chosen to position the windows in a region of nondestructive laser power density. In our case, the cell arms are 2.5 cm in diameter and 4.2 cm long, dimensions chosen to accommodate the diameter of the laser beam as well as the positioning of the quartz window. This sample chamber cannot be used with high carrier gas pressures, although these were not needed for our work. Experiments can also take place in ambient air, where a sample cell is not necessary.

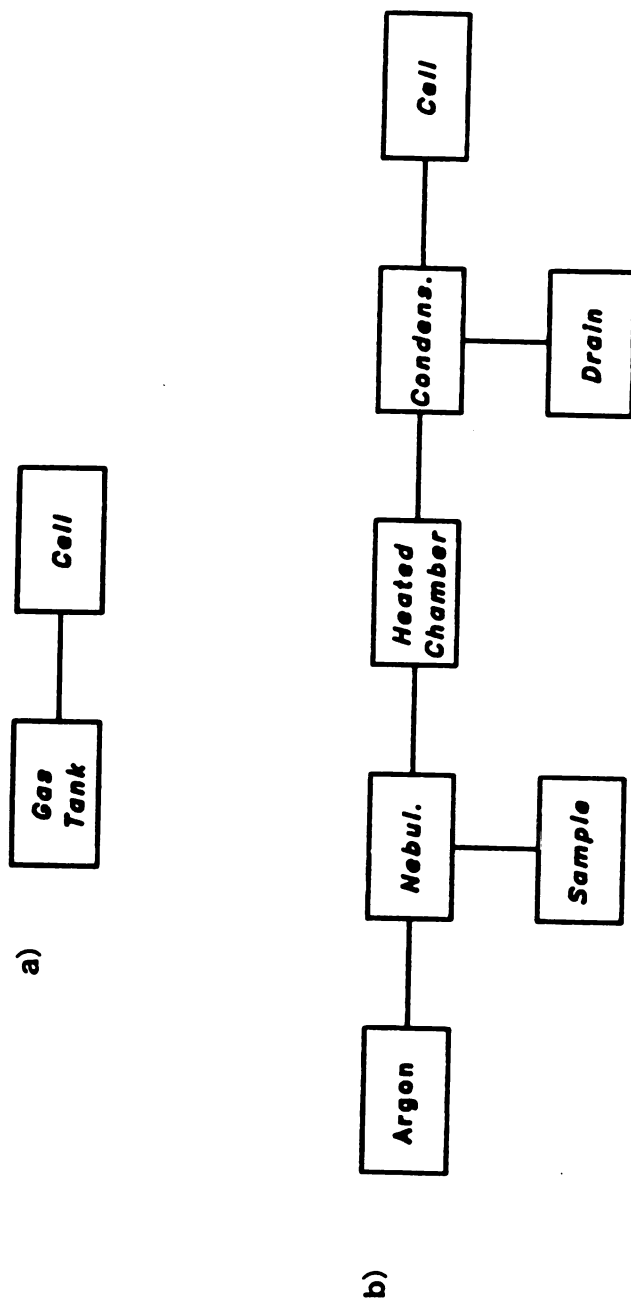


Figure 3-2. Block diagram of sample introduction systems:
a) for gases, b) for aerosols.

2. Aerosols

A block diagram of the components of a sample introduction system for the production of dry aerosols is shown in Figure 3-2b. This system consists of a crossed-flow pneumatic nebulizer, a heated spray chamber with a condenser, and the six-armed cross sample cell that was described above.

A large portion of everyday solution analysis is performed with nebulizers which generate an aerosol from the sample. The crossed-flow pneumatic nebulizer described by Donohue and Carter (78) was used here for aerosol introduction with LIBS, and is pictured in Figure 3-4. This design arose after a series of modifications (79-81). The nebulizer was constructed in our lab and used previously in other projects (82). Two four-inch stainless steel tubes, 0.095-in o.d., are used for solution uptake and carrier gas (mostly argon) inlet lines. A 1/4-in piece of 0.029-in o.d. stainless steel capillary column is silver-soldered into the tip of each inlet line. To avoid excessive backpressure, the length of fine-bore capillary tube is kept as short as possible. A high velocity stream of argon across the uptake line aspirates solution into the nebulizer chamber. Frequent capillary alignment is required for optimum nebulizer performance. Alignment is obtained by tightening the appropriate mounting screws for each capillary. Earlier nebulizer designs incorporated metal-jacketed glass capillaries (83) or all-glass capillaries which were frequently chipped or broken; this caused erratic, non-uniform nebulization. The incorporation of stainless steel capillaries has eliminated this problem. Adequate nebulizer performance was observed with argon flow rate of 3.0 l/min and greater. Care must be

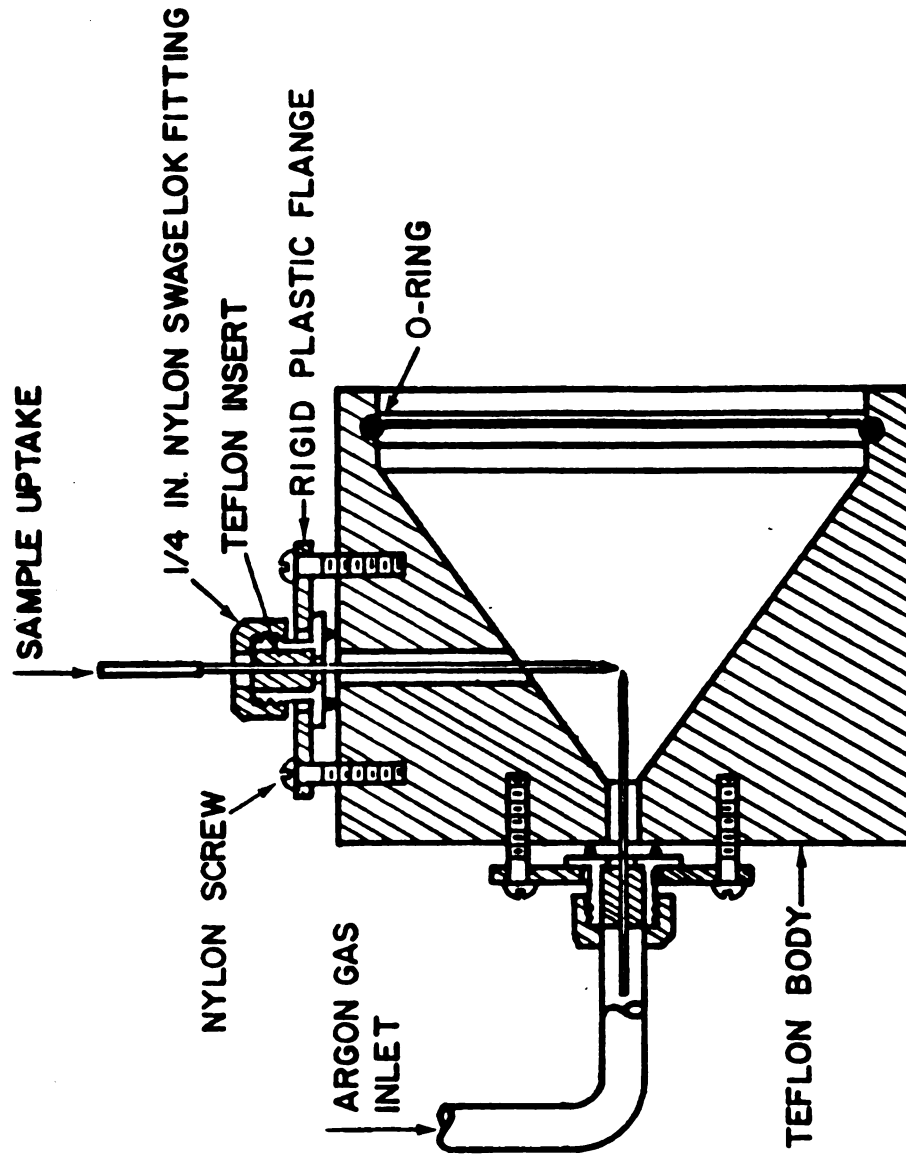


Figure 3-4. The crossed-flow nebulizer.

taken to provide a good fit of all components to ensure consistent positioning control during use.

The aerosol chamber, shown in Figure 3-5, is a design that has been described by Fassel and co-workers (84) for use with an ultrasonic nebulization system they developed. It slides into the nebulizer and is sealed by an O-ring. The design minimizes the number of large droplets which reach the heated chamber. The vaporization of such droplets causes gas flow pulsations which can lead to source instability. The aerosol chamber is easily interfaced to the heated chamber via an 18/9 male-to-male elbow.

From the aerosol chamber, the sample solution is carried by the argon stream into the heated spray chamber. There the droplets of solution are desolvated and the remaining dry salt particles and the solvent vapor are brought by the argon stream into the condenser, where the solvent vapor is condensed and removed; the dry aerosol remains in the carrier gas. Since water is continuously aspirated between samples, thermal equilibrium is established inside the heated chamber. Desolvation occurs in the spray chamber, while solvent removal occurs in the condenser. The desolvation system employed was developed by Veillon and Margoshes (68). The apparatus, shown in Figure 3-6, is constructed from a cylindrical, glass, heated chamber and a modified Friedrichs condenser. The heat is supplied by a heating tape (Briskheat, Standard Fibrox, 6' x 1", 624 W, Sybron/Thermolyne Co.) which encompasses the chamber. At a Powerstat (Superior Electric Co.) setting of 55 V, under nebulizing conditions, the inside temperature of the chamber reaches approximately 160 °C (85). In the water-cooled condenser, 98% of the solvent (water) is removed (86).

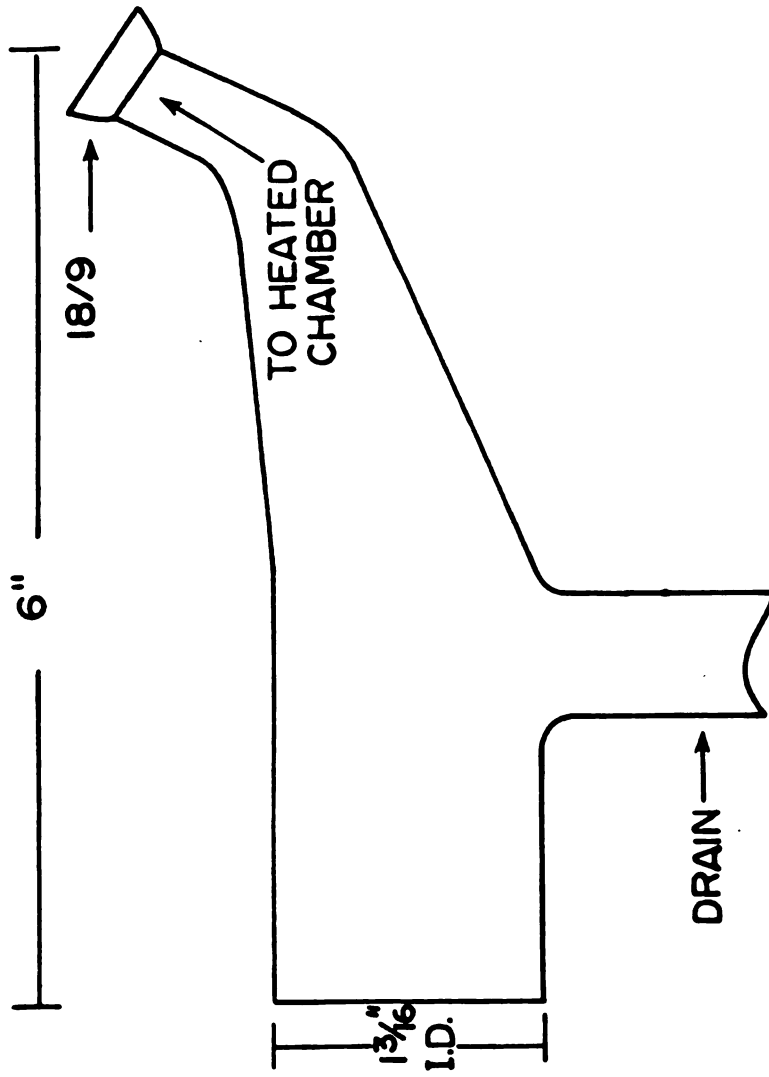


Figure 3-5. The aerosol chamber.

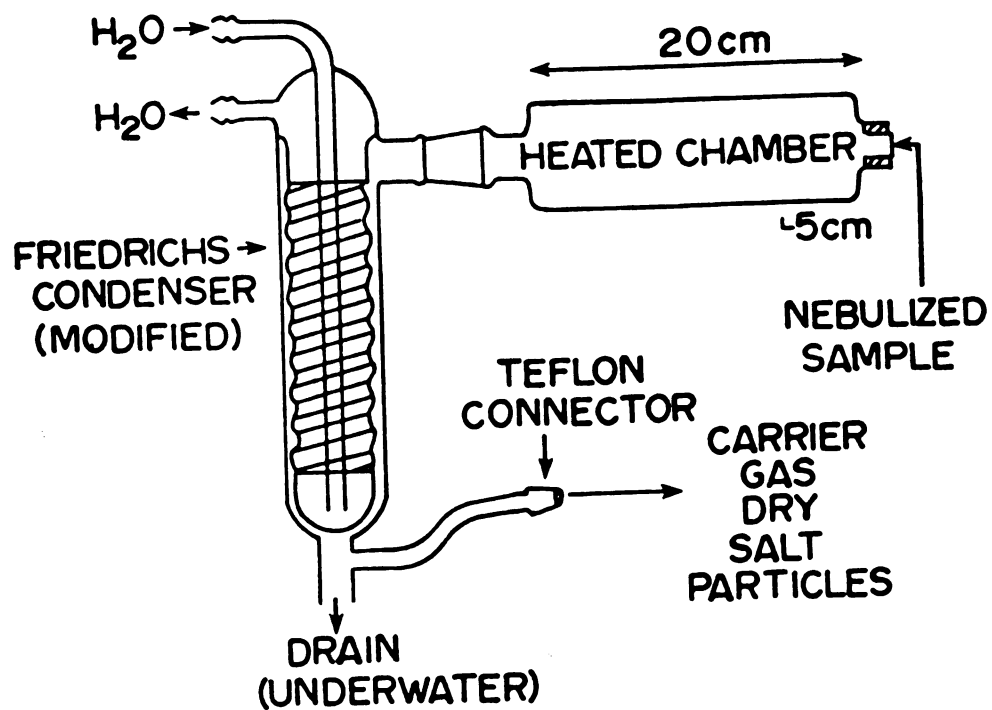


Figure 3-6. The desolvation system.

After desolvation, the dry aerosol is carried to the sample chamber, described above, through a Tygon tube.

3. Liquid Streams

a. Isolated Droplet Generator Approach

For solution introduction into a LIBS system, in the form of liquid streams, an Isolated Droplet Generator (IDG), constructed in our laboratories by Dr. P.M. Wiegand for other projects (4), was used. This IDG is based on the principles discovered by Rayleigh in 1879 (87,88) and further advanced by Schneider et al. (89-91), Hieftje et al. (92-99) and Boss and coworkers (100); its main characteristic is the induced breakup of a liquid jet.

Figure 3-7 shows the basic components of the IDG. A liquid is forced through a glass capillary with a velocity sufficient to cause the formation of a liquid jet. The capillary is attached to a rectangular piezoelectric crystal called a bimorph. When an oscillating voltage is applied to the bimorph, it causes the crystal to vibrate at the oscillation frequency. These vibrations are transmitted through the capillary to the surface of the liquid jet, which becomes dynamically unstable under the action of surface tension, and thus breaks at the resulting wave nodes into uniformly spaced droplets. The droplet stream can be further manipulated by selective charging and deflection of the individual droplets. This is done because in most instances the optimum droplet production rate is faster than that desired experimentally. In this case, the rate of droplet delivery can be slowed by trapping unwanted droplets by selective charging and deflection. A cylindrical charging electrode is placed at the point where droplets are forming

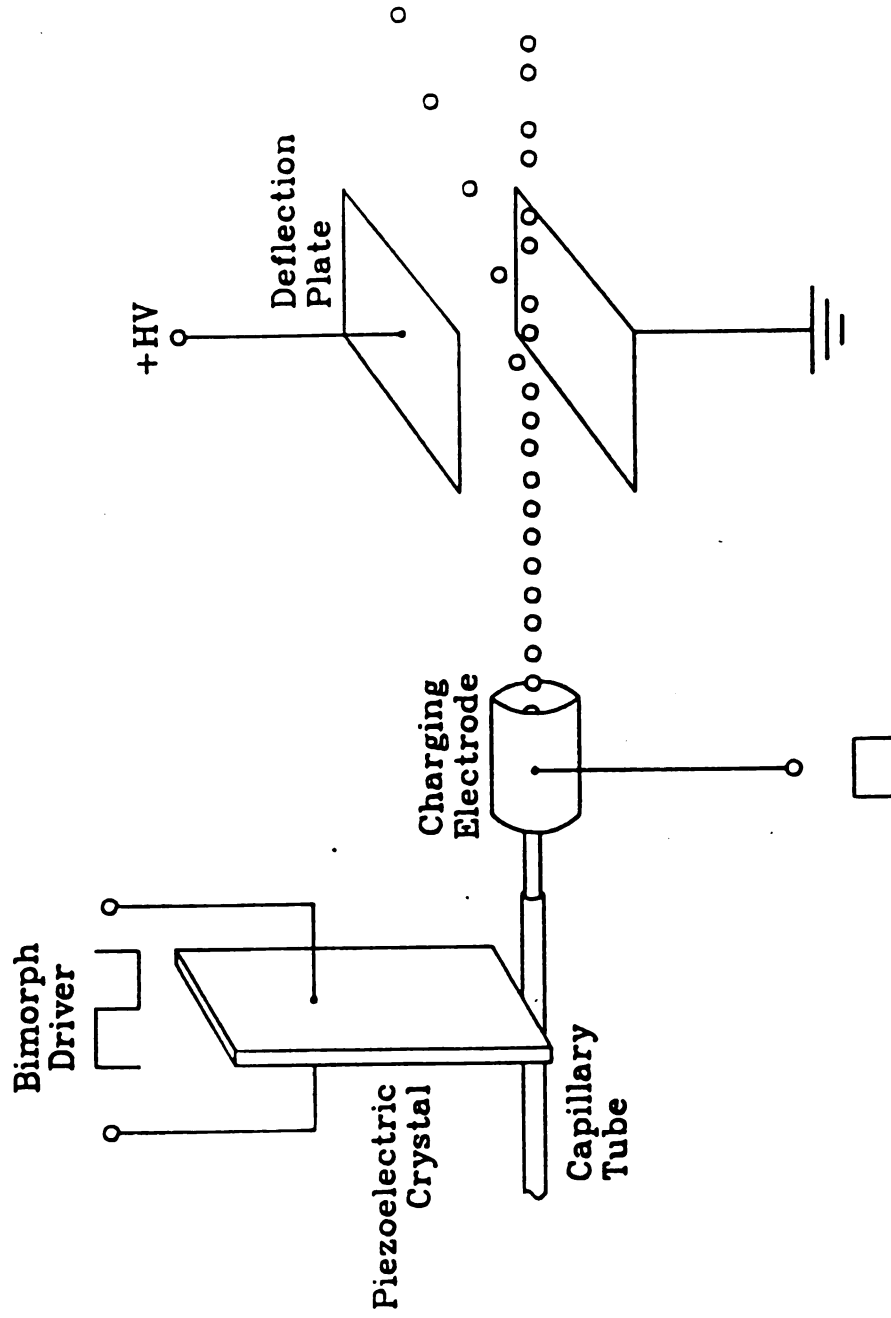


Figure 3-7. Basic components of the Isolated Droplet Generator.

from the liquid jet. If a voltage is applied to the electrode when the droplet breaks from the jet, a charge is imposed on the droplet by a process of induction. High voltage deflection plates are then used to deflect the charged droplets out of the main stream. The control system for the droplet generator (4) contains a versatile large scale integrated circuit timer for droplet production and pulsing. This device consists of five independent counters that can be configured and loaded under software control. One counter is used to clock the piezoelectric crystal, while two others are used for charging and phasing the droplets. In this manner, a wide variety of droplet streams can be produced. Since the waveforms originate from a crystal oscillator, frequency is both stable and reproducible. Several modes of operation are possible, such as single drop pulsing, droplet packet pulsing, and "droplet-on-demand" operation. Detailed description of the components and operation of the IDG can be found in Reference 4.

The Isolated Droplet Generator was interfaced to a LIBS apparatus as shown in Figure 3-8. The droplet stream is positioned so that it intersects the focal point of a Nd:YAG laser as shown in Figure 3-9. The active volume of the plasma contains one or more droplets depending on the bimorph frequency. A Strobotac strobe lamp synchronized with the IDG is used to observe the droplets. A "frozen" liquid stream appears when an optimum bimorph frequency is reached. Experiments were performed in the ambient air. Although an argon environment was desirable for reasons explained in a following chapter, several attempts to produce droplets in argon were not successful. Droplet introduction without charging or phasing was chosen to minimize the effects of slight fluctuations in the liquid stream or laser beam.

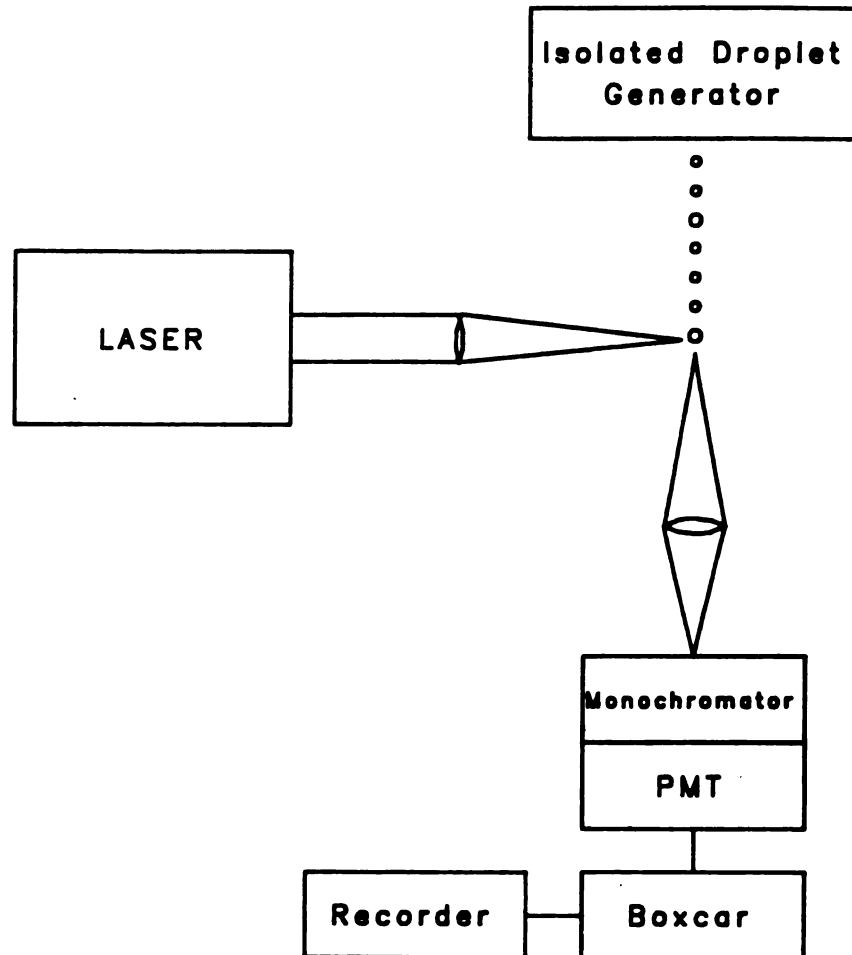


Figure 3-8. Schematic of the interface of the IDG with LIBS.

Droplets that are not introduced can be collected and recycled to avoid inefficiencies. In this experimental configuration the laser action causes breakdown of the medium, creation of the plasma and rapid vaporization of the microdroplets, as well as atomization, excitation and ionization of the analyte. The emission is gathered, spectrally resolved and detected in a conventional manner as shown in Figure 3-8.

A critical step in the operation of the IDG, and as a consequence in the interface of the IDG and LIBS, is the production of capillaries suitable for forming the liquid jet (4). Disposable micro pipets (Dade Hospital Supply Corp., Miami, Fla., 5-20 μ l size) were found to be suitable sources of controlled bore tubing for this application. The end of the pipet is fire-polished in a cool flame and periodically checked with a microscope or reticle until the desired diameter is obtained. Care must be taken to evenly heat the capillary tip, or else a skewed opening will be obtained. Capillaries 15-70 μ m in diameter were made by this method and used for IDG-LIBS. Smaller diameter capillaries can be produced as well, but frequent clogging and excessive backpressure prevent them from being experimentally useful. Before use, the capillaries must be flushed in the reverse direction to wash out any particles which may clog the constriction. To facilitate wash-out of the tubing, capillary lengths should be kept as short as possible. Typical lengths used were in the range 0.5 to 1.0 inch.

The capillaries then were mounted by gluing the capillary perpendicular to the bimorph at a distance of approximately 0.25 inch. from the capillary tip. A rigid-setting glue such as Duco Cement was used to facilitate transfer of the vibrations from the bimorph to the capillary without dampening. After gluing, the capillary-bimorph

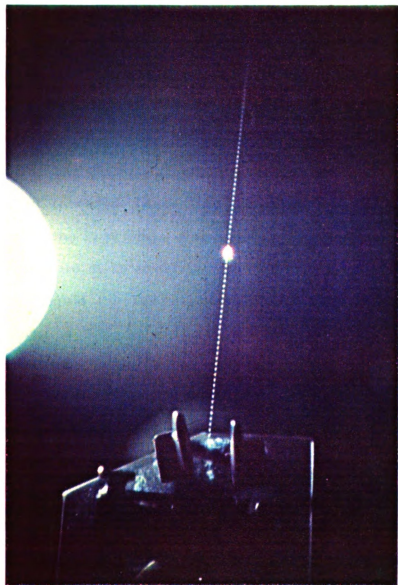
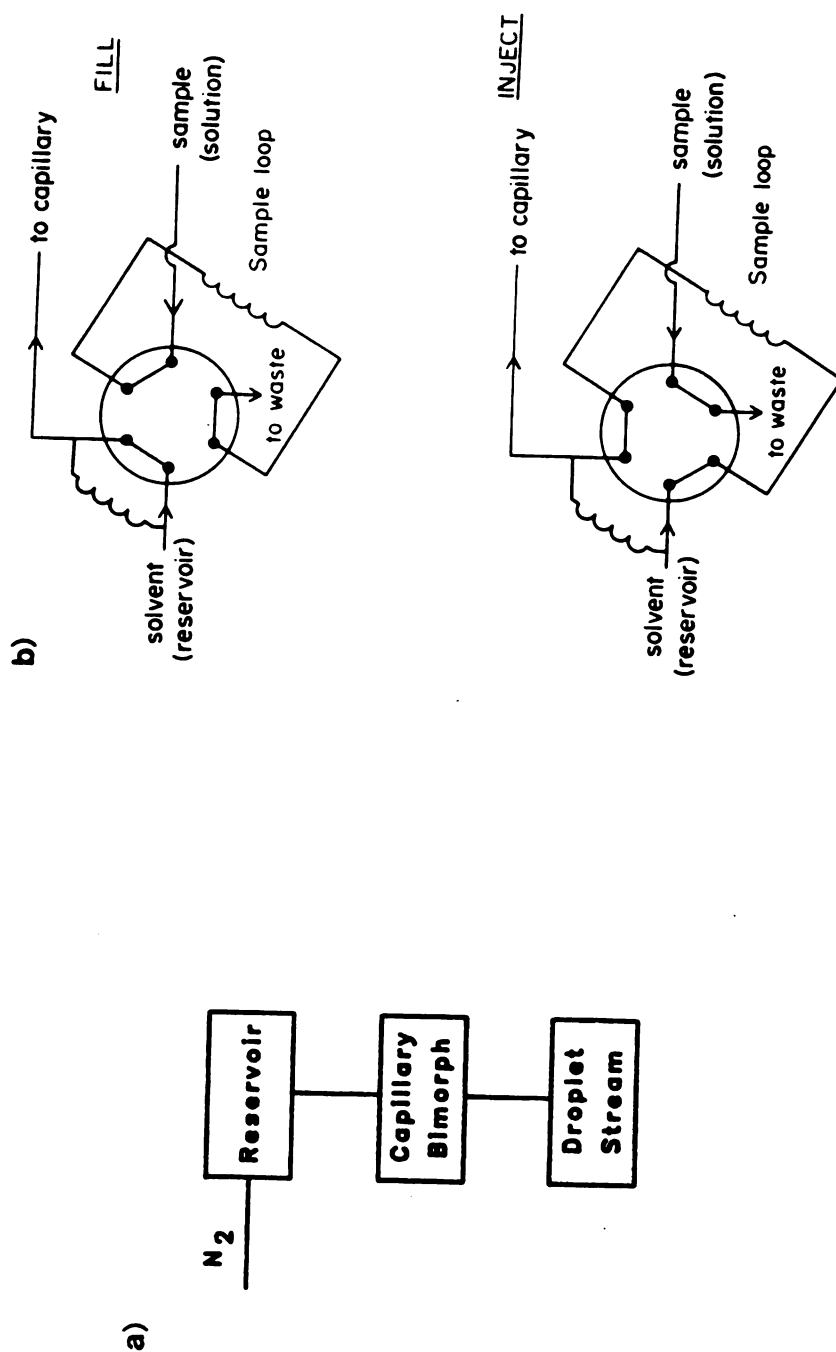


Figure 3-9. A picture of the "frozen" liquid stream intersecting the focal point of a Nd:YAG laser.

assembly is allowed to dry overnight before use. The type of bimorph used was the PZT-5H variety, 0.021" x 0.12" x 1.75", with the electrodes connected in a series positive configuration (Vernitron Piezoelectric Div., Bedford, OH).

In the initial experiments with the IDG-LIBS system, a constant pressure liquid delivery vessel, described elsewhere (4), was used to host the solution sample to be converted to a liquid stream. Nitrogen gas introduced through the cap of the reservoir forces the solution through the capillary with the attached bimorph on it and the droplet stream is created when the liquid jet departs from the capillary (Figure 3-10a). The liquid delivery system consisted of an aluminum cylinder with a threaded brass cap containing a Viton rubber seal. A polyethylene insert was placed within the aluminum cylinder. Regulated gas pressure at 10 to 60 psi was provided through a fitting in the cap, forcing liquid through a sintered metal filter to a 1/16" fitting also in the cap. A 0.45 μ m in-line filter (Rheodyne 7335) was attached to the outlet fitting. After the filter, a union adapts from 1/16" stainless steel tubing to 1/16" plastic tubing compatible with Cheminert fittings. The plastic tubing (Teflon or microline) was 0.04" i.d. and 0.07" o.d., which is a size easily force-fit onto the end of the capillary. The solution samples were filtered (with a 0.45 μ m nylon membrane filter) prior to their use since clogging of the filter element of the in-line filter would cause slower flow rates through the capillary and unstable droplet streams. Whenever the latter was observed, the filter element was replaced.

Although keeping the solution under study in a constant pressure reservoir enabled us to test the feasibility of IDG-LIBS interface, it



made any quantitative work impossible . The reason was that changing from one solution to another involved turning off the whole system, opening up the liquid delivery vessel to remove the previous sample solution and introduce the new one, and letting the system run to ensure removal of the old solution from the tubing. With such a complicated system, achieving exact identical parameters as used prior to solution change was more or less a matter of luck! An inexpensive and easy way to get around this problem was the use of a Flow Injection (FI) system, shown in Figure 3-10b.

b. Flow Injection-Isolated Droplet Generator Approach

It has been more than 10 years since the term flow injection analysis (FIA) was first used (101) to describe an analytical technique in which a discrete sample volume is injected into a continuously flowing carrier stream. Some of the earliest FIA papers reported that the technique could be used to present a small volume of sample to a sensor or an instrument without any prior chemical reaction. However, the first report of the FIA-atomic absorption spectroscopy (AAS) combination did not appear until mid-1979 (102). More recently, FIA based procedures, have made a great impact in many areas of chemical analysis. Analytical advantages such as high precision, high sampling rates for microliter sample volumes, and freedom from nebulizer or injector tip blockage problems have already been demonstrated (103-106) for the combined FIA-ICP-atomic emission spectroscopy technique. A critical review of FIA methods for flame AAS with a brief discussion of FIA-ICP methods has been presented by J.F. Tyson (107). There are also indications (such as a number of recent publications and

presentations at different conferences concerning FIA methodologies) of a growing interest in applications of FIA to atomic spectroscopy.

In our experiments, the interface of a flow injection system with the isolated droplet generator for sample introduction with the LIBS technique was done in the following way: A 6-port, 4-way Rheodyne valve was used as shown in Figure 3-10b. In the FILL position, solvent contained in the constant pressure reservoir flows continuously through the capillary while sample solution fills up a sample loop and is directed to waste. In the INJECT position, sample solution passes directly to waste while solvent going through the sample loop to the capillary forces the sample that was in the loop to the capillary and the latter reaches the laser spark region and gets analyzed.

Several different size sample loops were made from Teflon tubing of 0.8 mm i.d. Sample injection volumes between 70 μ l and 1.5 ml were used. In the FI-IDG configuration, the in-line filter was placed after the valve in such a way that solvent and sample solutions are filtered before entering the capillary. In the IDG-LIBS technique, stability of the liquid stream is very crucial because the droplet stream has to intersect the focal point of the laser beam precisely. Thus, any perturbation of the droplets may destroy the proper alignment. On the other hand, switching of the valve causes such a disturbance due to momentary pressure changes. In order to minimize this effect, a pressure release coil of 0.5 mm i.d. and 2 ml volume was placed between the solvent reservoir and the capillary with two T-joints.

D. Detection and Signal Processing Systems

The detection system consisted of a scanning monochromator (Model EU-700-56, Heath) and a photomultiplier module (Model EU-701-30, Heath). Photomultiplier tubes used were: RCA 1P28A and Hamamatsu R666 with extended red response.

A boxcar averager with gated integrator (Model 162-164, Princeton Applied Research, Princeton, NJ) was used for signal processing. Care was taken to scan the spectrometer more slowly than the integrating time of the boxcar to avoid artificial smoothing of the spectral features. The boxcar integrator is a versatile instrument for measuring repetitive signals, particularly those with short pulse durations and low duty cycles. It allows the recovery of signals that are time-related to a trigger signal and the rejection of those that are not.

In our first LIBS experiments, the boxcar was triggered by the Q-switch of the Nd:YAG laser. This triggering method was not very efficient because every firing of the laser did not result in breakdown and creation of a plasma, due to laser pulse-to-pulse fluctuations. An optical trigger system seemed more suitable for our application, initiating the signal processing only when the laser spark was observed. A commercially available Optical Trigger Detector (EG&G Princeton Applied Research, Model 1301) was utilized. This module was designed to be capable of picking up an optical signal in an electrically noisy environment and of developing from it a clean electrical trigger synchronized with the detected flash (108). It is based on the use of a fast photodiode which senses the light flash through use of an optical fiber positioned close to the event. To avoid triggering from the laser

light, instead of the laser plasma, a proper filter cutting off the IR region was clamped in front of the fiber optic.

Finally, the spectra were recorded on a variable range chart recorder (Model SR-255B, Heath Schlumberger).

CHAPTER IV

TIME-RESOLVED LASER-INDUCED PLASMA CHARACTERIZATION

The transient nature of the laser spark requires the use of time-resolved spectroscopy for plasma characterization. It has been reported in the literature, and shown in our work, that the microsecond time scale is the most useful region for analytical purposes. It was decided, therefore, that the laser plasma should be characterized through its optical emission, on a μs time-resolved basis.

As mentioned in the previous chapter, a boxcar averager with gated integrator was used for signal processing in order to obtain time-resolved, signal-averaged spectra. An optical trigger system initiated the signal processing. In all experiments, the quoted delay times are relative to the trigger pulse.

From the spectra shown and similar spectra with better wavelength resolution, the plasma was characterized according to its electron concentration, the nature of processes governing the continuum emission and its excitation and ionization temperature.

A. Background Emission Studies

The background emission from a laser plasma provides some direct insight into the nature of breakdown. Furthermore, the time profile of noise in the background emission determines the ultimate detection limits of the technique.

Figure 4-1. Argon Background Emission as a function of Wavelength:
a) Delay Time = 0.5 μ s (V_{PMT} = 350 V),
b) Delay Time = 1.0 μ s (V_{PMT} = 440 V),
c) Delay Time = 1.0 μ s (V_{PMT} = 350 V).

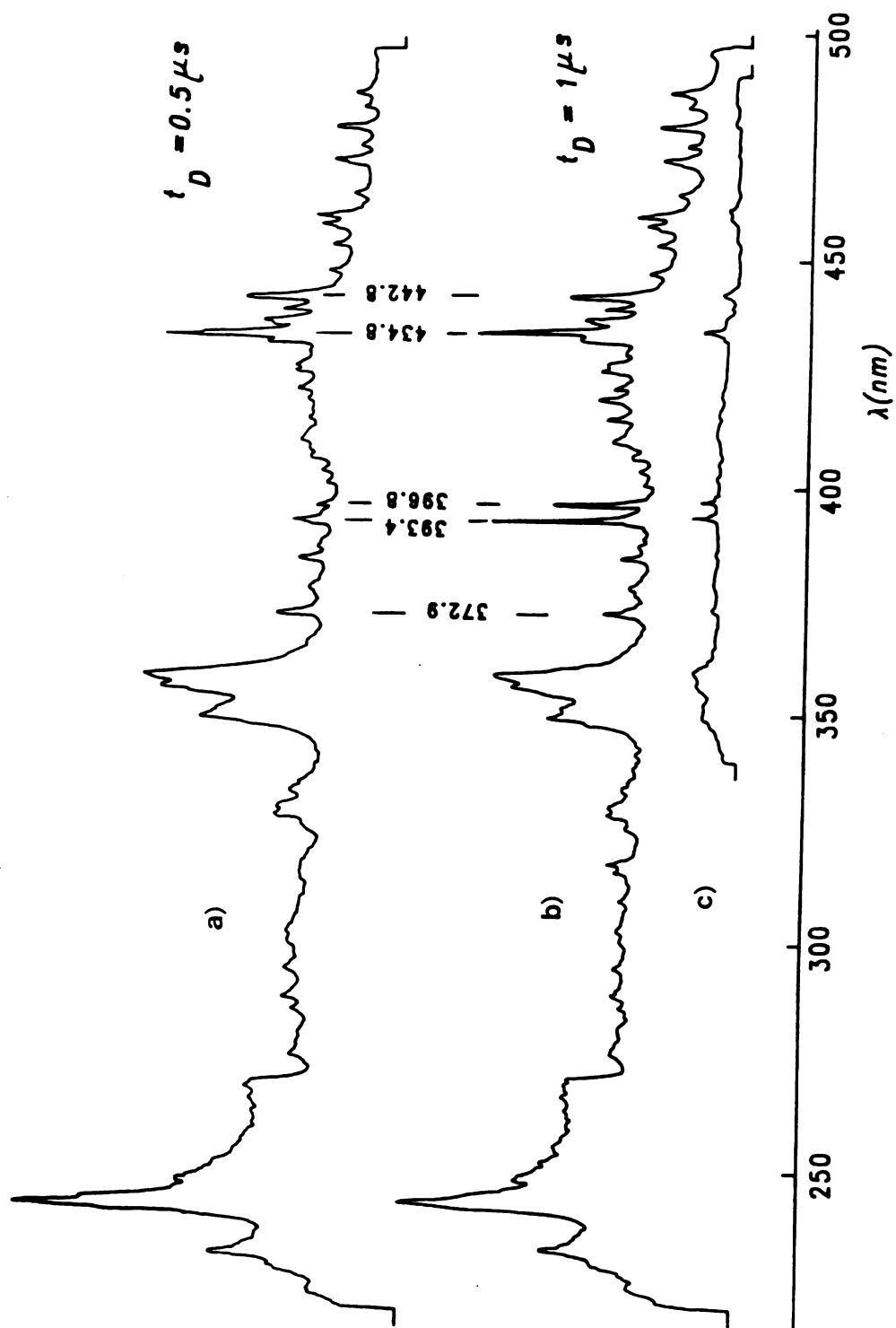


Figure 4-1

To identify regions of possible spectral interference, background emission spectra from 220 to 500 nm were observed at several delay times for argon and air (carrier gases used) plasmas. Representative spectra are shown in Figures 4-1, 4-2 and 4-3.

In general, shortly after plasma initiation, the dominant radiation is an optical continuum, resulting from bremsstrahlung and radiative recombination, mixed with ionic lines. Between 0.1 and 1 μ s, both of these contributions decay, leaving emission lines from neutral atoms which are seen out to 20 μ s or longer. At intermediate and late times ($> 5 \mu$ s) molecular features are also present (66). With time-resolved detection of the spark radiation, an observation period is selected when the continuum is reduced in intensity (but never zero) and the spectral interferences resulting from ionic lines are eliminated, while the neutral lines remain intense. Long-lived ion lines can also be used for analysis, particularly for elements such as calcium with strong ionic emission. Normally, ion lines are observed at early times $< 1 \mu$ s.

The most obvious feature in the background spectra is the continuum radiation observed. Continuum emission in a decaying plasma can arise from radiative recombination (free-bound transitions), or bremsstrahlung (free-free transitions). Radiative recombination occurs when a free electron combines with an ion into some bound state, with the excess energy being carried off by a photon. Bremsstrahlung, on the other hand, is a free-free transition in which a free electron, that is moving inside the electric field of an ion, emits a photon and the electron thereby decays to a lower energy state. The high energy requirements of bremsstrahlung radiation should be met immediately after the laser spark initiation, while the radiative recombination

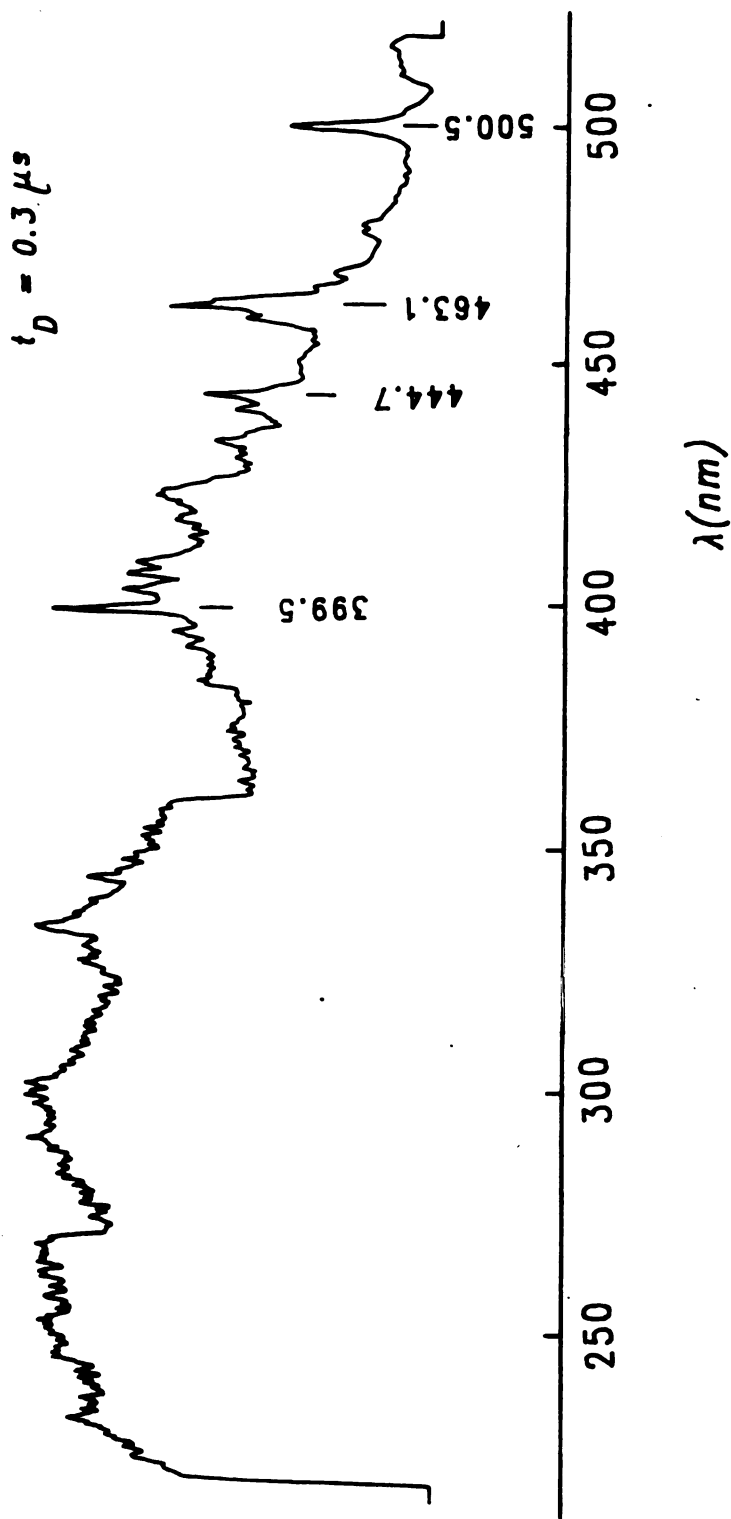


Figure 4-2. Air Background Emission as a function of Wavelength (plasma in the sample cell).

reactions should occur later in time, diminishing to acceptable levels within approximately 1 μ s. Prior to this time a high-intensity, noisy spectrum is obtained. Once radiative recombination has occurred, excited states of neutral atoms (e.g. Ar*, O*, N*) are formed. These atoms can then undergo radiative transitions to the ground state.

In Figure 4-1, spectra of an argon plasma are shown at different delay times. The spark was formed in the sample cell using the aerosol apparatus. A 500 ppm calcium solution was aspirated through the nebulizer. At 0.5 μ s after the trigger pulse, the continuum emission is very intense, and the prominent lines are argon ion lines (Figure 4-1a). At 1.0 μ s delay time, the continuum and the argon ion emission have decayed considerably, enabling the two calcium ionic lines (at 393.4 and 396.8 nm) to become distinguishable in the spectrum (Figure 4-1c). The same spectrum is shown in Figure 4-1b but with higher gain so that it can be seen better. Here, it is also obvious that argon atom lines in the region of 410 to 430 nm are very well revealed. At this point, it should be noted that ionic and atomic lines due to the carrier gas are much broader than those due to analytes.

In Figure 4-2, a spectrum of an air plasma is presented, 0.5 μ s after the initiation of the laser spark. The experimental configuration used was the same as the one mentioned in the previous paragraph. The only difference was that distilled water instead of calcium solution was aspirated through the nebulizer. The features of this spectrum are again the intense continuum emission and ionic nitrogen (mainly) and oxygen lines.

In Figure 4-3, spectra of an ambient air plasma are shown. This time the breakdown took place in the open air without using the

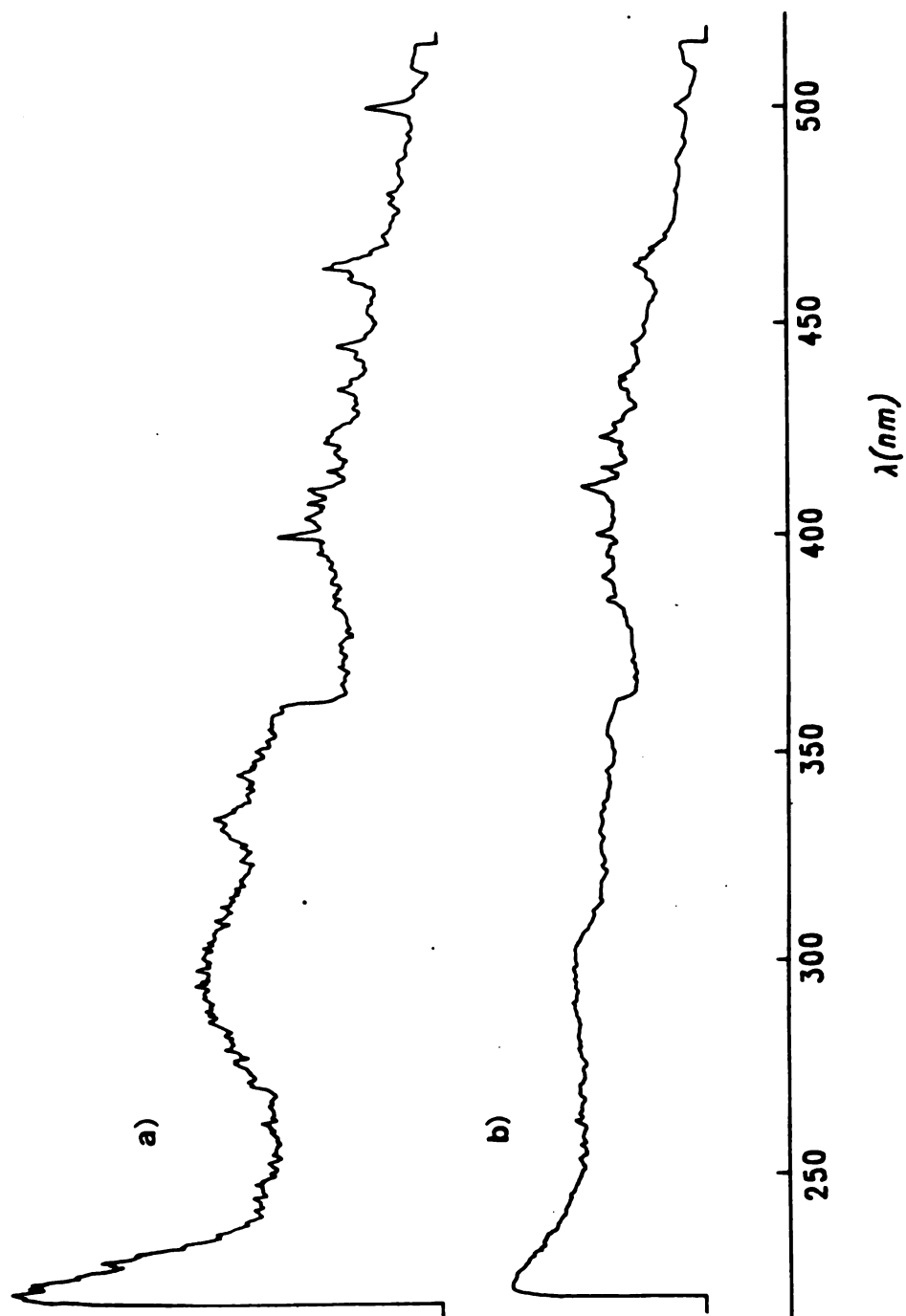


Figure 4-3. Ambient Air Background Emission as a function of Wavelength: a) Delay Time = 0.5 μ s, b) Delay Time = 1.0 μ s.

nebulizer-desolvation-sample cell system. The continuum, different in the UV spectral region (compared to that observed taken in the sample cell using compressed air from a tank), and nitrogen and oxygen ionic peaks are predominant at a delay time of 0.5 μ s. At 1 μ s after the trigger pulse, the continuum and ionic emission decrease in intensity, while atomic nitrogen and oxygen lines can be seen.

From the background spectra obtained we can conclude that under the same experimental conditions (same gain), background emission from an argon plasma is much higher than that from an air plasma. This comparison is illustrated in Figure 4-4, where the emission intensity is given in arbitrary units (a.u.).

B. Determination of the Plasma Temperature

If the source is not spatially resolved the resultant temperature is a population-averaged temperature as discussed by Boumans (109). This quantity is a parameter which describes the source but is not identical with the temperature of each layer of the source. Radziemski and coworkers (66) reported that in one case they spatially unfolded the plasma emission via Abel inversion and determined temperatures which were less than 5% higher than population averaged ones. They concluded that considering the uncertainties introduced by unfolding a small source of only approximate cylindrical symmetry, it was not clear that further effort on unfolding would have improved the temperature or electron density values. We have determined the population-averaged temperature.

Plasma temperatures are usually calculated from the ratios of neutral to neutral lines or ion to neutral lines, usually of the same

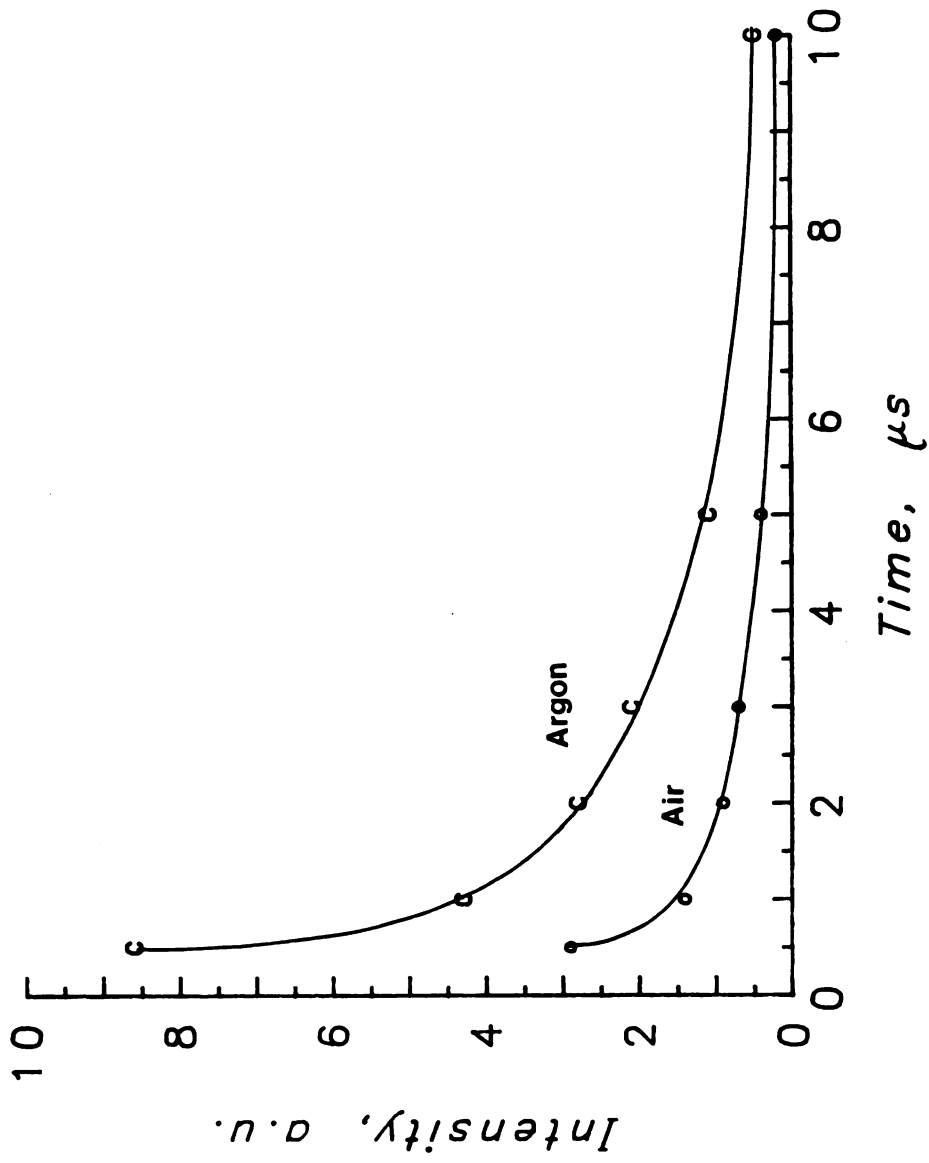


Figure 4-4. Comparison of Argon and Air Background Emission as a function of Time.

element (10). These intensities are combined with the Boltzmann equation or the Saha equation and the electron density to determine the excitation temperature and the ionization temperature, respectively. Agreement between ionization and excitation temperature is a necessary but not a sufficient condition for local thermodynamic equilibrium (the so called LTE condition).

a. Excitation Temperature Studies

Calculation of the excitation temperature requires the derivation of a relation between temperature and observed relative intensities.

The intensity I of a spectral line of wavelength λ emitted by a transition from an upper energy level E_2 to a lower energy level E_1 is given by:

$$I = C A_{2-1} N_2 / \lambda \quad (1)$$

where C is a proportionality constant, A_{2-1} is the transition probability (Einstein Coefficient), N_2 is the population of state 2 and λ is the central wavelength for an emission originating in an excited state of energy E_2 . For a Maxwell-Boltzmann distribution, N_2 can be expressed as

$$N_2 = N g_2 \exp(-E_2/kT) / Z \quad (2)$$

where N is the total number of atoms of the emitting species, g_2 is the statistical weight of state 2, E_2 is the energy of state 2 relative to the

ground state, k is the Boltzmann constant, T is the excitation temperature and Z is the partition function.

From Equations (1) and (2), we can derive:

$$I = C' g_2 A_{2-1} \exp(-E_2/kT) / \lambda \quad (3)$$

where $C' = C N / Z$. For determination of the excitation temperature, Equation (3) can be expressed in a more convenient form:

$$\log (I \lambda / g_2 A_{2-1}) = \log C' - E_2 / 2.303 k T \quad (4)$$

Equation (4) implies that a plot of the left hand side of the equation vs. E_2 results in a straight line with a slope which is inversely proportional to the temperature. When E_2 is expressed in cm^{-1} , the excitation temperature is given by:

$$T = -h c / 2.303 k (\text{slope}) \quad (5)$$

where h is Planck's constant and c is the speed of light.

Reif and coworkers (110) have shown the validity of the slope method for obtaining the excitation temperature. They stated that the technique yields correct values, if i) the wavelength response of the spectrometer is properly calibrated, ii) the emission intensity measurements are not affected by self-absorption and iii) accurate transition probabilities are available.

The first criterion can be met if the emission lines are observed over a small wavelength interval. For the second one, Knopps et al.

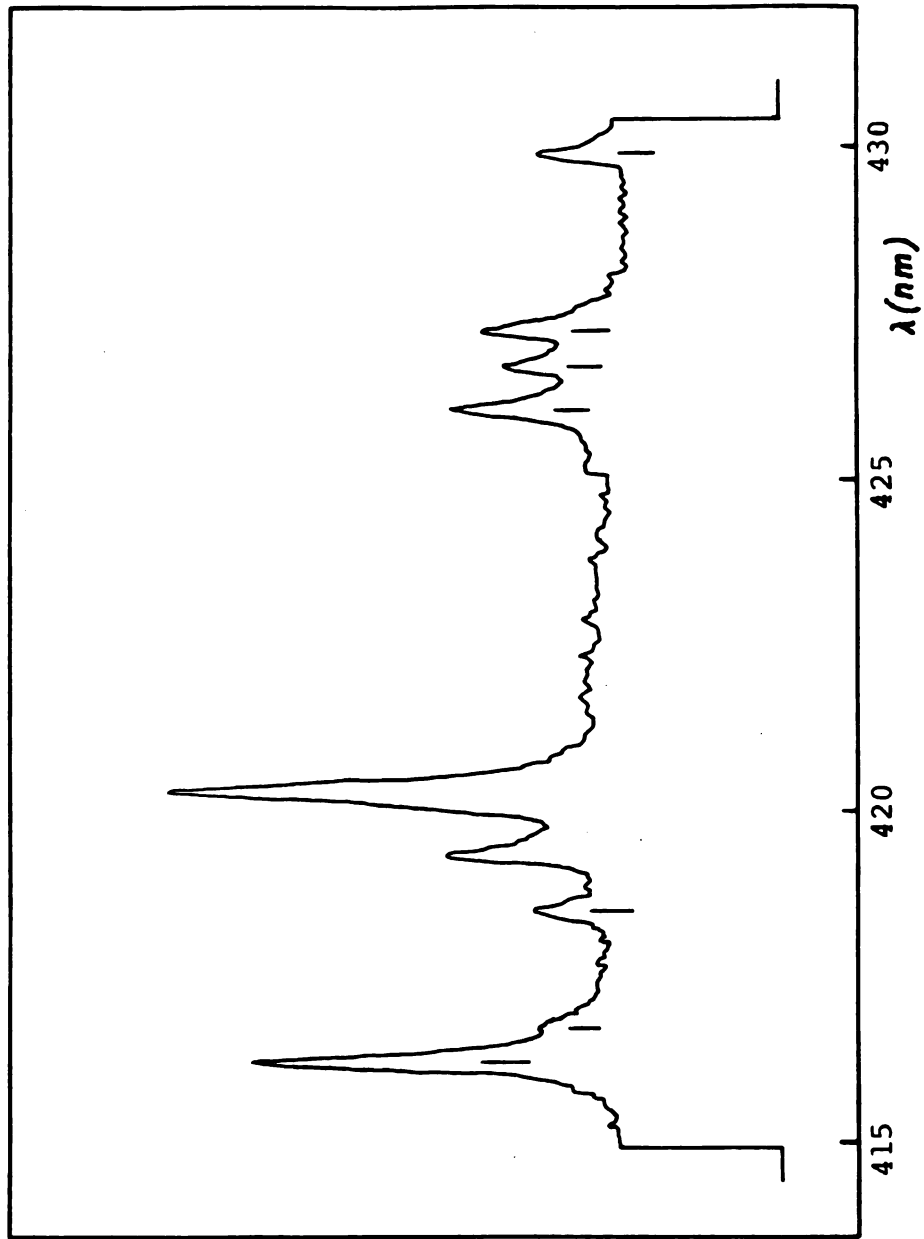


Figure 4-5. Spectrum of Neutral Argon Emission Lines at 3.0 μs

(111) and Tourin (112) have found that an unseeded argon plasma is transparent below 650 nm. Therefore, negligible self-absorption occurs below this wavelength. For the third requirement accurate transition probabilities were obtained from tables (113).

There are two major advantages of the slope technique: i) no light source other than the laser plasma is required and ii) there is no theoretical limit on the applicable temperature range.

In our experiments, we determined the excitation temperature of the plasma, created in an argon atmosphere in the sample cell, using the LIBS apparatus for aerosols. Water was aspirated through the nebulizer. A series of seven neutral argon emission lines, located between 415 and 430 nm, were chosen for this study. This spectral range is shown in Figure 4-5. A complete sequence of spectra of this region at different delay times is included in Appendix A, to show clearly the elimination of the continuum and argon ion lines at late times and the behavior of long lived argon atomic lines. The transition characteristics associated with the lines of interest, were obtained from tables (113) and are presented in Table 4-1. A monochromator slit width of 30 μm and a scan rate of 0.02 nm/s were used. The energy of the laser beam was 95 mJ/pulse. Spectra were obtained for times of 0.5, 1.0, 2.0, 3.0, 5.0, 10.0, and 25.0 μs after the creation of the plasma. Three such spectra were gathered at each particular time. After background subtraction, the peak intensities were measured and averaged from each set of the three spectra. The log of this average was calculated in the proper form and plots similar to Figure 4-6 were generated. The excitation temperatures were determined from the slope of each curve. Estimates of the error in the measurements were derived from the

Table 4-1. Argon Line Emission Parameters^a

λ (nm)	E_2 (cm ⁻¹)	g_2	A_{2-1} (10 ⁸ s ⁻¹)
415.9	117184	5	0.01450
416.4	117151	3	0.00295
418.2	118460	3	0.00580
425.9	118871	1	0.04150
426.6	117184	5	0.00333
427.2	117151	3	0.00840
430.0	116999	5	0.00394

a: See Reference 5.

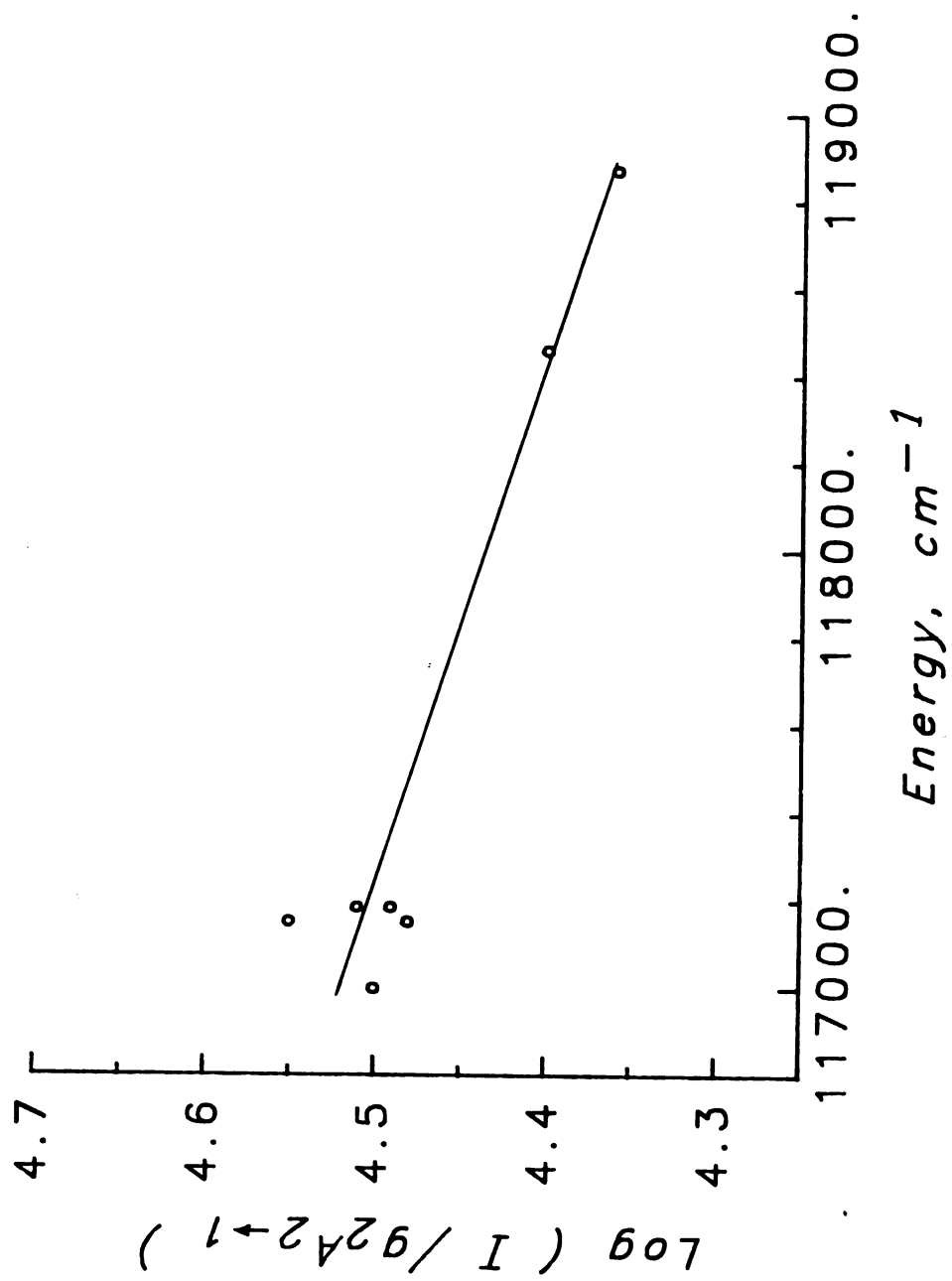


Figure 4-6. Excitation Temperature Slope Plot at 3.0 μs

uncertainty of the average and in the listed transition probabilities. The temperatures obtained, together with the relative standard deviation (RSD) of the measurements are listed in Table 4-2 and shown graphically in Figure 4-7. The temperature at 0.5 μ s is not reported because it has a very high RSD; this is caused by random errors associated with the high noise levels present in that spectral set.

The temperature values found are close to results published by other authors (66) for an air plasma, even though higher temperatures were expected for an argon plasma. This may be due to the continuous aspiration of water into the heated chamber. Water vapor reaching the sample cell because of desolvation inefficiency may be responsible for lowering the plasma temperature.

b. Electron Density Measurements

The dominant line-broadening mechanism in dense plasmas is Stark broadening caused by the electric fields of charged species which surround the radiating atoms. Stark broadening has also been found to be the major contributor to spectral line widths for many species in the laser plasma, especially at early times. Pressure broadening by neutral perturbers in laser-induced breakdown (LIB) plasmas generally yields a detectable contribution only if the neutral particle density is greater than the charged particle density by a factor of 10^3 (66), which in the LIB plasma occurs after 10 μ s. Even though temperatures are higher at early times and pressure broadening due to neutrals is greater, the electron and ion concentrations are also higher. As a result, at all but late times the Stark broadening dominates. Doppler broadening is also insignificant in most cases compared to Stark broadening. In general,

Table 4-2. Argon Plasma Excitation Temperature

Time (μs)	Temperature (K)	% RSD
1.0	14500	15
2.0	13700	13
3.0	11800	10
5.0	11200	11
10.0	10000	10
15.0	9400	10
25.0	8900	12

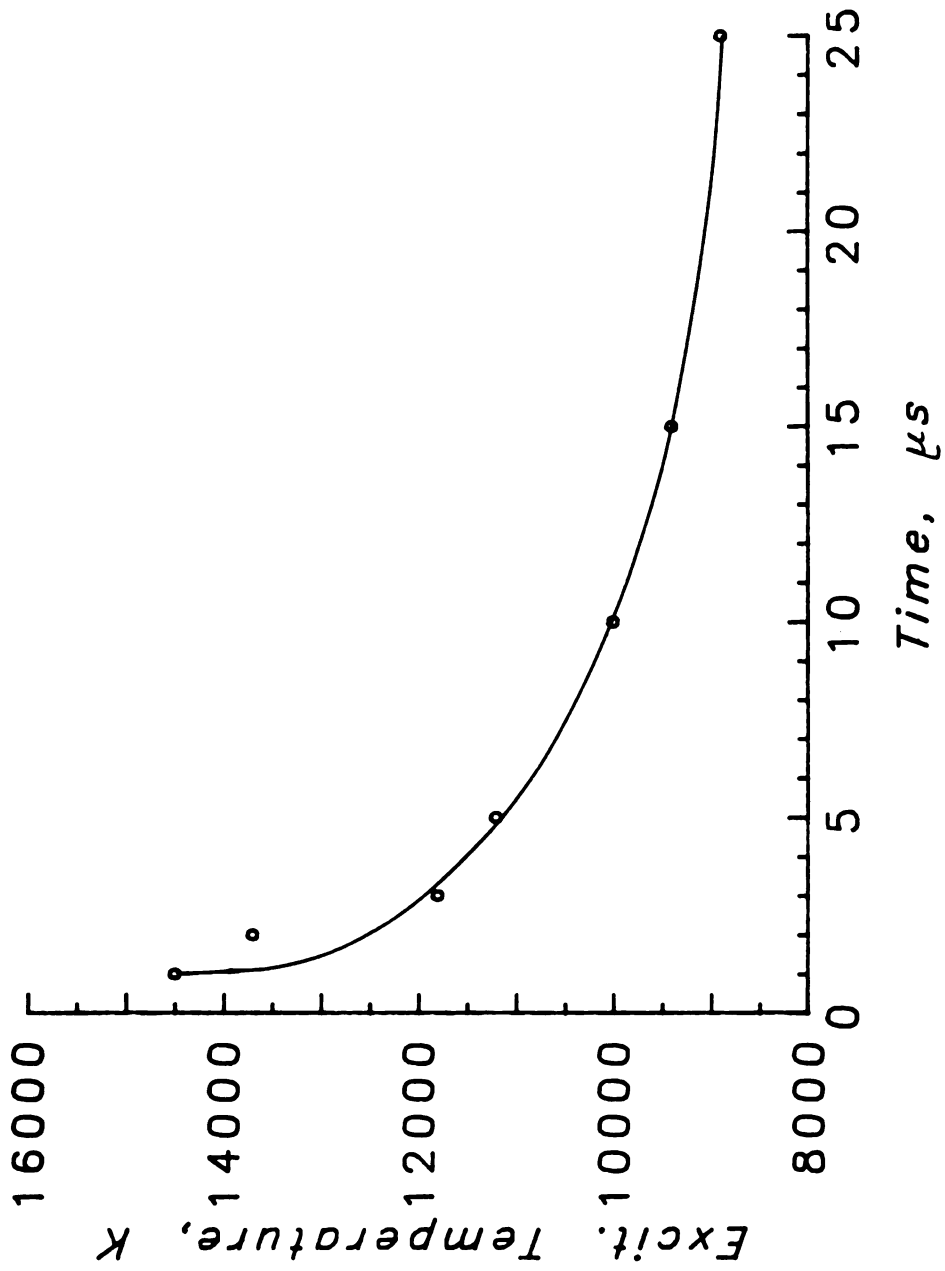


Figure 4-7. Excitation Temperature as a function of Time

electron densities are determined from the Stark widths of various lines using the theory developed by Griem (10,114). Because hydrogen is subject to a linear Stark effect, the hydrogen lines undergo pronounced broadening, on the order of a few nanometers, which depends almost entirely on the charged particle density. The hydrogen Balmer lines are H_ϵ (at 397.0 nm), H_δ (at 410.2 nm), H_γ (at 434.0 nm), H_β (at 486.1 nm) and H_α (at 656.3 nm).

H_β is useful as a density standard for electron densities (N_e) from about 10^{16} cm^{-3} to $3 \times 10^{17} \text{ cm}^{-3}$. Using H_γ at lower densities is of no particular advantage, although it can be useful up to $N_e = 10^{17} \text{ cm}^{-3}$, e.g., in cases where H_β is perturbed by impurity lines. However, use of H_δ enables measurements down to $N_e = 10^{14} \text{ cm}^{-3}$ and of H_α up to $N_e = 10^{19} \text{ cm}^{-3}$. In contrast to H_β , systematic errors in electron densities from the profiles of these lines may not be negligible, as remaining discrepancies between experiment and theory correspond to about 15% uncertainty in the electron density.

According to the Kolb and Griem theory of Stark broadening (115), the Stark width of a hydrogen line, when raised to the 3/2 power, is proportional to the electron density. The relationship is:

$$N_e = C(N_e, T) \Delta\lambda^{2/3} \quad (6)$$

where N_e is the electron density in cm^{-3} , $C(N_e, T)$ is a proportionality coefficient slightly dependent on the electron density and temperature and $\Delta\lambda$ is the width of the Stark broadened line.

In our work, experimentally obtained Stark-broadened emission profiles of the H_α line at 656.3 nm were used to measure the electron density.

The apparatus used for these measurements was the one designed for aerosols (nebulizer-heated chamber/condenser-sample cell configuration) with argon as the carrier gas and distilled water aspirated continuously. The source of hydrogen was the small amount of water vapor that escaped from the desolvation process and reached the sample cell. As mentioned above, the value of the proportionality coefficient is weakly dependent on temperature and electron density, both of which were not known. Because of that, coefficients tabulated by Griem (10) for electron-density determinations from (full) half-widths of Stark-broadened hydrogen lines for various reasonable temperatures and densities were averaged, and this was used to calculate N_e . The half widths, $\Delta\lambda$, were obtained by scanning slowly over the H_α line and monitoring the emission intensity on a strip chart recorder. The H_α line was used because on the one hand, it appeared very clearly in the spectra and on the other hand very high electron densities were expected, where this line is most suitable. To increase precision, three determinations were made of the H_α emission profile. Table 4-3 lists the results obtained for N_e at various times and the percent relative standard deviations. Figure 4-8 shows the Stark broadened H_α line at 656.3 nm, 4.0 μ s after the creation of the plasma. The energy of the laser beam was about 95 mJ/pulse and the slit width of the monochromator was 30 μ m. The dependence of electron density on time is shown graphically in Figure 4-9.

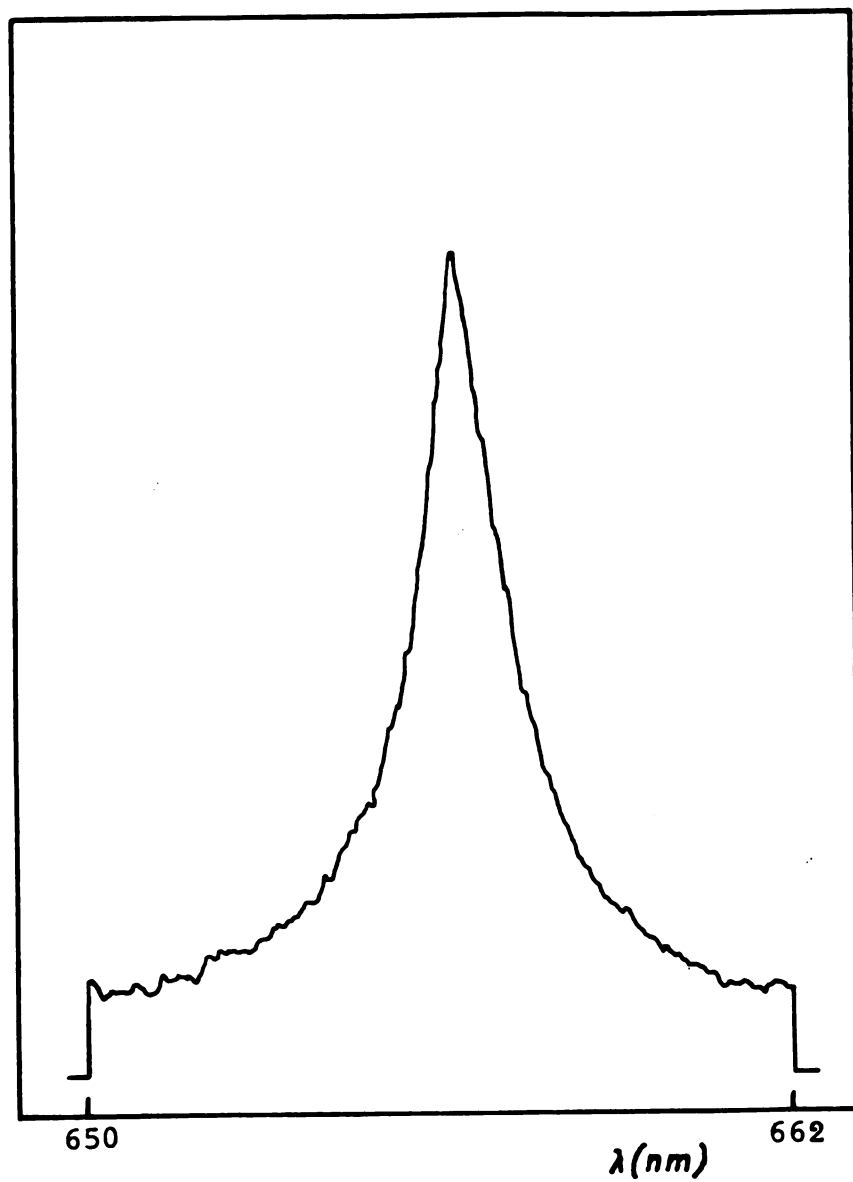


Figure 4-8. Stark Broadened H_α Line Profile at 4.0 μs

Table 4-3. Electron Densities determined from Stark profiles of the H _{α} emission

Time (μ s)	$\Delta\lambda(\text{\AA})$	$N_e \times 10^{-17} \text{ (cm}^{-3}\text{)}$	% RSD
0.5	32.4	6.4	25
1.0	26.4	5.4	20
2.0	20.4	4.2	10
3.0	18.0	3.4	10
5.0	14.4	2.5	12
10.0	10.8	1.3	15

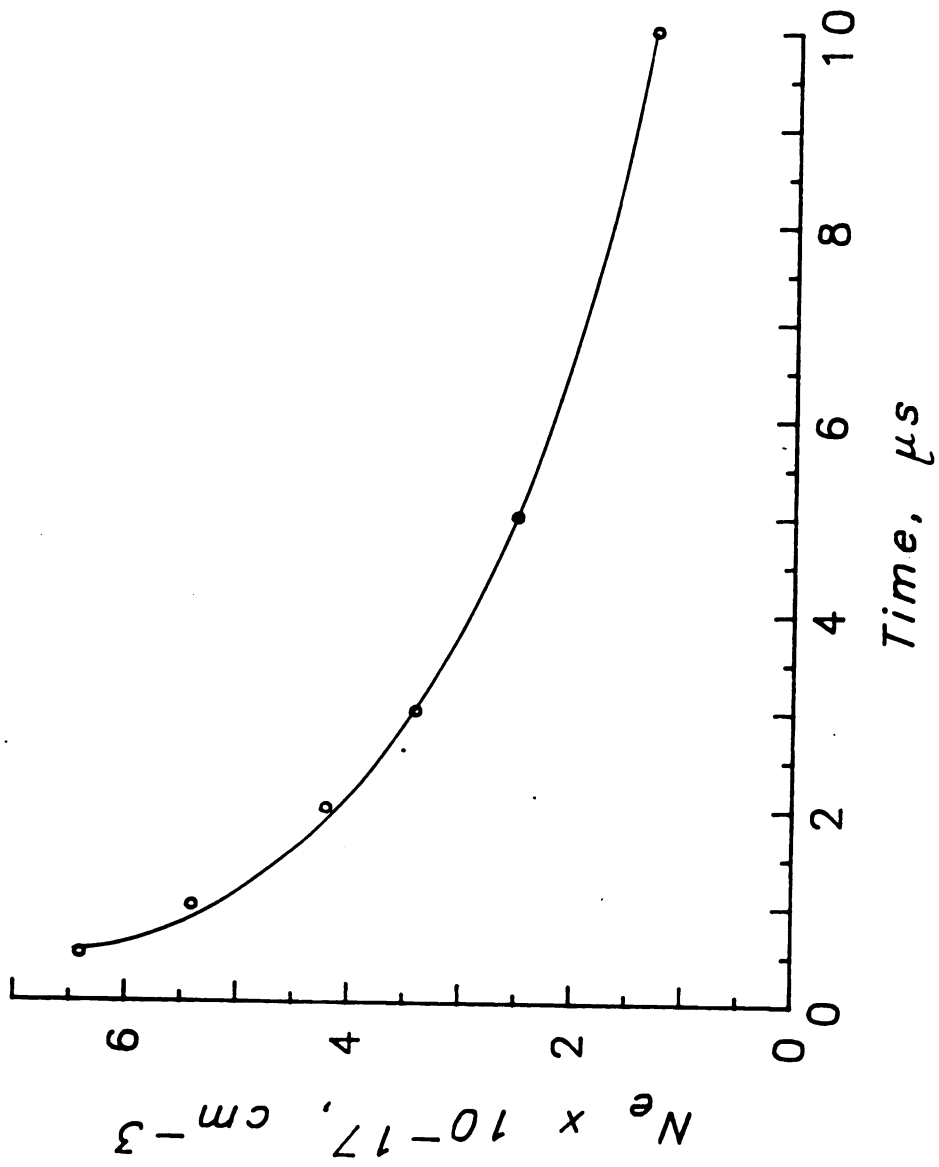


Figure 4-9. Electron Density as a function of Time

The values obtained for N_e fall into the same range as those reported by other authors (66).

c. Ionization Temperature Studies

For the determination of the ionization temperature of the laser plasma, the intensities of the Ca ionic line (CaII at 393.3 nm) and the Ca atomic line (CaI at 422.7 nm) were obtained while a 500 ppm calcium solution was aspirated into the nebulization/desolvation system. Argon was used as the carrier gas. Figure 4-10 shows the decay of the Ca atomic and ionic emission lines as a function of time. It is very surprising that the calcium ionic peak, slowly decaying, is still more intense than the atomic peak of the same element even at 25 μ s! Considering the general trend of the ionic lines to decay early in time as the electron concentration in the spark decays, this is an unusual behavior. However, similar observations have been reported in the literature (65,66) for the unresolved BeII doublet at 313.1 nm. The authors stated that this doublet could have been seen more than 20 μ s after plasma initiation, which was longer than the strong BeI line at 234.8 nm could have been observed (10 μ s). They even tried to explain and support this behavior theoretically.

The Saha equation describes the relationship between the degree of ionization, the ionization temperature and the electron pressure (P_e). Using Boumans' notation (5), the intensity ratio of an ion-atom pair is governed by the temperature (T) according to the equation:

$$\log (I^+/I) = -\log P_e + \log (g^+ A_{2-1}^+ \lambda / g A_{2-1} \lambda^+) \\ -5040 (V_{ij} + V_{q^+} - V_q) / T + 5/2 \log T - 6.18 \quad (7)$$

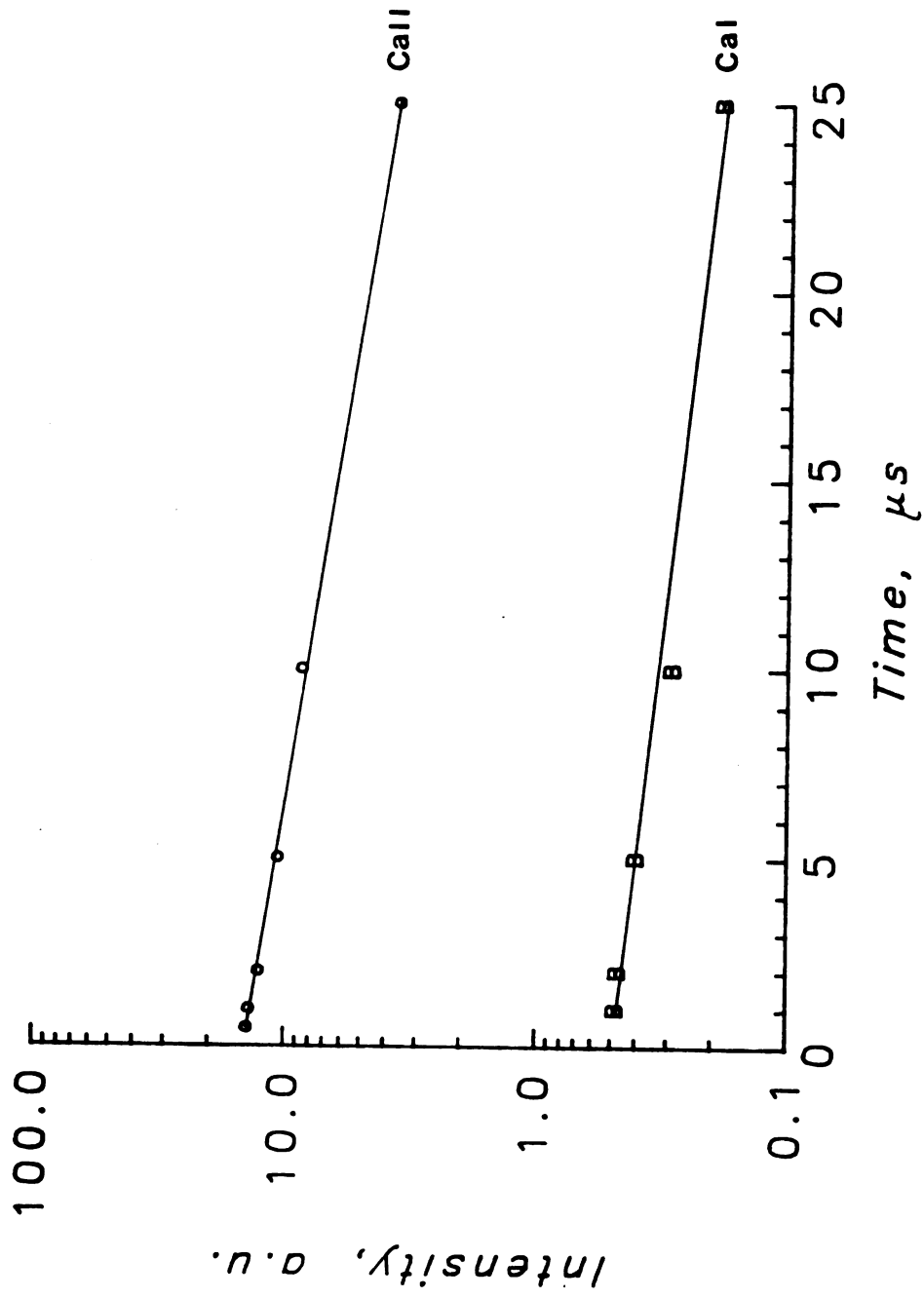


Figure 4-10. Calcium Emission as a function of Time

where the superscript "+" refers to the ions, V_e is the excitation level from which emission occurs, V_{ij} is the apparent ionization potential for the atom (and therefore contains the partition functions), and all other terms have been previously defined. According to Boumans, the apparent ionization potential for calcium is 5.83 eV. Using tables compiled by Corliss and Bozman (116), the gA values for the atom and ion lines were found to be 1.0 and 0.91 respectively. The excited state energy levels were obtained from spectral tables (117) and were 2.93 eV and 3.15 eV for the atom and ion, respectively. The electron pressure is related to the electron density by:

$$P_e = N_e T / 7.34 \times 10^{21} \quad (8)$$

With the electron densities calculated in the previous section and the intensity ratio of the Ca ionic and atomic lines, Equations (7) and (8) were solved on a minicomputer recursively for T at each time. The results obtained, averaged for three sets of intensity ratio pairs are listed in Table 4-4 and presented graphically in Figure 4-11. The ionization temperature at 0.5 μ s is not reported because of the high %RSD associated with it (40%), caused by high noise level present in the spectra.

We can point out that for delay times equal to or greater than 1 μ s, the excitation temperature agrees with the ionization temperature to better than 4%. Thus, the plasma behaves as if it were in, or very close to, local thermodynamic equilibrium at times at least equal to or greater than 1 μ s. Other authors (66) have reached the same conclusion

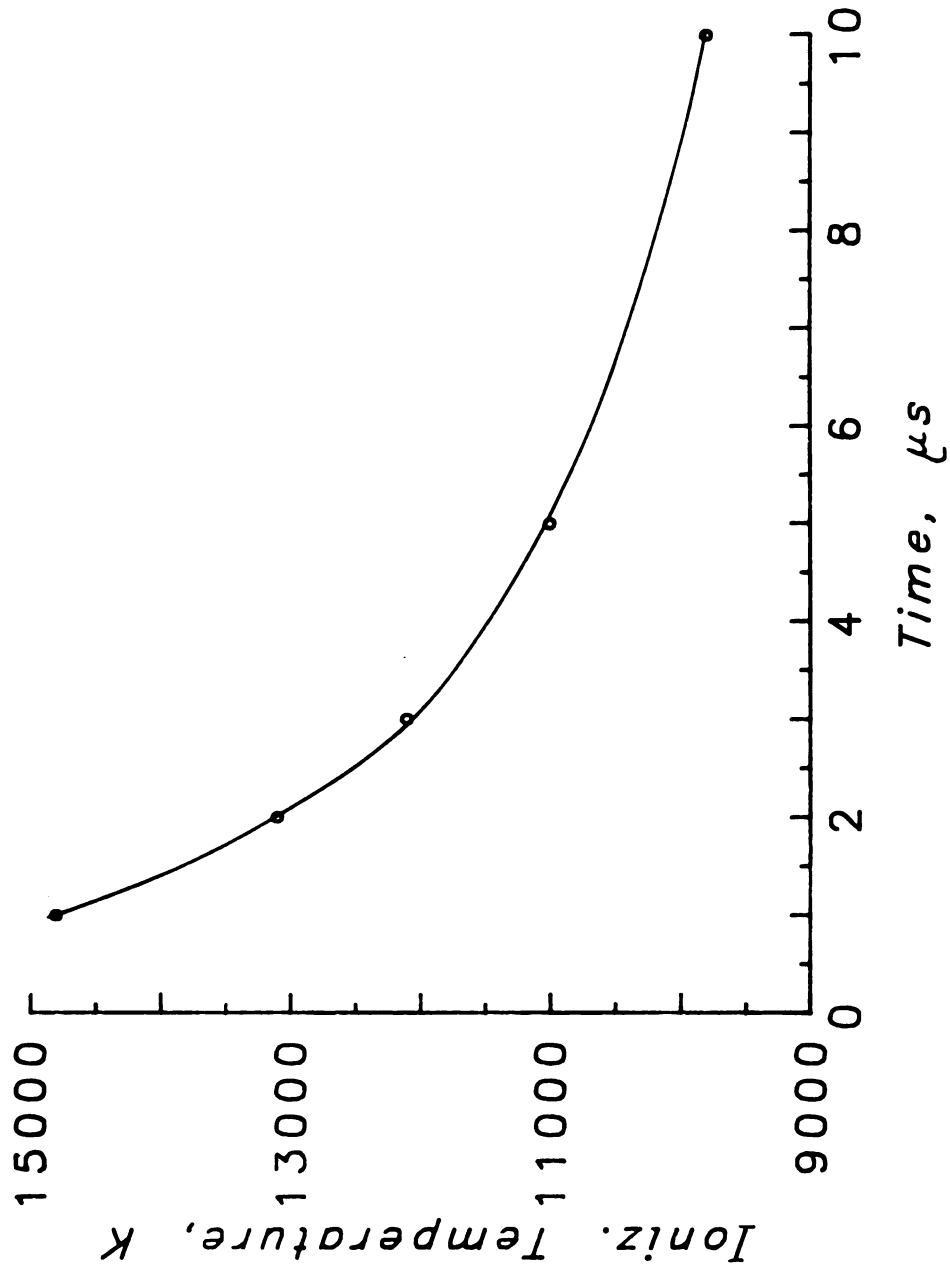


Figure 4-11. Ionization Temperature as a function of Time

Table 4-4. Argon Plasma Ionization Temperature

Time (μ s)	Temperature (K)	%RSD
1.0	14800	20
2.0	13100	13
3.0	12100	11
5.0	11000	10
10.0	9800	10

from experimental and/or calculated temperature values under conditions that were similar to those of the plasma under discussion. Their temperatures calculated from a LTE model agreed with experimental values although the computed values were higher at early times and decayed more rapidly.

CHAPTER V

APPLICATION OF LIBS TO SOLUTION SAMPLES

After characterizing the laser plasma, the system was applied to spectrochemical analysis of solution samples. Extensive qualitative work was done with several elements, based on time-resolved spectroscopic methods. During these studies many experimental parameters were optimized, which helped us improve our results and enabled us to obtain good quantitative information with the LIBS technique.

As mentioned in Chapters I and III, two different sample introduction approaches were used for the analysis of solutions. In the first approach, solutions were converted to dry aerosols by a nebulization / desolvation apparatus; in the second approach the liquid samples were converted to liquid streams of isolated nanoliter droplets by an isolated droplet generator. The similarities and differences in the two methods are discussed in the following sections and more detailed discussion on the comparison is included in Chapter VII.

In this chapter the importance of the time-resolved spectroscopy is shown for both sample introduction systems. Experimental conditions used are presented. Attempts at optimizing different parameters are described. Signal-to-background, signal-to-noise ratio plots, calibration curves and detection limits are given as well.

A. Spectrochemical Analysis with Time-Resolved Spectroscopy

It is obvious, from Figure 4-1 and the discussion on the background emission in the previous chapter, that some form of time discrimination technique is necessary to minimize the contribution of the initial spark background to the analytical signal. However, the optimum position in time to begin integration of the emission was not known. By time-resolving the plasma radiation with the boxcar averager, we can choose observation times that maximize the ratio of atomic (or ionic) emission to background. Since the optimum time is somewhat dependent on the species, time-resolved spectra should be obtained for each element.

1. Analyte Emission Studies

Figures 5-1 and 5-2 show a typical sequence of time-resolved spectra of an analyte. In Figure 5-1, spectra near the ionic calcium line (at 393.4 nm) are presented at several delay times. In Figure 5-2 the sodium "doublet" (at 589.0 and 589.6 nm) is shown at different times after the initiation of the laser plasma. These results were obtained using the aerosol apparatus with argon as a carrier gas and 200 ppm solutions of calcium and sodium, respectively. Spectra of the same elements and concentrations produced using the isolated droplet generator are included in Appendix B (Figures B1 and B2) for comparison. The main features are the same. High background emission and noise prevail at early times, preventing us from observing the lines of interest. At later times, analyte ionic or atomic lines are easy to see and identify. A noticeable difference between Figure 5-1 and B1 is the presence of a broad emission line, observed at 392.8 nm at times $< 1 \mu s$

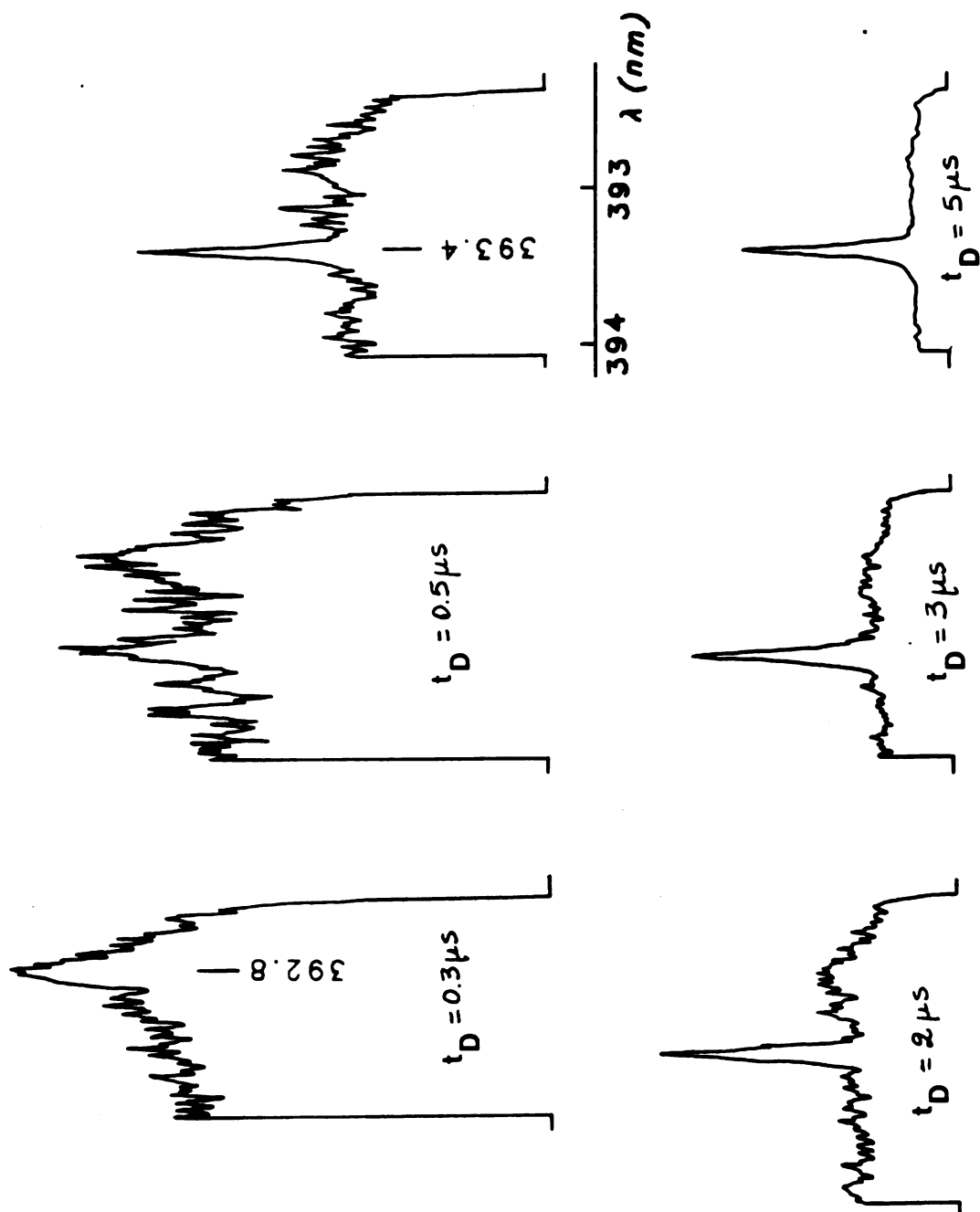


Figure 5-1. Time-Resolved Spectra of the Calcium ionic line (at 393.4 nm) obtained with the aerosol apparatus.

in Figure 5-1, which is not seen in Figure B1. This was identified as an argon ion line. The fact that experiments with the isolated droplet generator took place in ambient air while an argon environment was used for the nebulizer / desolvation / sample chamber system explains this difference. It is also obvious from Figure 5-1 that ion emission due to the carrier gas is broad and decays much faster than the sharp ion lines due to analytes. Another observation from comparison of Figures 5-1 and 5-2 is that analyte ionic lines decay faster than atomic ones. The same trend was found to be true for several lines and it can be noticed easily when both ion and atom emission is intense. At this point, we should mention that the behavior of the calcium ion and sodium atom emission from LIBS may be representative for ions and atoms, respectively, although we have to bear in mind that pronounced deviations might be observed (e.g., CaII vs. CaI and BeII vs. BeI).

Since time-resolution methods are very important for the LIBS technique, the time profiles of calcium ionic and atomic emission and the sodium doublet emission were observed. These experiments were performed using the nebulizer / desolvation / sample cell system with 500 ppm calcium and sodium solutions, respectively. Signals representing the emission were sent to a LeCroy Transient Digitizer (LeCroy Model 8013A) and then to a computer for data processing. The lines of interest were "scanned" taking a time profile at each wavelength. Three-dimensional (intensity vs. time vs. wavelength) plots are shown in Figures 5-3 and 5-4 for the ionic calcium lines. The wavelengths have a positive offset of about 0.1 nm according to the calibration of the monochromator. A "sample" of "raw" data for the production of the above plots is given in Appendix B (Figure B3). In

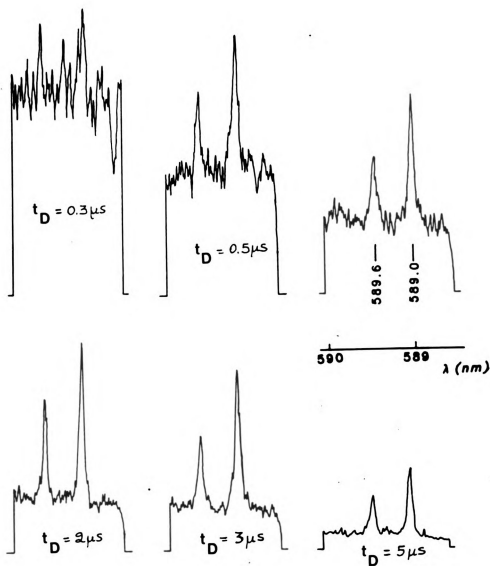


Figure 5-2. Time-Resolved Spectra of the Sodium Doublet (at 589.0 and 589.6 nm) obtained with the aerosol apparatus.

Figure B3, each point of the curves is the average of 300 data points. Time profiles were taken at the following wavelengths: a) 393.4 nm (ion line), b) 393.0 nm, and c) 394.2 nm (background emission). We can clearly see the difference between b) and c) curves due to the fast decaying ionic argon emission. All these features above are very profound in the 3-dimensional plots. The initial "spike" is the huge continuum emission that decays in less than 1 μ s. Similar time profiles and 3-dimensional plots were obtained for calcium and sodium atomic lines (Figures B4 and B5). In the calcium atomic line time profile (Figure B4), it seems that the continuum emission decays later in time (compared to that obtained for the calcium ion line). In fact this is an instrumental artifact which is observed at high amplifier gains. In general, the results obtained with the LeCroy transient digitizer agree very well with the time-resolved spectra obtained by the boxcar integrator.

Among the elements studied were: Lithium (LiI at 670.8 nm), Magnesium (MgII at 279.6 nm), Manganese (MnII at 257.6 nm), Aluminum (AlI at 396.2 nm), Potassium (KI at 766.5 nm), Cobalt (CoI at 345.4 nm), Chromium (CrI at 357.9, 359.4, 360.5, 425.4, 427.5, and 429.0 nm), Molybdenum (MoI at 379.8, 386.4, and 390.3 nm) as well as Calcium (CaI at 422.7 and CaII at 393.4 nm) and Sodium (NaI at 5890.0 and 589.6 nm). The optimum delay time for ionic emission was between 2-4 μ s and for atomic emission was between 3-7 μ s. The most suitable time was selected based on signal-to-background and signal-to-noise ratios presented in the next section.

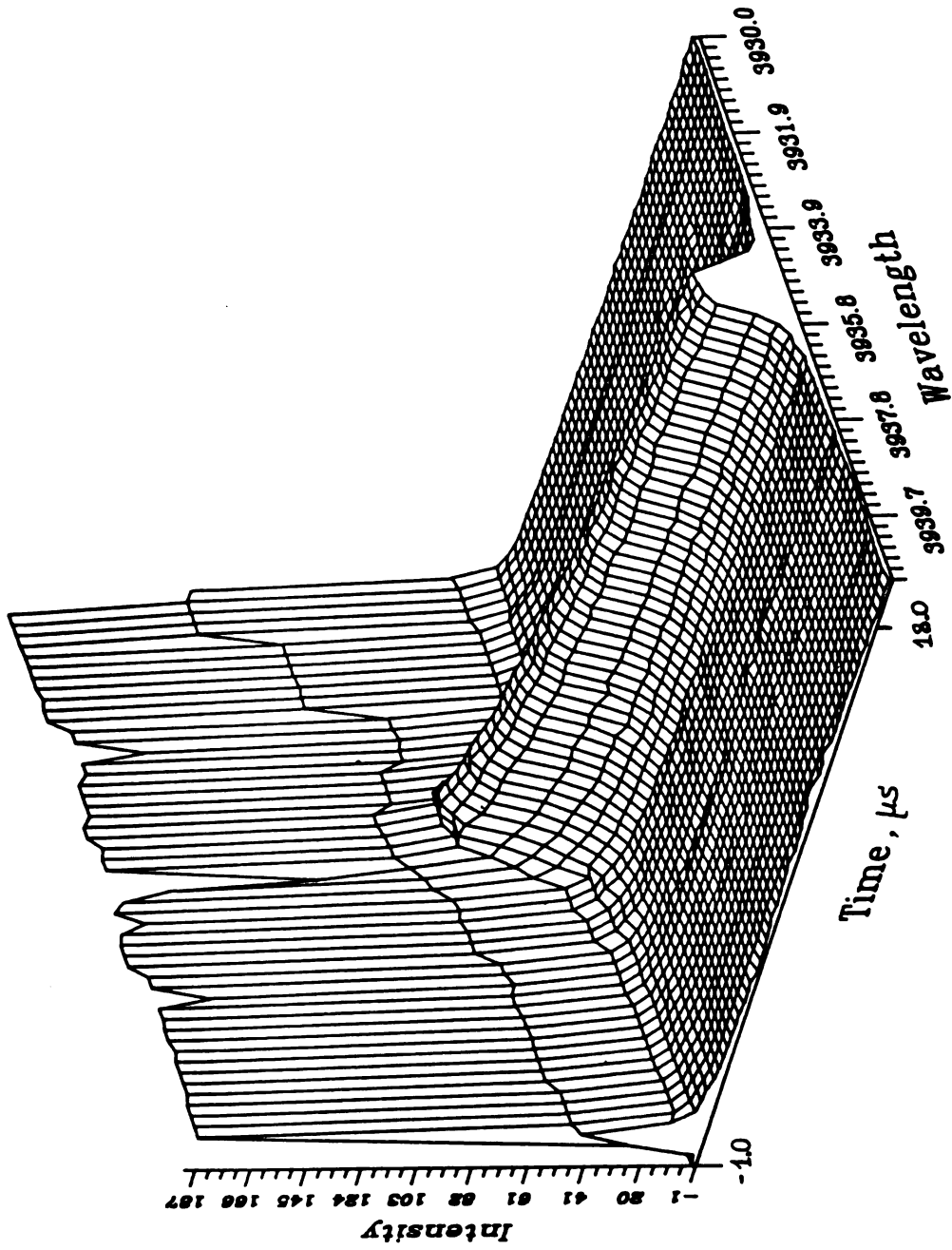


Figure 5-3. Three-Dimensional Plot (Intensity vs. Time vs. Wavelength) of the Calcium ionic line (at 393.4 nm) obtained with the aerosol apparatus.

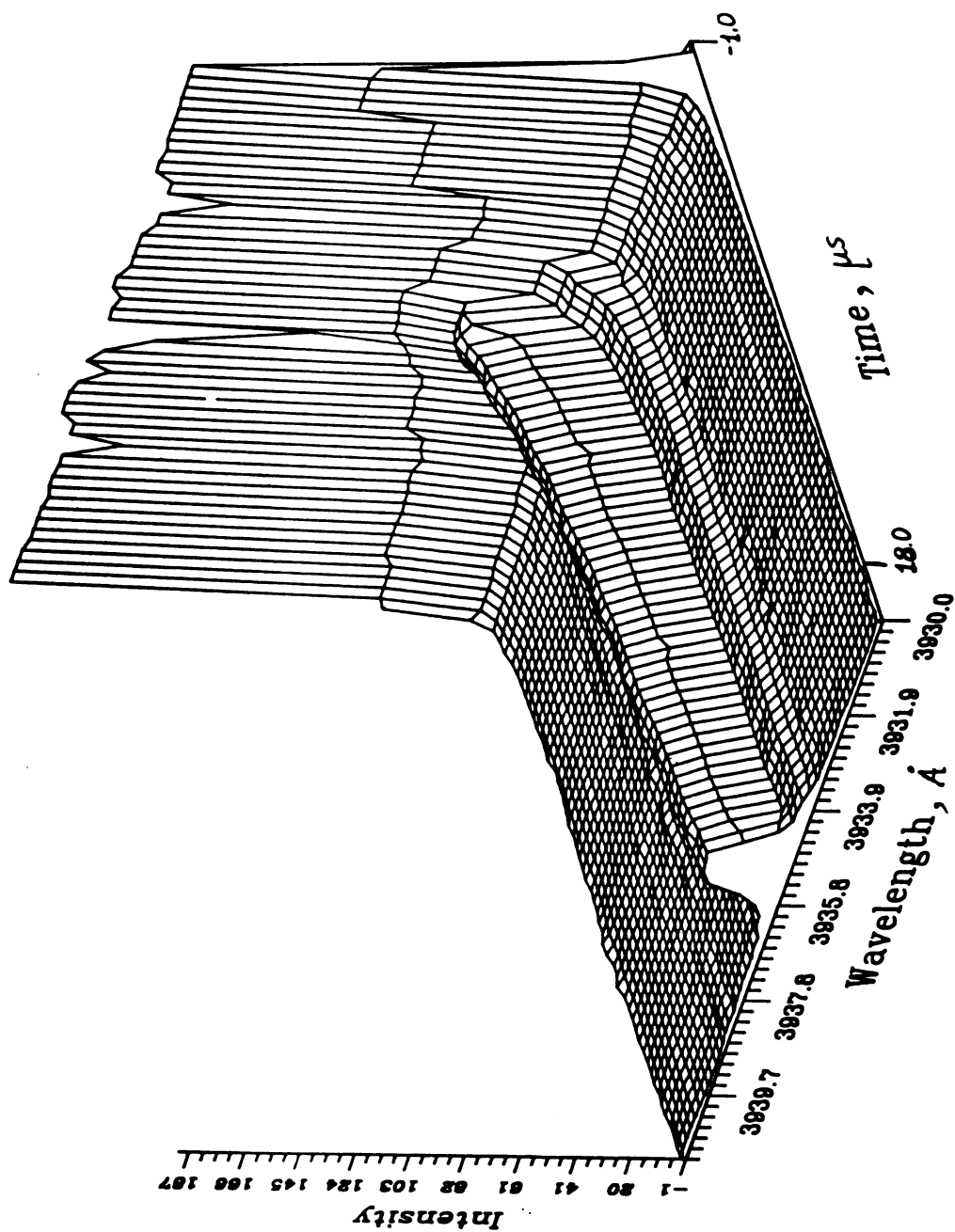


Figure 5-4. Three-Dimensional Plot (Intensity vs. Time vs. Wavelength) of the Calcium ionic line (at 393.4 nm), showing the argon ion line as well. The aerosol apparatus was used.

2. Analyte Signal-to-Background and Signal-to-Noise Studies.

Since our ultimate goal was to explore the possibility of using LIBS as an analytical method, the optimization of the signal-to-background and signal-to-noise ratios (SBR and SNR, respectively) was necessary. These ratios were determined from the time-resolved spectra of each analyte. SBRs and SNRs at different delay times are listed in Tables 5-1 and 5-2 for the calcium ion and sodium atom emission. They are also presented graphically in Figures 5-5 and 5-6, respectively.

The signal was calculated as the difference between the total emission and the background. The noise was estimated in two ways: by measuring the rms noise on the signal (after long averaging) and by measuring the noise on the background. The rms noise was taken as 1/5 of the peak-to-peak noise from the recorder tracing. This is a statistically valid way to estimate noise (118). For normally distributed noise, 99.7% of the instantaneous deviations from the mean are within ± 2.5 standard deviations. Thus, one standard deviation (the rms noise) represents 1/5 of the peak-to-peak excursions. Comparison of the background noise to the noise present in the analyte signal shows they are comparable at low concentrations, indicating that analyte-associated noise is negligible. Flicker noise, which is directly proportional to the magnitude of the signal, dominates at high concentrations. The main source of background noise was not identified. Note that even though the signal, background and noise levels are strong functions of delay time between plasma initiation and observation, the signal-to-noise ratio is a rather slowly varying function with time.

Table 5-1. Signal-to-Background and Signal-to-Noise Ratios for the calcium ionic line at 393.4 nm.

Time, μ s	SBR	SNR
0.5	17	50
1.0	34	68
2.0	126	81
3.0	252	105
5.0	212	88
10.0	172	42

Table 5-2. Signal-to-Background and Signal-to-Noise Ratios for the sodium atomic line at 589.0 nm.

Time, μs	SBR	SNR
0.5	1.9	62
1.0	4.3	95
2.0	9.0	116
5.0	18.0	118
10.0	17.0	100

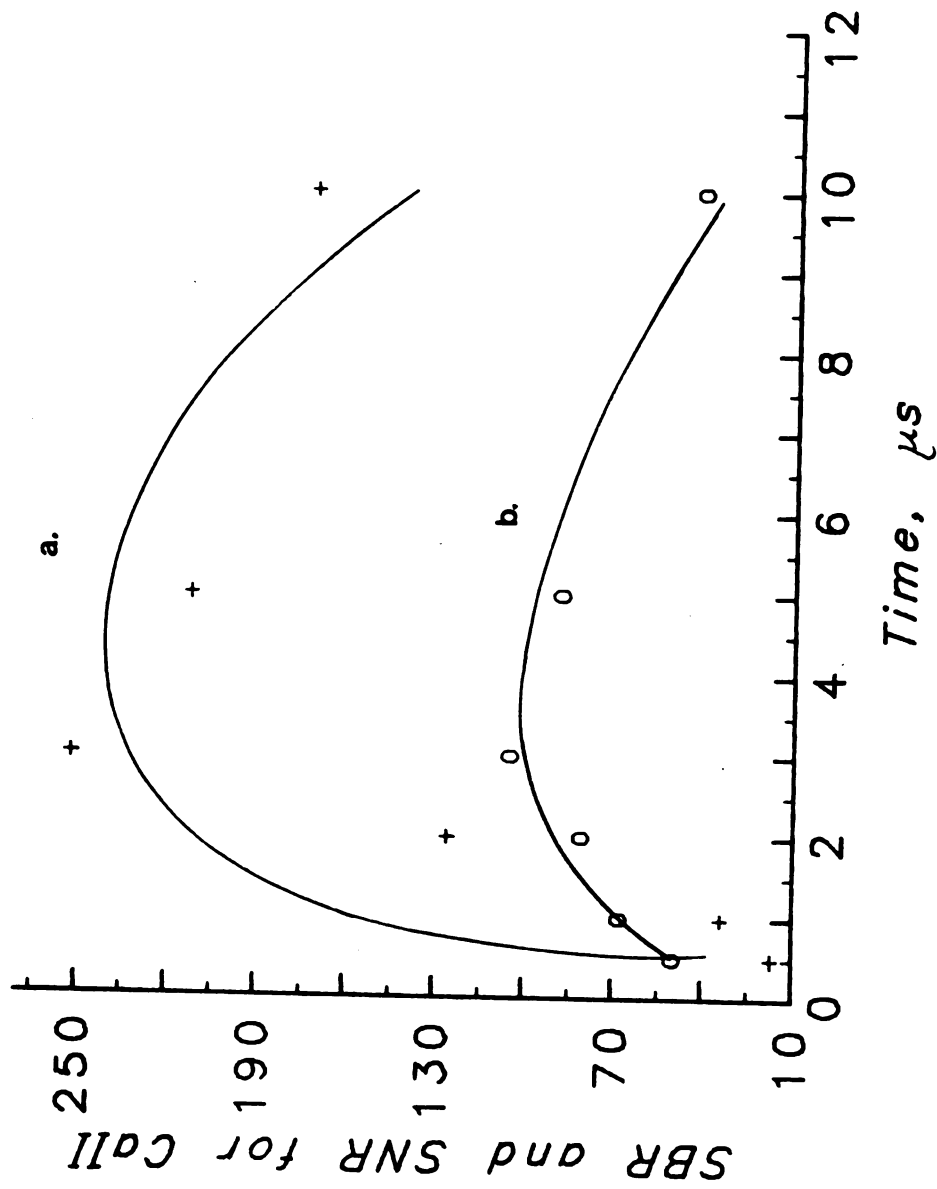


Figure 5-5. a) Signal-to-Background Ratio (SBR) vs. Time,
 b) Signal-to-Noise Ratio (SNR) vs. Time for the Calcium ion
 line (at 393.4 nm).

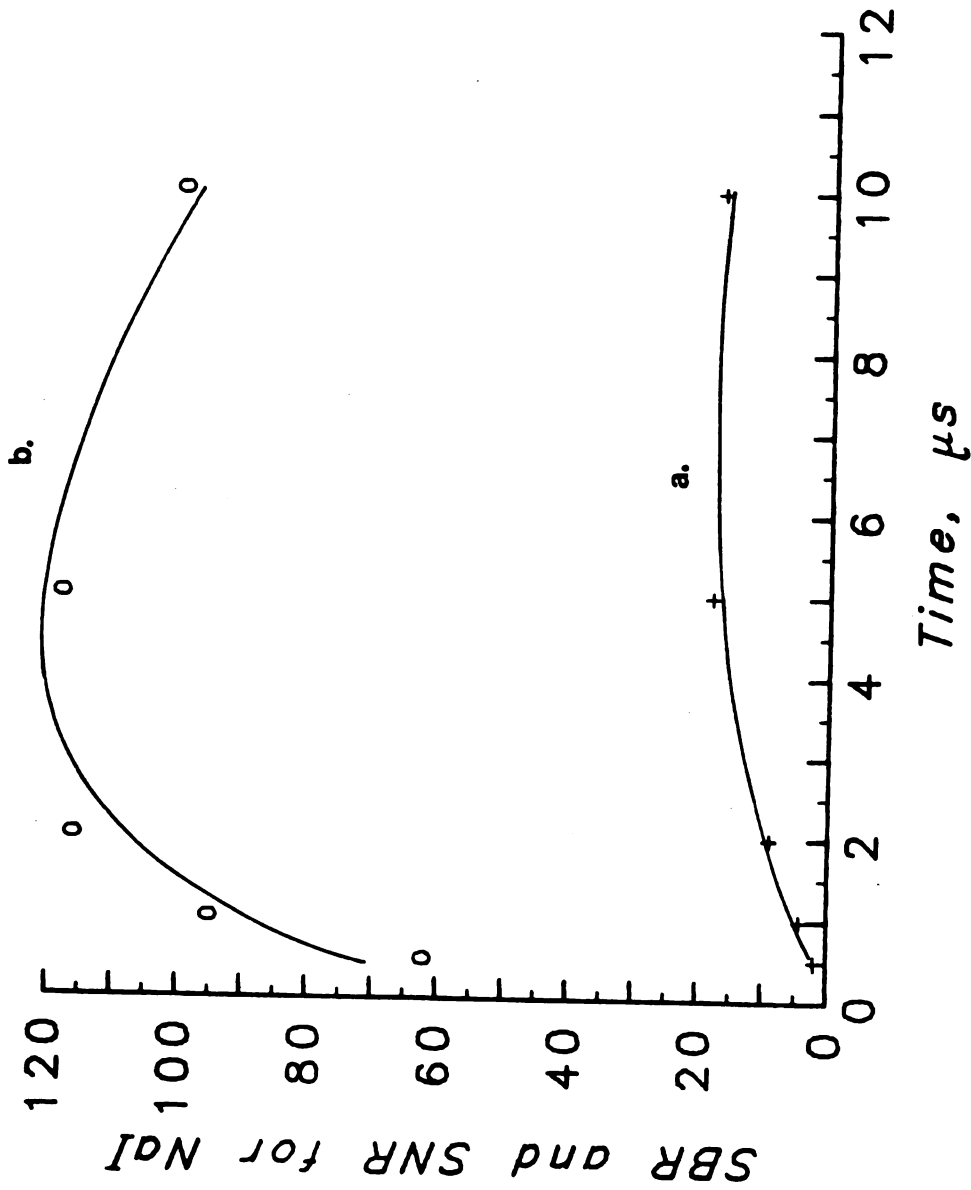


Figure 5-6. a) Signal-to-Background Ratio (SBR) vs. Time,
 b) Signal-to-Noise Ratio (SNR) vs. Time for the Sodium
 atomic line (at 589.0 nm).

From Figures 5-5 and 5-6, the optimum delay times, based on the highest SNRs, were around 3 μ s for the calcium ionic line and around 5 μ s for the sodium atomic line.

B. Effect of Laser Power on Signal

As mentioned in Chapter III, the only requirement of the laser is that it produce the power density required to cause breakdown in the material of interest. The energy of the laser beam should be greater than the threshold for breakdown of the carrier gas since vaporization of the solvent (in case of the liquid streams), atomization and excitation of the analyte should occur as well. Therefore, before examining the effect of laser power on the signal, measurements of breakdown thresholds in several media were taken. The results are tabulated in Table 5-3. As was expected from the literature (9), the breakdown threshold for argon was lower than that of air. It was also verified that in the case of an aerosol the thresholds decreased (66). The breakdown threshold of ambient air was lower than that of compressed air from a tank; this might have been caused by moisture, free ions or dust particles existing in the laboratory air. A dramatic drop in the threshold occurred when the laser beam was focused on the liquid droplets (produced by the IDG). The last three observations agree with other authors' experimental investigations (44); they mentioned that the presence of small solid or liquid particles in the laser's focal volume significantly decreased the threshold for air breakdown. They also found that the threshold was a function of wavelength, pulse duration, particle size, and material (with the spot size and the focal volume kept constant). Particularly, referring to liquid droplets, they showed that

Table 5-3. Laser-Induced Breakdown Thresholds

a). Plasma created in the sample cell using the apparatus for dry aerosols (nebulizer/desolvation system).

Breakdown Thresholds			
Carrier gas	Solution	Laser Power, mW	Laser Energy, mJ/pulse
argon	no solution	330 $\pm$ 10	33 $\pm$ 1
argon	dist. water	290 $\pm$ 10	29 $\pm$ 1
argon	Ca solution	300 $\pm$ 12	30 $\pm$ 1
air	no solution	400 $\pm$ 20	40 $\pm$ 2

b). Plasma created in a liquid stream using the isolated droplet generator.

Breakdown Thresholds		
Medium	Laser Power, mW	Laser Energy, mJ/pulse
ambient air (AA) + no stream	330 $\pm$ 10	33 $\pm$ 1
AA + dist. water droplets	86 $\pm$ 5	8.6 $\pm$ 0.5
AA + Mn solution droplets	110 $\pm$ 5	11 $\pm$ 0.5

the breakdown threshold of droplets decreased with increased droplet size.

Next, the effect of laser power on the total signal, background and analyte emission was studied. Results obtained with the aerosol experimental setup, using argon as a carrier gas and a 200 ppm calcium solution aspirated through the nebulizer, are shown in Figure 5-7. The calcium ion line at 393.4 nm was monitored and the total signal intensity measurements were taken at different laser power values. Background emission was reported at 394.1 nm for several laser power settings, as well. Log-log plots of emission intensity vs. power are presented in Figure 5-7. The laser power was measured before the focusing lens, because after the very tight focusing in the breakdown region the laser beam diffused considerably. The range of the laser power used was very narrow: 0.53-1.88 Watts (corresponding to laser energy values between 53 and 188 mJ/pulse), because of the nature of the LIBS experiments. Since the breakdown threshold imposed a lower power limit, emission was observed only at powers exceeding threshold. On the other hand, at high laser powers, the plasma grew large in size, became unstable and hard to image on the monochromator slit. Thus the signal intensity appeared to decrease at high powers (not being reliable any more). This fact set the upper limit of useful laser power values. For the experiments described here, powers in the range 0.9-1.0 W were typically used. The slopes of the log-log plots of intensity vs. power (Figure 5-7) were not meaningful since multiphoton absorption was not the predominant mechanism for the breakdown, and more likely a saturation effect caused the "plateau" region in our plots. Very similar

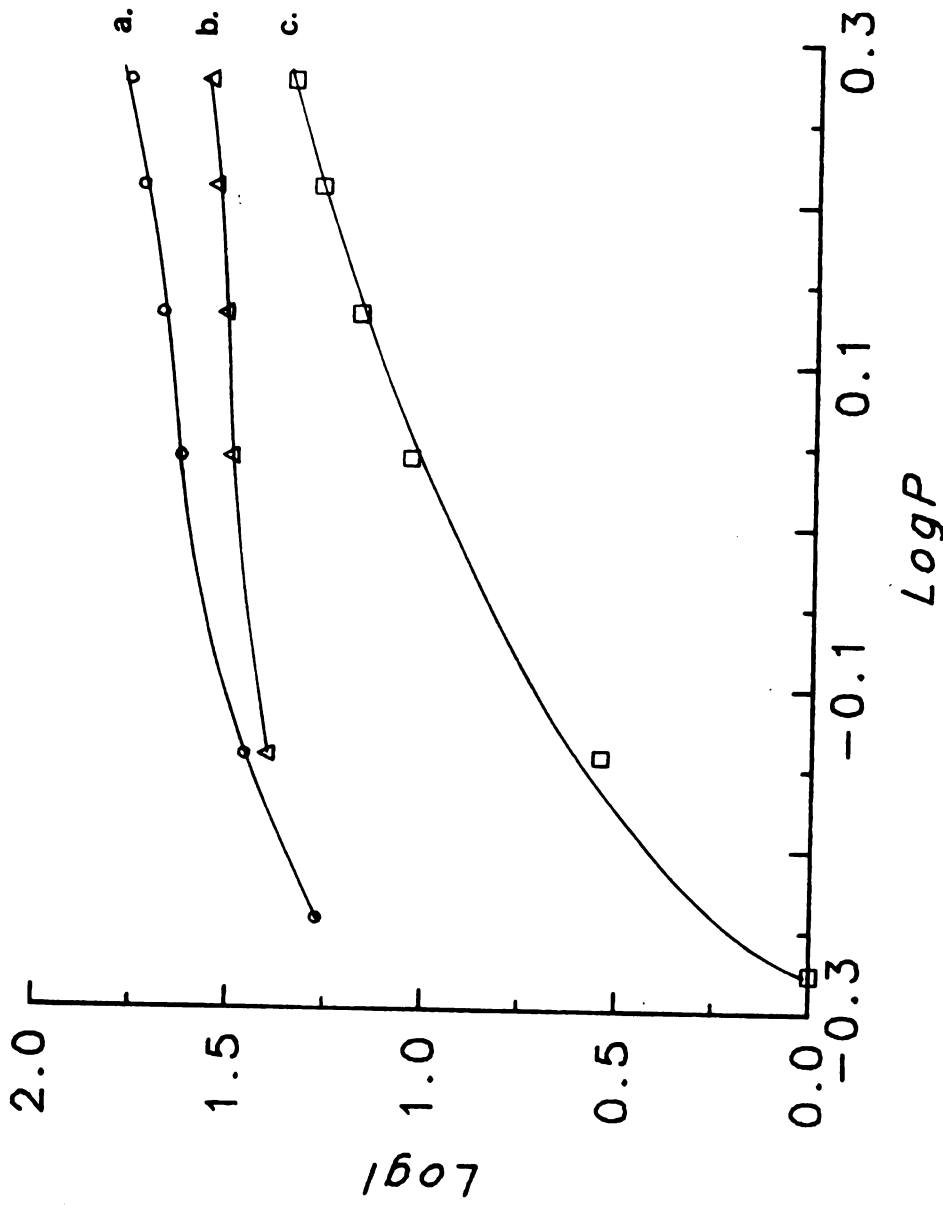


Figure 5-7. Log-log plot of Emission Intensity of the Calcium ion line as a function of Laser Power. a). total signal, b). calcium ion emission and c). background emission.

results were obtained for the effect of laser power on signal, using the droplet streams in the open air.

Our observations seem to agree with those of other authors (67), who reported that for an increase in laser energy from 60 to 140 mJ/pulse, the total emission intensity increased by 145%, whereas the ratio of analyte to background emission increased by only 20%. It was reported elsewhere (65) that laser energy (between 50 and 200 mJ/pulse) had no effect on the signal-to-noise ratios or detection limits.

C. Optimization of Experimental Parameters

Before exploring the potential of the LIBS technique as an analytical method, optimization of several parameters was attempted. The components of the experimental apparatus and the typical settings used for laser-induced breakdown spectroscopy are listed in the Table 5-4. In previous sections of this chapter, the importance of time resolution was discussed. To obtain the lowest detection limits, the delay time between plasma initiation and emission observation was chosen to give the highest signal-to-noise ratio. The effect of the laser power on the signal was also discussed previously. A laser energy range was selected that was sufficient for breakdown of the medium and atomization, ionization and excitation of the element of interest. On the other hand, very high laser power was avoided as producing an unstable plasma and causing erroneous results.

The slit width of the monochromator was selected such that it provided good resolution and at the same time collected enough radiation for detection.

Table 5-4. Experimental Apparatus and Settings used for Laser-Induced Breakdown Spectroscopy

A. Laser

laser	Quanta-Ray DCR Nd:YAG
wavelength	1064 nm
pulse width	10 ns
repetition rate	10 Hz
energy	90-100 mJ/pulse

B. Detection System

1. Spectrometer	Heath EU-700-56
grating	1180 lines per mm
slit width	30 μ m
slit height	1 cm
scan rate	0.05-1 A/s
2. Photomultiplier Module	Heath EU-701-30
photomultiplier tube	RCA 1P28A, Hamamatsu R666, 400-1000 V
3. Signal Processing	
a. boxcar averager	PAR 162 (Princeton Applied Research)
aperture delay	2-50 μ s
aperture duration	0.5 μ s
trigger	external, from laser Q-switch output or optical trigger + slope, + level
time constant	0.1 s
b. gated integrator	PAR 164 (Princeton Applied Research)
input	50 Ω , dc
time constant	10-100 μ s
averaging mode	exponential
4. Chart Recorder	
speed	0.2-0.5 in/min
span	1-10 V

The photomultiplier tube (PMT) voltage along with the amplifier gain determined the "adjustable" gain of the system. A combination of high PMT voltages with low amplifier gains resulted in less noise in the measurements.

The boxcar averager and gated integrator time constants (input and output) were chosen so that the highest signal-to-noise ratio would be obtained without distortion of the signal and within a reasonable analysis time. The spectrometer was scanned slowly to avoid attenuation of the signal peaks by the time constants of the electronics.

In addition to those parameters given in Table 5-4, the influence of several experimental conditions associated with each sample introduction system was studied and the results are given in the following sections.

1. Sample Introduction System for Aerosols

The effect of nebulizer argon flow rate on the analyte emission was studied. The results are presented in Figure 5-8. A 200 ppm calcium solution was used and the intensity of the calcium ion line was measured. In Figure 5-8 we can see that at the beginning the signal intensity increases as the argon flow rate increases because more solution is aspirated to the heated chamber and consequently more analyte reaches the laser plasma per unit time. At high flow rates, however, the emission intensity begins to decrease. This may be due to instability in the crossed-flow nebulizer, which is caused by the high argon flow rates. Also, at high argon flow rates a larger amount of water vapor may arrive at the sample chamber per unit time (due to desolvation inefficiency) and cool down the plasma. Then ionization and

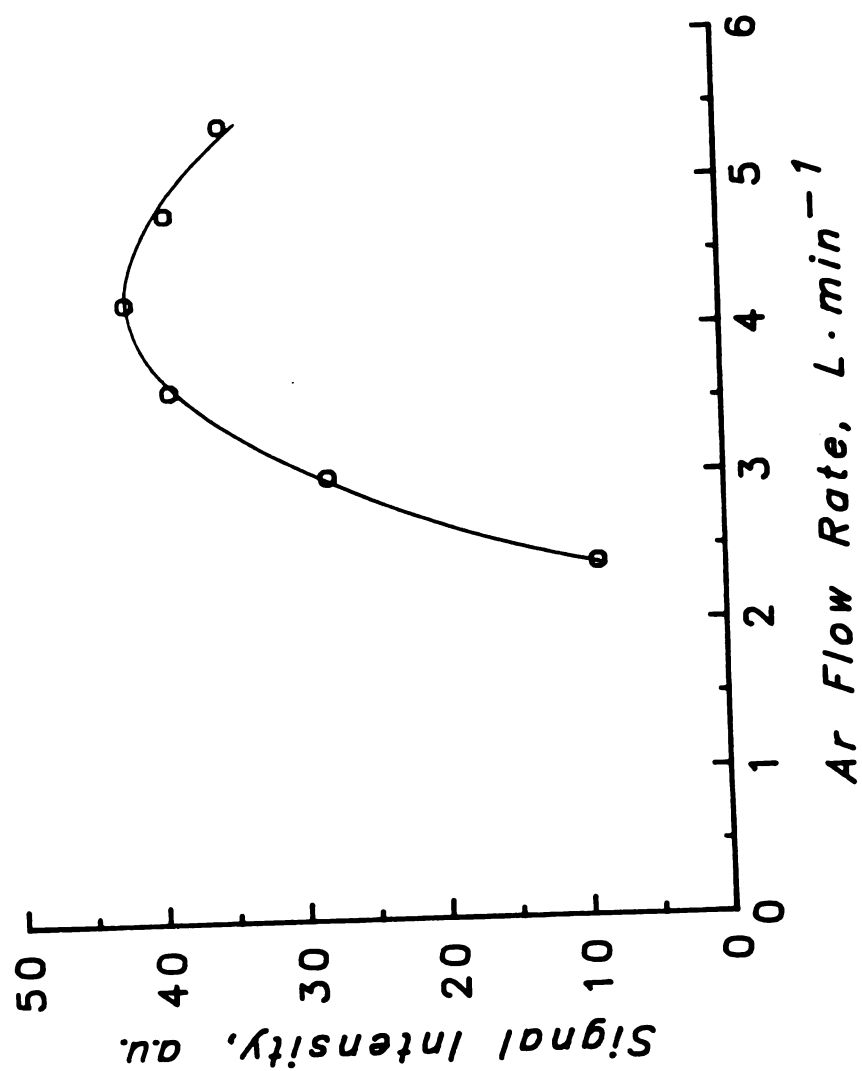


Figure 5-8. Effect of Nebulizer Argon Flow Rate on Analyte Emission.

excitation of the analyte is not complete, and as a result the emission intensity decreases. The optimum argon flow rate was found to be 4.2 l/min. In order to avoid much "dilution" of the dry aerosol in the carrier gas, a single channel peristaltic pump (Ismatek AMY8.1-AB2.5SR) was used. Solutions were pumped to the nebulizer at approximately 2.3 ml/min. Although the signal became less noisy (constant uptake rate), we still had to use high argon flow rates to keep the "net" uptake rate in the desirable range (0.17-0.25 ml/min). "Net" uptake rate is the amount of the solution that is actually aspirated into the heated chamber per unit time, since most of the sample goes to the drain. "Net" uptake rates were measured by observing the uptake rate of a solution (contained in a graduate cylinder) through the nebulizer and collecting the solution going through the drain in another graduate cylinder over a known time interval. This latter value was subtracted from the former to obtain the "net" uptake rate.

A better solution may be the use of an ultrasonic nebulizer which operates at much lower argon flow rates and produces a dense mist of the sample solution.

2. Sample Introduction System for Liquid Streams

The isolated droplet generator was also used here to introduce the sample solution to the laser plasma. The settings on the IDG are reported in Reference 4. Parameters that are crucial in the interface of IDG with LIBS were optimized and their effect on the emission intensity is discussed below.

The parameters affecting droplet production are capillary size, bulk flow rate through the capillary and applied bimorph frequency.

The capillary size is adjusted to produce droplets in a given size range and the transducer frequency is used to vary the size within this range. The bulk flow rate can also be adjusted even though low linear velocities are preferred as is explained in the next sections of this chapter.

a. Effect of the capillary size on analyte emission

The capillary size is associated directly with the size of the droplets produced, in accordance with the following equations (4):

$$V_d = F / f \quad (1)$$

where V_d is the droplet volume (ml), F is the bulk flow rate (ml s^{-1}) through the capillary and f is the production frequency. Since the volume of a sphere is given by the equation:

$$V = (4/3) \pi r^3 \quad (2)$$

the drop radius can be expressed as:

$$r_d = (3 F / 4 \pi f)^{1/3} \quad (3)$$

It is very difficult to measure the fire-polished capillary size, which is in the range of μm , and thus only approximate values can be given. Because of this we have calculated the drop radii for $f = 7 \text{ kHz}$ from measured bulk flow rates through the capillaries under study. A 200 ppm Ca solution was placed in the constant pressure reservoir and

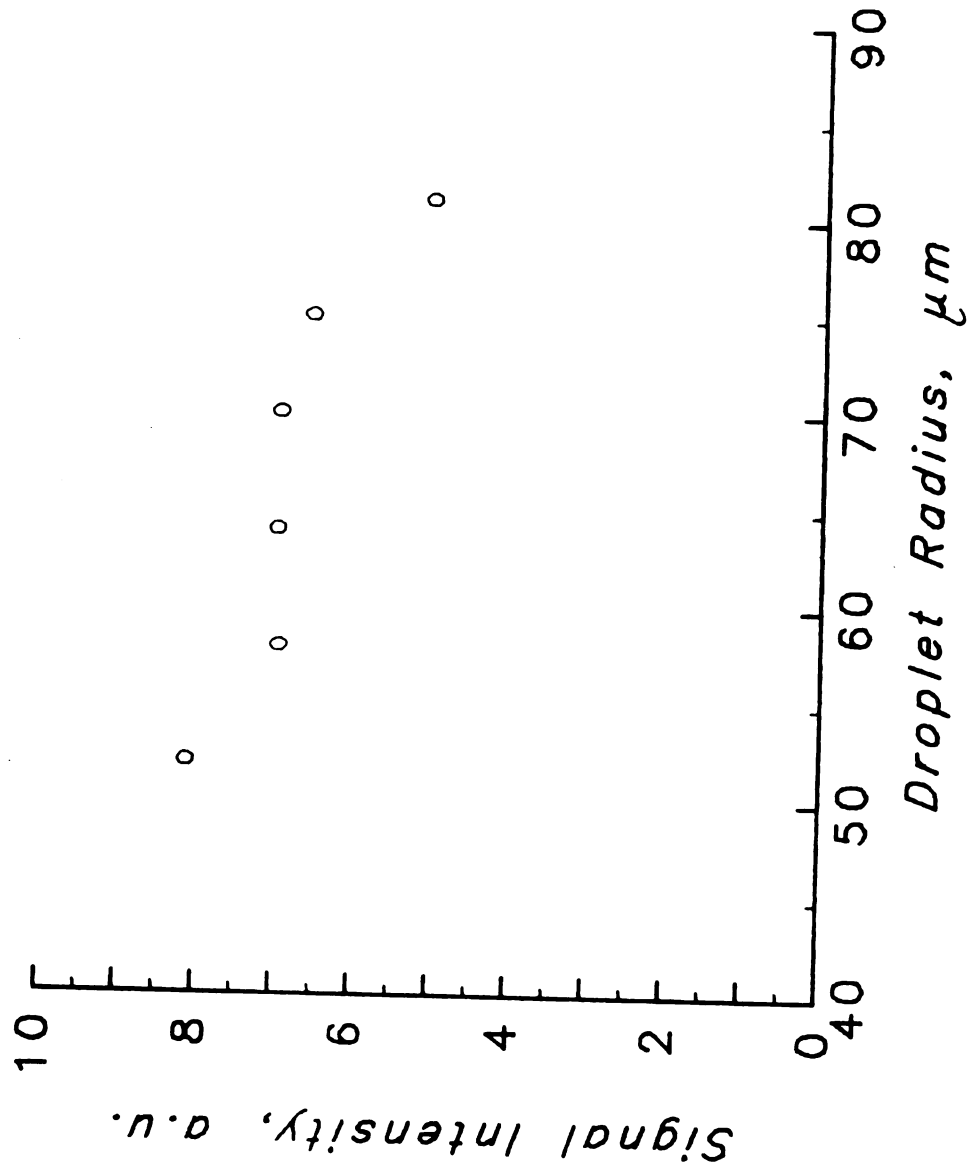


Figure 5-9. Effect of the Droplet Size on Signal Intensity.

the ionic calcium line at 393.4 nm was monitored. The signal intensity was plotted vs. drop radius as shown in Figure 5-9. The range of the drop radii was 52-86 μm and the volume of the droplets produced under the above conditions was 0.6-2.7 nl. From Figure 5-9, we can see that the signal intensity is almost constant for droplet radii between 58 and 75 μm . It increases for droplet sizes less than 55 μm in radius, while it decreases for those larger than 80 μm droplet radii. In fact, a stable stream cannot be formed from droplets larger than 85 μm in radius. It is obvious that at the "plateau" region there is a saturation effect, in the sense that the sample contained in the plasma region is not completely atomized or excited. For smaller droplets the atomization or excitation efficiency seems better, although the small size capillaries are very difficult to use because they get clogged easily.

b. Effect of bimorph frequency on analyte emission

In this series of experiments, the nitrogen pressure and the capillary size were kept constant while the bimorph frequency was varied. The production frequency determines the distance between the droplets when a stable stream is formed. With a 200 ppm calcium solution and measurements of the ion emission at 393.4 nm, we observed the following (See Figure 5-10). For bimorph frequencies less than 6 kHz the signal intensity increased with increasing frequency, reaching a "plateau" in the region between 6 and 12 kHz; it again decreased at higher frequency values. When a low frequency voltage was applied to the bimorph only one big drop was in the active plasma volume and this probably did not favor its complete desolvation or the atomization and excitation of the analyte. In the intermediate frequency range, 2-3

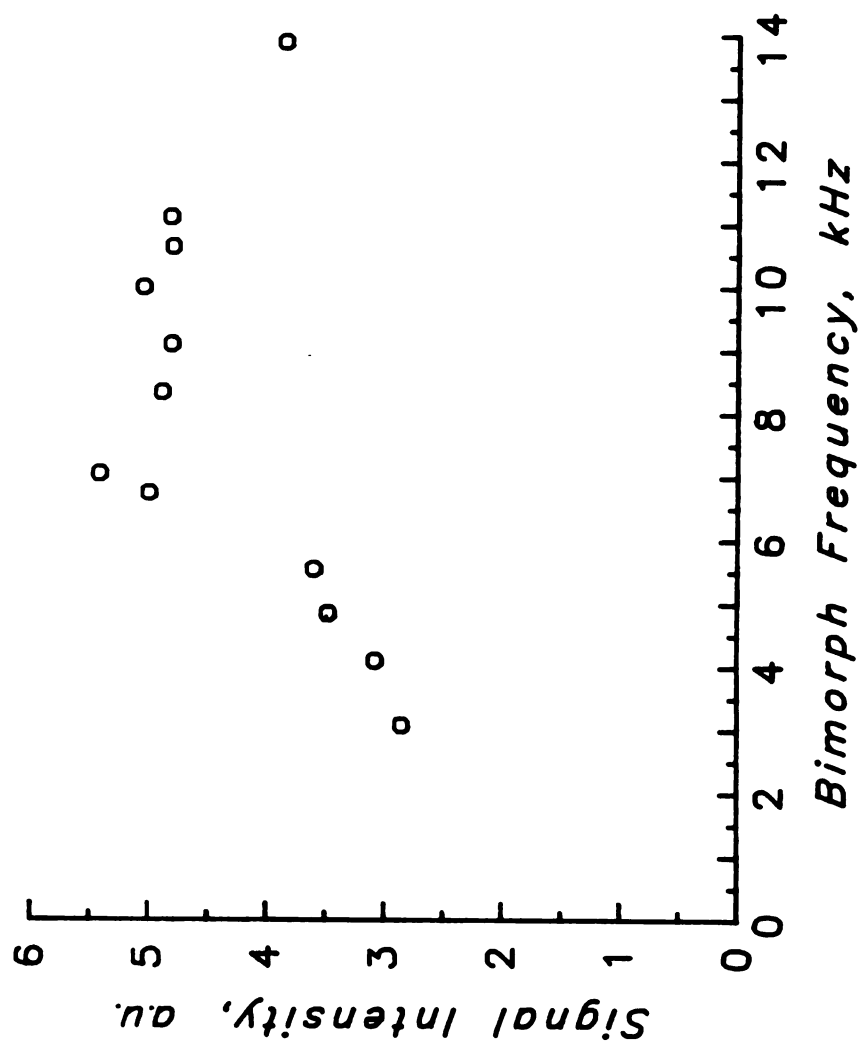


Figure 5-10. Effect of Bimorph Frequency on Signal Intensity.

smaller droplets were positioned in the plasma volume. It was in this region that the maximum possible signal intensity and highest precision were observed. At very high frequencies the emission decreased because it was difficult to form a stable droplet stream and many droplets were included in the laser spark, lowering the desolvation efficiency.

It should be mentioned that the "plateau" regions are very helpful for the optimization of the experimental conditions in this particular application (IDG-LIBS). This happens because in both cases (capillary size and bimorph frequency), it is extremely difficult to reproduce exactly the same capillary sizes or bimorph frequency settings. The fact that small changes do not affect the results appreciably is quite desirable.

c. Effect of reservoir pressure on analyte emission

Before we examined the dependence of the signal intensity on the reservoir pressure, we correlated the bulk flow rate of a solution through the capillary with the pressure of the liquid delivery vessel. Nitrogen gas regulated at 10 to 40 psi was introduced through the cap of the delivery vessel (see Chapter III). The bulk flow rate through the capillary was adjusted by increasing or decreasing the pressure. Flow rates were measured by collecting the effluent in a 10 ml graduate cylinder over a known time interval. The relationship between flow rate and pressure was linear at low pressures and showed curvature at high pressures as shown in Figure 5-11.

For the LIBS application the effect of nitrogen pressure on the signal was examined, while the capillary size and the bimorph frequency

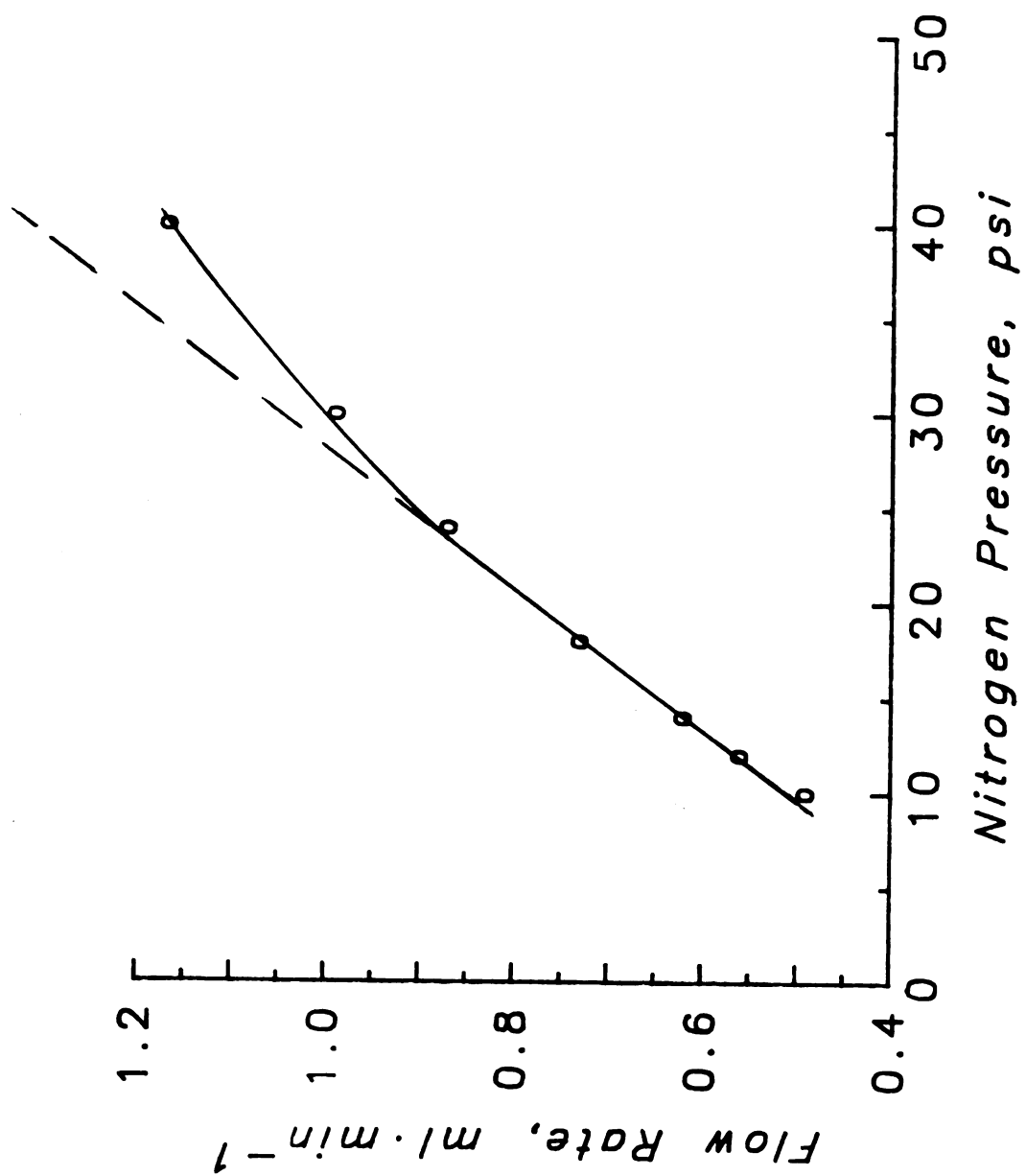


Figure 5-11. Flow Rate / Pressure Relationship for a 60 micron diameter capillary and in-line filter.

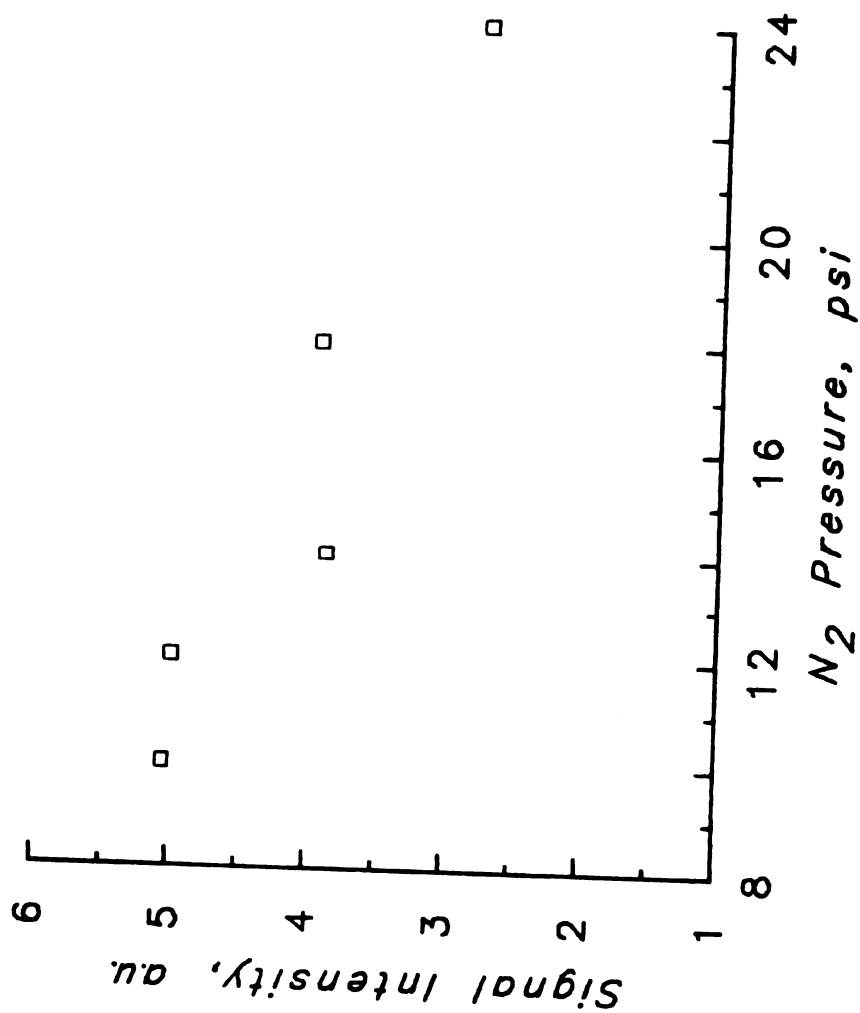


Figure 5-12. Effect of the liquid delivery vessel Pressure on Signal Intensity.

were kept constant. The same calcium solution and emission line were used. The results are shown in Figure 5-12. Since the pressure is almost linearly dependent on the bulk flow rate through the capillary and the other two parameters of the IDG (capillary size and bimorph frequency) are kept constant, the pressure change is translated as a small change in the droplet size. Therefore, the data points in Figure 5-12 follow the same general trend as in Figure 5-9.

d. Emission vs. Time Response as a function of sample injection volume.

As mentioned in Chapter III, in order to be able to use the IDG-LIBS technique for quantitative work, a flow injection system was added to the previous configuration. Because of dispersion that takes place during the mixing of the sample solution and the solvent (when switching of the valve occurs), emission-time response graphs were reported as shown in Figure 5-13. The data for these plots were taken for various injection volumes (sample loop sizes in other words) in the range 70 μ l-1.5 ml for a 200 ppm calcium solution. A capillary of 55 μ m diameter was used, with a bulk flow rate of 0.3 ml/min and a tubing diameter of 0.8 mm. The calcium ion emission was monitored as in all other studies. From Figure 5-13 it is obvious that the emission profiles are typical of an FIA-based system; i.e., with increasing injection volume, the peak height response approaches a "steady-state" signal. Unless we work with very low concentrations a small injection volume can be used, decreasing the analysis time considerably, while reducing the emission intensity only a small amount (note that curve A has a peak height = 50% the steady-state value). This is an advantage in two

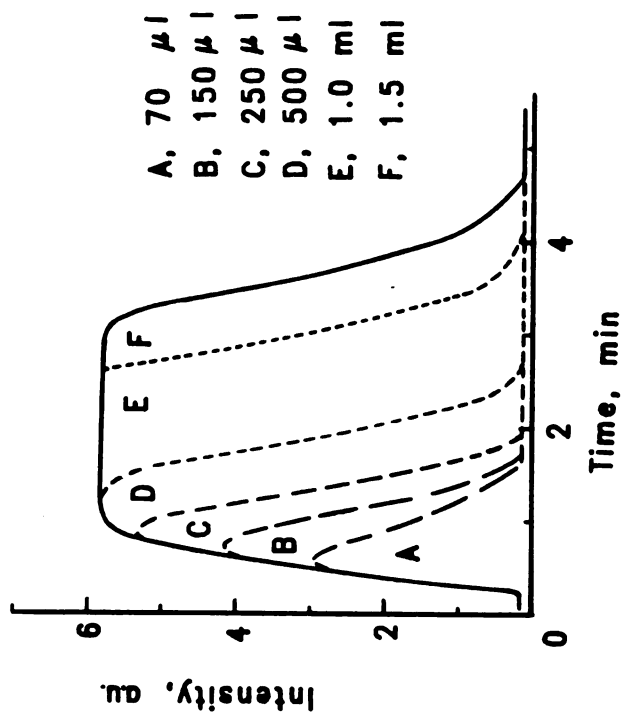


Figure 5-13. Emission vs. Time Response as a function of Sample Injection Volume.

ways: less sample is needed and faster analyses can be performed. For most of our experiments a 250 μ l injection volume was chosen as a good compromise value.

3. Sensitivity Dependence on Carrier Gas

We have also examined the effect of the media (carrier gases) used in our experiments on the sensitivity of the method, where sensitivity is defined as the slope of a calibration curve. Experiments were performed with the aerosol apparatus using separately argon and air as carrier gases. Calcium was the analyte in varying concentrations (100-500 ppm) and the ion line was measured. From the results shown in Figure 5-14, it is clear that the sensitivity using argon as the medium is much higher than that of air (in this particular case by a factor of 4). This should be kept in mind, when comparing the detection limits obtained with the dry aerosols and the liquid streams, since aerosols were analyzed in an argon environment and liquid streams in ambient air.

D. Quantitative Information with the LIBS technique

The first experimental setup for LIBS in gases was simple, consisting only of the laser and spectroscopic analysis system. However, when the method was applied to solution samples and particularly to liquid droplet streams, the apparatus quickly became very complicated. The long process of optimizing several experimental parameters, described earlier, was almost a necessity. Thereafter, the potential of LIBS as a quantitative analytical technique was explored.

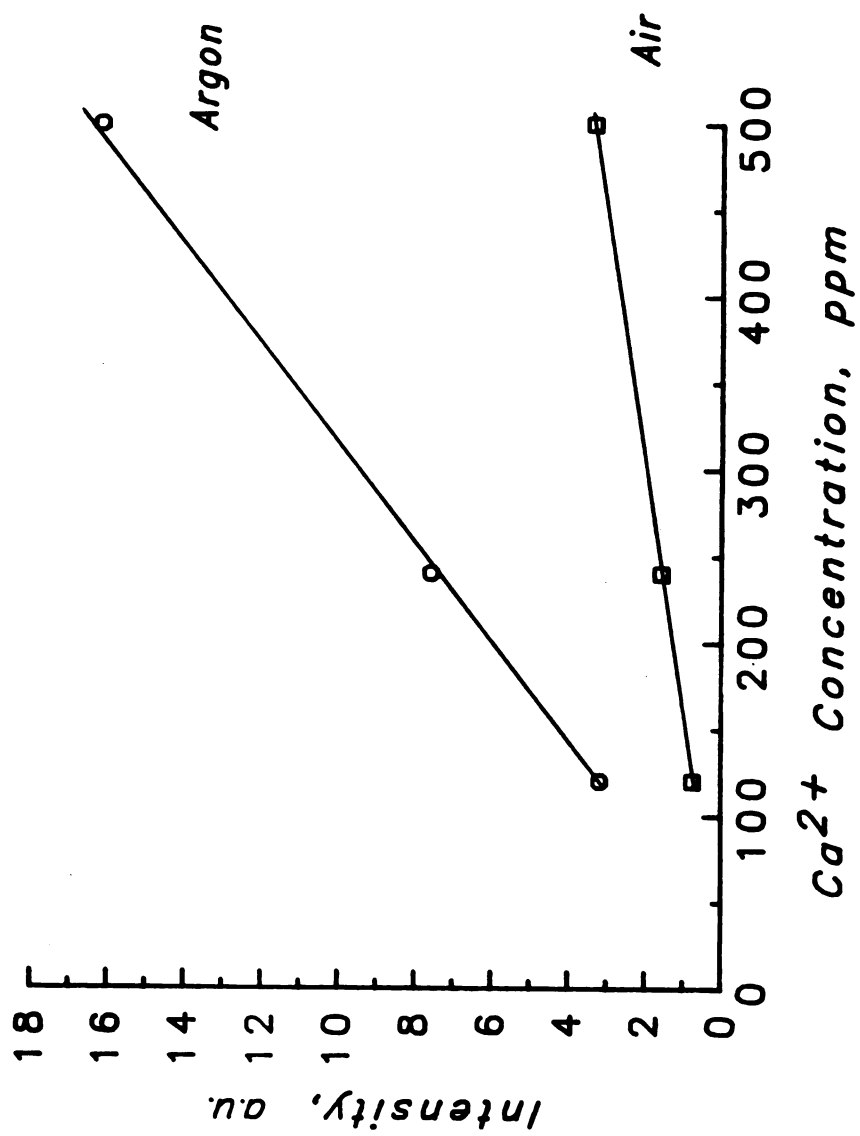


Figure 5-14. Sensitivity Dependence on Carrier Gas.

Calibration curves were obtained for many elements with both sample solution introduction systems and they were quite similar. Typical working curves for calcium and sodium are given in Figures 5-15 and 5-16, respectively. The former was taken with the flow injection / isolated droplet generator system and the latter with the nebulizer / desolvation / sample chamber configuration. Experimental parameters used for the calcium results, included: delay time = 4 μ s, droplet radius = 52 μ m, nitrogen pressure = 12 psi, bimorph frequency = 7.05 kHz, sample injection volume = 0.5 ml and laser energy = 100 mJ/pulse. The calcium ion line at 393.4 nm was monitored. For the sodium calibration curve, among the conditions used were: delay time = 5 μ s, laser energy = 95 mJ/pulse, argon flow rate through the nebulizer = 4.2 l/min and solution uptake rate = 0.24 ml/min with the peristaltic pump. The sodium atomic emission at 589.0 nm was measured. The optical trigger initiated the signal processing in both cases.

The linear dynamic range for calcium was approximately three orders of magnitude (0.5-1000 ppm), which was similar to that obtained for most of the elements studied. Sodium had a slightly shorter linear range. The deviation from linearity at high concentrations is most likely due to self-absorption. It should be pointed out that the plasma also became less stable at high analyte concentrations. Thus, the signal decrease may be caused by a combination of self-absorption and laser plasma instability. For each element, a log-log plot of intensity vs. concentration had a slope of unity. Slopes of calibration curves (sensitivities in other words) were different depending on the sample introduction system. With the liquid streams approach for calcium, the slope of the working curve was 0.17 l/mg. With the dry aerosol

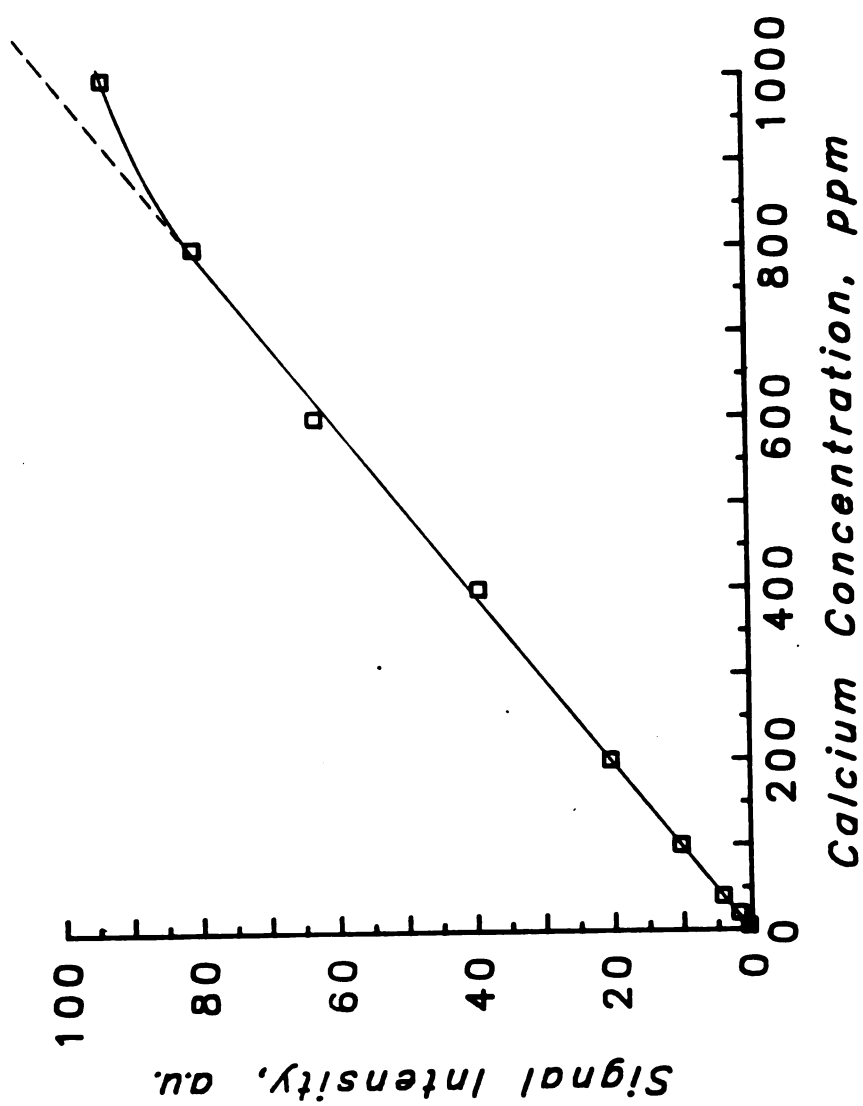


Figure 5-15. Calibration curve for calcium, taken by monitoring the ion line at 393.4 nm 4 μ s after the plasma initiation (solutions were introduced to the laser spark in the form of liquid droplet streams).

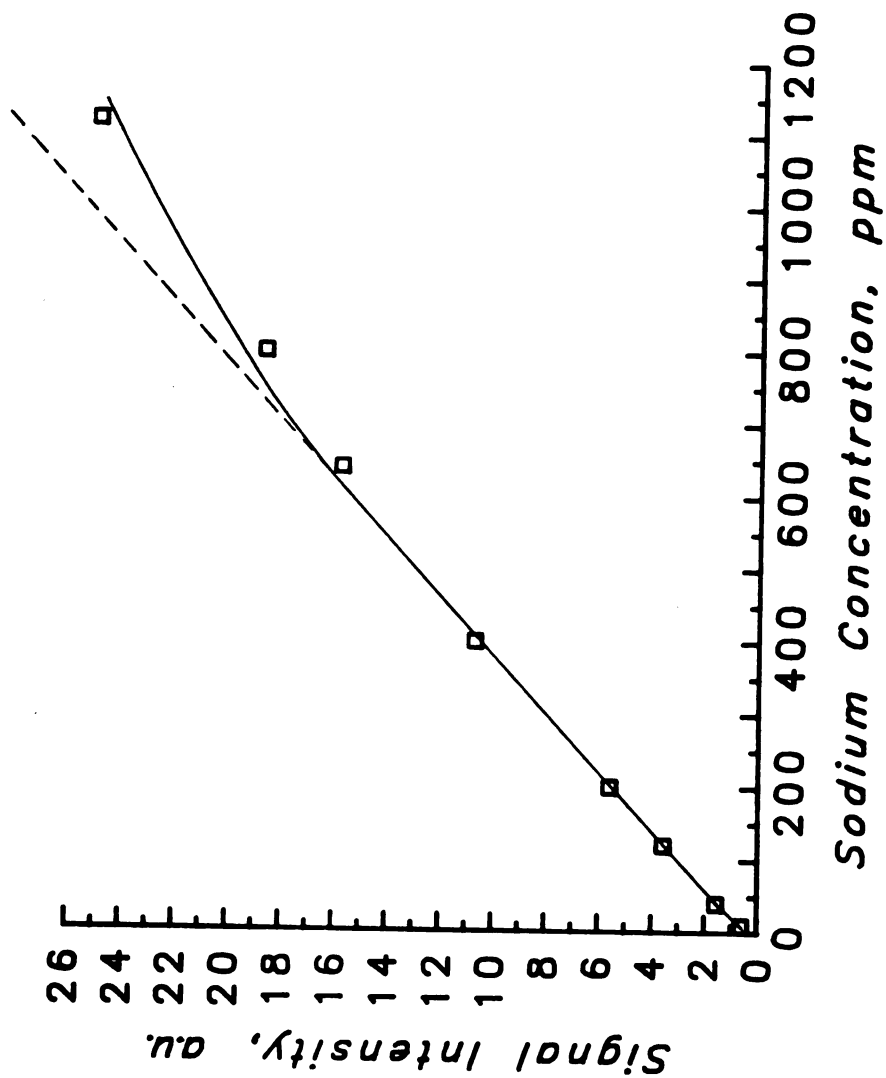


Figure 5-16. Calibration curve for sodium, taken by monitoring the atom line at 589.0 nm 5 μ s after the plasma initiation (solutions were introduced to the laser spark in the form of dry aerosols).

approach with the peristaltic pump, the slope of the same calibration curve was 0.10 l/mg, while without the pump it was 0.13 l/mg; however, the SNR (signal-to-noise ratio) was higher with the peristaltic pump due to the increased stability of the nebulizer.

The slope of the calcium calibration curve in Figure 5-15 is 0.173 ± 0.005 l/mg and the intercept is -0.0010 ± 0.0002 (which means that the working curve passes through zero). The correlation coefficient is 0.99996 and the relative standard error of the estimate (RS_e) is 1.5%. In the case of sodium, in Figure 5-16, the slope of the working curve is 0.025 ± 0.001 l/mg and the intercept is 0.537 ± 0.006 . The correlation coefficient of the same curve is 0.99999 and the relative standard error of the estimate is 2.5%. RS_es calculated for several elements were below 3.5%.

Detection limits (CL) for a series of elements were also determined for both dry aerosols and liquid streams and they are summarized in Table 5-5. The detection limit was defined as that analyte concentration that yielded a SNR = 3. The noise value used in these determinations was that of the background emission since small signal values result in signal variances which are small compared to those observed for the background. The limits of detection of the LIBS technique are in the ppm range for both sample solution introduction systems, as shown in Table 5-5. These numbers are much higher than those obtained by an ICP. However, the ICP is now a mature and commercially available source, while LIBS is a relatively new technique, used mostly for research purposes. A limitation of the LIBS method is the very small active volume of the laser plasma, which does not allow large quantities of analyte to be present at the focal point during the event. The

Table 5-5. Detection Limits for Various Elements in LIBS

Species	Analytical Line (nm)	C _L (LIBS:aerosol)		C _L (IDG-LIBS)		C _L (LIBS-Los Alamos) ^a	
		(ppm)		(ppm)		Spark in Liquids (ppm)	
Li I	670.78	0.2		0.3		0.006	
Na I	589.00	2.2		2.2		0.014	
Mg II	279.55	0.6		1.9		100.0	
Ca II	393.37	0.3		0.4		0.8	
Mn II	257.61	0.9		7.2		-	
Al I	396.15	9.4		5.2		20.0	

a: See Reference 69

sensitivity of laser-induced breakdown spectroscopy is in fact very high since low ppm levels of analyte can be detected in nl droplets (more obvious estimation in the case of the isolated droplet generator).

In the last column of Table 5-5, LIBS results obtained by other authors (69) working with solution samples are presented. The comparison cannot be direct since they used different laser source conditions. They also created the laser spark in a liquid medium instead of a gas where different breakdown mechanisms take place. On the other hand, the temperature of such a plasma is much lower than that obtained by an air spark at similar delay times because of the presence of the solvent. For the same reason, plasma temperatures in the liquid streams are expected to be lower than those in dry aerosols.

CHAPTER VI

INTERELEMENT STUDIES AND REAL SAMPLE ANALYSES

The ultimate goal when introducing a new analytical technique is to demonstrate its practical use in the analysis of real samples. The most common problems in all spectrometric methods involve the "matrix effects" where an interferent present in the analytical sample affects the magnitude of the spectral signal measured for the analyte.

It was expected that interferences would be minimal in the LIBS technique since the plasma temperature is very high. Interelement studies did, however, show a strong enhancement of the calcium ion emission when sodium was present in the sample. An increase in the intensity of the calcium ion line was also observed in the presence of aluminum. By contrast, the existence of phosphate in the sample solution did not affect the signal at all. The results of these studies are discussed in the following sections.

A. Effects of Sodium on Calcium Ion Emission

Since the calcium atom emission, as mentioned previously, is very weak, all the interelement studies were performed with the calcium ion line at 393.4 nm.

It has been noted, especially in hot flames and at low analyte concentrations, that the presence of an easily-ionized element in the sample, such as an alkali metal, can affect the degree of ionization of a

less easily-ionized element, such as calcium, by increasing the electron concentration in the flame and decreasing the extent of calcium ionization. Such elements are called ionization suppressants. The addition of an ionization suppressant is a common practice in flame atomic spectroscopy when easily-ionized elements are to be analyzed in high temperature flames (119-121).

In order to study the effect of sodium on the calcium ion emission in the LIBS technique, a series of calcium solutions was prepared in which the calcium concentration (5-100 ppm) was varied and the sodium concentration (1000 ppm) was held constant. A series of solutions containing calcium (5-100 ppm) with no added sodium was also prepared. Both series were analyzed using the two sample solution introduction systems described previously (see Chapter III) and delay times equal to 4 μ s. The results obtained with the dry aerosols apparatus are described here and shown in Figure 6-1. The calcium calibration curve taken with the addition of sodium started deviating from linearity at calcium concentrations higher than 60 ppm, which was rather unusual. The slopes of both calibration curves, taken with the dry aerosols apparatus, are listed in Table 6-1. From these values it is obvious that the addition of sodium to calcium solutions results in an increase in sensitivity and in the emission intensity of the calcium ionic line.

We would expect that the presence of an alkali metal would suppress the ionization of a less easily-ionized atom, which would have led to a decrease in the emission of calcium ions. Workers using N_2O / C_2H_2 flames have observed an enhancement of the calcium atom line with a simultaneous depression in the calcium ion emission when an ionization suppressant was added to the sample containing calcium (122,123). On

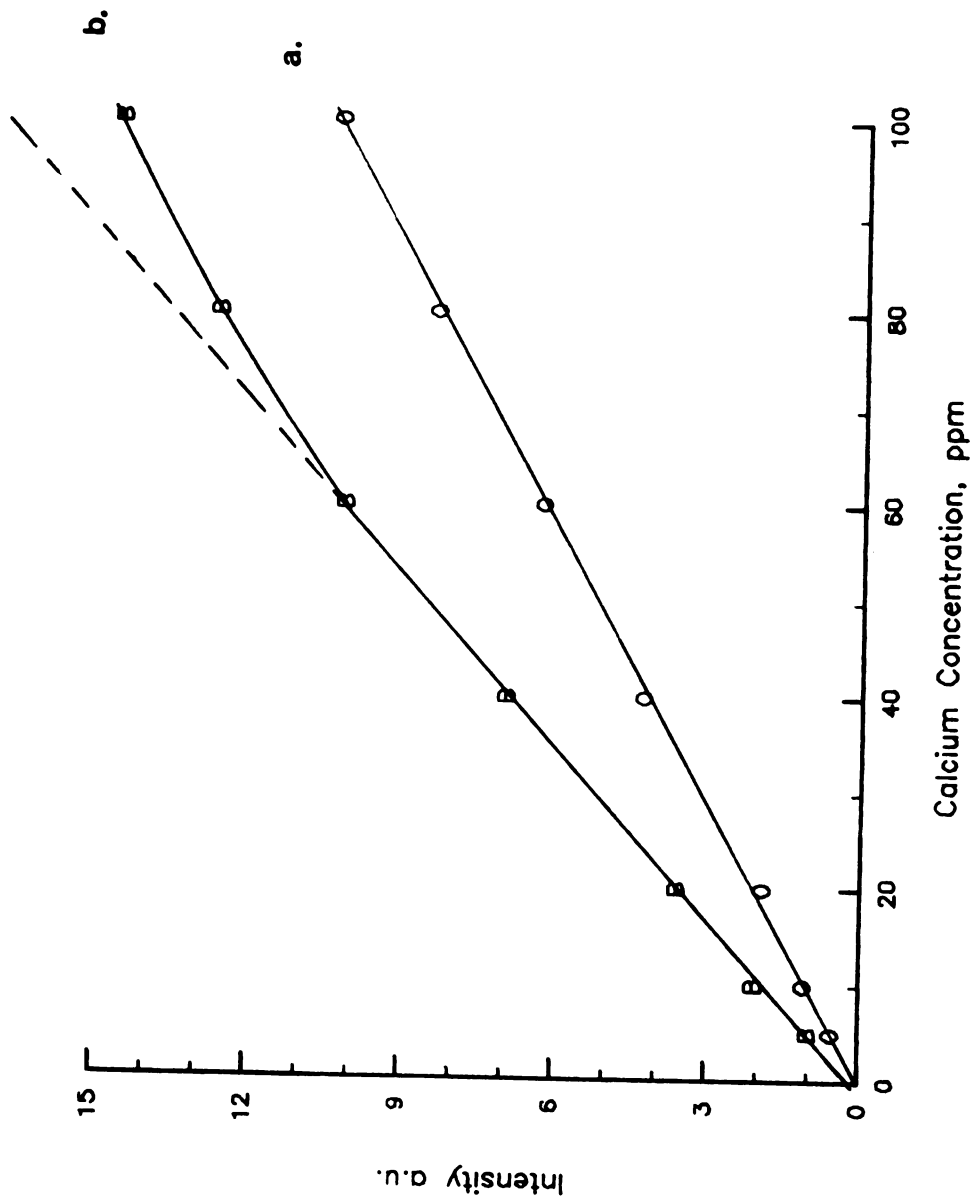


Figure 6-1. Calcium Calibration curves taken by monitoring the ion emission at 393.4 nm. a) Calcium Solutions (5-100 ppm), b) Calcium Solutions (5-100 ppm) + 1000 ppm sodium.

Table 6-1. Slope of Calibration Curves.

Standard Solutions	Slope
Calcium solutions (5-100 ppm)	0.102 ± 0.004
Calcium solutions (5-100 ppm) +1000 ppm Na	0.162 ± 0.007

the other hand, enhancement of both calcium atom and ion emission was observed on the addition of alkali metals in a miniature nanosecond spark source (86) and in a microwave plasma excitation source (124-126).

To get more information about the nature of the observed increase in the ion emission intensity, the emission was studied on a time-resolved basis. A solution of 100 ppm calcium and 1000 ppm sodium concentrations was prepared. The enhancement of the signal was plotted vs. time, as shown in Figure 6-2. Note that the maximum increase occurs at a time which is useful for analytical determinations (4 μ s). Direct comparison of the results shown in Figures 6-1 and 6-2 should not be attempted since different experimental parameters were employed.

In addition, a series of solutions was prepared with constant calcium concentration (100 ppm) and varying sodium concentrations (50-4500 ppm). Measurements were made 4 μ s after the creation of the laser spark. Significant enhancement was observed for sodium concentrations higher than 200 ppm. The results are shown in Figure 6-3, where it can be seen that the signal continues to increase with increasing sodium concentration. It appears that the percent enhancement is dependent on both sodium and calcium concentrations which causes the deviation of the calibration curve from linearity observed with the calcium solutions containing sodium. Since the extent of the enhancement depends on the calcium concentration, and since ionization is proportional to the inverse of the concentration, it appears that sodium increases the CaII population. However, since the emission from the CaII is actually enhanced, it would indicate that sodium is suppressing the ionization of CaII to higher states (CaIII, CaIV, etc.). Because the LIBS plasmas have

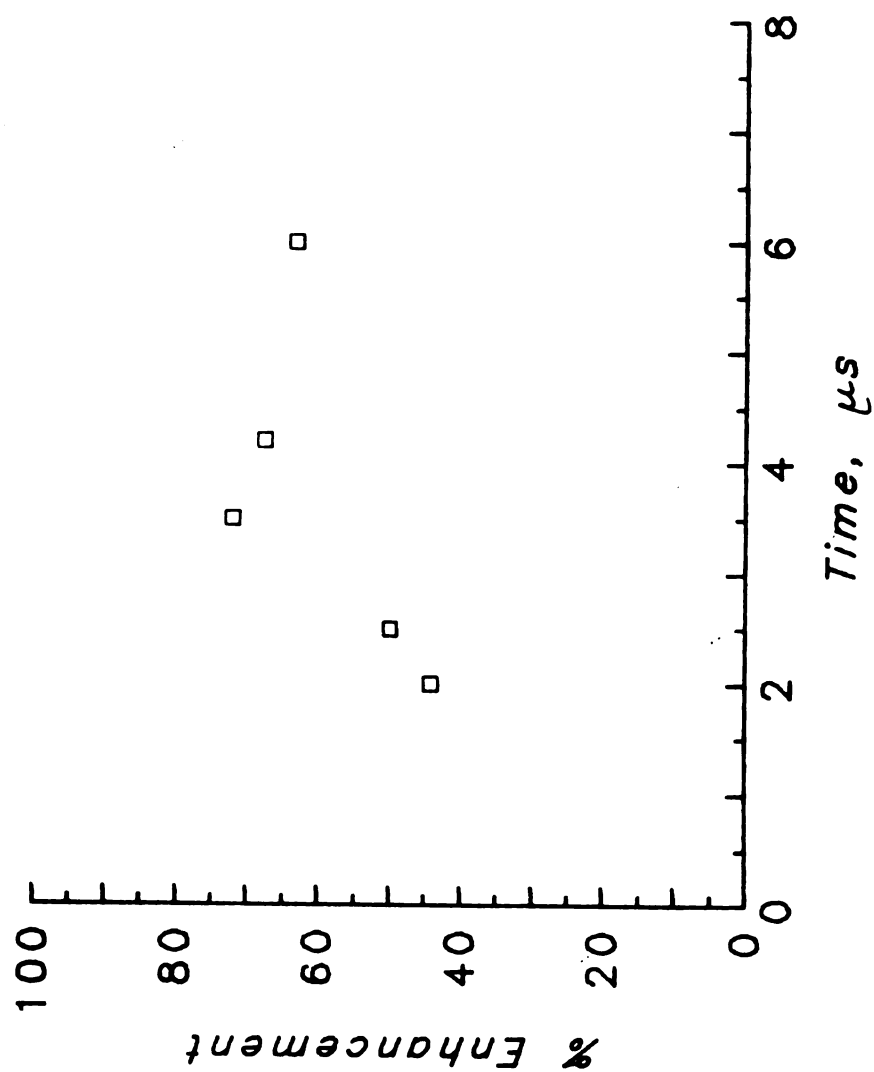


Figure 6-2. Time-Resolved Enhancement of 1000 ppm sodium on the Emission from 100 ppm Calcium.

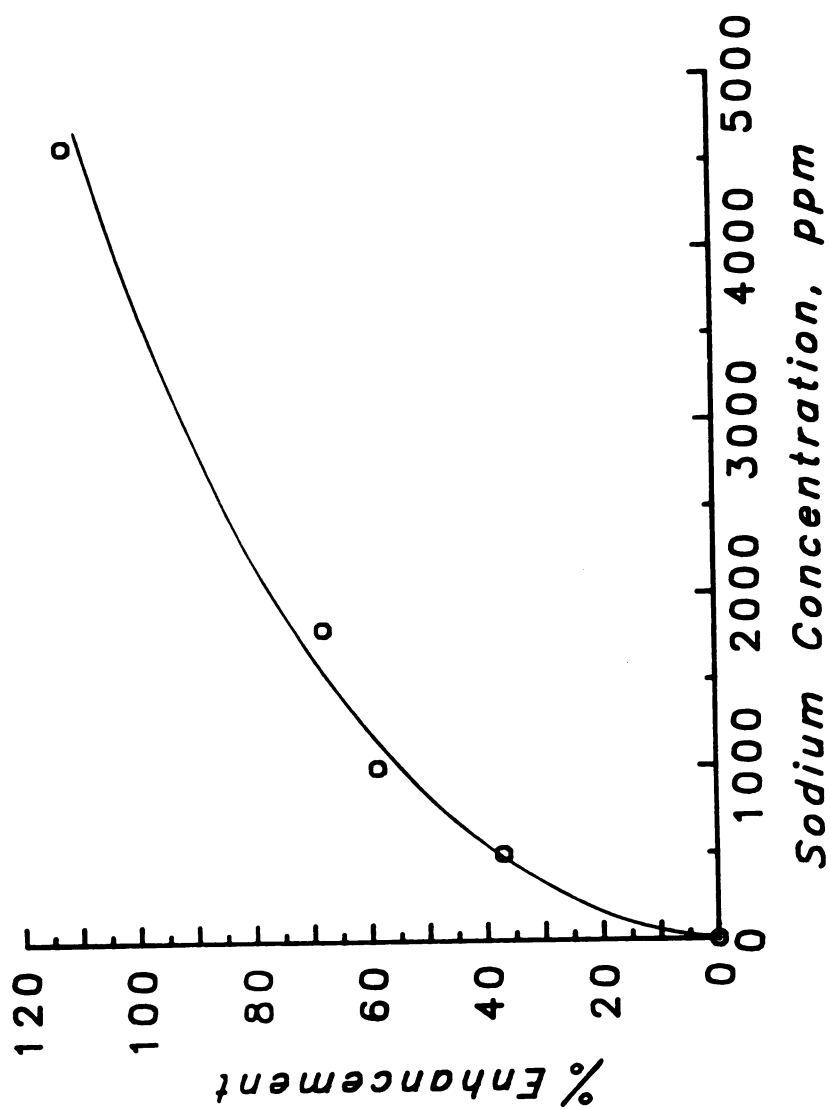


Figure 6-3. Enhancement of Sodium on the Emission from 100 ppm Calcium.

very high temperatures, the existence of such high ionization states is not surprising. Similar observations were made in liquid streams; however, the enhancement was not as large. This may have happened because of the lower plasma temperatures expected with liquid streams.

In conclusion, the enhancement caused by the alkali elements on the emission of the alkaline earths is a complex process. Not only is the process dependent on the concentration of both elements, but also the observed enhancement is a function of time. However, both dependencies can be explained qualitatively. The concentration of calcium determines its degree of ionization. On the other hand, the sodium concentration is important because it determines the degree of suppression of CaII to higher ionization states. For this reason, at a certain high sodium concentration a "plateau" in the percent enhancement of the calcium ion emission is expected. This "plateau" was never reached in our experiments since sodium concentrations higher than 4000 ppm introduced considerable instability to the plasma. Time is also a crucial parameter since analytes in higher ionization states should be present primarily at early times before the spark temperature decreases. However, our results are not conclusive because the calcium atom emission was not measured at the same time.

B. Effects of Aluminum and Phosphate on Calcium Ion Emission

Workers in the area of flame spectroscopy have shown that aluminum exhibits a marked depression on the emission of calcium in normal flames, such as the O_2 / H_2 , air / H_2 and air / C_2H_2 flames (127,128). This behavior is believed to be caused by the formation of refractory Al-Ca-O species that cannot be dissociated in the flame.

Workers using high temperature $\text{N}_2\text{O} / \text{C}_2\text{H}_2$ flames, however, have observed slight enhancements of the emission from calcium in the presence of aluminum (122). With microwave plasmas, a pronounced depression of calcium emission by aluminum has been reported (124).

In the LIBS technique, the presence of aluminum in calcium solutions caused a slight enhancement of the calcium ion emission, as shown in Figure 6-4. Thus, the usual depression is absent. The LIBS plasma is so hot that refractory species are completely dissociated. Instead, it appears that aluminum acts to suppress further ionization of CaII . At the high plasma temperatures, everything seems to exist in an elemental form.

The effect of phosphate on the calcium ionic emission was also examined. In total consumption burners, the existence of phosphate in the sample can alter the atomic concentration of calcium in the flame because of the formation of non-volatile complexes between the metal and the phosphate. It has been noted that the addition of phosphoric acid to a sample containing calcium causes a depression of the calcium emission, absorption or fluorescence that is highly dependent on flame temperature and residence time of the particles. In those cases, both aluminum and phosphate effects can be reduced by adding complexing agents such as EDTA to the sample solution. In experiments that we performed, there was no influence of phosphate on calcium ion emission even when the concentration was ten times higher than that of calcium.

The "resistance" of LIBS to those interferences that are prominent in flames is undoubtedly related to the high plasma temperature. Other high temperature sources, such as the ICP, show similar behavior, being free of pronounced aluminum or phosphate interferences.

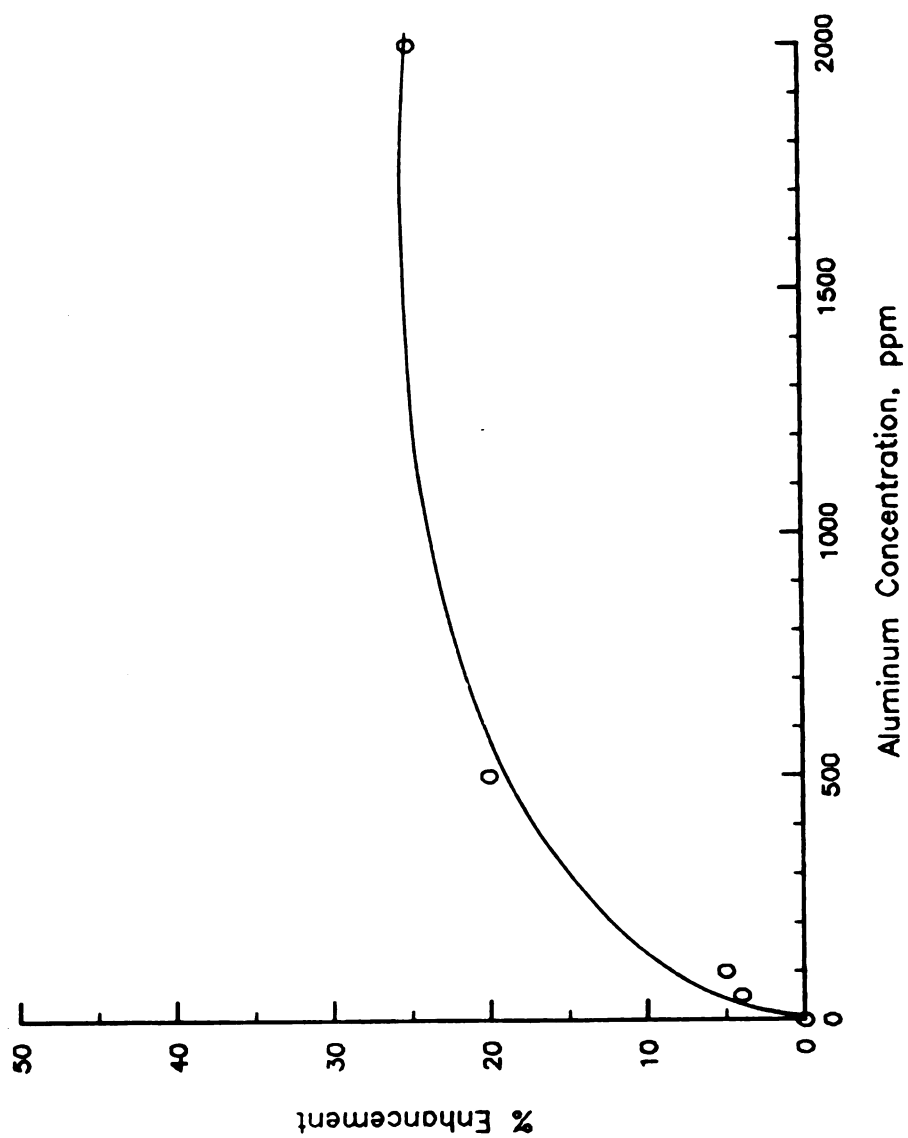


Figure 6-4. Enhancement of Aluminum on the Emission from 100 ppm Calcium.

C. Real Sample Analyses

After examining the interelement effects on the calcium ionic emission, the LIBS technique was applied to the determination of calcium in two simple real samples: tap and Red Cedar river water. The dry aerosol apparatus was used in both cases. Both samples were found to be approximately 100 ppm in calcium by the classical complexometric determination of calcium and magnesium with EDTA.

In the LIBS experiments the methods of external standards and standard additions (118) were used for comparison. The latter is used when it is difficult to duplicate the sample matrix to compensate for physical and chemical analyte interferences. The above methods were repeated with the addition of 1000 ppm of sodium to study its effect. Linear calibration curves were obtained, and their slopes as well as the calcium concentrations found in each case, are reported in Tables 6-2 and 6-3. Figure 6-5 shows the standard additions plots for both samples when 1000 ppm sodium was added. Figure 6-1 presents the calibration curves used for the external standards method with and without the addition of sodium.

With the standard additions method, the amount of analyte originally present in the solution can be obtained from a plot of the analytical signal vs. the concentration of the standard solution added into the same aliquots of sample solution. Then, the X-intercept of the plot gives the negative concentration that would have to be added to a "clean" sample to get the response given by the solution to which no addition was made.

Table 6-2. Calcium Determination in Tap Water

Method	Slope of Calibration Curve	Calcium Concentration (ppm)
Calcium External Standards	0.100 ± 0.005	118 ± 8
Standard Additions	0.094 ± 0.007	86 ± 5
Calcium External Standards	0.162 ± 0.007	95 ± 7
+1000 ppm Na		
Standard Additions	0.17 ± 0.02	94 ± 8
+1000 ppm Na		

Table 6-3. Calcium Determination in Red Cedar River Water

Method	Slope of Calibration Curve	Calcium Concentration (ppm)
Calcium External Standards	0.100 ± 0.005	128 ± 8
Standard Additions	0.085 ± 0.008	112 ± 8
Calcium External Standards	0.162 ± 0.007	102 ± 7
+1000 ppm Na		
Standard Additions	0.19 ± 0.02	92 ± 6
+1000 ppm Na		

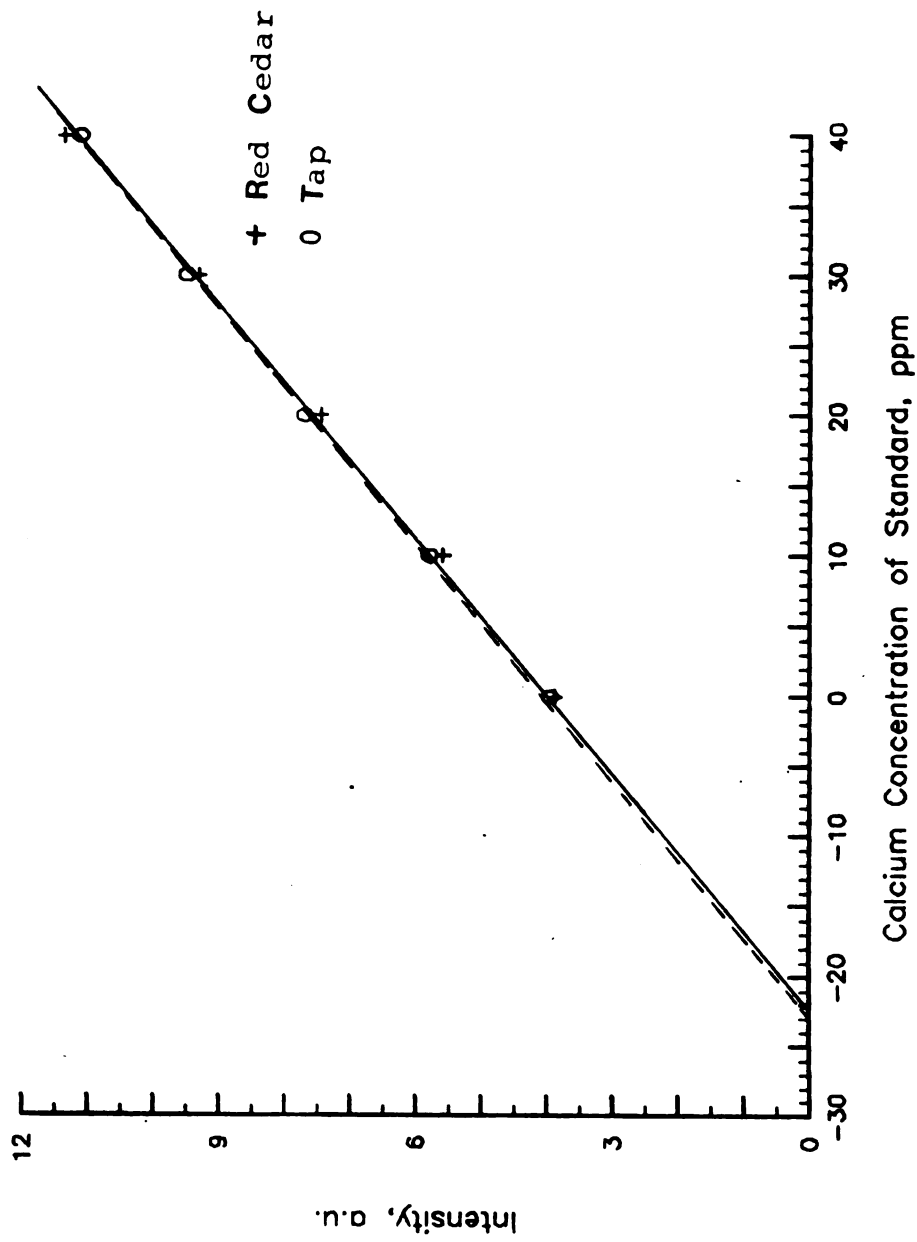


Figure 6-5. Standard Additions Analysis of Calcium in Tap and Red Cedar River Water Samples with the addition of 1000 ppm Sodium.

The experimental conditions used were the same as those reported in the previous chapter. In the method of standard additions, the best results were obtained when the original solutions were diluted by a factor of four. Linear calibration curves were found for standard additions up to twice as much calcium concentration as the expected value, deviating from linearity for higher concentrations. From the results shown in Tables 6-2 and 6-3, it can be seen that matrix effects become minimal when an easily-ionized element is added. This conclusion was drawn from the fact that calcium concentrations with the external standard method and the method of standard additions agree quite well.

It should be pointed out that the method of standard additions is very powerful, but it should be used with care. One of the requirements is that the slope of the calibration curves with external standards and standard additions methods should be the same, otherwise the standard addition procedure will not give accurate results.

From our experiments for the calcium determination in Red Cedar river water, the slopes of the external standard curve and the standard additions curve with and without the presence of sodium were barely the same, which causes one to doubt the reliability of the results.

It can be also verified from the slopes of the working curves that the presence of the alkali metals increases the sensitivity of the method.

Finally, although the real samples used were rather simple, they provided a means of illustrating the potential of LIBS as an analytical technique. It is expected that sample preparation procedures can be minimized by the laser-induced breakdown spectroscopy because of the very high temperatures associated with the laser plasma.

CHAPTER VII

COMPARISON OF THE TWO SOLUTION SAMPLE INTRODUCTION SYSTEMS

In the previous chapters, we described the application of a new spectrochemical technique to the analysis of solution samples. Laser-induced breakdown spectroscopy has been used mainly with gases and solids but only sparingly with the most common sample form, a solution sample! This might be due to the difficulty of introducing solutions into the laser spark.

In our work, we approached solution sample introduction from two directions. First, we used the "classic" way, which involves nebulization and desolvation of the solution, and second, a unique method of production of equally spaced isolated nanoliter droplets. Heretofore, results from both sample introduction systems have been presented. In this chapter a more detailed discussion of the similarities and differences of these two systems is presented.

In the experiments described, it should be noted that the laser-induced breakdown takes place in a gaseous medium. Therefore, the major gas breakdown mechanisms, described in Chapter II, are expected to take place; however, there is a difference. With the nebulization / desolvation / sample cell, a dry aerosol is carried by a flowing argon stream to the laser spark area. With the isolated droplet generator, on the other hand, a liquid droplet stream arrives at the laser focal point. In both cases, the presence of particles or droplets can alter the

breakdown mechanism and make theoretical predictions more difficult. The different breakdown thresholds obtained are an indication that additional processes occur.

A major characteristic of a plasma is its temperature. This is actually the factor that determines the potential of an atomic spectrometric technique. The higher the temperature the more elements can be determined by this technique. The great advantage of the LIBS method is the much higher plasma temperatures that can be achieved compared to those from other sparks or plasmas. Temperatures were measured for the laser plasma formed in argon with some water vapor, for the case of the aerosol apparatus, and are reported in Chapter IV. The presence of solvent, on the other hand, in the liquid stream experiments is expected to lower the temperature of the plasma. This might be a limitation to the isolated droplet generator method. Ways to get around this might be to use a second laser beam to provide the higher energy needed, or to combine laser breakdown with another spectroscopic technique used for the desolvation of the sample prior to its breakdown (e.g., an IR laser or a flame). Unfortunately, this would make a complicated instrumentation even more complicated.

The first experimental configuration used for solution samples, included the nebulizer / desolvation / sample cell system. One of the reasons a different sample introduction method was sought was the low efficiency of the desolvation system and the imprecision of nebulization. The operation of nebulizers is based on the use of a disrupting force, such as a carrier gas, to break the solutions into a mist. Although some nebulizers may produce nearly uniform-sized droplets (129), most of them do not, and droplet size discrimination can be achieved by

using special spray chamber geometries or aerosol modifiers inside the spray chamber. The mist is then carried as a cloud which reaches the area of the experimental event randomly in space and time.

By contrast, the isolated droplet generator converts the liquid jet into a stream of isolated droplets, identically spaced and uniform in size. The user can control droplet size and also has precise spatial and temporal control over the droplet delivery. In addition, considering the very small active volume of the laser spark, this feature becomes very important in achieving high precision. In fact, from our results, the %RSD was lower using the droplet streams than that with the dry aerosols, even though several other factors contributed to the final results. One of the negative factors is the creation of the breakdown in the ambient air with the IDG, instead of in an argon environment. The use of the latter is advantageous for several reasons: argon has a lower breakdown threshold, it gives a higher sensitivity to LIBS as an analytical technique as shown in Chapter V, and it is an inert gas which limits the chemical interferences. The last reason may not be so important in the LIBS application because at the delay times used everything seems to exist in an elemental form in the plasma region.

Not being able to confine the laser plasma in a sample cell when working with the IDG increases the chance that the liquid stream will become unstable in the laboratory environment. However, there are possible solutions to the problem such as introducing the droplet stream into a heated carrier gas stream.

The transient nature of the laser plasma made time-resolution spectroscopy necessary. This enabled us to minimize the carrier gas interference since the continuum emission and the ion lines due to the

medium decay much faster than the analyte signal that we are interested in. The time-resolved spectra obtained with both dry aerosols and liquid streams were very similar, as was shown in Chapter V.

One of our long range goals was to apply LIBS as a chromatographic detector for HPLC. Because of that an interface which would deliver HPLC effluent to the laser plasma with little dead volume and high efficiency was desirable. This was the main reason that we decided to test the isolated droplet production as a possible solution sample introduction system for LIBS. The above requirements for HPLC use are impossible to achieve with a desolvation system, because of the additional volume introduced to heat and desolvate the effluent. However, with the IDG, once the droplets are formed, no mixing with adjacent drops can occur. Thus, the dead volume is limited to that of a single droplet or a few nanoliters.

The addition of the flow injection system in the IDG-LIBS combination made the technique more flexible and created a new area of interest: application of flow injection analysis with LIBS. It should be mentioned that broadening the possibilities of the laser spark method increases the degree of the instrumental complexity. In general, the liquid streams apparatus was much more difficult to operate than the dry aerosol system because of the additional number of experimental parameters involved. Clogging of the capillaries was another problem. Filtering of the solution samples was necessary prior to their use with the IDG, which was not always the case with the nebulizer / desolvation system. It was also found that the in-line filter would clog rapidly if old solutions were used. This becomes a serious consideration since any clogging introduces instability in the liquid stream. To

alleviate this problem preservatives can be added to aqueous solutions to inhibit bacteria growth.

In general, the isolated droplet generator as a solution sample introduction system for LIBS may be more complicated than the dry aerosols apparatus, but it provides more versatility and allows LIBS to be interfaced to several other systems.

CHAPTER VIII

CONCLUSIONS AND FUTURE PROSPECTS

A. Conclusions

This dissertation has presented a relatively new analytical technique, which is called Laser-Induced Breakdown Spectroscopy. The technique was applied primarily to solution samples. The use of a laser source for the creation of a plasma makes the LIBS method very powerful. In fact the laser energy provided is sufficient to break down the medium, to desolvate the sample, and to atomize, ionize and excite the elements of interest. An advantage of this method is that experiments can take place in the ambient air.

A unique solution sample introduction apparatus was used to convert the sample into uniformly-spaced nanoliter droplets. The nebulization / desolvation approach was also employed for comparison purposes. The results of this comparison were discussed in the previous chapter.

Qualitative and quantitative studies of several elements were performed successfully. The limits of detection of the LIBS technique are in the ppm range, and are much higher than those obtained by some other atomic spectroscopic methods (e.g., ICP emission spectroscopy). A limitation of the LIBS technique is the very small active volume of the created laser spark, where all the processes have to take place.

Interelement studies showed that the method under study is "resistant" to matrix effects which are particularly pronounced in flame atomic spectroscopy. This happens because the laser plasma reaches very high temperatures. Simple real sample analyses were performed to examine the potential of the LIBS technique.

The interface of the LIBS method with isolated droplet production makes this technique very flexible for future applications in the area of solution samples. In addition, considering the extensive applications of the laser plasma for gases and solids, it makes laser-induced breakdown spectroscopy applicable to all types of samples.

B. Future Prospects

1. Improvements in Instrumentation

Since the LIBS instrumentation was set up in our laboratories for the first time, several improvements can be made. For the nebulizer / desolvation system, an increase in the sample introduction efficiency is expected if an ultrasonic rather than a pneumatic nebulizer is used. This should lower the detection limits considerably. Also, with the use of ultrasonic nebulization the size of the droplets produced can be controlled and optimized as in the case of the IDG. For the liquid stream approach, the computer control capability, provided with the existing isolated droplet generator, can be utilized for more flexibility (see Reference 4). In addition to that, modifications to the IDG instrumentation for easier use, will be very useful.

Various improvements can also be made in the electronics. A reliable high-gain, low-noise fast amplifier is a necessity for minimal distortion of the signal intensities and additional improvement in the

detection limits. A fast gated-PMT could be used to avoid viewing the initial continuum emission "spike" and eliminate any possibility of saturation of the PMT at early times and particularly at high gains. Automation of the apparatus would be another considerable improvement for data acquisition and signal processing. This would help in setting optimum parameters as well as in averaging enough data points for high SNRs.

2. Future Applications

In all of our experiments, the fundamental IR beam (at 1064 nm) of a Nd:YAG laser was used to provide sufficient energy for breakdown and the other processes associated with the excitation of the analyte. Since it is an invisible beam, it is quite difficult to work with; the green line at 532 nm (the first harmonic) would be a better choice as long as it can provide the required energy. The latter has been used successfully by other authors (46) in laser-induced explosion of water droplets. However, these workers did not use it for analytical applications and thus its capability in this regard is not known. Another advantage of the green line is that it is better collimated than the fundamental and therefore it can be transmitted easily with smaller divergence than the IR beam.

Addition of a second laser beam or another spectroscopic desolvation method might be necessary for improving detection limits, as has been reported by other authors (69). This implies very careful synchronization of the entire system, which in the case of the IDG, can be quite complicated.

Since LIBS is a variation of emission spectroscopy, multielement determinations can be performed as well. Selection of the best delay time for obtaining the highest sensitivity for each element should be done before obtaining any quantitative information. For simultaneous multielement analysis, this might involve a slight compromise in sensitivity, since each element has its own optimum observation time. However, from our results, it has been noted that the optimum time range for several elements is very similar. Therefore, simultaneous multielement determinations would involve only a slight reduction in sensitivity. The present detection system is practically limited to a single emission measurement at a time. Implementation of an optical multichannel analyzer (OMA) on the LIBS system would vastly improve the throughput of simultaneous multielement detection. Rapid gating of the detector might be necessary to reduce the background emission. This criterion is met by the Princeton Applied Research OMA III (130).

Laser-induced breakdown spectroscopy is easily applied to gaseous samples because of its nature. Therefore, another possible application of the laser spark is an on-line gas chromatographic detector, with elemental specificity. An unfortunate fact is that helium, which is a commonly used carrier gas for gas chromatography (GC), has a very high breakdown threshold. Because of this an appropriate mixture of two carrier gases must be tried in ratios that might lower this threshold. A similar effect has been noticed with certain mixtures of argon and neon (17).

Another application that was mentioned in Chapter VII is the use of LIBS as an HPLC detector. We have shown that LIBS can be successfully interfaced with the IDG. From studies that have been

performed by P.M. Wiegand (4) it was concluded that it should be possible to produce droplets with all common HPLC solvents. Initial results with selected solvents showed that both surface tension and viscosity affect the speed with which the jet forms a droplet stream. However, these effects were reproducible and could be compensated. Droplet charging of nonaqueous solvents was not possible for all solvents, but should work for most reverse-phase HPLC mobile phase systems. If the entire droplet stream can be sent to the excitation source, all common HPLC solvents should be usable. Having this information, the next step is to try the different HPLC solvents with the LIBS technique to study the possibility of using this system as an HPLC detector.

Finally, since we have introduced solution samples into the laser plasma in the form of liquid streams, using a flow injection system, another possible application is "real" flow injection analysis with LIBS. In this case, the system has to be optimized for the highest sensitivity, and lowest dispersion of the flow injection. This implies that the shortest possible tubing be used between the injection valve and the capillary. At the same time, it has to satisfy the requirements for the smooth operation of the IDG-LIBS combination, which demands a stable droplet stream.

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APPENDICES

APPENDIX A

**Argon Time-Resolved Spectra
obtained at various times after breakdown**

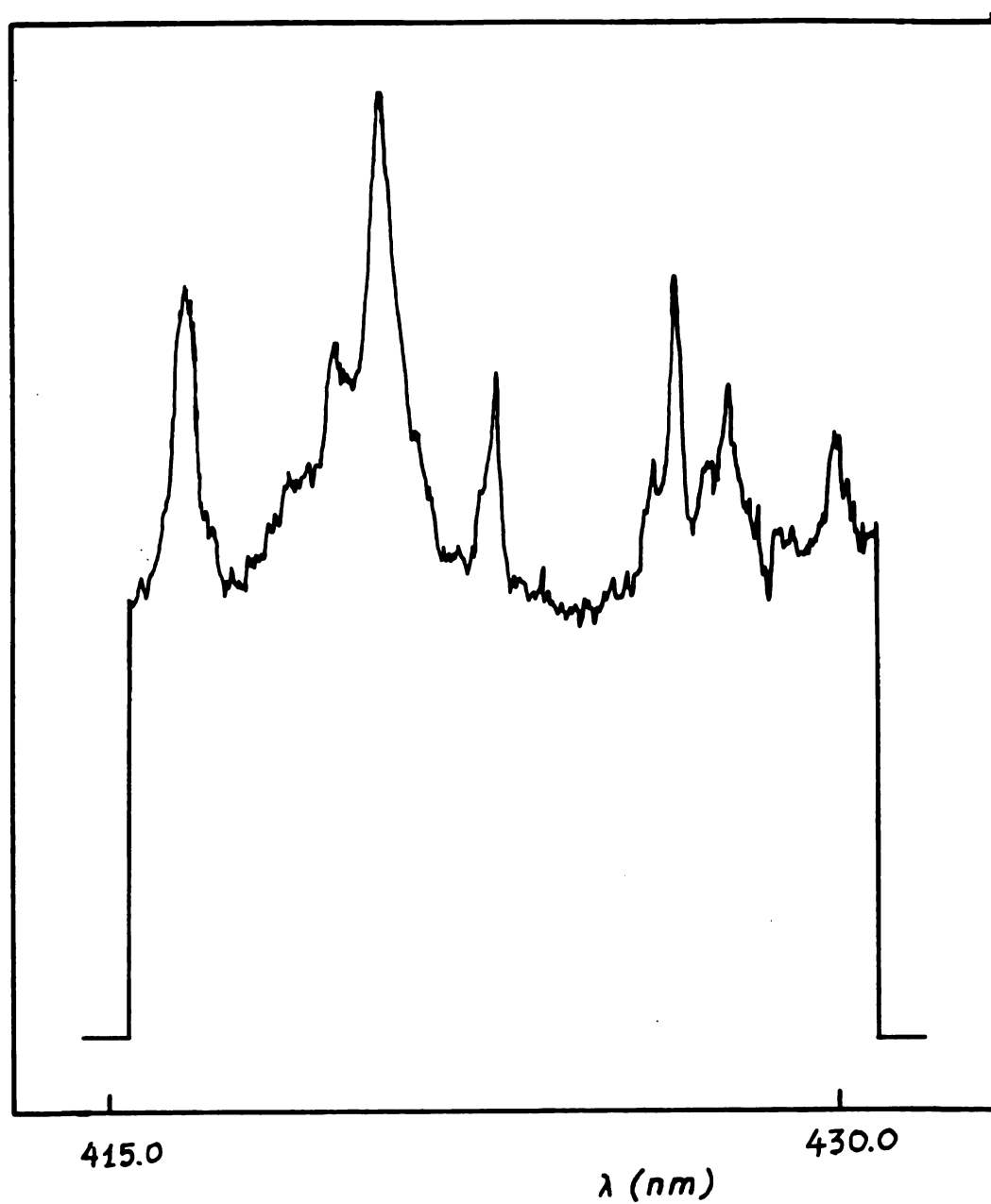


Figure A1. Argon Emission Spectrum at 0.5 μ s after Breakdown (Gain 1)

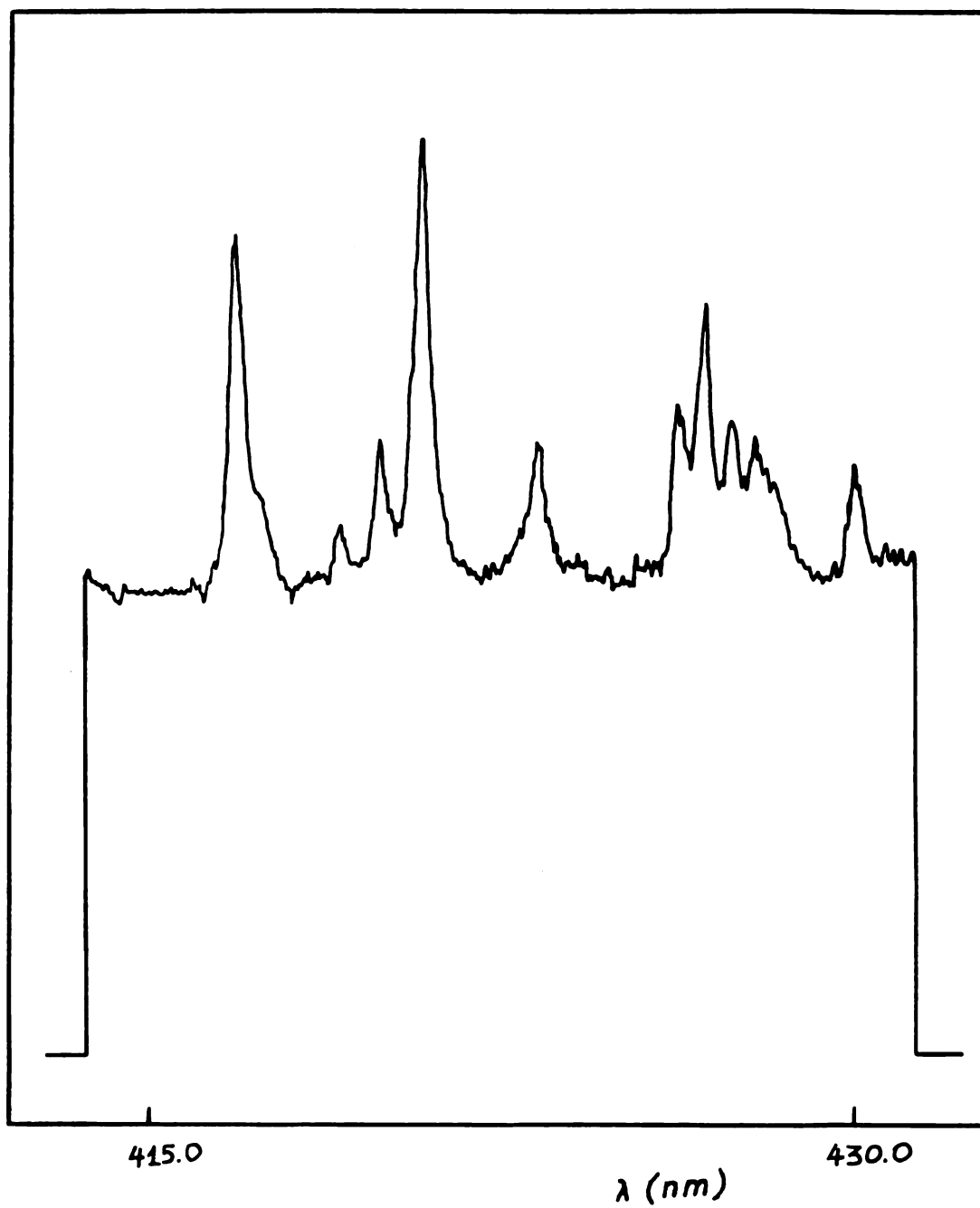


Figure A2. Argon Emission Spectrum at 0.7 μ s after breakdown (Gain 2)

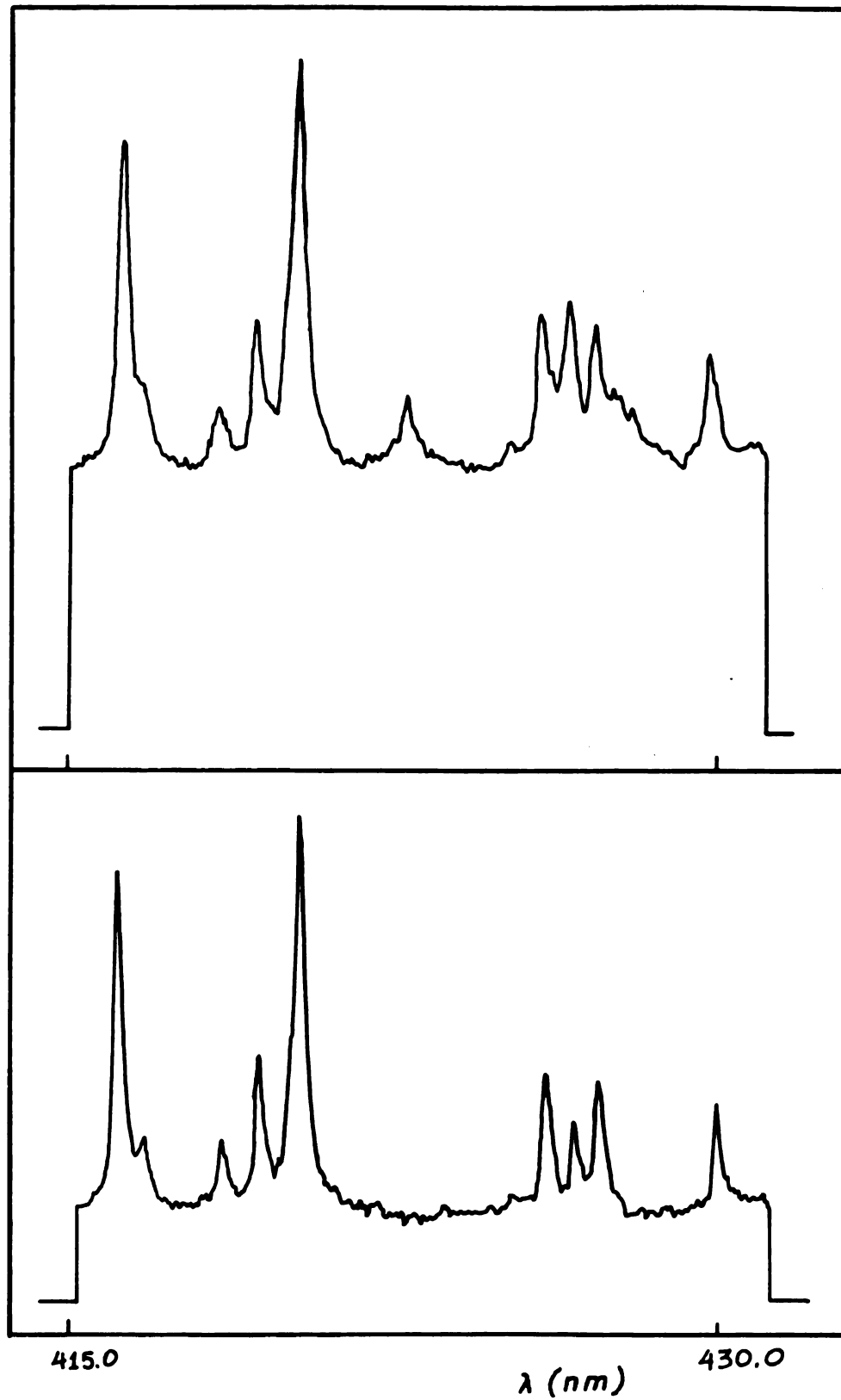


Figure A3. Argon Emission Spectra at 1 μ s (Spectrum A) and 5 μ s (Spectrum B) after Breakdown (Gain 2)

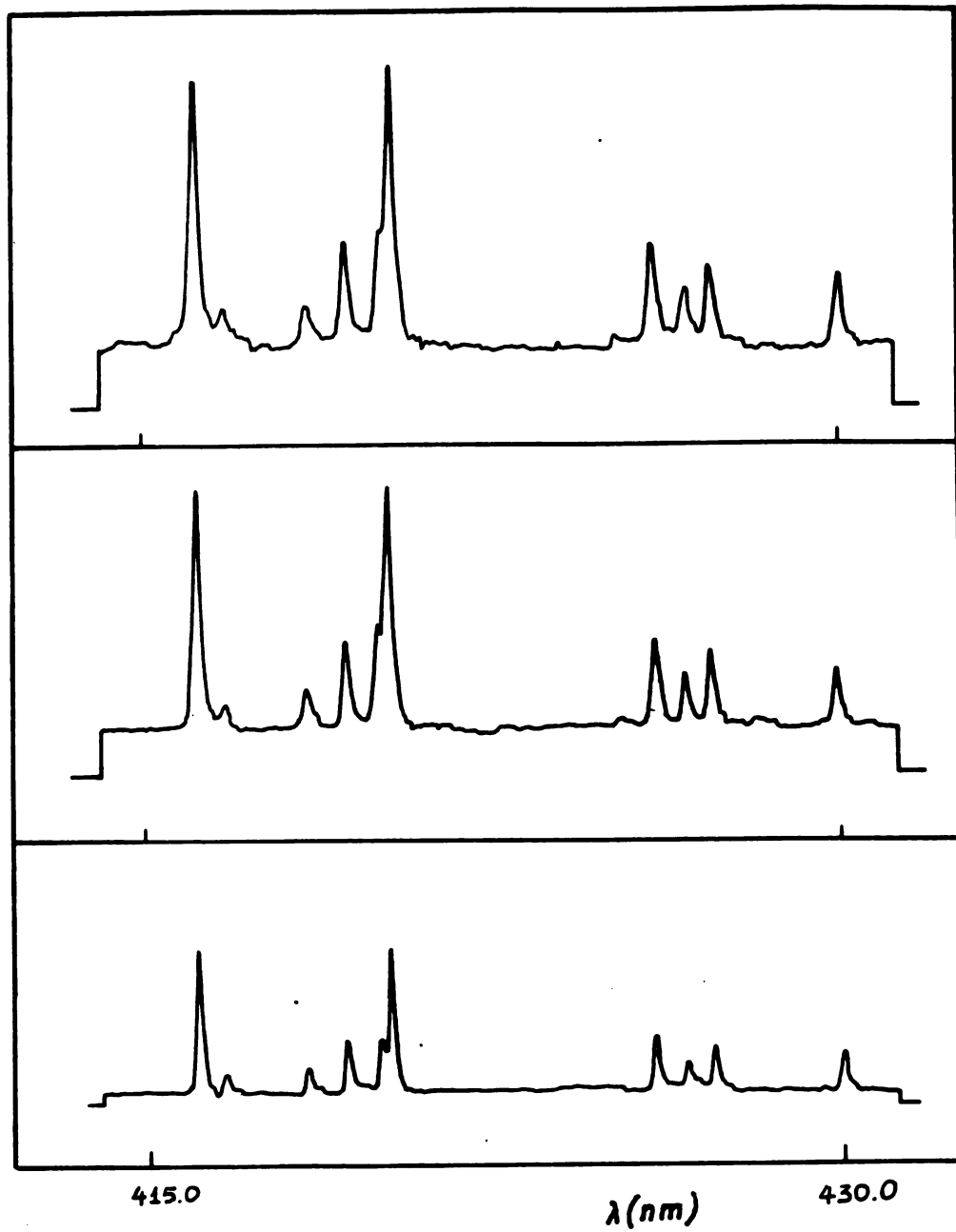


Figure A4. Argon Emission Spectra at 10 μ s (Spectrum A), 15 μ s (Spectrum B) and 25 μ s (Spectrum C) after Breakdown (Gain2)

APPENDIX B

Time-Resolved Spectra of analyte emission

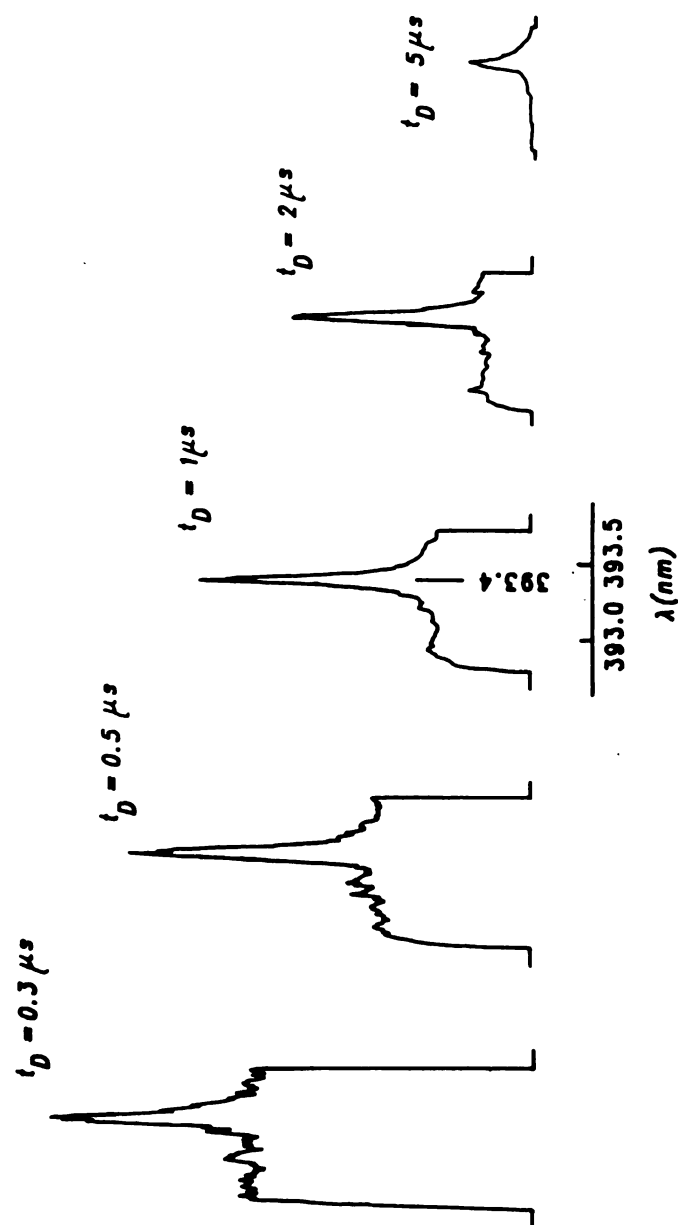


Figure B1. Time-Resolved Spectra of Calcium ionic line (at 393.4 nm) obtained with the Isolated Droplet Generator.

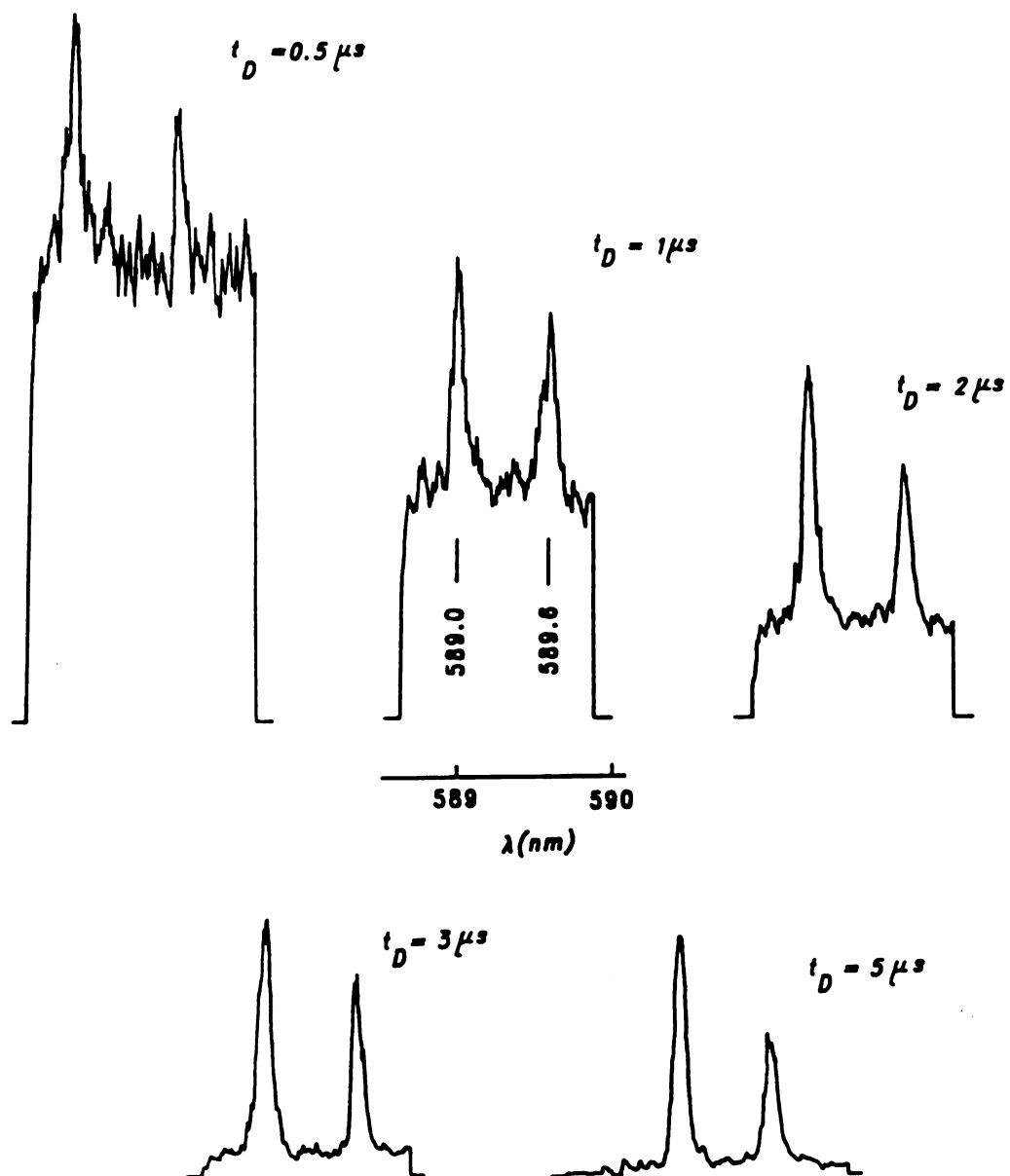


Figure B2. Time-Resolved Spectra of the Sodium Doublet (at 589.0 and 589.6 nm) obtained with the Isolated Droplet Generator.

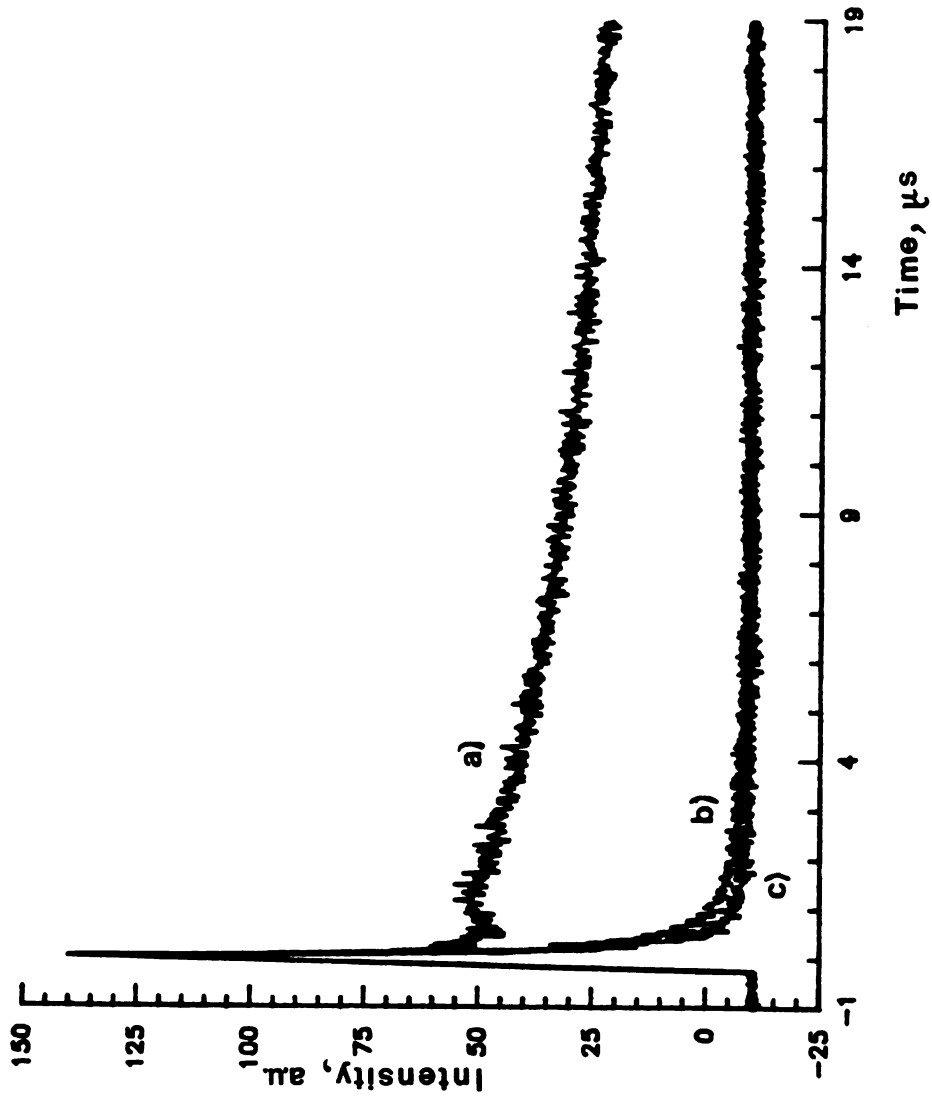


Figure B3. Emission Time Profiles at a) 393.4 nm, b) 393.0 nm and c) 394.2 nm for a 500 ppm calcium solution obtained with the aerosol apparatus.

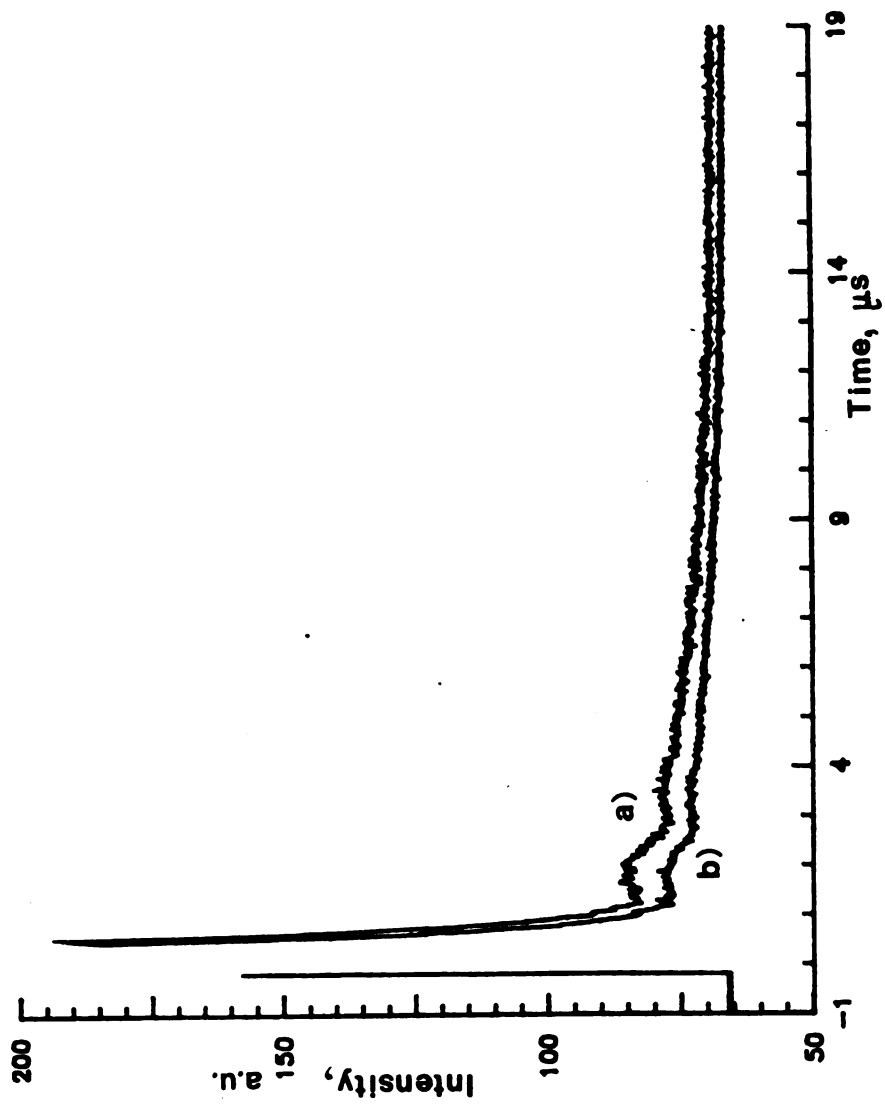


Figure B4. Emission Time Profiles at a) 422.7 nm and b) 422.4 nm for a 500 ppm sodium solution obtained with the aerosol apparatus.

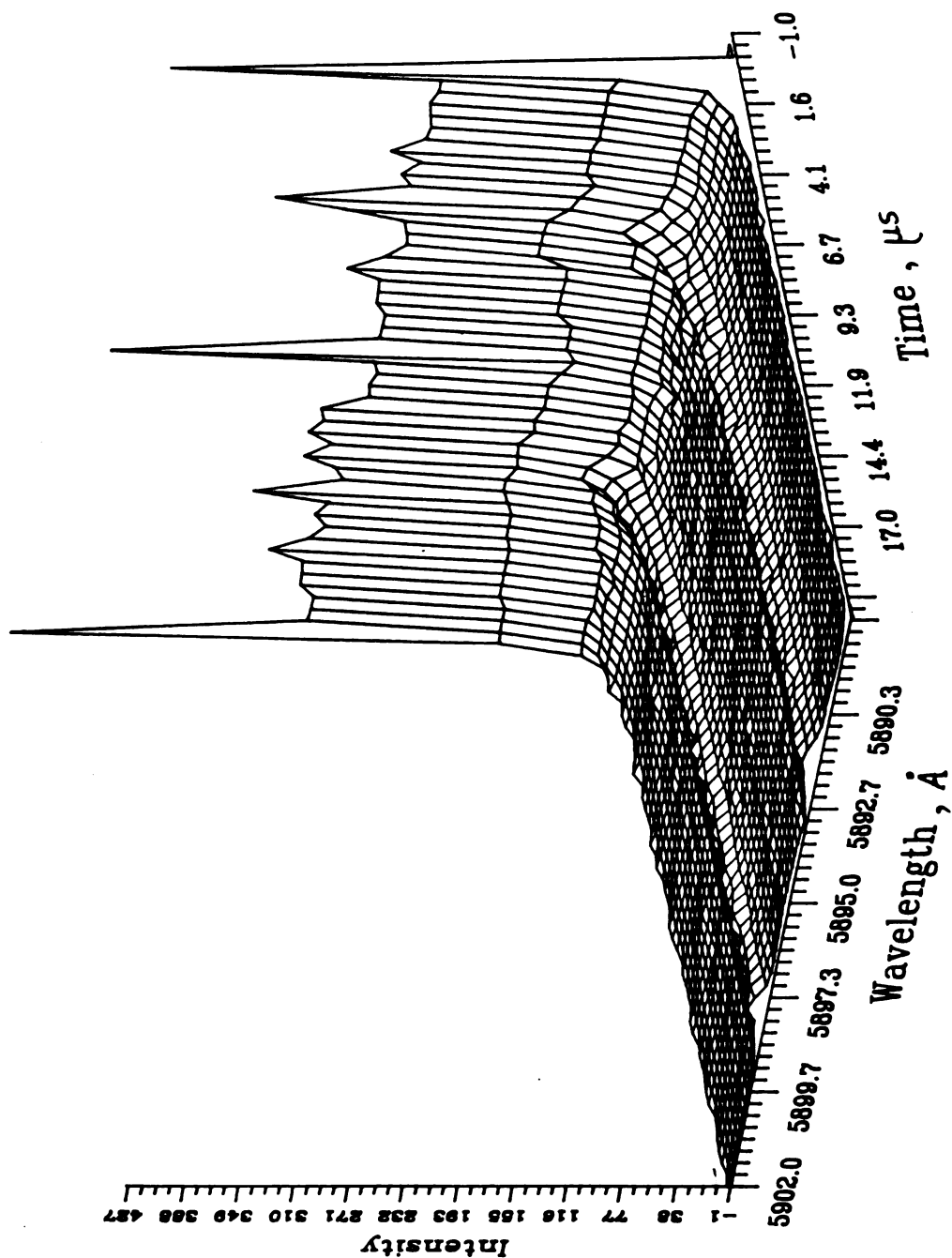


Figure B5. Three-Dimensional Plot (Intensity vs. Time vs. Wavelength) of the Sodium Doublet (at 589.0 and 589.6 nm) obtained with the aerosol apparatus.