ATOMIC EMISSION AND ATOMIC FLUORESCENCE SPECTROMETRY IN INDUCTIVELY COUPLED PLASMA

BY

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EDUCATION FOR INDEPENDENT THOUGHT

It is not enough to teach man a specialty. Through it he may become a kind of useful machine but not a harmoniously developed personality. It is essential that the student acquire an understanding of and a lively feeling for values. He must acquire a vivid sense of the beautiful and of the morally good. Otherwise he—with his specialized knowledge—more closely resembles a well-trained dog than a harmoniously developed person. He must learn to understand the motives of human beings, their illusions, and their sufferings in order to acquire a proper relationship to individual fellow-men and to the community.

ALBERT EINSTEIN
From New York Times
October 5, 1952
DEDICATION

This dissertation is sincerely dedicated to my wife, Christine Nikdel, and my mother, who have given me their love and encouraged me to obtain the endless knowledge within higher education. In their debt I will always be.
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I wish to take this opportunity to express my regard to the friends and colleagues who, through their interest and discussions, helped make this time pass so easily. I like to take particular pleasure in expressing special gratitude to my research director, Graduate Research Professor Dr. James D. Winefordner, for his constant sincerity, his steady guidance, and kindly inspiration throughout this work.

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ATOMIC EMISSION AND ATOMIC FLUORESCENCE SPECTROMETRY IN INDUCTIVELY COUPLED PLASMA

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Molecular emission spectra of native species (\textit{OH}, \textit{NO}, and \textit{NH}) in the argon inductively coupled plasma (ICP) have been studied as a function of height in the plasma, input power, and adjacent environment to the plasma. Similar studies were carried out with an ICP into which is introduced moderately concentrated solutions of elements forming stable monoxides, such as \textit{Sc}, \textit{Y}, \textit{Gd}, and \textit{Lu}.

Using a medium power (1.25-1.5 kW) ICP as an excitation source for atomic emission spectrometry with a glass concentric nebulizer, aqueous solutions of rare earth elements in pure solution and combined mixture of all the rare earth elements are measured except \textit{Pm}. Analytical lines and ICP characteristics for such measurements are given.

The characteristics of the emission line profiles of \textit{Ca}, \textit{Zn}, and \textit{Mg} in the inductively coupled plasma discharge were investigated by means of atomic fluorescence spectrometry. The combination of the experimentally obtained excitation and fluorescence curves of growth allowed the self-absorption and self-reversal effects on the emitted profiles to be
qualitatively detected. In such measurements the flame is used as a resonance detector. The results show that self-absorption, while present, is not severe and that self-reversal is absent in the observation zones commonly used for analytical measurements. Furthermore, the use of the ICP as excitation source in flame atomic fluorescence spectrometry permitted low limits of detection to be achieved with a simple experimental set-up.

An inductively-coupled argon plasma (ICP) is used as a narrow line radiation source for the excitation of atomic fluorescence in several analytically useful flames (nitrogen-separated air/acetylene and nitrous-oxide/acetylene). Detection limits for 14 elements are compared to atomic fluorescence detection limits using other radiation sources and to those of other atomic spectrometric techniques. Dominant noise sources which limit measurement precision at low and high concentrations and the significance of and correction for the scatter problem are discussed. The reduction of spectral interference observed in ICP-emission is demonstrated for the determination of zinc in unalloyed copper (NBS SRM-394 and 396). The technique is also applied to the determination of zinc in fly ash (NBS SRM-1633), cadmium and zinc in simulated fresh water (NBS SRM-1643), and copper and zinc in orange juice.

Atomic/ionic fluorescence in the ICP using a cw dye laser as an excitation source has been studied. Detection limits for elements such as Ba, Na, Li, and V are given. Also the results show the non-Local Thermodynamic Equilibrium excitation conditions in our low powered ICP.

Relative ionic and atomic fluorescence profiles for barium have been obtained in an argon inductively coupled plasma by exciting different transitions with a nitrogen-laser pumped tunable dye laser and measuring the resulting fluorescence pulses with a boxcar averager. Spatially resolved profiles are directly obtained without the need of an Abel inversion
procedure, with a volume resolution of approximately 0.2 mm$^3$. The profiles are given along the excitation axis as well as along the observation axis, for different heights above the coil and different input powers. At low heights, the ion profile resembles a hollow pencil with a typical double-peaked, asymmetric distribution, while the atom profile seems to be complementary to the ion profile. Some scatter from water is also evident at low heights. By tuning the laser at two excitation transitions sharing a common upper level, the temperature of the plasma could be evaluated.

The atomic and ionic fluorescences of iron, tin, barium and indium excited by flashlamp- and nitrogen laser-pumped pulsed dye lasers in the inductively coupled plasma (ICP) are studied. Noise sources are investigated and detectability is compared to the techniques of ICP-emission and laser-excited atomic fluorescence spectrometry.
CHAPTER ONE

INTRODUCTION

A - Atomic Emission

A.1 - History of the ICP

Early developments of electrodeless discharges. The low-pressure electrodeless discharge has been known since 1884. It was discovered first by Hittorf in experiments on the conduction of electricity through the noble gases.

Mavrodineanu and Hughes traced the rf-excitation of low-pressure gases for spectrochemical analysis to the work of Tesla in 1891. Then, Thomson, in 1927 published his experimental results along with the theory of the electrodeless discharge expressing the magnetic and electric field spatial distributions by Bessel functions, assuming constant plasma conductivity across the column. Later Babat, in 1942, discovered that a ring discharge can be maintained while the pressure is increased up to atmospheric level. Thus, Babat is the inventor of the modern day inductively coupled plasma discharge. However, the major interest developed only after Reed successfully showed that one can produce an "Induction Torch" where the plasma is observable above the torch and is useful as a heat source.

The discovery of stabilized induction heated plasmas operated at atmospheric pressure with flowing gases through an open-ended tube by Reed, has led to two major applications: first as an induction-arc for
engineers, and second as a spectrochemical excitation source for analytical chemists.

The main reason for the delay in developing a stable Inductively Coupled Plasma (ICP) after Babat's publication was the design of a reliable method of cooling and heat protection of the plasma. Water-cooled walls, water jackets, and porous dielectric walls were applied, but Reed's approach to a gas cooling system has proven most effective and is now universally accepted for spectrochemical applications.

Reed's work showed three attractive properties for the plasmas which were (i) high gas temperature, (ii) capability of being sustained in noble gas environments (important from free-atom lifetime consideration), and (iii) freedom from contamination by electrodes, which were not required.

After Reed, two groups (Greenfield et al. and Wendt and Fassel) independently investigated the potential use of induction-heated plasmas as an excitation source (i.e. vaporization, dissociation, decomposition cells, free atom/ion reservoir) for atomic emission spectrometry.

Fassel and co-workers studied a great number of variables for developing an analytically useful ICP system. Until 1969, Fassel and his group had experienced problems introducing samples into the high temperature zone of the plasmas. At that time Fassel and Dickinson were able to "punch a hole" through the center of the plasma by introducing high velocity carrier gas in the sample injector. However, this same solution had been used since 1964 by Greenfield et al. in England.

Trace analysis. The aim of analytical chemistry has been described as the chemical characterization of a sample in general and to introduce improved methods for this characterization. It has been stated that the requirements for an ideal elemental technique are (i) to give unbiased
results, (ii) to be sensitive and give low detection limits, (iii) need no sample pretreatment, (iv) to cover a broad range of elements (i.e. ideally measure all elements in the periodic table), (v) to possess a large dynamic concentration range, and (vi) to allow simultaneous multi-element determination.

Looking to the field of instrumental analysis, the optical techniques seem to be the most appropriate for analytical purposes. They are favored for their speed, ease of operation, as well as simple sample pretreatment. The possibilities of handling many samples, of giving high sensitivity, and of determining numerous elements simultaneously are the other important characteristics relating to this field.

The inductively coupled radio-frequency argon plasma (ICP), being an extremely efficient atomic/ionic emission source, has multi-element capability and the high gas kinetic temperature makes it less susceptible to the chemical interferences than lower temperature sources such as flames. (In general, chemical effects are less than 10%). The precision is comparable to flame atomic absorption (1-5%). The reported linear dynamic range approaches the capabilities of modern electronic equipment, which are indeed needed to take advantage of this feature, and exceeds the linear dynamic range of flame atomic absorption considerably.

The limits of detection reported most widely in the literature for emission spectrometry with the ICP usually lie in the range of 0.01-10 ng/mL and are one to three orders of magnitude lower than with high temperature flames in emission spectrometry.

A.2 - Theory and Mechanism of Excitation in the ICP

The principle of spectral analysis is based on the following principles: conversion of the element under study in the sample to the gas
phase by the excitation source, i.e. concentration in condensed phase to atoms or ions per unit volume in the gas phase c→n_M; transition of a certain number of these atoms/ions from the ground state to the excited state (or metastable state) M→M^*; conversion of the excitation energy into the spectral line radiation M^*→M+hν; selection of the radiation of the specific line from the total radiation of the source by the spectral instrument and its transformation by the recording system into a measurable signal from the line under study (e.g. photomultiplier photocurrent in case of photoelectric recording etc.).

A unit volume of the luminous source contains n_M atoms or ions of the analyte. The elementary phenomenon leading to the excitation of ground state atoms/ions and the quenching of the excited atoms/ions (M→M^*) are rather varied. These are collisions of atoms/ions with free electrons and heavy particles, atoms, ions, electrons and molecules of the gas in the source, as well as, in some cases, chemical reactions with the participation of M atoms/ions.

In practical spectral analysis, resonance lines of atoms/ions, corresponding to the transition from the nearest excited level to the ground state are often measured. In sources with a high concentration of electrons, e.g., in plasmas, the basic phenomenon which lead to the excitation of resonance levels and also to atomization/ionization are collisions with electrons. Collisions with heavy particles are less effective.\textsuperscript{16}

In the rf-excited, inductively coupled argon plasma, the population (concentration) of excited states and degree of ionization exceeds the values that correspond to the Boltzmann-Saha expression and this departure from LTE is postulated to be due to the influence of argon metastable atoms.\textsuperscript{16,17} Consider a volume element ΔV in the center of the ICP
at a given height (≈15 mm) above the induction coil. Let us assume that LTE conditions (T≈6000 K) in AV are disturbed by the creation of an over-population of argon metastable atoms (outside of AV) and representing this by a net inflow of metastables from the surroundings to AV. This inflow has a rate constant \( k_m \) (cm\(^{-3}\) s\(^{-1}\)) and its value depends on externally controllable factors such as power input in the coil region (energy addition region), the plasma gas flow conditions, type of ICP (two-flow argon ICP or a three-flow ICP with nitrogen as the plasma gas and argon as the carrier and auxiliary gas), and the height of AV from the induction coil.

Conservation of energy, charge and mass balance require \(^{16,18}\) (i) a net outflow of argon ions (Ar\(^+\)) and electrons from the coil region having a rate constant \( k_i \) (cm\(^{-3}\) s\(^{-1}\)) for ambipolar diffusion; (ii) a net outflow of argon atoms (Ar) in the ground state from the coil region having a rate constant \( k_a \) (cm\(^{-3}\) s\(^{-1}\)) for diffusion; and (iii) the following inter-relationships to apply

\[
k_i = (\frac{\overline{V}_i}{V_i})k = 0.73 \quad k = 1 - k_a,
\]

and

\[
k_a = 1 - (\frac{\overline{V}_m}{V_i})k_m = 0.27 \quad k = 1 - k_i,
\]

where \( \overline{V}_m \) is the weighted average excitation potential of the metastable atoms at 6000 K (\( \overline{V}_m \approx 11.58 \) eV), \( V_i \) the ionization potential of argon (\( V_i \approx 15.76 \) eV), and \( k_m \) is the rate constant of the inflow of argon metastable atoms from their surroundings to the volume \( \Delta V \).

The ionization of metastable argon atoms and argon atoms by electron impact and the reverse three-body recombination reactions occur within the volume \( \Delta V \), are given by equations 3 and 4 (metastable argon atom acts
as an \textit{ionizant}, i.e. as an \textit{early ionizable constituent}, eq. 3, and as an \textit{ionizer}, eq. 3a, having assigned the "dual role"):

\begin{align*}
\text{Ar}_m + e & \xrightleftharpoons[k_{21}^\text{}}{}[k_{12}^\text{}}] \text{Ar}^+ + 2e, \\
\text{Ar}_m + M & \xrightleftharpoons \text{M}^+ + e + \text{Ar}^+, \\
\text{Ar} + e & \xrightleftharpoons[k_{43}^\text{}}{}[k_{34}^\text{}}] \text{Ar}^+ + 2e.
\end{align*}

These rate constants are interrelated, for local thermodynamic conditions, by:

\begin{align*}
K_{\text{Ar}_m} &= k_{12} / k_{21}, \quad (\text{cm}^3 \text{s}^{-1} / \text{cm}^6 \text{s}^{-1}), \\
K_{\text{Ar}} &= k_{34} / k_{43}, \quad (\text{cm}^3 \text{s}^{-1} / \text{cm}^6 \text{s}^{-1}).
\end{align*}

where \( K_{\text{Ar}_m} \) and \( K_{\text{Ar}} \) are the Saha equilibrium constants in \( (\text{cm}^{-3}) \) defined by:

\begin{align*}
K_{\text{Ar}_m} &= n_{\text{Ar}^+ n_e} / n_{\text{Ar}_m}, \quad (\text{cm}^{-3} / \text{cm}^{-3}) \\
&= 4.83 \times 10^{15} (\text{cm}^{-3} K^{-3/2}) T^{3/2} (Z_i / g_m) 10^{(-5040(E_i - E_m) / T)},
\end{align*}

and

\begin{align*}
K_{\text{Ar}} &= n_{\text{Ar}^+ n_e} / n_{\text{Ar}}, \quad (\text{cm}^{-3} / \text{cm}^{-3}) \\
&= 4.83 \times 10^{15} (\text{cm}^{-3} K^{-3/2}) T^{3/2} (Z_i / g_o) 10^{(-5040E_i / T)},
\end{align*}

where \( Z_i \) is the partition function of Ar+ (dimensionless); \( T \) the absolute temperature (K); \( g_m \) and \( g_o \) are the statistical weights for metastable
argon and ground state argon (dimensionless); $E_m$(eV) the excitation energy of the relevant metastable level; $E_i$(eV) the excitation energy of argon.

For a steady state of the rate equation for Ar+ and electrons from equations 3 and 4, one would obtain the following:

$$\frac{dn_{Ar^+}}{dt} = k_m n_{Ar^+} n_e + k_{21} n_{Ar^+} n_e^2 - k_{12} n_{Ar_m} n_e,$$  \hspace{1cm} (9)

and

$$\frac{dn_e}{dt} = k_{12} n_{Ar_m} n_e + k_{34} n_{Ar^+} n_e^2 - k_{21} n_{Ar^+} n_e^2 - k_{43} n_{Ar^+} n_e^2 - k_i.$$  \hspace{1cm} (10)

Using the quasi-neutrality condition, $n_e = n_{Ar^+}$, combining the equations 1, 9, and 10 would give:

$$n_e^3 - K_{Ar} n_{Ar^+} n_e - 0.27 \left( k_m / k_{43} \right) = 0.$$  \hspace{1cm} (11)

The general solution of equation 11 is an expression for $n_e$ in terms of both $K_{Ar}$ and $k_m / k_{43}$. Two special cases are of interest in the ICP:

(a) $k_m / k_{43} \gg K_{Ar} n_{Ar^+} n_e$, this applies to an ICP; when $T=6000$ K, $n_e=10^{15} - 10^{16}$ cm$^{-3}$, in which the second term in equation 11 is negligible compared to $n_e^3$ and therefore:

$$n_e = \left( 0.27 k_m / k_{43} \right)^{1/3}, \text{ (non-LTE)}, \hspace{1cm} (12)$$

(b) for $k_m = 0$, equation 11 yields the Saha value of $n_e$:

$$n_e = \left( K_{Ar} n_{Ar^+} \right)^{1/2}, \text{ (LTE)}. \hspace{1cm} (13)$$

This model can describe a range of conditions between non-LTE (eq. 12) and complete LTE (eq. 13). The non-LTE model involving a mechanism in which metastable argon acts as both an ionizer and ionizant appears
to be a useful postulate, as it permits a qualitative understanding of
the high sensitivity of ionic lines, the high electron number density,
and the negligible ionization interferences observed in ICP's under op¬
timum operating conditions.

A.3 - Sensitivity and Growth Curve in ICP

Four analytical figures of merit of an atomic emission spectrometer
are: the sensitivity, the signal-to-noise ratio, the line to background
ratio, and the detection limit. The detection limit is usually expressed
as the concentration which produces a signal equal to three times of the
standard deviation of the blank. The standard deviation in the blank
is a difficult quantity to predict theoretically. Neglecting the noise
in the detection system, the following noise sources can be considered
in emission ICP studies: source flicker noise, variation in the aerosol
production, in the solvent evaporization, and in the volatilization of
the dry particles, and instabilities of the plasma (electrical or fluid
dynamic).

The ICP has the properties of a dynamic source in common with the
arc and the flame. It has a stationary high temperature zone (coil re¬
gion 10000 K) in a fast flowing gas stream maintained by forced and/or
free convection. Sample material injected into the gas stream quickly
passes into the high temperature zone. Nevertheless, the ICP, as an ex¬
citation source, has several disadvantages:

(a) concentration of the element in the condensed phase and the
atom/ion population in the excitation zone in the gas phase do not have
a known unique relationship; they are function of the analyte solution
uptake flow rate and of the carrier gas velocity in the source as well
as the plasma characteristics; (b) analyte injection is not efficient,
and so it has to be supplied at a low constant rate for maintaining a steady signal; also material that has been injected into the source cannot be used for further investigation and observation; (c) incomplete mixing, unstable flow and turbulence introduce fluctuations in signal and background, which raise the detection limit; and (d) it is almost impossible to understand the detailed performance of a dynamic source because of the transient nature and the interdependence of the mixing, heating, dissociation, excitation, and ionization processes to which the analyte is subjected, combined with the non-uniform velocity and temperature fields of the source.

The sensitivity, $S$, which is generally defined in analytical chemistry as the change of the signal per unit change of the analyte concentration is inversely related to the detection limit. For a linear calibration curve, it is the slope of this curve, which relates, in its simplest algebraic expression (eq. 14), the line radiance, $B$, in $(W \text{ cm}^{-2} \text{ sr}^{-1})$ with the analyte concentration $n_M$ in the gas phase $(\text{cm}^{-3})$. It is clear that to convert solute concentrations to emission of light a great number of intermediate physical processes are needed.

$$B = S n_M$$

In order to inject the sample solution to the plasma, a means of transport is needed. Thus, the solution is transported up by a nebulizer and is converted into a fine spray of droplets. The larger droplets fall into the drain tube and the smaller droplets are carried away to the plasma with carrier gas, which also drives the nebulizer. The ratio of the volume of droplets which remain in the carrier gas and those originally taken up is called the efficiency of the nebulizer ($\varepsilon_N$, in our case, is $=0.10$).
Actually the amount of liquid $V_1$ delivered per unit time (2.5 mL/min) is diluted by the carrier gas $V_g$ per unit time (0.5 L/min) by a factor of $V_1/V_g = 0.005$. The smaller droplets are introduced into the high temperature zone of the plasma. The solvent, which is usually water, evaporates and carrier gas, by the free jet expansion model, expands with a factor $T_g/T_r$, where $T_g$ is the kinetic gas temperature and $T_r$ is room temperature.

The fraction of the solvent in the droplets that can be evaporated depends on the kinetic gas temperature gradient, which the droplets must always pass before reaching the observation zone. Also the droplet size distribution is important, because complete evaporation of large droplets takes more time than small ones. This transit time is related to the linear velocity of the carrier gas, the temperature gradient as well as the droplet size and composition, because expansion of the gas will reduce the velocity. In the literature, no experimental results are available to locate the height in the plasma, where all droplets are just evaporated. However, similar experiments in flames\textsuperscript{20} suggest that solvent evaporation will be completed rapidly in the ICP.

The next step is volatization, in which a high kinetic gas temperature is needed to disintegrate the particle. If only analyte is injected, the dry particles will be very small. However, if an excess of another salt as a matrix is present, the dry particles will be larger. The boiling point of this salt can deviate greatly from that of the salt of the analyte. Thus, the amount of analyte released in the presence of a matrix is different from that without the matrix. This could produce a different signal level, which is generally called a chemical/physical interference effect.
As the solid particles are transported deeper into the plasma (the high temperature zone), their temperature will rise and start to boil and come into the gas phase state. At this point the relationship between the solution concentration, c, and the total vapor concentration, \( n_T \), of analyte species has been established. From here on, the most important processes are dissociation, ionization and excitation, which are all temperature (and time) dependent.

Let us consider each process separately, when the molecules of the original salt are in the gas phase, they will dissociate into free atoms. Because the solvent is water, the oxygen atoms from dissociation of water, could react with the free analyte atoms to form substantial monoxide species which has been observed for stable monoxides such as rare earths in this laboratory and will be shown in Chapter 2. The equilibrium can be shown as follows:

\[
\begin{align*}
\text{MO} & \rightleftharpoons \text{M+O}. \\
& \text{(15)}
\end{align*}
\]

The degree of atomization \( \beta_a \) can be calculated as follows:

\[
\begin{align*}
n_T &= n_M + n_{MO}, \\
K_d &= \frac{n_0 n_M}{n_{MO}}, \\
\beta_a &= \frac{n_M}{(n_M + n_{MO})} = \frac{K_d}{(n_0 + K_d)}, \\
& \text{where according to Boumans,}^{20} K_d, \text{ the equilibrium constant, can be calculated from eq. 17:}
\end{align*}
\]

\[
K_d = \frac{n_M}{(n_0 + n_{MO})} \approx 5 \times 10^{-24} \times 10^{-5040E_d/T_d},
\]

where \( n \)'s are denoted to the particle densities, \( T_d \) is the dissociation temperature (K) and \( E_d \) the dissociation energy in (eV) (see Table 1). Because
water is completely dissociated, the value for \( n_0 \) is the same as the number density of water molecules introduced by the nebulizer into the plasma, i.e. \( 5 \times 10^{16} \text{ cm}^{-3} \).

The next important gas phase process is ionization, which is comparable to the dissociation except that the products are ions and electrons. The degree of ionization is defined in the same manner. Because here we are interested in atoms only, the expression for \( (1-\beta_i) \) is used, i.e. the fraction of elemental species not ionized

\[
1-\beta_i = \frac{n_M}{n_M + n_M^+} = \frac{n_e}{n_e + K_i},
\]

where \( K_i \) is the Saha constant, and its numerical form is

\[
K_i = 4.83 \times 10^{15} \frac{T_i^{3/2}(Z_i/Z_a n_e)}{10^{-5040E_i/T_i}},
\]

where \( T_i \) is the ionization temperature in (K), \( E_i \) is the ionization energy in (eV), \( Z_i \) and \( Z_a \) are the partition functions for ion and atom (dimensionless). The result for \( (1-\beta_i) \) is shown in Table 1.

By combining these processes and assuming complete volatilization, the relation between the solute concentration and the free atom number density in the plasma can be expressed as

\[
n_M = \varphi c_0 (1-\beta_i), \tag{20a}
\]

and for ion is given by

\[
n_M^+ = \varphi c_0 \beta_i, \tag{20b}
\]

where \( \varphi \) is the conversion factor in \( \text{atoms cm}^{-3}/\mu \text{g mL}^{-1} \), and is given by

\[
\varphi = (N_A/M_A) (V_1/V_g) (T_r/T_g) (10^{-6}) \epsilon_n, \tag{20c}
\]

with
$N_A = \text{Avogadro's number}, \text{ atoms (molecules) per mole, } 6.0 \times 10^{23} \text{ (dimensionless)}; \ M_A = \text{atomic (molecular) weight of analyte, (g/mole), } \ n_M \text{ and } c \text{ are in (cm}^{-3}\text{) and (\mu g/mL), respectively.}$

The next important process in the gas phase is excitation, which is the process which transfers the atoms/ions from the ground state to the excited state. Upon returning to the ground state light is emitted, which the relation of emitted light and total number density of free atoms is given by:

$$J = I_1 n_M \exp\left(-\frac{E_{ex}}{kT_{ex}}\right), \tag{21}$$

where $E_{ex}$ is the excitation potential in (eV), $T_{ex}$ is the excitation temperature (K), $J$ the emittance expressed in $(W \text{ cm}^{-3} \text{ Sr}^{-1})$, $k$ is the Boltzmann constant (eV K$^{-1}$), and $I_1$ is an element dependent $(W \text{ sr}^{-1})$, (see Table 1), which is given by the equation 21a:

$$I_1 = \left(\frac{h \nu_{ul}}{4\pi}\right)(g_u/Z_a)A_{ul}, \tag{21a}$$

where

- $g_u =$ the statistical weight of the upper level, (dimensionless)
- $h =$ the Planck constant, (erg s) or $(W \text{ s}^2)$
- $\nu_{ul} =$ the frequency of the transition $u \rightarrow l$, $(s^{-1})$
- $Z_a =$ the partition function of the atom, (dimensionless)
- $A_{ul} =$ the probability of the transition $u \rightarrow l$, $(s^{-1})$.

A very important aspect is the quantity, $B$, the light emitted per sr per area element in the plasma source. However, when the intensity is measured, the detector receives its light from many different volume elements as far as they fall within the observation zone of the optics. In fact, the light emitted along the line of sight is collected over the
entire depth of the plasma. For a radially symmetric plasma at the center of the plasma, the radiance, $B$, emitted by a narrow beam of observation given by:

$$B = 2 \int_0^R J(r) \, dr.$$  \hfill (22)

The complete expression is found by substituting the equations 20 and 21 into the equation 22:

$$B = 2I_1 \phi \int_0^R a(r)(1 - \beta_1(r)) \exp\left(-\frac{E_{ex}}{kT_{ex}}\right) \, dr,$$  \hfill (23)

where the radial dependence of dissociation, ionization and excitation has been indicated. For ionic lines, expression 23 changes to 24:

$$B = 2I_1 \phi \int_0^R \beta_1(r) \exp\left(-\frac{E_{ex}}{kT_{ex}}\right) \, dr.$$  \hfill (24)

It is possible to calculate the sensitivity, $S$, with the aid of the complete equations 23 and 24, but ignoring the radial variation of the parameters (see Table 1). And the growth curve is given in Figure 1 in the log-log plot. For high $n_M$, the slope is 1/2, and for low $n_M$, the slope is 1.

Under some circumstances, it is logical to use the ionic line instead of the atomic line to take advantage of the high fraction ionized. Experimentally this has been recognized and it appears that it can be applied to a great number of elements (e.g., Ba, Mg, Fe, Mo, Nb, Pd, Ti, V, W, Ca, and rare earths).

In conclusion, it can be mentioned that (i) the fundamental parameters which determine the sensitivity in the ICP should be known, in order to optimize the analysis to obtain the best results; and (ii) the dependence of these parameters upon a change of operating conditions in
### Table 1

**CALCULATED VALUE OF SENSITIVITY IN ICP**

<table>
<thead>
<tr>
<th>Data</th>
<th>Element</th>
<th>Na</th>
<th>Ca</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ</td>
<td>(nm)</td>
<td>588.99</td>
<td>422.67</td>
<td>213.86</td>
</tr>
<tr>
<td>( I_1 )</td>
<td>(W sr(^{-1}))</td>
<td>5.92x10(^{-14})</td>
<td>3.75x10(^{-13})</td>
<td>2.52x10(^{-12})</td>
</tr>
<tr>
<td>( E_{ex} )</td>
<td>(eV)</td>
<td>2.10</td>
<td>2.93</td>
<td>5.80</td>
</tr>
<tr>
<td>( E_{d} )</td>
<td>(eV)</td>
<td>3.90(NaOH)</td>
<td>4.7(CaO)</td>
<td>4.0 (ZnO)</td>
</tr>
<tr>
<td>( E_{i} )</td>
<td>(eV)</td>
<td>5.14</td>
<td>6.11</td>
<td>9.09</td>
</tr>
<tr>
<td>( \exp\left(-E_{ex}/kT_{ex}\right) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \beta )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \left(1-\beta_{i}\right) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( S=B/n_M )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( (W \text{ cm sr}^{-1}) )</td>
<td>LTE</td>
<td>6.1x10(^{-21})</td>
<td>7.2x10(^{-21})</td>
<td>7.1x10(^{-23})</td>
</tr>
<tr>
<td></td>
<td>non-LTE</td>
<td>1.1x10(^{-22})</td>
<td>1.1x10(^{-22})</td>
<td>3.9x10(^{-23})</td>
</tr>
</tbody>
</table>

**LTE:** \( T_{ex}=T_{d}=T_{i}=5000 \text{ K} \)

**non-LTE:** \( T_{ex}=5000 \text{ K}; T_{d}=4000 \text{ K}; T_{i}=8000 \text{ K} \)

\( \text{ex=excitation, d=dissociation and i=ionization} \)
Figure 1. Growth Curve for Atomic Emission.
the plasma, such as a change in power, gas volume ratio, and observation height, must be known; from a practical analytical point of view, ignorance of these relevant data is not desirable.

B - Atomic Fluorescence

B.1 - History of Fluorescence

Previous Investigations. Although the fluorescence of atomic/ionic vapors was investigated by several physicists in the 19th and 20th centuries; the major advances began in 1955, when Boers, Alkemade, and Smit used atomic fluorescence for studying the principle of physical and chemical processes in flames. Alkemade also suggested the potential use of atomic fluorescence in analytical spectroscopy.

Although the principles of atomic fluorescence have been known for many years, its first use in analytical chemistry for spectrochemical analysis was by Winefordner and Vickers in 1964. Much of the credit for this is attributable to two research groups in particular, Winefordner's group in the U.S.A. (University of Florida) and West's group in England (Imperial College).

In atomic fluorescence, just as in atomic absorption, the sample is atomized and then by optical pumping with a suitable external light source radiationally excited. Here, however the radiation emitted by the deactivation of excited atoms is usually measured at 90° to the incident beam. In atomic fluorescence the intensity linearly depends upon the number of excited atoms/ions if there is negligible self-absorption. Since the fluorescence intensity from the excited species is controlled by the intensity of the exciting source, the intensity of this source (within the absorption profile) is much more important in AFS than in
AAS. It has been shown that the fluorescence intensity depends linearly on the excitation source intensity and the quantum efficiency of the transition involved.

It should be mentioned that these linearities are valid only for low intensity sources, such as Hollow Cathode Lamps (HCLs) metal vapor discharge lamps, xenon arcs, and Electrodeless Discharge Lamps (EDLs). In fact the use of high intensity sources, such as tunable dye lasers, may result in a near-saturation of the upper energy level involved in the fluorescence transition. Because of saturation, the fluorescence radiance (for two level atomic system) does not depend on the source intensity or quantum efficiency of the transition. Furthermore, self-absorption is minimized if the correct illumination geometry is used. Tunable dye lasers are fairly expensive and are now useful only for slow sequential single element determination. Therefore, laser excited atomic/ionic fluorescence with an inductively coupled plasma is not presently a useful analytical tool because of the single element limitation and the high cost of both sources. However, the use of lasers for diagnostic purposes in the ICP is promising, particularly for profiling the temperature, electron density, and velocity of the plasma, by means of laser-induced atomic/ionic fluorescence spectrometry.

The rf-excited inductively coupled argon plasma operating at 36 MHz and a maximum power output of 2.5 kW was used for the first time by Hussein and Nickless as an excitation source for atomic fluorescence spectrometry in conventional flames with an unsheathed air/propane flame as atomizer, and introducing 1000-4000 µg/mL metal solutions as source material into the plasma. Since then, no other research has been done on the use of ICP-excited flame atomic fluorescence spectrometry until we investigated this excellent source for use as an excitation source in
air/acetylene nitrogen-separated flame, which will be discussed in Chapter 3. In Chapter 4, tunable dye laser excitation with an ICP as atomizer/ionizer will be considered in more detail.

B.2 - Theoretical Considerations

Types of Fluorescence Transitions. Fluorescence spectrometry is based upon the absorption of radiation of a specific wavelength by an atomic/ionic vapor and deactivation of the excited atoms/ions, which are called "atomic/ionic fluorescence". Both absorption and the measured atomic/ionic emission processes occur at wavelengths that characterize the atom/ion species present at the reservoir giving an excellent selectivity to this phenomenon.

Resonance fluorescence occurs when excited species absorb and re-emit radiation of the same wavelength, i.e., the same two levels are involved in the excitation-fluorescence processes. This type of transition is the basis for the "resonance monochromator" described by Sullivan and Walsh.\textsuperscript{36} Resonance fluorescence has been the most useful in analytical atomic fluorescence spectrometry because resonance line intensities are significantly greater than the intensities observed with other types of atomic fluorescence. A variation of resonance fluorescence called thermally assisted resonance fluorescence occurs when the lower state is not the ground state, but a metastable, thermally populated state.

Direct line fluorescence occurs when an atom or ion radiationally is excited from the ground state to a state and then undergoes radiational de-excitation to a lower excited state and emits a photon of energy less than that which it absorbed (Stokes process).

Direct line fluorescence is most useful analytically when the scatter of source radiation, by particles within the atomizer, is the
predominant source of noise. All non-resonance processes can be Stokes or antistokes.

Direct line fluorescence variation called \textit{thermally assisted direct line fluorescence} occurs when the excitation process originates from a state above the ground state; the fluorescence process occurs to the ground state and is an antistokes process.

\textbf{Excited direct line fluorescence} involves all excited states in the excitation and fluorescence processes; the fluorescence transition can therefore be either Stokes or antistokes with respect to the excitation process.

\textbf{Stepwise line fluorescence} occurs when an atom or ion is radiationally excited to a state above the ground state, then is collisionally de-excited to some intermediate state from which it then radiationally de-activates, and emitting a photon with lower energy (Stokes) than that which is absorbed. \textit{Stepwise line fluorescence} finds its analytical usefulness when excitation source scatter is the predominant noise source and there is no possibility for direct line fluorescence or when the transition probabilities are not favorable.

\textbf{A thermally assisted stepwise line fluorescence} variation is also possible. An atom or ion is radiationally excited to some upper level and while it is in this excited state (short lifetime), it is thermally excited to a more energetic upper state from which it then radiationally deactivates to the ground state (the emission can be either Stokes or antistokes with respect to the excitation process).

\textbf{Sensitized fluorescence} occurs when one species, called the donor, is excited and transfers excitation energy to an atom of the same or another species, called the acceptor, either of which de-excites radiationally.
The final type of atomic fluorescence is **multiphoton fluorescence**. Two (or more)-photon absorption will be observed only with coherent sources of excitation (or with extremely intense non-coherent sources). The last two processes have little analytical usefulness at present.

Figure 2a shows the variety of atomic fluorescence transitions which are described. Several fluorescence processes shown in Figure 1b have been observed with laser excitation of some transition elements. \(^{37-39}\)

**Basic Fluorescence Signal and Analytical Curve of Growth Expressions.**

The theory of atomic fluorescence can be described in three parts: the absorption of radiation by the atomic vapor, the emission (fluorescence) of radiation by the excited atoms and the return of the sample into the atomic vapor within the volume of observation. These relationships are well treated in the literature. \(^{39-41,21,37}\)

The radiation absorbed by an atomic vapor is given by

\[
B_A = (\frac{\Omega_A}{4\pi}) \int_0^\lambda B_{\lambda} [1 - \exp(-k_\lambda \lambda)] \, d\lambda
\]  

(24a)

where \(B_A\) is radiance absorbed by atomic vapor in \(W \text{ cm}^{-2} \text{sr}^{-1}\), \(\Omega_A\) is the solid angle of exciting radiation collected upon the absorption cell in\(\text{sr}\), \(B_{\lambda}\) is the source spectral radiance in \(W \text{ cm}^{-2} \text{sr}^{-1} \text{nm}^{-1}\), \(k_\lambda\) is the atomic absorption coefficient for analyte atom at wavelength \(\lambda\), and \(\lambda\) is the length of the absorption cell in (cm) (see Figure 2b).

Evaluation of the integral after assuming the source type and optical density leads to the following formulas (see pages 27 and 28).

**Continuum Source at Low Optical Densities.** When using the continuum source (or broad line source), the source half-width is assumed to be wider than the absorption line width (source intensity over the absorption line width is constant). The fluorescence line radiance is given by
Figure 2a. Types of atomic fluorescence transitions (the spacings between atomic levels is not indicative of any specific atom). a, resonance fluorescence (either process); b, excited state resonance fluorescence; c, Stokes direct line fluorescence; d, excited state Stokes direct line fluorescence; e, antistokes direct line fluorescence; f, excited state antistokes direct line fluorescence; g, Stokes stepwise line fluorescence; h, excited state Stokes stepwise line fluorescence; i, antistokes stepwise line fluorescence; j, excited state antistokes stepwise line fluorescence; k, thermally assisted Stokes or antistokes stepwise line fluorescence (depending upon whether the absorbed radiation has shorter or longer wavelengths, respectively, than the fluorescent radiation); l, excited state thermally assisted Stokes or antistokes stepwise line fluorescence (depending upon whether the absorbed radiation has shorter or longer wavelengths, respectively, than the fluorescence radiation); m, sensitized fluorescence (D=donor; D*=excited donor; A=acceptor; A*=excited acceptor; hν_E=exciting radiation; hν_F=fluorescence radiation); h, two photon excitation-fluorescence (multiphoton processes involving more than two identical photons are even less probable than the two photon processes).
\[ D + h\nu_E \rightarrow D^* \]
\[ D^* + A \rightarrow A^* + D \]
\[ A^* \rightarrow A + h\nu_E \]
Figure 2b. Schematic Diagram of Atomic Fluorescence Sample Cell.
\[ B_F = C_2 B_{c\lambda_o} K_0 n_M Y l \Delta \lambda_D (\Omega_A/4\pi) f_{lu} \]  
(25)

where

\[ B_{c\lambda_o} = \text{continuum source spectral radiance at temperature of source and at wavelength } \lambda_o \ (W \ cm^{-2} \ sr^{-1} \ nm^{-1}) \]

\[ C_2 = (\pi/\ln 2)^{1/2}/2 \ (\text{dimensionless}) \]

\[ f_{lu} = \text{absorption oscillator strength (dimensionless)} \]

\[ = (mc/8\pi^2e^2)(g_u/g_1)A_{ul} \lambda_o^2 = 1.51(g_u/g_1)A_{ul} \lambda_o^2 \]

\[ l = (l l'/A_s) = \text{absorption or emission path length (in cm)} \]

\[ A_s = 2ll'+2ll'+2ll' = \text{total surface area of the cell (see Figure 2)} \]

\[ A_{ul} = \text{Einstein coefficient of spontaneous emission (in s}^{-1}) \]

\[ Y = \text{fluorescence quantum efficiency (dimensionless)} \]

\[ n_M = \text{concentration of species at lower level (in cm}^{-3}) \]

\[ \Delta \lambda_D = \text{Doppler half-width (in nm)} \]

\[ \Omega_A = \text{excitation source solid angle impinging in absorption cell (in sr)} \]

\[ K_0 = \text{modified absorption coefficient, } k_0/n_M f_{lu} \ (\text{in cm}^2) \]

\[ k_o = \text{absorption coefficient for pure Doppler broadening} \]

\[ = K_0 n_M f_{lu} = X \frac{\lambda_o^2}{c \Delta \lambda D C_2} \ (\text{in cm}^{-1}) \]

\[ X = (mc^2/e) = 3.0 \times 10^{-4} \ (\text{in cm}^2 \ s^{-1}) \]

\[ \lambda_o = \text{peak absorption or emission wavelength (in nm)} \]

\[ c = \text{speed of light (in cm s}^{-1}) \]

\[ m = \text{mass of electron (in g)} \]

\[ F_s = \text{source factor to account for saturation of energy levels (dimensionless)} \]

The quantum efficiency of a transition is defined by \[ Y = A_{ul}/(A_{ul}+K) \], where \[ A_{ul} \] is the emission transition probability, and \[ K \] is the probability of radiationless transitions.
Line Source at Low Optical Densities. When the source half-width is much smaller than the absorption line width, the fluorescence line radiance is given by

$$B_F = B_L K_0 N_M \gamma_1 \delta_{ul} (\Omega_A/4\pi) f_{lu}$$  \hspace{1cm} (27)$$

where

- $B_L$ = radiance of line source, \(W \text{ cm}^{-2} \text{ sr}^{-1} \text{ nm}^{-1}\);
- $\delta_{ul}$ = factor to account for finite line width of source compared to absorption line (dimensionless).

All the equations describing fluorescence spectral radiance presented so far are involved in absorption of radiation by atoms in the ground state.

In Figure 3, the log-log plots of spectral radiance vs atomic concentration are called growth curves. To convert growth curves to analytical calibration curves, two other terms must be considered. The first one relates solution concentration $c$ to number of atoms $n_M$ while the second one relates fluorescence radiance to detector output signal.

The relationship of $n_M$ and $c$ is given by

$$n_M = 10^{19} (R a c \varepsilon_n / Q f_e) (1 - \delta_1) g_o / Z$$  \hspace{1cm} (28)$$

where $c$ is the concentration of analyte solution in (\(\mu g/\text{mL}\)), $R$ is the solution uptake rate in (\(\text{mL/min}\)), $\varepsilon_a$ is the atomization efficiency (dimensionless), $\varepsilon_n$ is the aspiration efficiency (dimensionless), $Q$ is the flow rate of gases into the flame (plasma) in (\(\text{L/min}\)), $f_e$ is the gas expansion factor \((n_f T_f / n_T g_o)\), where $n_f$ and $n_T$ are the number of moles of flame gases at room temperature $T_f$ and gas temperature, $T_g$), $g_o$ is the statistical weight of the ground state, and $Z$ is the electronic partition function $Z = g_o + g_m \exp (-E_m / kT)$...
The relation between the fluorescence spectral radiance and the output signal is given by

$$\phi_F = 4\pi \Delta \lambda \gamma WHT \lambda A_s B_F R_T$$

(29)

Where $\phi_F$ is the signal in (V), $A_s$ is the area of the sample cell in (cm$^2$), $B_F$ is the fluorescence spectral radiance in (W cm$^{-2}$ sr$^{-1}$), $W$ and $H$ are the width and height of the slit (cm, cm), $T_\lambda$ is the transmittance of the monochromator at wavelength $\lambda$ (dimensionless), $\Delta \lambda$ is the spectral bandpass of the monochromator (nm), $\gamma$ is the photodetector sensitivity in (A W$^{-1}$), and $R_T$ is the electronic transfer function in (V A$^{-1}$).

B.3 - Noise and Detection Limits.

The signal measurement in an optical spectrometer is limited by the existence of fluctuations on the signal. However, the quantum nature of the radiation produces fluctuations, which are called "photon noise", or more generally "shot noise." Shot noise adds error to the desired signal, that may only be predicted statistically. In addition to the shot noises predicted from statistics, additional fluctuations occur due to "excess low-frequency" noise; such a noise has a spectral noise power inversely proportional to the frequency and is called "flicker noise."

The cause of these noise sources can be found in light sources, absorbing medium, detectors, and electronic measurement systems used in an optical spectrometry. There are two types of errors: (i) "systematic errors" which arise from procedural inconsistencies and errors (sample preparation, etc.), background, stray light, detector offset, etc. and could be corrected by blank subtraction, modulation, calibration, etc. and (ii) "random errors" which result from reading and digitizing errors which can be minimized by improved experimental technique.
The analytical figures of merit, are "relative standard deviation" which is the reciprocal of signal-to-noise ratio; "limit of detection" which is the detectable analyte concentration with a certain confidence level; and "the sensitivity" corresponding to the slope of the analytical calibration curve.

The limit of detection is defined\(^19\) by

\[
C_L = \frac{x_L - \bar{x}_{bl}}{(dS/dc)} = k \sigma_{bl}/S = (S/N)_{lim} (\sigma_{bl}/S),
\]

which link the limit of detection (concentration, \(C_L\)) and the sensitivity, \(S = (dS/dc)\), and the noise level (random errors) in the blank, \(\sigma_{bl}\) is obtained from a number (16 or more consecutive readings) of measurements of the blank, i.e. \(\bar{x}_{bl}\) and \(\sigma_{bl}\) are the average of the blank and standard deviation of the blank, and \(k\) is a protection factor to give a desired confidence level \((S/N)_{lim} = k = 3\) is chosen which gives 99.86% confidence level).

When one works near the limit of detection, one usually applies paired readings, the background, \(x_b\), at \(t=t_0\) and the signal-plus-background, \(x_{s+b}\), at \(t=t_0+\tau_s\); \(\tau_s\) is the sampling time. The signal reading corrected for background, \(\Delta x\), is given by\(^42\)

\[
\Delta x = x_{s+b}(t_0+\tau_s) - x_b(t_0)
\]

or in another form

\[
\Delta x = x_s(t_0+\tau_s) + (dx_b(t_0+\tau_s) - dx_b(t_0))
\]

where \(dx_b(t)\) is the statistical fluctuation in the meter deflection or integrator output due to the background alone. The signal-to-noise is
\[ S/N = x_s(t_0 + \tau_s) / \sigma_{\Delta x} \]  

(32)

with

\[ \sigma_{\Delta x} = \left[ (dx_b(t_0 + \tau_s) - dx_b(t_0))^2 \right]^{1/2}. \]  

(33)

From equation 33 the variance \( \sigma_{\Delta x}^2 \) can be expressed as

\[ \sigma_{\Delta x}^2 = dx_b(t_0 + \tau_s)^2 + dx_b(t_0)^2 - 2dx_b(t_0 + \tau_s)dx_b(t_0). \]  

(34)

For stationary background fluctuation, the variance is \( \sigma_b^2 \), which is the time-independent variance of \( dx_b(t) \). In order to be able to compare the signal-to-noise ratios obtained with different types of noise and with different measuring procedures, and to find optimum values of the various characteristic times, one would take advantage of the relation between the auto-correlation function and the spectral noise power.

The auto-correlation function of a continuously fluctuating signal \( dx(t) \) is defined by

\[ \psi_x(\tau) = dx(t)dx(t+\tau), \]  

(35)

and so

\[ \sigma_{\Delta x}^2 = 2\sigma_b^2 - 2dx_b(t_0 + \tau_s)dx_b(t_0) = 2(\psi_x(0) - \psi_x(\tau_s)), \]  

(36)

where

\[ \psi_x(0) = dx_b(t_0 + \tau_s)^2 = dx_b(t_0)^2 = \sigma_b^2, \]  

and

\[ \psi_x(\tau_s) = dx_b(t_0 + \tau_s)dx_b(t_0). \]
To calculate $\sigma_{\Delta x}^2$, the auto-correlation function is expressed in terms of the spectral noise power $S_{1b}(f)$ of the background current fluctuations and from the Wiener-Khintchine theorem:

$$\psi_X(\tau_s) = \int_0^\infty S_X(f) \cos(2\pi f \tau_s) df,$$  \hspace{1cm} (37)

where

$$S_X(f) = S_{1b}(f) |G(f)|^2,$$

and $G(f)$ is the frequency response of the (linear) measuring device. Since, the noise power is a squared quantity, only the square of the absolute value of the frequency response is needed. Then, we have

$$\psi_X(\tau_s) = \int_0^\infty S_{1b}(f) |G(f)|^2 \cos(2\pi f \tau_s) df.$$ \hspace{1cm} (38)

One would obtain the relation between the variance and the spectral noise power as follows:

$$\sigma_{\Delta x}^2 = 2 \int_0^\infty S_{1b}(f) |G(f)|^2 (1-\cos(2\pi f \tau_s)) df.$$ \hspace{1cm} (39)

Because $\cos(2\pi f \tau_s) = 1$, for $\tau_s = 0$, $\sigma_{\Delta x}^2$ is therefore a function of the sampling time $\tau_s$; and as $\tau_s \to 0$ both $\sigma_{\Delta x}$ and $\chi_s$ approach zero.

The spectral noise power (noise power per unit frequency interval) for shot noise in terms of current fluctuations is given by

$$(S_{1b})_{sh}(f) = S_0 2e \sum_{j=1}^n \frac{I_j}{2} \sum_{j=1}^n R_j e^{2}$$ \hspace{1cm} (40)

where $e$ is the elementary charge in (C), $i_j$ is the $j$-th component in the current, emitted e.g. by a photocathode in (A), and $R_j$ is the corresponding
electron count rate in (counts s\(^{-1}\)). The spectral noise power considered as a function of frequency \( f \) is called the noise spectrum. The dimension of \( S_i \) is \((A^2 s)\). The bars denote average values. Noise spectra for an ICP have been evaluated in this laboratory.

The major sources of flicker noise (or excess low-frequency noise, 1/f noise) involve random drift of light sources, analyte production, and detection. The spectral noise power for flicker noise in terms of current fluctuations is given by

\[
(S_i)_{f_1}(f) = \sum_{j=1}^{n} \left( \frac{K_j^2}{f} \right) \bar{I}_j^2 = \sum_{j=1}^{n} \left( \frac{K_j^2}{f} \right) R_j e^2
\]  

(41)

where \( f \) is the frequency, \( K_j^2 \) is a constant with unity dimension which describes the low-frequency stability of the noise source and \( i_j \) and \( R_j \) are as before.

There are peaks occurring in the noise power spectrum which are due to oscillations (organ-pipe) in the plasma torch system. They may extend to the audible frequency range and are called "whistle noise" (specially for fluorescence torch configuration).

Another source of noise existing in electrical circuits and components but insignificant compared to the other noises when photomultipliers are used, is the "thermal (Johnson) noise" which are due to the random thermal motion of electrical charge carriers in any conductor.

When combining all the noises from different origins into a total noise expression, care must be taken in the method of addition. For example, if two noises with r.m.s. values \( \sigma_a \) and \( \sigma_b \) exist together, the r.m.s.-value of the total noise \( \sigma_T \), is given by

\[
\sigma_T = (\sigma_a^2 + \sigma_b^2 + 2C_{\sigma_a \sigma_b})^{1/2}
\]

(42)
where $C$ is a correlation coefficient, and its value is unity, in the case of complete statistical correlations (both have a common origin), and its value is zero, in the case when both noises are completely uncorrelated.

For systems which are shot noise limited, modulation of the signal, regardless of the modulation frequency will not improve the signal-to-noise ratio. For systems which are additive flicker noise limited, it is necessary to "modulate" only the signal and not the background. One must keep in mind about the suppression of "excess low-frequency noise" that the gain in signal-to-noise ratio by modulation is limited to that modulation frequency at which $(S/N)_{\text{shot}} \approx (S/N)_{\text{flicker}}$. At modulation frequencies above this limit, additive flicker noise still decreases, but shot noise is unaffected by modulation and sets a final limit to the S/N gain by modulation.

In conclusion, one could say, in practice the absolute magnitude of both signal and the noise in the signal have little use. However, the signal-to-noise ratio can be useful and is directly related to the applicability of any method for an analysis. The signal-to-noise ratio allows the limiting detectable concentration to be defined and is used to determine the values of the experimental parameters at which the limit of detection as well as the maximum signal-to-noise ratio at higher concentrations occur.

Detection limits (atoms per cm$^3$) of hot gases are given for AFS, AAS and AES$^{21}$ in Table 2. The conversion factor from atoms/cm$^3$ to $\mu$g/mL is given by

$$\psi = \frac{n_f}{c} = \left( \frac{N_\text{A} \epsilon_\text{a} V_\text{a}}{Q \epsilon_\text{r} M_\text{A}} \right) 10^{-6}, \left[ \frac{\text{atom/cm}^3}{\mu\text{g/mL}} \right]$$

where
Table 2
COMPARISON OF CALCULATED DETECTION LIMITS FOR SEVERAL FLAME/PLASMA SPECTROSCOPIC METHODS

<table>
<thead>
<tr>
<th>Method</th>
<th>( \lambda_0 ) (nm)</th>
<th>( \text{Limit of Detection, atoms cm}^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda_0 = 300 )</td>
<td>( \lambda_0 = 600 )</td>
</tr>
<tr>
<td>ATOMIC FLUORESCENCE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laser, Typical operating</td>
<td></td>
<td></td>
</tr>
<tr>
<td>values (( \lambda_0 = 300 ) nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detector noise limit</td>
<td>( \overline{D} = 10^2 \text{s}^{-1} )</td>
<td>10²  10²  10²</td>
</tr>
<tr>
<td>Detector noise limit</td>
<td>( \overline{D} = 10^4 \text{s}^{-1} )</td>
<td>10⁴  10³  10³</td>
</tr>
<tr>
<td>Background noise limit</td>
<td></td>
<td>10⁵  3x10⁴  3x10⁴</td>
</tr>
<tr>
<td>Laser, Saturation (( \lambda_0 = 300 ) nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detector noise limit</td>
<td>( \overline{D} = 10^2 \text{s}^{-1} )</td>
<td>2x10⁻¹  2x10⁻¹  2x10⁻¹</td>
</tr>
<tr>
<td>Detector noise limit</td>
<td>( \overline{D} = 10^4 \text{s}^{-1} )</td>
<td>2x10⁰  2x10⁰  2x10⁰</td>
</tr>
<tr>
<td>Background noise limit</td>
<td></td>
<td>10²  3x10¹  3x10¹</td>
</tr>
<tr>
<td>ATOMIC ABSORPTION (Source noise limited - ( \lambda_0 = 300 ) nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xenon Arc Source</td>
<td>4x10⁸</td>
<td>8x10⁸  4x10⁹</td>
</tr>
<tr>
<td>Hollow Cathode Discharge</td>
<td>7x10⁷</td>
<td>1x10⁸  7x10⁸</td>
</tr>
<tr>
<td>ATOMIC EMISSION (Background noise limited)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \lambda_0 = 300 ) nm</td>
<td>10⁹</td>
<td>10⁹   10⁴</td>
</tr>
<tr>
<td>( \lambda_0 = 600 ) nm</td>
<td>10⁵</td>
<td>10⁴   3x10³</td>
</tr>
</tbody>
</table>
\( N_A = \text{Avogadro's number, atoms (or molecules) per mole, } 6.0 \times 10^{23}, \text{ dimensionless} \)

\( M_A = \text{atomic (molecular) weight of analyte, g/mole} \)

\( F = \text{transport rate of sample solution as determined by nebulizer, cm}^3/\text{s} \)

\( \varepsilon = \text{efficiency of nebulization and desolvation (fraction of sample solution transported to chamber and flame which actually gets into flame or plasma and becomes desolvated particles), dimensionless} \)

\( \beta_v = \text{efficiency of vaporization of particles in flames or plasma to produce submicroscopic species, dimensionless} \)

\( \beta_a = \text{efficiency of atomization, i.e., fraction of submicroscopic species (atoms, molecules, ions) which end up as atoms, dimensionless} \)

\( Q = \text{flow rate of unburnt gases (at room temperature) into flame, cm}^3/\text{s}. \)
CHAPTER TWO
MOLECULAR EMISSION SPECTRA
AND ATOMIC EMISSION SPECTROSCOPY IN ICP

A - Molecular Emission Spectra

A.1 - Introduction

The rf-excited, inductively coupled argon plasma (ICP) is becoming increasingly popular as an excitation source for atomic (and ionic) emission spectrometry. Outstanding advantages of this plasma include its long-term stability, and the very high temperatures achieved throughout a considerable volume of the plasma. The temperatures appear to be sufficiently high to bring about essentially complete decomposition of almost all molecules introduced into the plasma in the form of aqueous aerosols. As a result, emission spectroscopy using the ICP is relatively free of those types of interferences well known in flame spectroscopy, that are related to stable chemical compound formation.43

In various regions of the plasma, however, molecules exist and their emission spectra can be observed. When an aqueous aerosol containing inorganic salts is aspirated through the center of a toroidal plasma, many processes (desolvation, possibly hydrolysis, melting, sublimation and vaporization, and molecule decomposition) take place in a manner analogous to that occurring in flames, except that argon plasmas contain a much lower concentration of oxygenated species than do most analytical flames. Metal monoxides appear to exist briefly in the center of the plasma for some distance above the rf coil before decomposing into metal atoms and
ions in the region where emission measurements are generally made (≈ 15 to 25 mm) above the coil. Higher in the plasma, oxides are again formed as metal atoms react with entrained atmospheric oxygen (or with the oxygen produced from water dissociation).

Other sources of molecular emission from the plasma include OH emission, arising from incomplete decomposition of aspirated water, and emissions arising from the entrainment of atmospheric gases, starting where the plasma "tail flame" emerges from the plasma torch. Emissions resulting from atmospheric gases and their reaction products include those of \( \text{N}_2, \text{N}_2^+, \text{NH} \) and \( \text{NO} \). The conditions under which molecular emissions can be observed from argon plasmas are discussed in this chapter. Particular attention has been paid to the \( \gamma \)-band system of \( \text{NO} \), which extends from 200 to 280 nm, a wavelength range in which many elements have their most useful emission lines.

Molecular emissions are also observed when gases other than argon are used for plasma gas flows, such as in nitrogen-cooled argon plasmas, when organic solvents are aspirated, or when various gases or vapors are introduced as samples.

A.2 - Experimental

The instrumentation used in this study is described in Table 3. A schematic diagram of the experimental system is shown in Figure 4. The present study involved the use of both the conventional (short) torch and a long (for fluorescence studies) torch (see Figure 5). By extending the quartz tube above the load coil in the long torch, mixing of ambient atmosphere with the plasma is eliminated and cooling of the plasma due to the mixing is also reduced. The upper end of the long torch becomes cloudy with use and causes transmission losses where observations of emission are made below the end of the quartz tube. Therefore, conventional torches
<table>
<thead>
<tr>
<th>Component</th>
<th>Model, Manufacturer</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP Torch Assembly Generator</td>
<td>Pt-1500 Torch Assembly and HFP-1500D RF Generator</td>
<td>0.55-1.5 kW</td>
</tr>
<tr>
<td></td>
<td>Plasma Therm, Inc., Kresson, NJ 08053</td>
<td>10-16 L/min Ar Plasma (coolant) gas flow</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;0.5 L/min Ar auxiliary gas flow rate</td>
</tr>
<tr>
<td>ICP Short Torch</td>
<td>Laboratory Constructed - (see Figure 5)</td>
<td>40 psi (20 mL/min Solution Uptake Rate)</td>
</tr>
<tr>
<td>ICP Long Torch</td>
<td>Laboratory Constructed - (see Figure 5)</td>
<td>&lt;1 L/min Ar gas flow rate</td>
</tr>
<tr>
<td>ICP Nebulizer</td>
<td>Concentric</td>
<td>1 mm slit height</td>
</tr>
<tr>
<td></td>
<td>Ring Glass - T 220 - A2</td>
<td>25 mm slit width</td>
</tr>
<tr>
<td></td>
<td>J. E. Meinhard Assoc., Santa Anna, CA 92705</td>
<td>(0.05 nm spectral bandwidth)</td>
</tr>
<tr>
<td>Monochromator</td>
<td>E-700 Monochromator, Heath Co., Benton Harbor, MI</td>
<td>-1000 V</td>
</tr>
<tr>
<td></td>
<td>49022 (0.35 m, f/6.8, 1180 grooves 1nm, Glazes at 250 nm, 2nm/mm)</td>
<td></td>
</tr>
<tr>
<td>Photomultiplier</td>
<td>R-928, Hamamatsu TV Corp., Ltd., Middlesex, NJ 08846</td>
<td></td>
</tr>
<tr>
<td>Current-to-Voltage Converter</td>
<td>Model 427, Keithley Instrument Co., Cleveland, OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>44139</td>
<td></td>
</tr>
<tr>
<td>Recorder</td>
<td>Model Potentiometric, Texas Instrument, Houston, TX</td>
<td></td>
</tr>
<tr>
<td></td>
<td>77006</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4. Schematic Diagram of Experimental Set-up Used in present Emission Studies.
Figure 5. Schematic Diagram of ICP Torches (all quartz tubing has wall thickness of 1 mm).
A. Short (Conventional) Torch
B. Long ("Fluorescence") Torch
are of the short variety. Unfortunately, mixing of ambient air occurs where the torch is terminated.\footnote{44}

A.3 - Results and Discussion

**Molecular Emissions from Unsalted Plasmas.** The emission from a pure argon plasma consists essentially of Ar atom lines superimposed on a background continuum due to Bremsstrahlung and ion-electron recombination processes. We have observed all recorded Ar I lines\footnote{45} in the range 340-600 nm. A weak Ar II line at 480.6 nm has been observed in the plasma core by Truitt and Robinson.\footnote{46} Most commercial argon contains several \(\mu\)g/mL of carbon as low molecular-weight hydrocarbons, CO and CO\(_2\). These traces lead to C I lines at 193.09 nm and 247.86 nm, but emissions of molecular species (e.g. CN) derived from these trace impurities have been observed only in high-powered plasmas, such as that of Greenfield et al.\footnote{47}

**OH Emission.** The OH molecule is the most ubiquitous molecular emitter in unsalted plasmas. Even when water is not injected as an aerosol, the "after-flame" above the plasma torch shows emission from the \(A^2\Sigma^+ - X^2\Pi\) (0,0) band in the vicinity of 306.4 nm. This is apparent in published background emission spectra,\footnote{46-49} whether water has been injected or not, both for low-powered (0.5 - 2 kW) and for high-powered (2 - 7 kW) plasmas. Where no water is aspirated, the emission arises from entrained atmospheric water vapor. OH emission is minimized when no water is aspirated and a long plasma torch is used, the plasma being observed through the torch wall (made of Spectrosil quartz in our case). The (1,0) band of the same system is usually also apparent through the wavelength range from 281 to 300 nm. Parts of the (1,1), (2,2) and (0,1) bands can also be seen between 310-350 nm. The relative intensities of lines of the (0,0) band between 307 and 309 nm have been used\footnote{50} to obtain OH-rotational temperatures in the plasma.
NH emission. The most prominent NH emission band, which is at 336.0 nm, has been reported in the high-powered, nitrogen-cooled plasmas of Greenfield et al. and is recorded as a weak emission in the "afterflame" of low-powered argon-cooled plasmas. NH emission also occurs when air is introduced into the coolant stream of a 4 kW Ar plasma. We have observed NH emission in an argon plasma operated at low plasma gas flow (10-15 L/min), at 0.55 - 1.5 kW, viewed 18-20 mm above the induction coil, with ambient air and with air being flushed through the plasma box to prevent overheating. In Figure 6, spectra are given of OH and NH (306-338 nm) obtained under these conditions (1.5 kW power, 12 L/min Ar, and 18 mm observation height); NH has a very strong, sharp Q branch (0,0) at 336.0 nm (A^3Π - X^3Σ^-).

The influence of ambient air versus flushed air on the variation of the NH emission signal to background at 336 nm (resulting with water aspiration) as a function of observation height above the load coil and for two power levels is shown in Figure 7a. For the case of the lower power (1.0 kW) plasma, ambient air surrounding the plasma results in a rather sharp maximum, whereas flushed air surrounding the plasma spreads the maximum out over about 10 mm. This is apparently a result of considerable air entrainment over a greater observation height in the latter case compared to the former case. At higher input powers (1.5 kW in our case), the extent of air entrainment is greater in both cases than for lower power, the maximum occurs at about the same height (≈ 25 mm), and the breadth of the maximum are approximately the same in both cases. In Figure 7b, the linearity of NH emission to background signals at 336 nm with variation in nebulizer pressure (or solution aspiration rate) is shown. NH emission has been used as the basis of a method of determining NH4+ in solution. The NH4+ is oxidized by hypobromite to give
Figure 6. Emission Spectra of OH and NH in the wavelength Region of 306-338 nm. Experimental Conditions: ICP input power, $P=1$ kW; Observation height above load coil, $z=24$ mm; Plasma Gas Flow Rate, $R=15$ L/min; Monochromator Slit Width $W=50$ μm; Monochromator Slit height, $H=1$ mm; Nebulizer Gas Pressure, $N=40$ psi; Solution Nebulization Flow Rate, $F=2$ mL/min.
Figure 7a. NH Emission Signal to Background Signal at 336.0 nm Band Head vs Observation Height. Experimental Conditions: $R=15$ L/min; $W=25$ μm; $H=1$ mm; $N=40$ psi; $F=2$ mL/min (water).

Key: Solid line $P=1.0$ kW; Broken line $P=1.5$ kW; ☯ Air flushed into box (housing) containing torch. ★ Ambient air in box (housing) containing torch.
1-MISSION (336 nm)/BACKGROUND EMISSION (336 nm)
Figure 7b. NH Emission Signal to Background Signal at 336.0 nm Band Head vs Nebulizer Pressure. Experimental Conditions: same as above for 5a except z=20 mm and air flushed into box (housing) containing torch.
nitrogen, which is then passed into a low-powered (1 kW) plasma. Only very weak NH emission is seen when concentrated ammonium salt solutions are aspirated directly into the plasma.

**NO emission.** NO emission which arises from air entrainment in the plasma flame has been noted by Truitt and Robinson\(^46\) and by Scott and Strasheim.\(^52\) The major bandhead of the \(\gamma\)-band system of NO \((A^2\Sigma^+ - X^2\Pi)\) is at 247.1 nm; the fine structure of several bands can be observed from 200-280 nm in a plasma operated at 1.1 kW and viewed at a height of 24 mm above the coil. In Figure 8a, spectra are shown in the \(\gamma\)-band system of NO (200-280 nm) and the (1,0) band of the \(A^2\Sigma^+ - X^2\Pi\) transition of OH (281.1-300 nm) obtained under the above conditions. A slow scan (expanded) of the 232-248 nm region, including the two strongest NO bands, (0,1) and (0,2), is shown in Figure 8b, and the (1,0) band (210-215 nm) is shown in detail in Figure 8c. The last of these bands has been suggested\(^52\) as a possible cause of difficulty in determinations of zinc using the Zn I line at 213.86 nm. The superimposition of this line on some of the fine structure of the NO emission has also been noted by Larson et al.\(^53\)

In Figure 9a, continuum background spectra are given for 3 input power levels; the Ar emission is observed through the quartz wall of the long torch to eliminate ambient air entrainment. At 0.55 kW, the background signal is virtually at the photomultiplier dark current level. With an increase in input power, the background signal level increases as one would expect for a "blackbody" radiator. In Figure 9b, the variation of NO emission (at 214.9 nm) to background emission (also at 214.9 nm) with observation height is shown for several different experimental conditions. It is apparent that at the lower input power (1.0 kW), the ratio increases from an undetectable level at around 10-15 mm, depending upon the atmosphere surrounding the plasma. At higher input power (1.5 kW), the ratio
Figure 8. Emission Spectra (γ-band) of NO and A^2Σ^+ - X^2Π Band of OH.
Experimental Conditions: P=1 kW; R=15 L/min; z=24 mm; W=50 μm; H=1 mm; N=40 psi; F=2 mL/min.

a. Spectral Range of 200-280 nm Showing γ-Band of NO and A^2Σ^+ - X^2Π Band of OH.
Figure 8:  

b. Expanded Spectral Range of 232-248 nm showing (0,1) and (0,2) NO bands.  
c. Expanded Spectral Range of 210-216 nm showing (1,0) NO band.
Figure 9a. Argon Plasma Continuum Background Observed Through Quartz Tubing of Long Torch vs λ. Experimental Conditions: R=15 L/min; W=25 μm; H=1 mm; N=40 psi; F=2 mL/min (Water); z=20 mm.

Key: ⊙ P=0.55 kW; ◇ P=1.0 kW; △ P=1.5 kW
The dark current level in this studies is ≈0.5 nA(5x10^{-10} A)
Figure 9b. NO Emission Signal to Background Ratio at (1,0) Band Head at 214.9 nm vs Observation Height. Experimental Conditions: R=15 L/min; W=25 μm; H=1 mm; N=40 psi; F=2 mL/min (water).

- Argon flushed into box (housing) containing torch.
- Air flushed into box (housing) containing torch.
- Ambient air in box (housing) containing torch.

Key: Solid line P=1.0 kW; Dashed line P=1.5 kW
NO EMISSION (214.9 nm)/BACKGROUND EMISSION (214.9 nm)

OBSERVATION HEIGHT (mm)
reaches a maximum at \( \approx 25 \text{ mm} \) for all "atmospheric conditions," the maximum having the greatest amplitude for ambient air and to lowest for an Ar flush.

**Other Molecular Emissions.** Other emission spectra are readily observed when various gases, vapors and liquids are injected into the plasma include those of \( \text{O}_2 \) and \( \text{O}_2^+ \) (from oxygen),\(^{46,47} \) \( \text{N}_2 \) and \( \text{N}_2^+ \) (from nitrogen),\(^{46,47} \) \( \text{CN} \) and \( \text{C}_2 \) (from hydrocarbons, \( \text{CHCl}_3, \text{CCl}_4 \), and \( \text{CO} \)),\(^{54} \) \( \text{CO} \) (from the aspiration of methanol into a nitrogen-cooled plasma),\(^{47} \) \( \text{PO} \) (from \( \text{PCl}_3 \)) and \( \text{SO} \) (from \( \text{SO}_2 \)).\(^{55} \)

**Molecular Emissions from Salted Plasmas.** The existence of metal oxides, both in the central region a few millimeters above the rf coil and in the outer part of the "tailflame" at heights of 25-50 mm, can be demonstrated clearly by aspirating moderately concentrated solutions of elements with rather stable monoxides, e.g., 1000 \( \mu \text{g/mL} \) of \( \text{Y}, \text{Sc}, \text{Gd}, \text{Sm}, \text{Lu} \) and \( \text{Zr} \).\(^{56} \) In all of these cases, the molecular emissions from the monoxide appear in a different part of the visible spectrum from the atom and ion lines of the same element. It is apparent, by visual observation of an inductively coupled argon plasma that at least four rather distinct zones exist: (i) a preheating (\( \approx 0-10 \text{ mm} \)) where poor analyte atomic or ionic signal to background ratios occur but with a very bright background; (ii) a narrow zone (\( \approx 10-15 \text{ mm} \)) where fairly intense atomic and ionic emission occurs but also where monoxide emission is seen; (iii) the analytical zone (the pencil system, \( \approx 20-30 \text{ mm} \)) where ionic and atomic emission measurements are generally made because of the excellent line-to-background ratios; (iv) the plume region (\( > 35 \text{ mm} \)) where the plasma gases have expanded and cooled and where considerable ambient air is entrained; in this region monoxide emission can again occur, but where atomic and ionic emission signals to background ratios are quite poor. The location of these zones
depends on a complex fashion upon power levels, plasma gas flows, nebulizer pressure, torch configuration, and analyte species. Although many workers who use the ICP as an emission source are aware of these phenomena, little information has appeared in the literature concerning the presence of molecular emission produced by salt introduction (as well as unsalted plasmas—see above discussion) into the ICP and therefore the less knowledgeable worker might attempt measurement of radiation (especially emission, but also absorption or fluorescence) under conditions where the signal-to-background ratio is far from optimal.

In Figure 10a-f, typical monoxide emission spectra of several species observed in the plume region (~45 mm) are given. It should be stressed that these spectra are the result of aspirating high concentrations of the specific species into the plasma and of observations in the plume region. Therefore, such emission will rarely affect analytical measurements by AEICP. Nevertheless, monoxide emissions do occur and workers should be aware of its existence. In Figure 11a and 11b, the variation of emission signals of several species (atomic, ionic, and molecular) with observation height are shown. For Y, the maximum for Y(II) occurs at a higher height than for Y(I) which occurs at a higher height than Y0. For Lu, the maximum for Lu(II) occurs at a higher height than for LuO; the emission signal for Lu(I) was rather low and constant over the observation height range of 10 to 45 mm.

B - Rare Earth Analysis

B.1 - Introduction

The analysis of rare earths in materials by chemical methods is plagued with separation and detection difficulties, and so most workers have resorted to spectroscopic measurement techniques. Fassel has reviewed
Figure 10. Monoxide Emission Spectra of Several Species in Spectral Range of 465-475 nm and 590-630 nm. Experimental Conditions: \( P = 1.1 \) kW; \( R = 16 \) L/min; \( N = 30 \) psi; \( F = 1.5 \) mL/min; \( W = 25 \) \( \mu \)m; \( H = 1 \) mm; \( z = 45 \) mm. Backgrounds e and f are at dark current level \( \approx 0.5 \) nA (5 \( \times \) 10\(^{-10}\) A).

a. 1000 ppm Gd (GdO emission bands in 610-628 nm range)

b. 500 ppm Sc (ScO emission bands in 590-620 nm range)

c. 500 ppm Y (YO emission bands in 590-630 nm range)

d. 500 ppm Y (YO emission bands in 590-630 nm range)

<table>
<thead>
<tr>
<th>Element</th>
<th>Monoxide Band Heads (nm)</th>
<th>Intensity ( ^{(a)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdO</td>
<td>618.268, 620.086</td>
<td>110,110</td>
</tr>
<tr>
<td></td>
<td>621.171, 622.093</td>
<td>110,110</td>
</tr>
<tr>
<td>ScO</td>
<td>601.707, 603.617</td>
<td>160,620</td>
</tr>
<tr>
<td></td>
<td>606.431, 607.265</td>
<td>490,440</td>
</tr>
<tr>
<td></td>
<td>607.930, 610.187</td>
<td>620,320</td>
</tr>
<tr>
<td></td>
<td>610.993, 611.597</td>
<td>370,370</td>
</tr>
<tr>
<td></td>
<td>614.870, 613.393</td>
<td>180,150</td>
</tr>
<tr>
<td></td>
<td>618.809, 619.290</td>
<td>150,150</td>
</tr>
<tr>
<td>YO</td>
<td>597.204, 598.764</td>
<td>1300,1000</td>
</tr>
<tr>
<td></td>
<td>600.360, 601.987</td>
<td>740,620</td>
</tr>
<tr>
<td></td>
<td>603.660, 613.206</td>
<td>500,1400</td>
</tr>
<tr>
<td></td>
<td>614.836, 616.508</td>
<td>1100,820</td>
</tr>
<tr>
<td></td>
<td>618.223, 619.982</td>
<td>560,590</td>
</tr>
<tr>
<td></td>
<td>621.796</td>
<td>450</td>
</tr>
</tbody>
</table>

\( ^{(a)} \) W. F. Meggers, C. H. Corliss, and B. F. Scribner, NBS Monograph 145, Part I (1975). (They are relative intensities for DC arc)
EMISSION SIGNAL (RELATIVE UNITS)

WAVELENGTH (nm)
Figure 10f. \( \text{H}_2\text{O} \) Background in 590-650 nm range.
Figure 10b. 1000 ppm Lu (LuO emission bands in 465-475 nm range)
e. H₂O Background in 465-475 nm range.

<table>
<thead>
<tr>
<th>Element</th>
<th>Monoxide Band Heads λ(nm)</th>
<th>Intensity (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LuO</td>
<td>466.175, 467.231</td>
<td>630, 310</td>
</tr>
<tr>
<td></td>
<td>468.416, 469.546</td>
<td>420, 270</td>
</tr>
<tr>
<td></td>
<td>470.800, 473.500</td>
<td>190, 100</td>
</tr>
</tbody>
</table>

(a) Same as fig. 10 a, c, d
Figure 11. Emission Signals of Several Species vs Observation Height.
Experimental Conditions: Same as Figure 10.

a. 500 ppm Y
   " Y0 band head at 614.84 nm. (band head intensity=1100)
   □ Y atom line at 619.17 nm. (atom line intensity=1200)
   △ Y ion line at 508.74 nm. (ion line intensity=1100)
Figure 11b. 500 ppm Lu

⊙ LuO band head at 466.18 nm. (band head intensity=630)
⊙ Lu atom line at 500.11 nm. (atom line intensity=800)
△ Lu ion line at 499.41 nm. (ion line intensity=800)
EMISSION SIGNAL (nA)

OBSERVATION HEIGHT (mm)
spectroscopic methods which have been extensively used for the quantitative determination of rare earth metals. Flame spectra of rare earth elements were observed by Rains et al.\textsuperscript{58} who aspirated non-aqueous solutions of these elements into an oxy-hydrogen flame. Reducing flames to aid in atom production were used by Fassel et al.\textsuperscript{59} who were successful in obtaining analytically useful line spectra of these elements in fuel rich flames by introducing ethanol solution of the elements.

Further studies by Mossotti, Fassel and others\textsuperscript{60-62} on these elements provided over one thousand absorption lines in the optical region which were successfully used for quantitative determination of rare earth elements by atomic absorption spectrometry.

Amos and Willis\textsuperscript{63} in their study observed that when higher temperature flames were employed as an absorption cell, the degree of ionization of rare earths became significant. Determination of traces of rare earths by atomic absorption with electrothermal atomization and by d.c. arc emission spectroscopy was discussed by Dittrich and Borzym.\textsuperscript{64}

Dickinson and Fassel\textsuperscript{65} with an ultrasonic aerosol generator and desolvation facility in their ICP determined detection limits for La and Ce. Later Fassel and Kniseley\textsuperscript{13} reported ICP detection limits of rare earths which were superior to those from flames. Souilliart and Robin\textsuperscript{66} used a high power (6.6 kW) ICP and ultrasonic nebulizer in the study of rare earth metals. In this study, we have used a conventional moderate power (1.25-1.5 kW) ICP with a glass concentric pneumatic nebulizer for the determination of detection limits (LOD) and linear dynamic ranges (LDR) of rare earth elements in pure solution and in a mixture of all the rare earth elements.
B.2 - Experimental

Preparation of Standards. Individual stock solutions of 1000 µg/mL of each rare earth element as well as mixtures of the elements were prepared by dissolving reagent grade pure oxides (ignited at 600°C for 4 hr) in hot 3 M HCl. Successive dilutions were made before each determination using distilled-deionized water. A solution of hydrochloric acid in deionized water was used as the blank.

Apparatus. Instrumental setup is given in Figure 4, and a 2 kW inductively coupled plasma (Plasma Therm Inc., Kresson, NJ) with a 27 MHz radio frequency generator was used in conjunction with a glass concentric nebulizer. The nebulizer solution flow rate was controlled with a syringe pump (Sage Instruments, Div. of Orion Research Inc., Cambridge, MA). A list of major instrumental components of the ICP system used in this study is given in Table 4.

Limits of detection (LOD) and linear dynamic ranges (LDR) were measured by integrating the electrometer signal for 10 s. The LOD was taken to be that concentration equivalent to a signal three times that of the standard deviation of 16 consecutive, integrated blank readings.

Experimental Conditions. The plasma system was operated at argon flows specified by the manufacturer. The ICP power was maintained at 1.25-1.5 kW throughout all measurements; the nebulizer solution flow rate was maintained at 2.2 mL min⁻¹ and the cooling gas was controlled to 16-20 L min⁻¹. A spherical lens (image 1:1), placed in a 3" metal tube, was used to focus the emission beam to the monochromator entrance slit. The entrance slit of the monochromator was set at 30 µm in width because it was the lowest value, which could be used and 2 cm in height; the exit slit was adjusted to a width of 16 µm to reduce the signal from the background emission. The ICP was mounted on an adjustable (x-y-z) table so that the
Table 4
SPECIFIC COMPONENTS OF EXPERIMENTAL SYSTEM

<table>
<thead>
<tr>
<th>Component</th>
<th>Model #</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP Torch assembly</td>
<td>PT 1500</td>
<td>Plasma Therm Inc., Kresson, NJ</td>
</tr>
<tr>
<td>RF Generator</td>
<td>HFP-1500D</td>
<td></td>
</tr>
<tr>
<td>Nebulizer</td>
<td>T-220-A2</td>
<td>JE Meinhard Associates, Santa Anna, CA</td>
</tr>
<tr>
<td>Monochromator</td>
<td>1870</td>
<td>SPEX, Metuchen, NJ</td>
</tr>
<tr>
<td>Photomultiplier</td>
<td>R-818</td>
<td>Hamamatsu Corp., Middlesex, NJ</td>
</tr>
<tr>
<td>High voltage power supply</td>
<td>224</td>
<td>Keithly Instruments, Cleveland, OH</td>
</tr>
<tr>
<td>Current/voltage convertor</td>
<td>601</td>
<td>Keithly Instruments, Cleveland, OH</td>
</tr>
<tr>
<td>Integrator</td>
<td></td>
<td>Lab Constructed</td>
</tr>
</tbody>
</table>
observation height could be adjusted with respect to the monochromator. The optimum plasma observation height was found to be 12 mm above the load coil of the ICP.

B.3 - Results and Discussion

The observed detection limits and linear dynamic ranges of rare earth elements with the lines used for measurement (also energies of levels and gA values are given) are summarized in Table 5. The linear dynamic ranges were obtained by measuring the relative emission signals of selected analysis lines vs concentration of metal ions in solution. The analytical calibration curves are linear over a concentration range of ≈5 orders of magnitude for all of the elements being studied. As representative examples, calibration curves for La, Ce, Eu, Dy, Ho, and Lu are presented in Figures 12, 13 and 14.

Comparison of the results of this work with that of other authors indicates that the condition employed in this study have resulted in similar or better limits of detection as others reported in the literature. It is also clear from the LODs obtained in the mixture of elements that matrix interferences are negligible in the ICP.

In the present studies, only ion lines were found to be sufficiently intense for analytical measurements of rare earth metals. Ion lines (see Table 4) were selected on the basis of maximum of intensity and minimum spectral interference and background. The detection limits obtained in this study in pure aqueous solutions or rare earth mixtures are similar to or superior to those reported in two previous studies of ICP excitation of rare earths. The excellent linear dynamic ranges in this study should be stressed; unfortunately, LDRs were not obtained in any of the previous studies.
Table 5

LIMITS OF DETECTION AND LINEAR DYNAMIC RANGES OF RARE EARTH METALS

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>Energy Levels (K)</th>
<th>( g_A \times 10^8 ) (s(^{-1}))</th>
<th>Limits of Detection ng/mL</th>
<th>Linear Dynamic Range (dimensionless)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>This Work--ICP</td>
<td>Previous Works--ICP</td>
</tr>
<tr>
<td></td>
<td>Pure Soln.</td>
<td>Mixture</td>
<td>Ref. (13)</td>
<td>Ref. (66)</td>
<td></td>
</tr>
<tr>
<td>La(_{II})</td>
<td>394.91</td>
<td>3250-20565</td>
<td>5.0</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>379.48</td>
<td>1971-28315</td>
<td>2.3</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Ce(_{II})</td>
<td>394.27</td>
<td>0-25360</td>
<td>2.0</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Pr(_{II})</td>
<td>391.89</td>
<td>2998-28509</td>
<td>2.0</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>390.8</td>
<td>4437-30018</td>
<td>1.9</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Nd(_{II})</td>
<td>401.22</td>
<td>5086-30002</td>
<td>5.2</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Sm(_{II})</td>
<td>360.95</td>
<td>2238-29935</td>
<td>3.9</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>442.43</td>
<td>3910-26540</td>
<td>1.3</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Eu(_{II})</td>
<td>420.50</td>
<td>0-23774</td>
<td>3.2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>412.97</td>
<td>0-24208</td>
<td>1.9</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>381.97</td>
<td>0-26173</td>
<td>4.8</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Gd(_{II})</td>
<td>376.84</td>
<td>633-27162</td>
<td>8.3</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>342.25</td>
<td>1935-31146</td>
<td>19.0</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>336.22</td>
<td>633-30367</td>
<td>12.0</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Tb(_{II})</td>
<td>350.92</td>
<td>0-28488</td>
<td>NR(^b)</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Element</td>
<td>Wavelength</td>
<td>Transition</td>
<td>Intensity</td>
<td>Life</td>
<td>Spin</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>------------</td>
<td>-----------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Dy II</td>
<td>353.17</td>
<td>0-28307</td>
<td>19.0</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Ho II</td>
<td>345.6</td>
<td>NR^b</td>
<td>NR</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Er II</td>
<td>349.91</td>
<td>440-29011</td>
<td>9.9</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>337.28</td>
<td>0-29641</td>
<td>13.0</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Tm II</td>
<td>384.80</td>
<td>0-25980</td>
<td>1.1</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Yb II</td>
<td>369.42</td>
<td>0-27062</td>
<td>0.74</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>328.94</td>
<td>0-30392</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lu II</td>
<td>350.74</td>
<td>0-28503</td>
<td>0.20</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

a. See Reference (67).
b. NR = not recorded.
Figure 12. Analytical Calibration Curves for Lanthanum and Cerium.

- Single element
- \( x \) in mixture
Figure 13. Analytical Calibration Curves for Europium and Dysprosium.

- single element
- x in mixture
Figure 14. Analytical Calibration Curves for Holmium and Lutetium.

- single element
- x in mixture
CHAPTER THREE

ATOMIC FLUORESCENCE SPECTROMETRY
IN THE FLAME USING ICP AS A NEW EXCITATION
SOURCE "ICP-EXCITED FASF"

A - ICP Diagnostics Using the ICP-Excited Flame AFS

A.1 - Introduction

Many physical parameters of the inductively coupled plasma (ICP) source for analytical spectroscopy have been investigated. The recent review by Barnes contains an extensive list of references covering fundamental operating principles and methodologies. Emission profiles of several elements for several experimental conditions have been reported by Human and Scott, who used a pressure-scanning Fabry-Perot interferometer to obtain the profiles. These authors concluded that the spectral profiles of the lines emitted for the elements investigated (Ca, Sr, Ar) depended upon the height of observation and that, although self-absorption and self-reversal were observed at certain heights, these phenomena did not occur for a range of at least three orders of magnitude (1-1000 μg/mL) indicating the excellent characteristics of the ICP as an emission source.

This work reports preliminary results showing how several limiting characteristics of the ICP emission profiles can be derived if the ICP is used as an excitation source for atomic fluorescence spectrometry. The emission of selected atomic species introduced into the plasma is monitored via the fluorescence signal observed when a given (low) concentration of the same element is aspirated into an air-acetylene or another
suitable gas mixture flame. Therefore, the flame acts as a resonance monochromator.\textsuperscript{70-73} This procedure is capable of providing in a very simple way \textit{qualitative but unequivocal} information about the line profile of the ICP emission without sophisticated instrumentation such as high resolution monochromators of Fabry-Perot interferometers. These latter approaches are the only ones giving complete quantitative information about the true line profiles. However, the fluorescence technique, not only clearly detects self-absorption, but is especially sensitive to incipient self-reversal of the emission line profile.

This information is obtained from the experimental log-log plot of three curves of growth: the first one, is the \textit{excitation curve of growth}, in which a fixed low concentration is used in the flame while increasing concentrations are aspirated into the ICP, (i.e., the flame acts as a resonance monochromator);\textsuperscript{73} the second one, is the \textit{fluorescence curve of growth}, (i.e., the conventional curve of growth obtained with a fixed (high) concentration of a selected element in the ICP while aspirating increasing concentrations of the same element into the flame); and the third one, is the \textit{common emission curve of growth}, in which the emission from the ICP is directly plotted \textit{vs} the concentration of the analyte in it.

The results obtained for the elements Zn, Mg and Ca verify the expected behavior of these curves.

A.2 - Theoretical Considerations

The interaction between the radiation emitted by the ICP and the absorbing atoms in the flame is described by the following "excitation function" \textsuperscript{74-76,21,37}

\[
\int_{\text{abs}} E_{\lambda}^{\text{exc}} (\lambda) \alpha_f(\lambda) d\lambda = \int_{\text{abs}} E_{\lambda}^{\text{exc}} (\lambda) \{1 - \exp[-k_f(\lambda)L]\} d\lambda
\]  \text{ (44)}
in which the integral is extended over the entire absorption line width (i.e., the width over which \( k_f(\lambda) \) differs markedly from zero). Here the terminology is as follows:

\[
E_{\lambda, \text{exc}}(\lambda) = \text{spectral irradiance of the ICP as a function of wavelength at a given height and at a given analyte concentration, evaluated at wavelength } \lambda, \ J \ s^{-1} \ cm^{-2} \ nm^{-1};
\]

\[
a_f(\lambda) = \text{fraction of radiation absorbed at any wavelength } \lambda, \text{ dimensionless;}
\]

\[
k_f(\lambda) = \text{absorption coefficient of analyte atoms in the flame, usually given by the product of } k_o \text{ (peak absorption coefficient for a purely Doppler broadened profile) and the Voigt profile function, cm}^{-1}; \text{ for a given resonance line and under given conditions and flame temperature, } k(\lambda) \text{ is proportional to } n_f, \text{ the flame atomic concentration, over all the absorption line, for all values of } n_f.
\]

\[L = \text{interaction length for the absorption process in the flame, cm.}\]

The spectral irradiance of the ICP, \( E_{\lambda, \text{exc}}(\lambda) \), can be regarded as the product of the blackbody spectral irradiance at the wavelength considered and at the ICP emission temperature and the total absorption factor which is a function of the concentration in the ICP and of its emission depth in the direction of the flame.

When the interaction process is studied by means of the resulting fluorescence emission in the flame, then the fluorescence radiance is given by the following proportionality:
\[
B_F = \left\{ \int_{\text{abs}} \int_{\text{exc}} E_\lambda (\lambda) \left\{ 1 - \exp\left[-k_f(\lambda)L\right] \right\} d\lambda \right\} \left\{ \int_{\text{abs}} \int_{\text{exc}} \left\{ 1 - \exp\left[-k_f(\lambda)L\right] \right\} d\lambda \right\} \left\{ \int_{\text{abs}} \int_{\text{exc}} k_f(\lambda)d\lambda \right\} \right\} \left\{ \int_{\text{abs}} \int_{\text{exc}} [A_t(n_f, \lambda)]/[\int_{\text{abs}} k_f(\lambda)d\lambda] \right\} \right\} \right\} \right\} \right\} \right\}
\]

Equation 45 is equal to Equation 44 multiplied by a term which takes into account the self-absorption of the fluorescence radiation leaving the flame. Here, \( A_t(n_f, \lambda) \) is the total absorption factor for the fluorescence radiation in the flame, \( n_f \) is the flame atomic concentration, and \( \lambda \) is the (homogeneous) fluorescence depth. Equation 45 simplifies for the two usual limiting cases of line and continuum excitation sources and for negligible fluorescence self-absorption. In fact, if \( n_f \) is low, then the second factor at the right hand side of Equation 45 is unity.

If the ICP acts as a spectral line source, the \( k_f(\lambda) \) can be considered constant and equal to its peak value, \( k_{\text{max}}^f \). Equation 45 then reduces to Equation 46.

\[
B_F \simeq \left\{ 1 - \exp\left[-k_{\text{max}}^f L\right] \right\} \int E_\lambda (\lambda) d\lambda \right\}.
\]

Thus the ICP may act as a line source if its overall spectral emission profile is narrower than the absorption profile in the flame, even though its higher temperature would cause the Doppler halfwidth to be larger than that in the flame by a factor of approximately the square root of two (assuming a Maxwellian velocity distribution exists).

If the ICP acts as a spectral continuum because, at high concentrations, self-absorption has broadened the emission profile to such an extent that it becomes larger than the absorption profile in the flame, then Equation 45 reduces to Equation 47.
\[ B_F \propto E_{\lambda_{\text{exc}}}^{\lambda_0} \int \{1 - \exp[1 - k_F(\lambda) L]\} d\lambda \Delta \lambda_{\text{exc}}^{\lambda_0} A_t(n_F L) \]  

(47)

in which \( E_{\lambda_{\text{exc}}}^{\lambda_0} \) is the constant irradiance of the ICP over the absorption line profile.

Therefore, when the interaction between the ICP emission and the resonance absorption profile in the flame is monitored by the fluorescence emitted from a constant concentration of flame atoms, a slope of unity for low concentrations in the ICP and a limiting slope of zero for high concentrations in the ICP should be obtained. This limiting zero slope will hold, irrespective of the amount of self-absorption, as long as self-reversal does not affect the ICP emission profile. When this happens, i.e., when the ICP emission profile starts showing a dip in the center, this dip will be reflected immediately in the fluorescence signal, and a negative slope will be observed in the experimental plot.

On the other hand, the ICP-excited fluorescence curve of growth obtained by aspirating in the flame increasing concentrations of analyte should give the following information:

(i) if the asymptote at high \( n_F \) has a slope near -0.5, then the ICP, at that particular height and atom density \( n_p \), behaves like a line source, i.e., its spectral profile is narrower than the absorption profile in the flame;

(ii) when self-absorption is large in the ICP emission, this curve of growth should approach a region of zero slope, which indicates that the emission profile is broader than the absorption profile; and

(iii) the absence of self-reversal in the emission profile can be inferred unequivocally by the combined observations of this curve of growth with the previously described excitation curve of growth obtained at the same experimental settings.
These results, which are summarized in Table 6, can be obtained from Equations 45-47, by assuming that the self-absorption factor for the fluorescence cannot be considered negligible and remembering that $A_t(n_f)$ and $A_t(n_f^L)$ vary linearly with $n_f$ at low $n_f$ values and with $n_f^{3/2}$ at high $n_f$ values.

A.3 - Experimental

Figure 15 shows the experimental arrangement used. The ICP source (ICP 1500 Plasma Therm., Inc., Kresson, N.J.) was focused on the aperture of a chopper and subsequently onto the flame by means of spherical quartz lenses. In order to minimize pre- and post-filter effects, a rectangularly shaped burner was used and care taken to optimize properly illumination and observation geometries. Furthermore, in order to avoid possible inhomogeneities in temperature and composition, the flame was shielded by another similar flame, which could in turn be surrounded by an inert gas flow.

The fluorescence was collected by a spherical quartz lens and directed onto the entrance slit of a small monochromator (Jobin-Yvon, H-10, 8 nm/mm reciprocal linear dispersion); the slit width and height were set, unless otherwise stated, at 50 µm and 10 mm, respectively. The output signal of a photomultiplier (Hamamatsu 1P28) was fed to a lock-in amplifier (840 Autolock, Keithley, Cleveland, Ohio) and then to a chart recorder. For the emission measurements, the ICP image was focused directly onto the entrance slit on a 0.35-m monochromator (2 nm/mm reciprocal linear dispersion, 25 µm slit width, 15 mm slit height Model No. EV-700, Heath, N.Y.). Neutral density filters (Corion, Massachusetts) allowed the verification of the linearity of the response of both emission and fluorescence photomultiplier and associated detection electronics.
Table 6
THEORETICAL LIMITING SLOPES FOR THE THREE CASES
CONSIDERED IN ABSENCE OF SELF-REVERSAL (a)

<table>
<thead>
<tr>
<th>Technique</th>
<th>Atom Density in the Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Very Low</td>
</tr>
<tr>
<td>Emission</td>
<td>1</td>
</tr>
<tr>
<td>Excitation</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom Density in the Flame</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very Low</td>
</tr>
<tr>
<td>Flourescence (line source excitation)</td>
</tr>
<tr>
<td>Flourescence (continuum source excitation)</td>
</tr>
</tbody>
</table>

(a) When self-reversal in the source is effective at high concentrations, the slope of the emission technique decreases and that of the excitation technique becomes negative. When self-reversal occurs in the flame, the high density slopes will display similar trends. Self-reversal in the flame here means that a temperature gradient exists in the flame and should not be confused with the post-filter effect.

37
Figure 15. Layout of the experimental set-up used.
Standard solutions were made from reagent grade chemicals, dissolved in the minimum amount of HCl, and brought to the desired concentration level with deionized water.

A.4 - Results and Discussion

Figures 16, 17 and 18 show the excitation curves of growth obtained for the elements Mg, Zn, and Ca when a constant low concentration of each element (1, 1, and 10 ug/mL, respectively) was aspirated into the air-acetylene flame and the ICP concentration was varied from 10 to 20,000 ug/mL. This last concentration caused no problem in the operation of the ICP, although a deposit was observed after prolonged operation on the aerosol injection orifice. A similar effect was also reported by Larson and Fassel when aspirating high sodium concentrations.

As one can deduce from these figures, the general limiting trends predicted by the theory are qualitatively well verified experimentally. In the case of magnesium, Figure 16 shows that self-reversal in the ICP is totally absent at the heights which are commonly used for analysis (curves b and c). Indeed, to observe self-reversal (curves d and e) it was necessary to increase the observation height to 37 mm above the coil, in a region practically never utilized for analysis. One can also note the utility of detecting incipient self-reversal in the ICP by means of the flame fluorescence signal, since the ICP emission is still increasing, although with a smaller slope (curve f). Figure 16 shows also clearly (see insert c) that at an observation height of 13 mm above the coil, the emission is still increasing almost linearly (slope of 0.9) and the fluorescence is also increasing (slope of 0.6); this indicates that self-absorption in the ICP is not very pronounced even at concentrations as high as 20,000 ug/mL. This unique feature of the ICP as an excitation source indicates that it behaves as an optically thin discharge. When
Figure 16. Emission and Excitation curves of growth for Mg at 285.2 nm.  
(a) ICP emission, height of observation above coil, z=18 mm;  
(b) ICP excitation curve, z=18 mm; 1 µg/mL of Mg aspirated  
into the air-acetylene flame; (c) same as (b) but at z=25 mm;  
(d) same as (b) but at z=30 mm; (e) same as (b) but at z=37  
mm; (f) emission from ICP at z=37 mm; (g) ICP emission (upper  
line) and excitation (lower line) curves for the three con¬  
centrations reported in the abscissa at z=13 mm. All curves  
were obtained at an operating power of 1.5 kW.
Figure 17. Emission and Excitation curves of growth for Zn at 213.9 nm. (a) ICP emission, z=18 mm; (b) ICP excitation curve, z=18 mm, 1 μg/mL of Zn aspirated into the air-acetylene flame; (c) ICP emission (upper line) and excitation (lower line) curves for the three concentrations reported in the abscissa at z=37 mm. All the curves were obtained at an operating power of 1.5 kW.
Figure 18. Emission and Excitation curves of growth for Ca at 422.7 nm. (a) ICP emission at z=37 mm; (b) same as (a) but at z=13 mm; (c) Excitation curve, z=37 mm, 10 µg/mL of Ca aspirated into air-acetylene flame; (d) same as (c) but at z=13 mm; (e) same as (c) but at an operating power of 1 kW. All other curves were obtained at 1.5 kW.
self-absorption broadens the line and the emission curve reaches a slope of $\approx 0.5$ (curve a), the excitation curve approaches a slope of zero (curves b and c).

Even more striking are the results for zinc presented in Figure 17. In fact, no sign of self-reversal is observed even at 37 mm above the coil, while self-absorption seems to be complete at this height (see insert c). The results obtained with calcium (Figure 18) are similar to those for magnesium and zinc. As with Mg, Ca emission shows self-reversal at 37 mm above the coil (curve c), and this increases at a power of 1 kW (curve e).

Figures 19 and 20 show the fluorescence curves of growth for Mg and Zn in the air-C$_2$H$_2$ flame obtained at several fixed concentrations in the ICP. By recalling the conventional behavior of the fluorescence curves of growth (see Table 6), one can conclude from both figures that the ICP should be considered essentially a "line" excitation source compared to the absorption profile in the flame. Indeed, all the fluorescence curves (a to d in both figures) have a slope close to -0.5 for high analyte concentrations in the flame. Moreover, the intersection points of the asymptotes for the curves are not significantly displaced from each other when the concentration in the ICP increases from 1,000 to 20,000 $\mu$g/mL. This indicates that the $a$-parameter (which is indicative of the ratio between collisional and Doppler broadening) is not changing much, which is in qualitative agreement with the behavior shown by the excitation curves of growth, obtained at the same heights, of Figures 16 and 17. This is as expected, since the major source of collisional broadening would be interaction with the argon plasma gas.

Since at 37 mm above the coil, zinc self-absorption was essentially complete (see Figure 17, insert c), flattening of the fluorescence growth
Figure 19. Fluorescence curves of growth for Mg at 285.2 nm and at z=18 mm. The different curves correspond to different concentrations in the ICP: (a) 1,000 µg/mL; (b) 4,000 µg/mL; (c) 8,000 µg/mL; (d) 20,000 µg/mL.
Figure 20. Fluorescence curves of growth for Zn at 213.9 nm and at z=18 mm. The different curves correspond to different concentrations in the ICP: (a) 1,000 μg/mL; (b) 4,000 μg/mL; (c) 8,000 μg/mL; (d) 20,000 μg/mL. The insert (e) in the figure shows the difference in the results obtained at z=37 mm, when the ICP concentration is fixed at 1,000 μg/mL (lower curve) and at 20,000 μg/mL (upper curve).
Figure 6
curve should be observed at this height when 20,000 μg/mL of Zn is aspirated in the ICP. Results, shown in the insert (e) of Figure 20, verify that a flattening is indeed observed at the highest ICP concentration. However, for analyte concentrations in the flame above 2,000 μg/mL, a negative slope in the fluorescence growth curve still occurs, which could probably be explained by the additional broadening of the absorption profile in the flame.

**A.5 - Detection Limits**

Although considered beyond the scope of the present work, the limits of detection were measured with the present non-optimized system for the three elements investigated. Sixteen consecutive integrated blank measurements were performed by aspirating water into the air-acetylene flame and the highest concentration of the element into the plasma. When water was aspirated into the plasma, the noise level remained essentially the same. The slit width of the fluorescence monochromator was set at 1 mm for Ca and Zn and at 50 μm for Mg. The actual concentrations aspirated into the flame were 0.01 μg/mL for Mg, 0.1 μg/mL for Zn and 0.1 μg/mL for Ca. The calculated detection limits (at 3 times the standard deviation of the blank) were found to be 13, 4, and 23 ng/mL for Zn, Mg, and Ca, respectively.

Although the experiment arrangement was not optimized for illumination and collection efficiencies, the detection limits are equivalent or within an order of magnitude of those obtained with conventional atomic fluorescence excited by an electrodeless discharge lamp (Ca) or an Eimac-Xe continuum source (Mg, Zn). These detection limits are similar or better than those reported by Hussein and Nickless for a 36 MHz (2.5 kW) induction-coupled plasma and an air propane flame.
B.1 - Introduction

The inductively-coupled argon plasma (ICAP) has been demonstrated\[13\] to be an excellent source for emission spectrometry. However, the spectral characteristics of the emission from this source, such as high intensity, excellent short and long term stability, narrow linewidth and freedom from self-reversal, make it an ideal radiation source for the excitation of atomic fluorescence in flames.

The first reported use of a radiofrequency, induction-coupled plasma (36 MHz, 2 kW, Model SC15, Radyne Ltd., U.K.) as an excitation source for flame atomic fluorescence spectrometry (AFS) by Hussein and Nickless\[34\] resulted in relatively poor detection limits\[35\] (see Table 8) which probably contributed to the absence of further development of the ICAP as a source for AFS. However, the tremendous growth in the use of the ICAP for emission in the last decade has resulted in significant improvement in sample introduction and plasma stability,\[78\] which now makes the ICAP an excellent source for AFS as seen in part A.

The advantage of the ICAP compared to other AFS sources is its flexibility with respect to the availability of intense atomic and ionic line radiation for many elements. Changing from one element to another is simply a matter of aspirating a different solution into the plasma, taking less than one minute. The availability of many intense non-resonance and ionic lines allows scatter correction to be easily performed using the two-line technique.\[79\]

ICAP-excited AFS can also offer an alternative to ICAP-emission when spectral interferences which are observed with monochromators of medium resolution (>0.01 nm spectral bandpass) significantly limit
emission analysis. Interferences in emission due to changes in the plasma background radiation (which require a background correction procedure) are not observed using AFS and line spectral interferences which cannot be resolved may be reduced or eliminated because of the spectral selectivity of flame AFS, based on differences in atomization, excitation, and ionization properties of the flame and plasma; on differences in quantum efficiencies between analyte and interferent lines; and on the property of the flame as a resonance detector with an effective spectral bandwidth equivalent to the width of the absorption transition.

We have investigated the application of the ICAP as an excitation source for atomic fluorescence using a simple optical setup, low resolution monochromator, and nitrogen-separated air/acetylene and nitrous-oxide/acetylene flames. Detection limits obtained for 14 elements are compared to AFS detection limits using other excitation sources and to detection limits of other atomic spectrometric techniques, such as flame atomic absorption and ICAP-emission. The noise sources limiting precision at low and high concentrations are delineated and the effect of various instrumental parameters such as spectral bandpass and ICAP nebulizer pressure on signal-to-noise ratios is described. The scatter problem is evaluated and the two-line method is applied for scatter correction. ICAP-emission and ICAP-excited AFS are applied to the analysis of zinc in unalloyed copper (NBS SRM-394 and 396) and the AFS technique is employed to correct for a zinc-copper spectral interference at the 213.9 nm line in ICAP-emission. ICAP-excited AFS is also employed for the analysis of copper and zinc in orange juice, zinc in fly ash (NBS SRM-1633) and cadmium and zinc in simulated fresh water (NBS SRM-1643).

B.2 - Experimental

Instrumentation. The instrumentation used in this study is described in Table 7 and a diagram of the arrangement of experimental components.
### Table 7
**INSTRUMENTATION AND OPERATING PARAMETERS**

<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
<th>Operating Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ICAP</strong></td>
<td>PT-1500 torch assembly and HFP-1500D RF generator (Plasma Therm Inc., Kresson, N.J.)</td>
<td>1.5 kW power, 15 L/min argon coolant flow rate</td>
</tr>
<tr>
<td><strong>Nebulizer</strong></td>
<td>Concentric-ring glass nebulizer T-220-A2 (J. E. Meinhard Assoc., Santa Anna, CA)</td>
<td>Nebulizer pressure optimized for individual elements - from 15 to 35 psi (Solution Uptake Rate=1.75 mL/min)</td>
</tr>
<tr>
<td><strong>Emission monochromator</strong></td>
<td>EU-700 monochromator (Heath Company, MI), 0.35-m focal length, f/6.8 aperture, 1180 groves/mm, grating blazed for 250 nm, adjustable slits, 2 nm/mm reciprocal linear dispersion</td>
<td>1 mm slit height 25 μm slit width (effective 0.05 nm spectral bandpass)</td>
</tr>
<tr>
<td><strong>Fluorescence monochromator</strong></td>
<td>H-10 monochromator (UV-V) (JY Instruments, Metuchen, N.J.) 0.1-m focal length, f/3.5 aperture, 8 nm/mm reciprocal linear dispersion, holographic grating with 1200 groves/mm, with 0.05, 0.5, 1, 2 mm slits providing spectral bandpasses of 0.4, 4, 8, and 16 nm, respectively.</td>
<td>2 mm slit width except where noted in text; 1 cm slit height</td>
</tr>
<tr>
<td><strong>Emission photomultiplier</strong></td>
<td>R-928, (Hamamatsu TV Corp. Ltd., Middlesex, N.J.)</td>
<td>1000 V</td>
</tr>
<tr>
<td>Equipment Description</td>
<td>Specifications and Details</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------------------------------</td>
<td>------------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Fluorescence photomultiplier</td>
<td>1P28, (RCA Corp., Harrison, N.J.)</td>
<td></td>
</tr>
<tr>
<td>Current-to-Voltage Converter</td>
<td>Keithley 427 (Keithley Instrument Company, Cleveland, Ohio)</td>
<td></td>
</tr>
<tr>
<td>Lock-in Amplifier</td>
<td>Keithley 840 Autoloc amplifier, wideband</td>
<td></td>
</tr>
<tr>
<td>Recorder</td>
<td>Texas Instruments, Houston, TX</td>
<td></td>
</tr>
<tr>
<td>Nebulizer and mixing chamber for flame</td>
<td>Perkin-Elmer adjustable nebulizer and mixing chamber with flow spoiler (Perkin-Elmer Corp., Norwalk, Conn.)</td>
<td></td>
</tr>
<tr>
<td>Burner heads</td>
<td>Circular stainless steel capillary burner head with auxiliary sheath</td>
<td></td>
</tr>
<tr>
<td>Lenses</td>
<td>Spectrosil, 5 cm diameter, 9 cm focal length</td>
<td></td>
</tr>
<tr>
<td>Mirror</td>
<td>5 cm aluminum-coated spherical with 5 cm focal length (Klinger Scientific Corp., Jamaica, N.Y.)</td>
<td></td>
</tr>
</tbody>
</table>

600 to 900 V, depending on background emission from flame

1 or 3 second time constant

600 Hz

5-8 mL/min aspiration rate
is shown in Figure 21. Radiation from aqueous solutions of the analyte element aspirated into the ICAP is modulated at 600 Hz and focused by spherical quartz lenses on the separated flame. A reflector is placed behind the flame to provide a double-pass system. The fluorescence monochromator is placed 4 cm from the flame center and the viewing area is centered 2 cm above the burner head. A light trap is placed opposite the flame from the monochromator to reduce stray light and scatter effects. Once optical alignment is attained, the only ICAP parameters that must be optimized for different elements are the argon pressure to the nebulizer and the concentration of the solution nebulized. Torch position is not critical, since the entire emission area above the coils is focused on the area of the flame viewed by the fluorescence monochromator.

Emission measurements from the ICAP were performed as described previously in Chapter 2.

**Excitation Source (ICAP) Solutions.** The solutions used for excitation of analyte emission from the ICAP contained 10 to 20 mg/mL of the analyte. Whenever possible, these "excitation" solutions were prepared by acid dissolution of the high purity metal or metal oxide, although other compounds (nitrates, chlorides, etc.) were employed when the former were not available. The selectivity of the fluorescence technique using line source excitation (i.e., its ability to discriminate against spectral interferences) depends on the spectral purity of the line source, and if significant interferent contamination exists in the excitation solution, interferent emission will be excited in the ICAP which may degrade the selectivity. The effect of such contamination is discussed more fully for the analysis of zinc in unalloyed (high-purity) copper.

The use of solutions of such high concentrations does not significantly degrade the ICAP performance by clogging the sample orifice of
Figure 21. Diagram of Experimental Layout of Components for Measurement of ICAP-excited AFS and ICAP-emission.
the torch or the nebulizer during an 8-hour working day. However, to prevent such degradation on prolonged use, which would result in source intensity drift, the torch is cleaned after a day's use in a solution of 1:3 V:V HNO₃/HCl.

**Fluorescence Standards.** Standards for AFS measurements were prepared from the same solutions used for excitation in the ICAP using serial dilution with deionized water and sub-boiling distilled acids prepared in this laboratory.

**Sample Preparation.** The samples analyzed by ICAP-excited AFS and ICAP-emission were prepared as follows:

1) Orange juice - dry ashing procedure is described by McHard et al.

2) Fly ash (NBS SRM-1633) - wet ashing procedure is described by Epstein et al.

3) Unalloyed copper (NBS SRM-394 and 396) - dissolution of 1 g of copper is carried out in 10 mL of sub-boiling distilled HCl with dropwise addition of sub-boiling distilled HNO₃ until complete, reduction in volume after dissolution by evaporation to 2 mL, and finally the solution is diluted to a volume of 100 mL.

4) Simulated Fresh Water (NBS SRM-1643) - direct analysis is performed.

**B.3 Results and Discussion**

**Limits of Detection.** As shown in Table 8, limits of detection for many of the elements examined using ICAP-excited AFS approach, equal, or even exceed in one case (Mo) the best atomic fluorescence detection limits ever obtained in similar flames (i.e., nitrogen-separated air/acetylene or nitrogen-separated nitrous-oxide/acetylene) using a relatively conservative time constant (3 s) or integration time (1 s) and a
<table>
<thead>
<tr>
<th>Element</th>
<th>λ(nm)</th>
<th>Flame</th>
<th>ICAP-excited AFS&lt;sup&gt;c,d&lt;/sup&gt;</th>
<th>ICAP-omission</th>
<th>AFS line&lt;sup&gt;h&lt;/sup&gt;</th>
<th>AAS&lt;sup&gt;i&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>308.2</td>
<td>S-NOA</td>
<td>1000</td>
<td>23</td>
<td>120</td>
<td>30</td>
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<tr>
<td>As</td>
<td>235.0</td>
<td>S-AA</td>
<td>5000</td>
<td>142</td>
<td>70</td>
<td>100</td>
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<tr>
<td>Ca</td>
<td>422.6</td>
<td>S-AA</td>
<td>10</td>
<td>4</td>
<td>0.3</td>
<td>1</td>
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<tr>
<td>Cd</td>
<td>228.8</td>
<td>S-AA</td>
<td>0.8</td>
<td>&gt;23</td>
<td>1.5</td>
<td>10</td>
</tr>
<tr>
<td>Co</td>
<td>240.7</td>
<td>S-AA</td>
<td>11</td>
<td>&gt;23</td>
<td>1.5</td>
<td>10</td>
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<tr>
<td>Cr</td>
<td>357.8</td>
<td>S-AA</td>
<td>2</td>
<td>23</td>
<td>0.3</td>
<td>3</td>
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<tr>
<td>Cu</td>
<td>324.7</td>
<td>S-AA</td>
<td>2</td>
<td>23</td>
<td>0.3</td>
<td>2</td>
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<tr>
<td>Fe</td>
<td>248.3</td>
<td>S-AA</td>
<td>6</td>
<td>&gt;20</td>
<td>0.6</td>
<td>10</td>
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<tr>
<td>Mg</td>
<td>285.2</td>
<td>S-AA(fr)</td>
<td>0.09</td>
<td>1.6</td>
<td>0.09</td>
<td>0.1</td>
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<tr>
<td>Mn</td>
<td>279.5</td>
<td>S-AA</td>
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<td>12</td>
<td>0.5</td>
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<tr>
<td>Mo</td>
<td>313.3</td>
<td>S-NOA</td>
<td>400</td>
<td>&gt;37</td>
<td>750</td>
<td>30</td>
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<tr>
<td>Element</td>
<td>Wavelength (nm)</td>
<td>Flame Type</td>
<td>Detection Limit (ng/g)</td>
<td>Limit (ng/g)</td>
<td></td>
<td></td>
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<tr>
<td>---------</td>
<td>----------------</td>
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<td>------------------------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>283.3</td>
<td>S-AA</td>
<td>800</td>
<td>142</td>
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<tr>
<td>V</td>
<td>318.5</td>
<td>S-NOA</td>
<td>400</td>
<td>&gt;17</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318.4</td>
<td></td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318.3</td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>213.9</td>
<td>S-AA</td>
<td>0.5</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* Wavelengths of major fluorescence line(s) contributing to the fluorescence spectral intensity. Since the spectral bandpass of the monochromator is 16 nm, other lines may contribute some intensity.\(^5\)

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

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

*d* From references 34, 35 (SNR=2).

*e* Predicted ICAP-emission limits of detection\(^3\) for the same line(s) used to excite AFS.

*f* Commercial multi-element limits of detection\(^4\) based on SNR = 2 for ICAP-emission.

*g* State-of-the-art limits of detection for ICAP-emission using pneumatic nebulization (SNR=2).\(^5\)

*h* Line source atomic fluorescence detection limits in a similar flame (SNR=2).\(^3\)

*i* Atomic absorption detection limits (SNR=2).\(^6\)

*j* Limit of detection based on the normal analytical line, not the most sensitive line.\(^4\)
rigorous (SNR = 3) definition of detection limit. While the fluorescence
detection system for ICAP-excited AFS is well optimized for a background
shot-noise limited, dispersive system, using double-pass optics, light
traps and a very low resolution (spectral bandpass = 16 nm) monochromat-
tor, the optical transfer of the ICAP emission to the flame can be im-
proved by at least an order of magnitude by the use of an ellipsoidal
reflector placed off-axis or behind the plasma to collect a much
larger solid angle of emission. This should improve detection limits by
the increase in the light gathering power, assuming scatter does not be-
come a significant noise source. We are presently collecting only about
2 percent of the source radiation using 5 cm spherical lenses with a
focal length of 9 cm.

The ICAP-excited AFS detection limits are a function of the atomic
emission intensity from the ICAP and the flame background emission inten-
sity. Shot-noise induced by the flame background emission is the limit-
ing noise source at the detection limit using the 16 nm spectral bandpass
with both separated air- and nitrous-oxide/acetylene flames. The effect of
spectral bandpass (slit width) on the signal-to-noise ratio (SNR), and thus
on the detection limit, is shown in Figure 22 for cadmium in an air/acetylene
and vanadium in a nitrous-oxide/acetylene flame. In the former flame, the
SNR shows a slight decrease upon changing from a 16 nm spectral bandpass
(2 mm slits) to a 4 nm spectral bandpass (0.5 mm slits), which is consist-
tent with the changes in solid angle observed using the H-10 monochromator
without focusing optics. Geometrical considerations show that over 2 cm
of flame height are observed by the collimator although the vignetted
region is considerably extended, due to the small collimator effective
aperture (2.86 cm). In all cases, the slit width is such that the over-
all width of the flame is viewed by the collimator. The considerable
Figure 22. The Effect of Slit Width on the ICAP-excited AFS signal-to-noise ratio from (■) cadmium in a nitrogen-separated air/acetylene flame and (☆) vanadium in a nitrogen-separated nitrous-oxide/acetylene flame. (20 ng/mL Cd; 100 µg/mL V)
decrease in SNR upon a further 10-fold decrease in spectral bandpass is due to a change of the dominant noise from flame background-induced shot-noise to photomultiplier dark-current shot-noise and/or electronic noise. In the case of vanadium in the nitrous-oxide/acetylene flame, the more significant decrease in SNR for the decrease in spectral bandpass from 16 to 4 nm is likely due to the exclusion of fluorescing lines from the bandpass which decreases the signal more than the case of cadmium, which involves one fluorescing line. The less significant decrease in SNR observed in the change from 4 nm to 0.4 nm is also due to the exclusion of fluorescing lines and geometrical considerations, since the flame background-induced shot-noise is still limiting at the smaller bandpass.

For some elements, the ICAP-excited AFS detection limits are within an order of magnitude of the best reported ICAP-emission detection limits (Zn, Cr, Cd, Mg, Cu) listed in Table 8. Furthermore, the ICAP-excited AFS detection limits are better or equal to the detection limits obtainable on a commercial ICAP spectrometer for these same elements. These detection limits are representative of what we can obtain using our medium resolution monochromator (0.04 nm spectral bandpass) for ICAP-emission.

Of further interest is a comparison of detection limits for ICAP-excited AFS and ICAP-emission using the same line. A recent publication by Winge et al. estimated detection limit capabilities for the prominent lines of 70 elements emitted in an ICAP excitation source. Their estimated detection limits using the lines with the best signal-to-background ratio are very close to the experimentally determined detection limits for a commercial ICAP instrument which were presented in Table 8. The predicted ICAP-emission detection limits for the atomic resonance lines which we used to excite fluorescence are also presented in Table
8. It is interesting to note that for every element (except Pb) determined in a nitrogen-separated air/acetylene flame, the ICAP-excited AFS detection limits are from two to twenty times better than the predicted ICAP-emission detection limits for the same lines.

When detection limits are determined at the same line, the factors which must be considered are the solid angle of the ICAP-emission focused on the flame versus the solid angle viewed by the emission monochromator, the emission intensity of the excitation solution (10 mg/mL) in the ICAP versus the emission intensity of the solution used to determine the ICAP-emission detection limit, the noise sources limiting detection for each technique, and the efficiency of emission and fluorescence excitation, collection and detection. Although the signal in ICAP-excited AFS will lose with respect to factors such as the fluorescence quantum efficiency (typically 0.01 - 0.05 in an air/acetylene flame) and monochromator collection efficiency (since only a small percentage of fluorescence radiation is collected), ICAP-excited AFS will gain based on the solid angle of collection of ICAP-emission and relative background emission intensities of the ICAP and the nitrogen-separated air/acetylene flame. The qualitative significance of these factors are illustrated by the improvement of the "same line" ICAP-emission detection limits using ICAP-excited AFS as a detection system, as shown in Table 8.

**Precision and Linearity.** In Figure 23(A), a typical ICAP-excited AFS analytical growth curve is shown, in this case for zinc, which is linear over slightly less than 4 orders of magnitude. In Figure 23(B), a precision plot is shown for this same element, based on sixteen 1 second integrations at each data point and repeated twice. The analytical precision at high concentrations is on the order of one to 2 percent and is primarily limited by the source (ICAP) stability. This is in
Figure 23. ICAP-excited AFS analytical growth curve (A) and precision curve (B) for zinc in a nitrogen-separated air/acetylene flame at 213.9 nm.
RELATIVE FLUORESCENCE

(A)

LIMIT OF DETECTION

0.001 0.01 0.1 1 10 100
ZINC CONCENTRATION (µg/ml)

(B)

% R.S.D. (conc.)

0.1 1 10 100
agreement with other researchers\textsuperscript{71,17} who have reported the ICAP precision to be limited primarily by fluctuations in the nebulization and sample transport system to about one percent.

The long term stability of the ICAP emission is excellent,\textsuperscript{17} on the order of a few percent over long time periods, and thus its use to excite fluorescence represents a considerable advantage over many previous sources used for AFS such as electrodeless discharge lamps, which must be carefully thermostatted\textsuperscript{90} under certain conditions, and the Eimac short-arc xenon lamp,\textsuperscript{91} which has a much lower intensity in the ultraviolet.

\textbf{Scatter.} The problem of scattered radiation is perhaps the most significant interference in AFS when resonance transitions are employed. Scatter can occur from environmental sources, such as reflections off mirrors and burner heads, but this type of scatter is only significant when it becomes a dominant noise source due to either source-induced shot-noise or flicker. The latter is a problem with some pulsed dye lasers,\textsuperscript{92} where pulse to pulse variations may be ten percent at a minimum. In ICAP-excited AFS, we observed environmental scatter to be significant only for those elements with detection limits less than about 5 ng/mL, and even in the case of magnesium, with a detection limit of 0.09 ng/mL, the scatter signal was not a significant noise source.

The other type of scattered radiation is that due to undissociated matrix particulates in the analytical flame. This scatter has been categorized as primarily being of the Mie variety (i.e., due to particulates much larger than the wavelength of scattered radiation)\textsuperscript{73,93} and does not have an easily defined relationship to wavelength as Rayleigh scatter does (I \alpha \lambda^{-4}). An error in accuracy will result from this type of scatter, since it may be mistaken for atomic fluorescence. The scatter
interference is much more severe using continuum excitation sources than line sources, because of the greater spectral width of the former.

The primary method for correction using line excitation sources, the two line technique,\textsuperscript{73,94} is based on the narrow linewidth of the atomic fluorescence and the assumption that the scatter signal does not change appreciably in the wavelength vicinity of the atomic fluorescence line. Another line from the source, which does not excite significant analyte or matrix fluorescence, is found near to the analyte line and the scatter signal is measured at that line, corrected for the relative intensities of the two lines, and subtracted from the signal excited by the analyte source line.

The ICAP is the ideal source for scatter correction using the two-line technique because of the great number of intense ion lines excited by the plasma. The ionic population of air/acetylene and electron-buffered (1 mg/mL K as KCl) nitrous-oxide/acetylene flames is insignificant for most elements and thus these ion lines are available for scatter correction along with many other non-resonance transitions. These lines are equally as useful for the correction for broad band molecular fluorescence interferences although such interferences would be expected to be more severe with a continuum source than a line source.

The magnitude of the matrix-scatter interference in ICAP-excited AFS was investigated for the zinc 213.9 nm line using a 5 percent high-purity lanthanum solution. The scatter signal was equivalent to a concentration of 60 ng/mL Zn and could be corrected for completely using the Cd II line at 214.4 nm generated by 10 mg/mL Cd in the ICAP. It should be noted that any solutions used for production of "scatter-correction" radiation in the ICAP must be significantly free of analyte or an over-correction may result. Comparison of analyte emission line intensity and
scatter correction emission line intensity from the ICAP is made experimentally using a 5 percent high-purity lanthanum solution.\textsuperscript{73,95} The presence of analyte contamination in the scatter correction solution aspirated into the ICAP can be evaluated by observing if any signal is generated by an analyte standard in the flame. In general, care must be taken that the "scatter correction" solution does not emit spectral components capable of exciting fluorescence within the spectral bandpass of the monochromator.

Another possible method for scatter correction using the ICAP is based on the shape of the "excitation" curve of growth.\textsuperscript{72} The technique is similar to the method described by Haarsma \textit{et al.},\textsuperscript{96} which takes advantage of the self-absorption of the source at high concentrations. In the concentration range on the plateau region of the excitation curve of growth the fluorescence intensity will not appreciably increase while the emission intensity and thus the scatter will increase. Aspirating two different high concentrations of the element being determined into the plasma and knowing the effect of the two different concentrations on the fluorescence and the emission signals, one can calculate the scatter signal and subtract it out.

8.4 - Applications

\textbf{Zinc in Unalloyed Copper (NBS SRM-394 and 396).} The determination of trace zinc in high purity copper is a difficult analytical problem using either atomic absorption or ICAP-emission. The major zinc resonance line at 213.856 nm is subject to a direct spectral interference by the copper 213.853 nm non-resonance transition (11203 - 57949 cm\textsuperscript{-1}). This interference has been reported\textsuperscript{73} for flame atomic absorption analysis and requires an electrodeposition of the copper from solution\textsuperscript{97} or a high-resolution atomic absorption technique employing wavelength modulation.
and line-nulling\textsuperscript{98} before accurate analysis can be performed. The problem using ICAP-emission is illustrated in Figure 24 by a scan of the wavelength region of the zinc 213.856 nm line for the unalloyed copper SRM 396. While the majority of the copper lines are easily resolved, the 213.853 nm line cannot be with the resolution available in spectrometers typically used for ICAP-emission. Even with an echelle spectrometer, this line pair has been shown to exhibit an overlap.\textsuperscript{98} The emission from this line at a concentration of 10 mg/mL copper is equivalent to the emission from approximately 20 \(\mu\)g/mL of zinc, making analysis impossible without the use of zinc-free copper for matrix-matching. The Zn II line at 206.2 nm can be used for the determination of zinc by ICAP-emission without line spectral interference from copper, although background correction by scanning over the wavelength region of the line is still required to correct for a change in the background level caused by either stray light due to copper emission or changes in the plasma background. The zinc detection limit for this line was found to be approximately 4x worse than at the 213.9 nm line, in agreement with the results of Winge et al.\textsuperscript{83} While SRM 394 was analyzed (375 \(\mu\)g/g certified value), SRM 396 (4.7 \(\mu\)g/g certified value) could not be analyzed because of its low zinc concentration, the poorer detection limit and the continuous background in the vicinity of the 206.5 nm Zn II line generated by the copper matrix. The background was equivalent to approximately 1 \(\mu\)g/mL zinc at this wavelength. The analysis values for SRM 394 were approximately 10 percent less than the certified value, indicating a slight interference by ICAP-emission.

The determination of zinc in both SRM 394 and 396 by ICAP-excited AFS is summarized in Table 9 along with the ICAP-emission results. The AFS results agree well with the certified values. There is no significant
Figure 24. Wavelength scans of (A) 20 µg/mL zinc and (B) 10,000 µg/mL copper as SRM 396 (unalloyed copper) illustrating the spectral interferences observed in ICAP-emission for zinc analysis in copper.
### Table 9
SAMPLE ANALYSIS USING ICAP-EXCITED AFS AND ICAP-EMISSION

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Certified Value ($\mu$g/g)$^a$</th>
<th>Analyzed Values ($\mu$g/g)$^b$</th>
<th>ICAP-excited AFS</th>
<th>ICAP-emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unalloyed copper (SRM-394)</td>
<td>Zn</td>
<td>$375 \pm 38$</td>
<td>$376 \pm 3$</td>
<td>$325 \pm 25$</td>
<td></td>
</tr>
<tr>
<td>Unalloyed copper (SRM-396)</td>
<td>Zn</td>
<td>$4.7 \pm 0.3$</td>
<td>$4.8 \pm 0.1$</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>Fresh water (SRM-1643)</td>
<td>Zn</td>
<td>$0.065 \pm 0.003$</td>
<td>$0.0656 \pm 0.0008$</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>$0.008 \pm 0.001$</td>
<td>$0.0079$</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>Fly ash (SRM-1633)</td>
<td>Zn</td>
<td>$210 \pm 20$</td>
<td>$219 \pm 4$</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>Orange juice</td>
<td>Cu</td>
<td>e</td>
<td>$0.57$</td>
<td>$0.60$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>e</td>
<td>$0.45$</td>
<td>$0.46$</td>
<td></td>
</tr>
</tbody>
</table>


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

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

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

$^e$Not a standard reference material.
fluorescence excited at the 213.853 nm copper line in the flame, due to a combination of the relatively low thermal population in the air/acetylene flame of the 11203 cm\(^{-1}\) energy level and the quantum efficiency of the fluorescence process. This combination effectively minimizes copper spectral interference in ICAP-excited AFS by more than a factor of 10\(^4\) compared to the ICAP-emission case. The effect of the flame as a resonance monochromator is not significant in this example, since even 10 mg/mL Cu in the ICAP did not excite any fluorescence from the Cu 213.853 nm line.

When the 16 nm spectral bandpass is used on the fluorescence monochromator, several resonance copper lines at 216.5 nm, 217.8 nm, and 218.2 nm are included. Although no spectral interference is observed when a pure zinc solution (20 mg/mL) is used for excitation in the ICAP, we found that our supposedly 99.99+ zinc standard contained about 5 \(\mu\)g/mL copper, indicating a purity of less than 99.98. This was enough copper to excite fluorescence at the resonance copper lines, and although no interference was observed for the analysis of SRM 394 in the part-per-million concentration range, a slightly higher value (approximately 20 percent greater) than the certified value for SRM 396 was obtained using the 16 nm spectral bandpass. The enhancement due to the copper fluorescence from the resonance lines, equivalent to approximately 10 ng/mL zinc, was completely eliminated by using the 0.4 nm spectral bandpass. A scatter signal of approximately 4 percent for SRM 396, equivalent to 2 ng/mL zinc, was observed and corrected for using the Cd II 214.4 nm line.

**Fly Ash (NBS SRM-1633) and Trace Elements in Water (NBS SRM-1643).**

Zinc was determined in fly ash and cadmium and zinc in simulated fresh water by ICAP-excited AFS. No chemical interferences were observed in
either case, and the results are presented in Table 9. Excellent agreement with the certified values was obtained.

**Orange Juice.** The determination of copper and zinc in Florida orange juice was performed using both ICAP-excited AFS and ICAP-emission. The optical arrangement for the former was as described in reference 81. Agreement of results between the two techniques was good, as illustrated in Table 9. Matched-matrix standards were employed so that background correction by wavelength scanning was not required.

In the analysis of orange juice for zinc by ICAP-emission, a series of wavelength scans through the vicinity of the 213.9 nm zinc line showed not only the gradually increasing continuum background from the argon plasma but also superimposed on this background were bands of the $\gamma$-system of NO ($A^2\Sigma^+ \rightarrow X^2\Pi$) degraded to shorter wavelengths, resulting from the entrainment of the ambient air, with bandheads at 214.91 nm and 215.49 nm. Furthermore, the phosphate present in the matrix blanks and in the orange juice produced a strong emission at 213.620 nm. However, the monochromator resolution was sufficient to eliminate the effect of these spectral interferences.

For the copper analysis by ICAP-emission, the wavelength scans from 323 nm to 326 nm showed several lines of argon (323.45, 323.681, 324.369, and 325.76 nm) and strong OH bands (323.5 and 325.7 nm) with some less intense OH peaks at other wavelengths (323.7, 324.4, and 324.7 nm). Under our experimental conditions, the argon lines and OH bands caused no problems in the copper analysis at the 324.7 nm line.
CHAPTER FOUR

ATOMIC FLUORESCENCE SPECTROMETRY IN ICP WITH DYE LASER EXCITATION "LASER-EXCITED AFS IN ICP"

A - cw Dye Laser As An Excitation Source in ICP

A.1 - Introduction

The radio frequency inductively coupled plasma has become a widely-used tool for multi-element atomic emission analysis.\textsuperscript{99,100} Investigation of excitation processes in spectroscopic systems is very important for the full realization of any new tool's analytical utility. This is particularly true in the case of plasma sources, where the excitation mechanisms have been shown to be different from those in flames.\textsuperscript{101,17} Mermet and Trassy\textsuperscript{102} designed a special rf plasma torch atomic absorption measurement, and Wendt and Fassel\textsuperscript{8} determined elements which are strong monoxide formers by atomic absorption measurements in an rf plasma. Using electrodeless discharge lamps as the primary excitation source, Montaser and Fassel\textsuperscript{103} reported atomic fluorescence in the ICP tail plume (3-5 cm above coil). Higher signals for fluorescence than emission were obtained for cadmium, zinc, and mercury, but a special torch configuration was required.

In this work, the analytical utility of a continuous-wave (cw) argon ion pumped dye laser excitation source and a conventional ICP torch atomizer/ionizer was investigated. A cw dye laser was chosen for this study because: (i) large fluorescence signal levels resulted for those elements capable of undergoing excitation, by the dye laser used; (ii)
amplitude modulation of the laser allowed use of synchronous detection techniques; and (iii) the instrumental system was relatively simple.

The major drawback in using a cw laser is the limited wavelength range (from 575 to 620 nm with a 5 W pump). Smith et al.\textsuperscript{104} used a similar cw dye laser with a nitrous oxide/acetylene flame and determined the possibility of overcoming the limited wavelength range by using excited lower states and a variety of nonresonance fluorescence processes in order to increase the number of elements which could be measured. The higher excitation temperatures in the ICP will increase the populations of the excited lower levels and should give greater excitation flexibility with the cw-laser-ICP than was available in the previous cw laser-flame studies.\textsuperscript{104} This work is a continuation of the Smith et al.\textsuperscript{104} study. Although the ICP has much higher excitation temperatures, the lack of complete thermodynamic equilibrium in the ICP was not necessarily expected to give predictable results as in combustion flames.\textsuperscript{105}

A.2 - Experimental

A block diagram of the experimental system is shown in Figure 25. The Rhodamine 6G cw dye laser, pumped by all lines of the 5 W argon ion laser, produced \(\approx 1\) W peak output power over the tuning range from 575 to 620 nm. Output power dropped off quickly near the wavelength limits. Typically the spectral bandwidth of the dye laser was \(\approx 0.05\) nm. The laser beam was chopped (260 Hz) and focused into the ICP plasma. The ICP was mounted on an adjustable (x-y-z) table so that any part of the plasma could be illuminated by the laser without disturbing the alignment of the laser with respect to the monochromator (0.35 m; f/6.8; 2 nm/mm).

Because two different areas of the plasma were investigated (the intense analyte pencil region above the coil (0.5-2.5 cm above the coil),
Figure 25. Block Diagram of ICP-CW Laser Fluorescence Spectrometer.
ICP - CW LASER FLUORESCENCE SPECTROMETER
where atomic emission measurements are performed, and the cooler tail plasma (3-5 cm above the coil) where mixing of ambient air with the plasma occurs, two slightly different optical arrangements were needed. In studies of tail plume fluorescence, the monochromator slit was placed parallel to the laser beam at right angles to the plasma axis. A spherical lens was used to focus the laser beam to ≈1 mm while passing through the plasma. For atomic fluorescence measurements in the analyte pencil area, the monochromator slit was placed in a vertical position similar to that used in flame emission measurements. It was found that atomic fluorescence signals could be increased by a factor of 2-3x through matching the fluorescing volume of the plasma to the monochromator observation area by using a cylindrical lens that focused the laser beam (normally 1 cm in diameter) to a 1 cm x 1 mm column at the analyte pencil in the plasma. For spatial fluorescence profiles, the monochromator slit was placed perpendicular to the focused horizontal laser beam so that ≈1 mm x 0.3 mm spatial resolution was possible. The monochromator slit width was adjusted to 70 μm (spectral bandpass of 0.14 nm) for all emission studies and 300 μm (spectral bandpass of 0.6 nm) for all fluorescence studies; the slit widths were determined by maximizing the signal-to-noise ratio.

Major components of the system are listed in Table 10. The plasma system was operated at combined Ar flows of 17 L/min. (Cooling flow rate = 15 L/min; plasma flow rate = 1 L/min; nebulizer flow rate = 0.5 L/min.) The right angle nebulizer supplied with the plasma system was replaced with the concentric nebulizer listed in Table 10; the nebulizer flow rate was controlled with a syringe pump (a 1.5 mL/min flow rate was simple to maintain and operate). Reflected power was kept to a minimum by the automatic matching network. Limits of detection for the ICP in
<table>
<thead>
<tr>
<th>Component</th>
<th>Model #</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon Ion Laser</td>
<td>550</td>
<td>Control Laser Corp. Orlando, FL</td>
</tr>
<tr>
<td>Dye Laser</td>
<td>491</td>
<td>Coherent Radiation, Palo Alto, CA</td>
</tr>
<tr>
<td>Chopper</td>
<td>125</td>
<td>Princeton Applied Research, Princeton, NJ</td>
</tr>
<tr>
<td>ICP</td>
<td></td>
<td>Plasma Therm, NJJC, Princeton, NJ</td>
</tr>
<tr>
<td>Torch Assembly</td>
<td>T-220-A2</td>
<td>JE MEINHARD ASSOCIATES, Kresson, NJ</td>
</tr>
<tr>
<td>Rf Generator</td>
<td>EU-700</td>
<td>Coherent Radiation, Palo Alto, CA</td>
</tr>
<tr>
<td>Nebulizer</td>
<td></td>
<td>GCA McPherson, Chicago, IL</td>
</tr>
<tr>
<td>Monochromator</td>
<td></td>
<td>RCA, Somerville, NJ</td>
</tr>
<tr>
<td>Photomultiplier</td>
<td></td>
<td>Keithly Instruments, Cleveland, OH</td>
</tr>
<tr>
<td>Current/Voltage Converter</td>
<td></td>
<td>Keithly Instruments, Cleveland, OH</td>
</tr>
<tr>
<td>Lock in Amplifier</td>
<td></td>
<td>Keithly Instruments, Cleveland, OH</td>
</tr>
<tr>
<td>Integrator</td>
<td>840</td>
<td>Lab Constructed, Cleveland, OH</td>
</tr>
</tbody>
</table>

Table 10

SPECIFIC COMPONENTS OF EXPERIMENTAL SYSTEM
the atomic emission mode were found to be similar to those previously reported.

Atomic fluorescence signals were measured with a synchronous detection system. For measuring limits of detection (LOD), the lock-in output was integrated for 10 s. The LOD was taken to be that concentration equivalent to a signal 3 times that of the standard deviation of 16 consecutive, integrated blank readings. Aqueous standards of analytical grade reagents were made using deionized water.

Noise sources were characterized in two ways. Background and analyte noises were studied by placing neutral density filters between the plasma and the monochromator and by varying the analyte concentration, respectively. Peak to peak noise for a 1 s lock-in time constant was measured as a function of the average signal output.

A 300 W EIMAC xenon arc continuum source was substituted for the laser for comparison purposes. Two spherical lenses were used to focus radiation from the lamp through the chopper and into the rf plasma.

A.3 - Results and Discussion

For atomic emission measurements, optimal measurements in the ICP were made in or just above the analyte pencil region. For normal operation (powers of 1.2-1.5 kW), the background and analyte emission was so intense that the fluorescence could not be separated from the background and/or analyte emission noise coming through the lock-in amplifier. In Figure 26, the relative intensity profiles for fluorescence, emission, and background are shown for sodium at 589.0 nm. The emission LOD for sodium (RF power of 1.2-1.5 kW and measured at 3 cm above the plasma load coil in the tail plume) was 0.2 ppm; instability of the tail plume resulted in this poor LOD.
Figure 26. Relative Intensity Profile for Sodium (589.0 nm, 1 \( \mu g \) mL\(^{-1} \) Na, 2.5 cm above coil, 1.2 kW).

...... Na fluorescence

----- Na emission

----- background
RELATIVE INTENSITY PROFILE - lateral
HIGH POWER - 1.2 KW
1 ppm Na  589.0 nm
2.5 cm above coil

---

FLUORESCENCE
EMISSION
BACKGROUND
By decreasing the power of the plasma in order to decrease the background, and by measuring the fluorescence in the analyte pencil region, the fluorescence signal-to-noise ratio (SNR) increased dramatically. In Figure 27, the relative sodium spatial intensity profile for this case is shown. Both background and analyte emission signals were greatly reduced, the fluorescence signal now being ≈20x the emission signal at the optimum power for sodium fluorescence which was 700 W. In fact, the bright fluorescence signal of a 2 μg/mL Na solution was readily observable by eye.

In Table 11, LODs are given for the elements with excitation transitions in the wavelength range of the laser system. Included for comparison are the values obtained by Smith et al.\textsuperscript{104} for excited-state flame fluorescence with the same cw dye laser. Also listed in Table 11 are atomic emission (with ICP) LODs. The analytical calibration curves for Ba and Na, shown in Figure 28, have a linear dynamic range of at least 5 orders of magnitude. Elements studied which gave no measurable fluorescence for 1000 μg/mL aqueous solutions included Mo, Rh, Sc, Sr, Cd, and U.

Contrary to our expectations, it is important to note that elements having fluorescence lines involving excited lower states resulted in poorer LODs with the ICP than with a flame.\textsuperscript{104} In fact, for many other elements having potentially useful atomic transitions, no fluorescence signals were observed even though observable atomic emission signals for these levels involved were present. For example, in the case of Ba, the Ba atomic ground state resonance transition at 553.5 nm which was used by Smith et al.\textsuperscript{104} was outside of the wavelength range of the dye used in the present studies and so could not be investigated. No fluorescence signals for Ba could be found for any of the excited state atomic transitions
Figure 27. Relative Intensity Profile for Sodium (589.0 nm, 1 μg mL$^{-1}$ Na, 1.5 cm above coil, 0.7 kW). Key to lines same as in Figure 26.
RELATIVE INTENSITY PROFILE - lateral
LOW POWER - 0.7 KW
1 ppm Na 589.6 nm
1.5 cm above coil
Table 11
LIMITS OF DETECTION (μg/mL)

**CW - LASER FLUORESCENCE**

<table>
<thead>
<tr>
<th>SPECIES - Wavelength</th>
<th>FLAME</th>
<th>ICP</th>
<th>EMISSION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na (I) 589.0</td>
<td>.0003</td>
<td>.0001</td>
<td>.0002</td>
</tr>
<tr>
<td>Ba (I) 553.7</td>
<td>.04</td>
<td>ND</td>
<td>--------</td>
</tr>
<tr>
<td>Ba (II) 455.4</td>
<td>------</td>
<td>.006(^a)</td>
<td>.0001</td>
</tr>
<tr>
<td>Li (I) 610.3</td>
<td>.5</td>
<td>.4</td>
<td>.003(^b)</td>
</tr>
<tr>
<td>V (I) 609.0</td>
<td>.3</td>
<td>5.</td>
<td>--------</td>
</tr>
</tbody>
</table>

\(^a\) excited at 585.4 nm  
\(^b\) excited at 670.7 nm
Figure 28. Analytical Calibration Curves for Na and Ba with ICP-cw Dye Laser Spectrometric System.
FLUORESCENCE INTENSITY (ARBITRARY UNITS)

ANALYTE CONCENTRATION

0.1 1.0 10 100 1000 10^4 10^5 10^6 10^7 ng/ml

0.1 1.0 10 100 1000 10^4 ug/ml

Na

Ba

LOD

LOD
within the wavelength range of our dye laser and listed by Smith et al. in their flame study. In contrast, however, large signals for barium ion fluorescence were observed. Suitable barium ion transitions exist in the wavelength range of the dye laser and are shown in Figure 29 along with detection limits for various excitation-fluorescence possibilities. These results for Ba show that analytical line selection is best made on the basis of highest laser power for the excitation wavelength and high spontaneous emission transition probability for the observed fluorescence transition. In addition, many elements are best observed as ions in the ICP; unfortunately, many ion lines exist in the higher energy end of the spectrum which negated studies with the present cw dye laser.

Although the operation of the plasma at lower power is undesirable for emission spectrometry (presumably due to lower effective excitation temperatures), this does not necessarily follow for fluorescence measurements in the ICP. No visible change in the toroidal nature of the plasma was apparent at the lower powers used and relative stability (as judged by relative recorder fluctuations) was the same for all powers. The excitation process for our low power rf plasma was evaluated according to the procedure described by Boumans and DeBoer. They found in a 1 kW plasma that the ratio of Ba(II) emission intensity at 455.4 nm to that of the Ba(I) line at 553.5 nm was 300x that expected for an excitation source at 5858 K in local thermodynamic equilibrium (LTE). The system in this study gave comparable results at 1 kW power; even at the lowest power used (0.6 kW), the emission intensity ratio Ba(II)/Ba(I) was 90x the LTE expected value for a temperature of 5850 K (see Figure 30). Therefore, non-LTE excitation is most likely taking place at the lower powers used in this study just as at the 1 kW power used by Boumans and DeBoer.
Figure 29. Barium Ion Energy Level Diagram.

Transition (1): $\lambda = 493.4$ nm; $gA = 0.19 \times 10^8$ s$^{-1}$
Transition (2): $\lambda = 455.4$ nm; $gA = 0.90 \times 10^8$ s$^{-1}$
Transition (3): $\lambda = 585.3$ nm; $gA = 0.19 \times 10^8$ s$^{-1}$
Transition (4): $\lambda = 614.2$ nm; $gA = 0.38 \times 10^8$ s$^{-1}$

<table>
<thead>
<tr>
<th>Limits of Detection (µg/mL)</th>
<th>Excitation $\lambda$ (nm)</th>
<th>Fluorescence $\lambda$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>585.3</td>
<td>585.3</td>
</tr>
<tr>
<td>&gt;1000</td>
<td>585.3</td>
<td>614.2</td>
</tr>
<tr>
<td>200</td>
<td>614.2</td>
<td>585.3</td>
</tr>
<tr>
<td>100</td>
<td>614.2</td>
<td>614.2</td>
</tr>
</tbody>
</table>
BARIUM ION ENERGY LEVELS

\[
\begin{align*}
&\text{Ba(II)} & & 0 \\
&1.\pi = 5.2 \text{ eV} & & \\
&\text{Ba(I)} & & \\

\end{align*}
\]

Energy Levels:
- \(493.4 \text{ eV} \quad g_A = 1.9\)
- \(455.4 \text{ eV} \quad g_A = 0.90\)
- \(585.3 \text{ eV} \quad g_A = 1.9\)
- \(614.2 \text{ nm} \quad g_A = 0.8, (10^8 \text{ sec}^{-1})\)
- \(A = 200 \text{ ng/m}^3, B = 100 \text{ cm}^{-1}\)
Figure 30. Barium ion emission at 455.4 nm to Barium atom emission at 553.5 nm for non-LTE study.
All noise measurements of analyte fluorescence, analyte emission, and ICP background at two powers 1 kW and 0.6 kW were found to be limited by "shot noise" except for the case of high concentration fluorescence which is analyte "flicker noise" limited. Thus, the ICP is "shot noise" limited.42

Results with the 300 W EIMAC xenon arc lamp for Cd, Ba, Na, Zn, Mn, Ca, U, Eu, Mg I, and Mg II were all negative except for magnesium (I) at 285.2 nm. Magnesium, which traditionally gives the best results of any element with EIMAC excitation, produced a detection limit of 0.3 µg/mL at 500 W plasma power. On this basis, it was concluded that sources with excitation temperatures similar to that of the EIMAC xenon arc lamp are unsuitable for use as a primary excitation source in the present ICP-AFS system.

B - Relative Spatial Profiles of Barium Ion and Atom in the Argon Inductively Coupled Plasma As Obtained by Laser Excited Fluorescence

B.1 - Introduction

The electron, atom, ion concentration and the temperature are among the most relevant physical figures of merit of the inductively coupled argon plasma discharge (rf-ICP) and are certainly the critical parameters characterizing the usefulness of this device as an atomizer, ionizer and exciter in analytical spectroscopy.68 Such parameters are known to vary as a function of input power, plasma and nebulizer gas (argon) flow rates, analyte species and matrix types, nebulizer and torch design and rf generator type and coupling mechanism.

Any modeling of the plasma processes and therefore any prediction of the optimal analytical conditions to be used rely on the value of the above mentioned parameters. However, as clearly stated by Kornblum and
these quantities must be obtained as a function of the spatial coordinates \((x,y,z)\) in the plasma and not merely as an integrated, average line of sight measurements. Thus, when the data are obtained via the emission or absorption techniques, an Abel inversion procedure is usually applied to convert the values into radially resolved information. Among the limitations of the Abel inversion technique, we may include (i) a precise measurement of the lateral intensity distribution at a number of discrete steps (or continuous scan) over the entire width of the plasma is needed, (ii) the step width must be smaller than the distance over which the intensity changes appreciably, and so at least 20 steps are needed, (iii) the exact location of the central point of the intensity distribution is needed or else large errors in the radial signals lead to anonuleus (even negative) signals at \(r=0\), (iv) the plasma must be exactly symmetrical and (v) the solution of the Abel integral equation must be solved via a computer, which is not a serious limitation but does place an additional burden on the processing of even a relatively simple set of measurements.

So far, all spatial studies in the ICP have been carried out via Abel inverted emission and/or absorption measurements to obtain relative concentration and temperature profiles. Kornblum and DeGalan have measured axial and radial distribution of temperature, electron concentration and element concentration in a rf-ICP at atmospheric pressure operated at 2 kW and 50 MHz and at 0.5 kW and 50 MHz. They also studied the interference of cesium and phosphate on calcium and magnesium in the above mentioned low power plasma. Mermet et al. have also measured radial intensity profiles in an argon plasma operated at 1.3 kW and at 40 MHz in order to determine spatial excitation temperatures and electron concentrations. Kalnicky et al. have measured
spatially resolved excitation temperatures and electron concentrations in the observation zone of a 27 MHz, Ar rf-ICP operated at 1 kW, this being the plasma and experimental conditions commonly used in commercial rf-ICP systems.

It is well known that diagnostic techniques based upon elastic light scatter (Rayleigh or Mie scatter) and inelastic light scatter (fluorescence or Raman scatter) are capable of direct spatial resolution with no need for an Abel inversion procedure to be performed. The fluorescence technique, both atomic and molecular, is well suited to obtain spatially resolved information on concentration of species and temperature, as it has been shown theoretically and in some cases experimentally. However, the high temperature and excitation capabilities of the ICP makes the fluorescence measurements with conventional excitation sources exceedingly difficult, because of the low signal-to-noise ratio, if one attempts to obtain a reasonably good (≈1 mm³) resolution. The use of a pulsed, tunable dye laser and gated detector will combine the advantages of spatial resolution (because of the high collination of the excitation beam) and good signal-to-noise ratio (because of the gated operation of the detection system, if the photomultiplier tube does not saturate because of the strong d.c. emission background).

For the first time, to the author's knowledge, experimental spatially resolved fluorescence intensity profiles of barium ions and atoms in an ICP plasma, were obtained by measuring the signal from a small plasma volume (≈0.2 mm³) excited by a nitrogen laser pumped, tunable dye laser. The aim of this work is to show the great information capability of such technique, rather than to give an extensive discussion of the results obtained in terms of the physical processes occurring in the discharge.

We will discuss the feasibility of the laser excited fluorescence method
in obtaining absolute concentration profiles of species as well as temperature profiles.

B.2 - Experimental

A block diagram of the experimental set-up is shown in Figure 31. Individual components as well as model numbers and manufacturers\(^{116}\) are collected in Table 12. The actual experimental operating conditions are given in the figure's captions. The barium concentration used throughout all measurements was 100 \(\mu g/mL\). The choice of this concentration resulted in a good signal to noise ratio also for the far-edge signals in both excitation and observation directions. Moreover, all measurements taken with 100 \(\mu g/mL\) were free from self-absorption and/or self-reversal (post filter) effects. This was demonstrated experimentally by varying 10 times the barium concentration (down to 10 \(\mu g/mL\)) and obtaining the same profile as that given by 100 \(\mu g/mL\), the only difference being the tenfold decrease of the fluorescence intensity.

As seen from Figure 31, the laser beam was directed into the ICP by means of two plane mirrors. A small aperture (1 mm) was placed in the excitation direction, approximately 50 cm away from the ICP. Because of the slight divergence of the laser beam its diameter throughout the ICP was measured to be approximately 3 mm. The ICP discharge is imaged at 1:1 magnification out the entrance slit of the monochromator whose height is fixed at 1.0 mm and whose slit width was typically set at 0.07 mm. Thus, the discharge volume over which the measurements are averaged was approximately 0.2 mm\(^3\). It must be noted, however, that the linear resolution in the excitation axis (\(x\) in Figure 31b), dictated by the slit width, and that in the observation axis (\(y\) in Figure 31b), dictated by the laser beam diameter, are different. As far as the height of observation is concerned (\(z\) in Figure 31b), this will of course be determined by the slit
Figure 31. a) Schematic diagram of the experimental set-up; b) geometrical arrangement referred to in the other Figure Captions.
<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
<th>Operating Parameters</th>
</tr>
</thead>
</table>
| rf-ICP    | PT-1500 Torch Assembly  
            HPF-1500D rf Generator,  
            Plasma Therm Inc.,  
            Kresson, N.H. | 0.7-1.5 kW  
Argon Plasma Gas  
Flow rate: 15 L/min |
| Nebulizer | Concentric ring glass nebulizer, T 230-A3,  
J. E. Meinhard Assoc.,  
Santa Anna, CA | Nebulizer gas pressure set at 40 psi, except where noted in text. |
| Torch #1  | Plasma Therm torch, modified as described by Genna et al.117 with 1 mm side arm for Ar plasma (coolant) gas |  |
| Torch #2  | Plasma Therm Torch, unmodified |  |
| Monochromator | EU-700, 0.35-m focal length; 1180 grooves/mm grating, blazed at 250 nm; f-6.8; 2 nm/mm reciprocal linear dispersion. Heath Co., Benton Harbor, MI | Slit height: 1 mm, slit width: 0.070-0.075 mm, unless otherwise noted in the text. |
Table 12—continued.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photomultiplier</td>
<td>R-928 (Hamamatsu Co., Middlesex, N.J.)</td>
</tr>
<tr>
<td>H.V. Power Supply Current</td>
<td>Keithley 244</td>
</tr>
<tr>
<td>to Voltage Converter</td>
<td>Keithley 247</td>
</tr>
<tr>
<td></td>
<td>(Keithley Co., Cleveland, OH)</td>
</tr>
<tr>
<td>N₂-Laser</td>
<td>UV-14</td>
</tr>
<tr>
<td>Dye Laser</td>
<td>DL-</td>
</tr>
<tr>
<td>Trigger generator</td>
<td>E-H Research Laboratories Inc., Oakland, CA</td>
</tr>
<tr>
<td>Boxcar Integrator</td>
<td>160-162</td>
</tr>
<tr>
<td></td>
<td>Princeton Applied Research, Princeton, N.J.</td>
</tr>
<tr>
<td>Recorder</td>
<td>Servagor, Gelman Instruments Co., Ann Arbor, MI</td>
</tr>
</tbody>
</table>

See Weeks et al.¹¹⁶
height or by the laser diameter, whichever is smaller. It is worth stressing that the slit height was set at 1.0 mm mainly to decrease the ICP d.c. background emission seen by the photomultiplier, rather than merely to improve the spatial resolution. A low power, He-Ne laser was used to assure proper alignment of the two apertures. Finally, the linearity of operation of the photomultiplier was always checked with the insertion of neutral density filters during the measurement procedure. This simply consisted in tuning the dye laser at the appropriate excitation wavelengths (either 455.4 nm or 614.2 nm), adjusting the ICP housing by an x-y-z adjustment constructed from a milling table (see Figure 31b) to allow excitation of the desired spatial element and measuring the resulting fluorescence pulse with a monochromator-photomultiplier-boxcar averager system. Several x-y-z values were monitored. Conventional line of sight integrated emission measurements were also taken to provide a direct comparison with the fluorescence data. However, no attempt was made to transform such averaged values into radial values.

8.3 - Results and Discussion

The Ba resonance ionic fluorescence and emission intensities at 455.4 nm obtained at 12 mm above the coil are shown in Figures 32-34 as a function of the input power to the plasma. In these Figures, the profiles are taken along the excitation axis. The characteristic features which can be derived from these figures are (i) both fluorescence and emission profiles show an asymmetric hollow pencil configuration, indicating a remarkably inhomogeneous distribution of barium ions, (ii) the asymmetry and the depth of the trough change as the power increases, the hollow pencil becoming deeper and the asymmetry being rotated over 180° with respect to the plasma axis, (iii) the emission profile is wider than
Figure 32. Resonance ionic fluorescence and emission profiles for barium at 455.4 nm. Experimental conditions: ICP power $P = 0.7$ kW; monochromator slit: width $w = 75$ μm, height $H = 1$ mm. Solution nebulization flow rate $F = 2.0$ mL/min; nebulizer pressure: 40 psi; barium concentration: 100 μg/mL; $z = 12$ mm; $y = -1.50$ mm. Fluorescence profile taken along the excitation axis.

a) fluorescence profile
b) emission profile
Figure 33. Resonance ionic fluorescence and emission profiles for barium at 455.4 nm. ICP power: $P = 1.1$ kW; monochromator slit width = 70 μm. All other conditions as in Figure 32. Fluorescence profile taken along the excitation axis.

a) fluorescence profile; $y = -1.50$ mm
b) emission profile; $y = -1.50$ mm
c) water scatter; $y = 0.0$ mm
d) corrected fluorescence; $y = 0.0$ mm
Figure 34. Resonance ionic fluorescence, emission and scatter profiles for barium at 455.4 nm. ICP power: $P = 1.5$ kW; monochromator slit width = 70 µm; $y = 0.00$. All other conditions as in Figure 32. Fluorescence profile taken along the excitation axis.

a) uncorrected fluorescence profile
b) emission profile
c) scatter profile
d) corrected fluorescence profile
the fluorescence profile, especially at lower powers, (iv) the trough is less pronounced in the emission profile as compared to the fluorescence profile (both items iii and iv are understandable in terms of the integrated emission measurements as compared to the spatially resolved fluorescence measurements, and (v) perhaps the most curious observation is that at the center of the plasma, at this observation height, a scatter signal is clearly evident when water was aspirated (see Figures 33 and 34). The position of the maximum scatter signal was displaced about 1 mm along each axis (x and y) from the central geometric axis of the plasma. This asymmetry might be determined by the alignment of the nebulizer tube and the precision of manufacture of the orifice. Extensive checks were made to insure that this signal was not due to other sources. Wavelength scanning of both laser and monochromator showed that the signal was not due to the carry-over of barium contamination in the spray chamber. Moreover, careful cleaning of the whole nebulizer/torch assembly gave no reduction in the signal, showing that it was not due to scattering from solid impurity particles carried from nebulizer or aerosol tube when water was aspirated into the plasma. As shown in the subsequent figures, the scatter signal decreases in importance with height of observation. It seems therefore justified to conclude that this scatter indicates the presence of minute water droplets. Further measurements have confirmed the presence of these droplets at heights up to 15-18 mm above the coil when nebulizer gas pressures of 30-40 psi are used and at least up to 12 mm even when the pressure is reduced to 25 psi.

A similar trend is also observed when the fluorescence profile is taken along the observation axis (Figures 35 and 36). Here, however, the trough tends to be filled when the input power increases.
Figure 35. Resonance ionic fluorescence profile for barium at 455.4 nm. ICP power: $P = 1.5$ kW. All other conditions as in Figure 32. Fluorescence profile taken along the observation axis.

a) $x = -1.0$ mm  
b) $x = 0.0$ mm  
c) $x = 1.5$ mm
Figure 36(i). Resonance ionic fluorescence profile for barium at 455.5 nm. x = 1.5 mm. All other conditions as in Figure 32. Fluorescence profile taken along the observation axis.

a) ICP power: $P = 0.7$ kW
b) ICP power: $P = 1.1$ kW
c) ICP power: $P = 1.5$ kW
Figure 36(ii). Same as in Figure 36(i) except for $x = -1.0 \text{ mm}$.

a) ICP power: $P = 0.7 \text{ kW}$
b) ICP power: $P = 1.1 \text{ kW}$
c) ICP power: $P = 1.5 \text{ kW}$
Figures 37-39 represent the fluorescence profiles obtained at an observation height of 18 mm above the coil, again along both the excitation and observation axis. These figures clearly show that (i) the asymmetry in the profile is still observed and it is more pronounced along the laser axis as compared to the monochromator axis, (ii) the profile starts flattening out, even at low powers, when the measurements are taken, for both x and y, displaced from the plasma center, (iii) there is no significant increase in the width of the profiles as compared to that at 12 mm, (iv) the H₂O scatter is now insignificant, and (v) the trough in the profile decreases with increasing input power, indicating an approach to a more uniform distribution of species.

When the observation height is increased to 24 mm above the coil, the hollow pencil configuration turns into a rather broad, fairly uniform distribution, at least along the laser axis (see Figures 40-42). It seems logical to conclude that the plasma expands radially with height while its optical depth increases. This fact is indeed confirmed by the presence of self-absorption effects at high concentrations at these and greater heights from the results seen in chapter 3 and the work of Human and Scott. By increasing the input power, the distribution becomes narrower.

Figures 43-45 show similar measurements at 12 mm above the coil obtained at tuning the laser at 614.2 nm while still observing the fluorescence at 455.4 nm. The laser transition originates from an excited metastable barium ion level and reaches the same level from which the fluorescence at 455.4 nm is emitted, i.e., we are now observing the antistokes direct line ionic fluorescence. The overall profile distribution does not seem to change from one already observed in the previous figures, and similar results are also obtained when the observation height is increased.
Figure 37(i). Resonance ionic fluorescence profile for barium at 455.4 nm. z = 18 mm. All other conditions as in Figure 32. Fluorescence profile taken along the excitation axis.

a) y = -1.0 mm
b) y = 1.0 mm

(ii). Same as (i). Fluorescence profile taken along the observation axis.

a) x = 0.0 mm
b) x = 2.0 mm
Figure 38(i). Resonance ionic fluorescence profile for barium at 455.4 nm. $z = 18$ mm; monochromator slit width: $W = 70$ μm; ICP power $P = 1.1$ kW. All other conditions as in Figure 32. Fluorescence profile taken along the excitation axis.
   a) $y = -1.0$ mm
   b) $y = 1.0$ mm

(ii). Same as (i). Fluorescence profile taken along the observation axis.
   a) $x = 0.0$ mm
   b) $x = 1.5$ mm
Figure 39(i).  Resonance ionic fluorescence profile for barium at 455.4 nm.  
\[ z = 18 \text{ mm}; \text{ monochromator slit width } W = 70 \text{ \mu m}; \text{ ICP power } P = 1.5 \text{ kW}. \]  
All other conditions as in Figure 32.  Fluorescence profile taken along the excitation axis.  
\begin{align*} 
a) & \quad y = -1.0 \text{ mm} \\
b) & \quad y = 1.0 \text{ mm} \\
\end{align*}  

(ii). Same as (i).  Fluorescence profile taken along the observation axis.  
\begin{align*} 
a) & \quad x = 0.0 \text{ mm} \\
b) & \quad x = 1.5 \text{ mm} \\
\end{align*}
Figure 40(i). Resonance ionic fluorescence and emission profiles for barium at 455.4 nm. $z = 24$ mm. All other conditions as in Figure 32. Fluorescence profile taken along the excitation axis.
   a) emission; $y = -1.0$ mm
   b) fluorescence; $y = -1.0$ mm
   c) fluorescence; $y = 1.0$ mm

(ii). Resonance ionic fluorescence profile for barium at 455.4 nm. $z = 24$ mm. All other conditions as in Figure 32. Fluorescence profile taken along the observation axis.
   a) $x = 0.0$ mm
   b) $x = 2.0$ mm
Intensity (Arbitrary Unit) vs. X (mm) and Y (mm)
Figure 41(i). Resonance ionic fluorescence and emission profiles for barium at 455.4 nm. $z = 24 \text{ mm}$; ICP power $P = 1.1 \text{ kW}$; monochromator slit width $W = 70 \text{ \mu m}$. All other conditions as in Figure 32. Fluorescence profile taken along the excitation axis.

a) emission; $y = -1.0 \text{ mm}$

b) fluorescence; $y = -1.0 \text{ mm}$

c) fluorescence; $y = 1.0 \text{ mm}$

(ii). Resonance ionic fluorescence profile for barium at 455.4 nm. Conditions as in (i). Fluorescence profile taken along the observation axis.

$x = 0.5 \text{ mm}$
(1) and (11)

Intensity (Arbitrary Unit)

$X \text{ (mm)} \rightarrow$

$Y \text{ (mm)} \rightarrow$
Figure 42(i). Resonance ionic fluorescence and emission profiles for barium at 455.4 nm. $z = 24$ mm; ICP power $P = 1.5$ kW; monochromator slit width $W = 70$ $\mu$m for fluorescence, 50 $\mu$m for emission. All other conditions as in Figure 32. Fluorescence profile taken along the excitation axis.

a) emission; $y = -0.5$ mm
b) fluorescence; $y = -0.5$ mm

(ii). Resonance ionic fluorescence profile for barium at 455.4 nm. Conditions are the same as in (i). $x = 0.5$ mm. Fluorescence profile taken along the observation axis.
Figure 43(i). Antistokes direct line ionic fluorescence profile for barium at 455.4 nm (excitation wavelength 614.2 nm). All other conditions as in Figure 32. Fluorescence profile taken along the observation axis.

a) $x = -1.0$ mm
b) $x = 0.0$ mm
c) $x = 1.5$ mm
Figure 43(ii). Same as Figure 43(i). Fluorescence profile taken along the excitation axis.

a) $y = -1.5$ mm
b) $y = 2.0$ mm
Figure 44(i). Antistokes direct line ionic fluorescence profile for barium at 455.4 nm (excitation wavelength 614.2 nm). ICP power $P = 1.1$ kW; monochromator slit width $W = 70$ μm. All other conditions as in Figure 32. Fluorescence profile taken along the observation axis.

a) $x = 0.0$ mm
b) $x = 1.5$ mm
Figure 44(ii). Same as Figure 44(i). Fluorescence profile taken along the excitation axis.
a) $y = -2.0 \text{ mm}$
b) $y = 0.0 \text{ mm}$
c) $y = 2.0 \text{ mm}$
Intensity (Arbitrary Unit)

X (m)
Figure 45(i). Antistokes direct line ionic fluorescence profile for barium at 455.4 nm (excitation wavelength 614.2 nm). ICP power $P = 1.5$ kW; monochromator slit width $= 70 \mu$m. All other conditions as in Figure 32. Fluorescence profile taken along the observation axis.

a) $x = 0.0$ mm  
b) $x = 1.5$ mm

(ii). Same as (i). Fluorescence profile taken along the excitation axis.

a) $y = -2.0$ mm  
b) $y = 0.0$ mm
However, some points are worth being stressed here (i) the fluorescence technique is versatile, since many combinations of excitation/fluorescence wavelengths can be found, (ii) obviously, even if present, scattering would not affect the results here, (iii) the concentration of a metastable level rather than that of the ground state is sensed here. This has interesting possibilities for measuring the plasma temperature. Indeed, the ratio of the antistokes to resonance fluorescence gives an immediate qualitative indication of the excitation (ion) temperature profile for the transitions considered, under those particular experimental conditions. Figure 46 shows both the resonance fluorescence profile and the antistokes fluorescence profile on the same scale; the ratioing of these profiles should reproduce the temperature profile.

In an attempt to follow the atom distribution as well as the ion distribution, the resonance atomic fluorescence of barium was observed by tuning the laser at 553.5 nm. The resulting profile along the excitation axis is shown in Figure 47 for three different powers. It is interesting to note the ion and atom profile are complementary to each other. In fact, the atom distribution is narrower than the ion distribution and peaked almost at the position where the ion profile show a minimum. Presumably, the barium atom distribution would be much less sensitive to the temperature variation than the barium ion distribution.

Finally, a spatial profile of the ionic resonance fluorescence was obtained in the same conditions as those reported in Figure 32 and at three different powers. This was done in order to ascertain if major differences in the profiles could be found with the two torches, indicating some artifact with the torch used for obtaining the reported profiles. As Figure 48 indicates, the commercial torch shows the same double-peaked,
Figure 46. Resonance and antistokes ionic fluorescence of barium at 455.4 nm. Profiles taken along the observation axis. ICP power $P = 0.7$ kW; $x = -1$ mm; $z = 12$ mm. Other conditions as in Figure 32.

a) resonance ionic fluorescence
b) antistokes ionic fluorescence
Figure 47. Resonance atomic fluorescence profiles for barium at 553.5 nm. Nebulizer pressure: 25 psi; monochromator slit width W = 150 μm. All other conditions as in Figure 32. Fluorescence profile taken along the excitation axis.

a) corrected fluorescence, P = 0.7 kW
b) corrected fluorescence, P = 1.1 kW
c) corrected fluorescence, P = 1.5 kW
d) scatter profile, P = 0.7 kW
e) scatter profile, P = 1.1 kW
f) scatter profile, P = 1.5 kW
Figure 48. Resonance ionic fluorescence profile for barium at 455.4 nm as obtained with Torch #2 (see Table 12). Conditions are the same as in Figure 2 except for $y = 1.0$ mm.

a) ICP power $P = 0.7$ kW
b) ICP power $P = 1.1$ kW
c) ICP power $P = 1.5$ kW
asymmetric distribution along the excitation axis. We therefore believe that the obtained profiles are representative of the relative distributions of the barium species in the plasma.

C - Pulsed Dye Laser as an Excitation Source in ICP

C.1 - Introduction

The advantages of the inductively-coupled plasma (ICP) as an atomic/ionic vapor cell for emission spectrometry have been well documented. The high temperature (~6000 K) as well as long residence time experienced by the analyte makes the ICP extremely effective for vaporization, atomization, and/or ionization processes and also produces an extremely complex and intense spectrum with many analytically useful atomic and ionic emission lines. There are, however, inherent disadvantages to the ICP when used for emission spectrometry (ICP-AES). A high resolution monochromator is required to isolate the analyte emission from the plasma background and matrix element emission. Background correction procedures are mandatory for accurate analytical determinations using the ICP for emission. Most significant, however, is that the detectability of the present ICP-AES method is fundamentally limited by the characteristics of the technique itself. Although some improvement may be expected from refinements in nebulization design and increases in rf power applied to the plasma, only a major development similar to the development of electrothermal atomization for atomic absorption spectrometry will result in "orders of magnitude" improvement in ICP-AES detection limits.

One major advantage that the technique of atomic fluorescence spectrometry (AFS) exhibits over other atomic spectrometric techniques is the direct dependence of sensitivity on the intensity of the excitation
source (short of saturation of the spectral transition). Application of the ICP to AFS measurements should thus provide an extremely effective combination. The inert gas atmosphere provides a high quantum efficiency and the high temperature will not only reduce chemical interferences, but will also increase the number of analytically useful fluorescence transitions. Background correction using ICP-AFS is not as critical as in ICP-AES since matrix-induced changes in the plasma background are not observed or are easily corrected for by blocking the laser, and spectrometers of moderate resolution are satisfactory. Most important, however, is the simplicity of improving detection limits by increasing source intensity.

Several investigators have used the ICP as an atomic/ionic vapor cell for AFS. Using electrodeless discharge lamps as the excitation source, Montaser and Fassel\textsuperscript{103} reported atomic fluorescence in the ICP tail plume (3 to 5 cm above the coil). Better detection limits for fluorescence than emission were obtained for cadmium, zinc and mercury using a special torch configuration. In section A of this chapter we have investigated the application of a continuous-wave dye laser to AFS in the ICP for barium, sodium, lithium, and vanadium. We were restricted, however, by the limited wavelength range of our laser and found that a power level of 0.7 kW provided the best signal-to-noise ratio (SNR).

At the present state-of-the-art, the pulsed tunable dye laser is the most useful laser for the excitation of fluorescence in atomic vapor cells because of the wide wavelength range that can be covered. In this investigation, we have studied the application of two such lasers, a flashlamp-pumped dye laser and a nitrogen laser-pumped dye laser, to the excitation of atomic and ionic fluorescence in the ICP.
The nitrogen laser-pumped dye laser (UV-14, Molelectron Corp., Sunnyvale, CA)\textsuperscript{116} and the flashlamp-pumped dye laser (CMX-4, Chromatix Inc., Sunnyvale, CA)\textsuperscript{118,119} were used as the excitation sources for AFS in the ICP. The experimental system was similar to that described in section A of this chapter with the following modifications. Experimental measurements with the flashlamp-pumped dye laser were made using rhodamine 6G laser dye, frequency doubling, and narrowing of the spectral bandwidth of the laser to approximately 0.003 nm using a high finesse etalon. The laser radiation was focused by a lens (Spectrosil, 2.5 cm diameter, f.1.=30 cm) to a spot 0.1 to 0.2 cm in diameter 1.5 to 2.5 cm above the coil in the pencil region of the plasma. The resulting fluorescence was focused 1:1 on the 0.35-m monochromator which employed a 3 mm slit height and 0.5 mm slit width (spectral bandpass =1 nm). The photomultiplier was modified for pulsed, high current operation\textsuperscript{116} and synchronous gated (boxcar) detection was employed. A stripchart recorder and integrator were used for readout. Experimental measurements with the nitrogen laser-pumped dye laser were as described by Weeks et al.\textsuperscript{116} and Omenetto et al.\textsuperscript{120} as well as the detection and signal processing systems for both lasers. The forward power to the ICP was 0.65 kW for the atomic lines and 1.1 kW for the ionic lines studied.

C.3 - Results and Discussion

Flashlamp-pumped dye laser. Detection limits for laser-excited ICP-atomic fluorescence spectrometry (LICPAFS), ICP atomic emission spectrometry (ICPAES), and laser-excited flame AFS (LFAFS) are given in Table 13. For the two elements investigated, the detection limits for LICPAFS were approximately two orders of magnitude worse than the best ICPAES detection limits which are reported in the literature using pneumatic
Table 13

DETECTION LIMITS (ng/mL)

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>FLUORESCENCE WAVELENGTH (nm) (\lambda_{excitation}/\lambda_{fluorescence})</th>
<th>LICPAFS Pulsed(^c)</th>
<th>LICPAFS cw(^d)</th>
<th>LFAFS Pulsed</th>
<th>ICPAES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron(^a)</td>
<td>FeI 296.7/373.5</td>
<td>50</td>
<td>-</td>
<td>0.06(^e)</td>
<td>26(4.3)(^h), 0.2(^i)</td>
</tr>
<tr>
<td>Tin(^a)</td>
<td>SnI 300.9/317.5</td>
<td>500</td>
<td>-</td>
<td>3(^f)</td>
<td>200(111)(^h), 6(^i)</td>
</tr>
<tr>
<td>Barium(^b)</td>
<td>BaI 455.4/455.4</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>1(1.3)(^h), 0.06(^i)</td>
</tr>
<tr>
<td></td>
<td>BaII 614.2/455.4</td>
<td>30</td>
<td>6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Indium(^b)</td>
<td>InI 410.2/410.2</td>
<td>300</td>
<td>-</td>
<td>0.8(^g)</td>
<td>400(187)(^h), 30(^i)</td>
</tr>
</tbody>
</table>

\(^a\)Flashlamp-pumped dye laser.
\(^b\)Nitrogen laser-pumped dye laser.
\(^c\)This work, with detection limit defined as 3 x std. deviation of the noise using an observed time constant of 1 s.
\(^d\)Continuous wave dye laser detection limit (Section A of this chapter).
\(^e\)LFAFS detection limit using the same transition as LICPAFS with a 10 s time constant and multipass cell (Ref. 118).
\(^f\)LFAFS detection limit using the same transitions as LICPAFS with a 1 s time constant and single pass cell (Ref. 119).
\(^g\)LFAFS detection limit using the same transitions as LICPAFS with a time constant from 0.5 to 5 s and a single pass cell (Ref. 116).
Table 13--continued.

**h** Best ICPAES detection limits using our monochromator/detection system with a 0.3 s time constant; estimated ICPAES detection limits (Ref. 83) for same lines in parenthesis.

**i** State-of-the-art ICPAES detection limits using pneumatic nebulization (Ref. 85).
nebulization, although they are almost identical to the best detection limits that we can obtain with our instrumentation by ICPAES. Furthermore, they are within an order of magnitude of the estimated detection limits for ICPAES published by Winge et al. for the same lines.

Of more significance, however, since they were performed with the same laser system, is a comparison of LFAFS with LICPAFS. The LFAFS detection limits using a nitrogen-separated air-acetylene flame are two to three orders of magnitude better than the LICPAFS detection limits. While a factor of 3 difference in laser power resulting from losses in reflective optics used to direct the laser beam into the ICP (3 mirrors and 1 lens compared to only 1 mirror for the LFAFS system) can account in a small part for the poorer LICPAFS detection limits, the greatest effect is undoubtedly due to the greater background emission (and noise) of the plasma. The LICPAFS and LFAFS detection limits were obtained under shot-noise limited conditions. In Figure 49, the effect of rf power on the SNR of the fluorescence signal from 10 μg/mL Fe at power levels of 0.65 kW and 1.25 kW is shown. While the background signal increases by a factor of approximately 18 with increasing power, the SNR decreases by approximately 4 fold, characteristic of a shot-noise limited system.

Factors influencing the signal and SNR for the LFAFS and LICPAFS methods include: efficiency and rate of atom production; quantum efficiency of the atomic transition; luminosity of the entrance optical-monochromator-detection system; and background emission of the atomization system. The efficiency and rate of atom production in the flame and ICP depends on the rate and efficiency of sample introduction; although no measurements were made of this parameter, it is assumed that the ICP is a much more efficient atomizer. Similarly, it is also assumed
that the ICP is a much less efficient quencher of excited atoms as compared to combustion flames. The luminosity (throughput) of the LFAFS system (16 nm spectral bandpass and an f/3.5 aperture) was much greater (≈64x) than that of the LICPAFS system (1 nm spectral bandpass and an f/6.8 aperture). Finally, the background emission of the ICP is several orders of magnitude greater than that of the nitrogen-separated air/acetylene flame.

As shown in Figure 49, detector/electronic noise (the noise contributed by the detector and electronics in the absence of photons striking the detector) is a major noise source at low ICP power levels (0.65 kW), although the dominant noise is ICP background emission shot-noise. At the higher ICP power level used (1.25 kW), the ICP background emission shot-noise is the only major noise source. The noise sources in an ICP analysis will therefore vary from detector/electronic noise at very low background emission intensities, through a region of moderate background emission intensity where background emission shot-noise is dominant, to finally, at high background emission intensities, background emission flicker is the major noise source. The best region to perform an analysis, based on signal-to-noise ratio considerations, is the background emission shot-noise limited region (when the background emission is essentially a continuum over the spectral bandpass of the wavelength dispersive device). In the detector/electronic noise region, the noise is not a function of optical throughput, so the SNR (i.e., the signal component) may be increased by increasing the throughput. In the background emission flicker noise region (again, under conditions of a continuum background, which we observed for the elements we investigated), the noise may be decreased at a rate faster than the signal by decreasing the spectral bandpass, thus again improving the SNR. Thus, methods of
Figure 49. Recorder tracings of laser-excited atomic fluorescence signals from 10 μg/mL iron in the ICP.

(A) Detector/electronic noise with photomultiplier shutter closed.
(B) Baseline and fluorescence signal at 0.65 kW forward power to the ICP.
(C) Baseline and fluorescence signal at 1.25 kW forward power to the ICP.
improving the SNR for the aforementioned noise regions place one in the background emission shot-noise limited region. Here, an increase or decrease in spectral bandpass does not change the SNR as long as the upper or lower noise regions, where new noise sources are added, are not too closely approached. The SNR can be improved in the background emission shot-noise limited region by increasing the optical throughput by means other than increasing the spectral bandpass, such as increasing the f-number of the optical system to match that of the spectrometer. This method will be effective until the background emission flicker noise region is reached, where further increases in throughput will not improve the SNR.

As mentioned previously, the throughput of the LFAFS system is much greater (≈64x) than the throughput of the LICPAFS system. Figure 49 illustrated the LICPAFS analysis to lie in the background emission shot-noise limited region (0.65 kW) close to the detector/electronic noise limited region. The significantly lower background level of the separated flame would thus place the LFAFS analysis far into the detector/electronic noise region using the optical throughput of the LICPAFS system. Therefore, the increased throughput of the LFAFS system significantly improves detection limits using flames compared to the ICP for laser-excited AFS, as was illustrated in Table 13.

**Nitrogen Laser-pumped Dye Laser.** Detection limits shown in Table 13 are similar to those observed for the flashlamp-pumped dye laser, relative to the other techniques listed. The limiting noise sources for LICPAFS (with the nitrogen laser-pumped dye laser) were a combination of radiofrequency interference noise from both the ICP and the nitrogen laser (using the 15 ns gate) and the background emission shot-noise from the plasma.
The expected improvements in LICPAFS detection limits due to an improvement (compared to flames) in the quantum efficiency and in the restricted volume of the analyte in the plasma (which is optimal for laser excitation) are more than offset by the increase in the background intensity of the ICP compared to separated flames. The detection limit differences between LICPAFS and ICPAES are largely due to the duty cycle differences in the measurement systems (cw compared to 1 μs or 5 ns pulsed times the repetition rate) under shot-noise limited conditions (flashlamp-pumped) or radio-frequency interference/shot-noise limited conditions (nitrogen laser-pumped). Barium fluorescence, for example, is saturated using the nitrogen laser-pumped dye laser, so the fluorescence intensity is significantly greater than the emission intensity when measured over the gatewidth of the boxcar averager used for signal processing. Nevertheless, the ICPAES detection limit under continuous d.c. processing conditions is about the same as the LICPAFS detection limit. In such cases, improvement in AFS detection limits can only be obtained by using lasers of greater duty cycle, assuming complete, uniform illumination of the atomic vapor by the intense central (spatial) portion of the laser beam.

The major noise source at high concentrations in LICPAFS is flicker noise due to pulse-to-pulse variations (intensity and spatial) of the laser; a similar noise component was observed in flame cells. Analytical growth curves for the elements studied were linear up to approximately 1000 μg/mL.
As stated in the literature the ICP is an excellent source of excitation for atomic/ionic emission spectroscopy. Based on the results presented in Chapter 2, one can minimize molecular interferences by minimizing ambient air mixing with plasma gas; a more common way is to use a longer torch. In practice, as time passes, the torch becomes cloudy and spectral analysis proves difficult. The second way would be to design a new induction torch configuration allowing use of an argon (or nitrogen)-separated plasma or simply by making a smaller housing for the torch and flushing it with argon or nitrogen. Doing this and using a 1 m JY monochromator would result in a lower detection limit for atomic/ionic emission spectrometry. Also, the use of liquid argon because of lower impurity than the commercial argon would be beneficial.

Since the behavior of heating and decomposition of dry particles injected into an argon and a nitrogen ICP discharge have been investigated with a computer simulation technique by Barnes and Nikdel\textsuperscript{121} and it was shown that the nitrogen ICP discharge overall is more effective than the argon ICP discharge, it would be interesting to verify their results experimentally by using a high power rf-generator with nitrogen as a plasma gas in atomic/ionic emission spectrometry. Also, from the diagnostic point of view "laser induced fluorescence" with a N\textsubscript{2}-pulsed
dye laser or excimer-laser in this type of ICP would provide valuable information to spectroscopists, in the field.

The effectiveness of the nitrogen ICP is probably due to a large population (concentration) of metastable nitrogen molecules which are then mixed with a thermally vaporized metallic species in the induction torch. The large excess and long life-time of the metastable nitrogen permits multiple excitation-emission cycles to occur during the resident time of the analyte in the torch which is based upon the energy transfer from metastable nitrogen molecules to the metal atoms/ions.

From the results presented in Chapter 3, we can conclude: (i) that the ICP is undoubtedly an excellent excitation source as far as its spectral emission characteristics are concerned. In agreement with the results of Human and Scott\textsuperscript{69} the very long linear concentration ranges obtained are due to the remarkably low self-absorption and to the absence of self-reversal at the heights used for analytical measurements. Results are preliminary and must be considered on a qualitative basis only. For example, the spatial (height) resolution was low; the results are an average over the stated height ±5 mm; (ii) similar information concerning ionic emission can be obtained provided that a sufficient density of ions is created in the flame atomizer; here one can use two ICP's to study the ion characteristic in plasmas.

Several other conclusions can be derived from the experimental evaluation of characterization of the ICP as an excitation source in atomic/ionic fluorescence spectrometry in Chapter 3: (1) as stated originally, the ICP has been confirmed to be an extremely versatile and intense excitation source for the atomic fluorescence determination of all the elements investigated; (2) the ICP combines the versatility of a continuum source with the high spectral irradiance and selectivity of a line source;
(3) The excellent multi-element excitation capability of the ICP simplifies the application of the 2-line method of correcting for scattering problems using resonance transitions because of the many neutral as well as ionic lines are available; (4) the spectral selectivity of the atomic fluorescence technique is shown to be advantageous in certain analytical applications where the emission technique is plagued with spectral interferences. The ICP proved to be an excellent excitation source for atomic fluorescence, allowing low detection limits to be obtained. Because of its extreme versatility (due to the excitation capability of a great number of elements), this source could prove to be useful for selected, specific applications in which the fluorescence technique presents fewer problems than the emission technique. Therefore, even though the ICP has been shown to be of marginal use as an atomizer in atomic fluorescence, its potential as an excitation source is worthy of more investigation, particularly when the experimental facilities are already available in the laboratory and where spectral interferences cause problems with the emission technique using the available spectrometer resolution.

In addition to this, several promising future areas of application for this source can be devised and are discussed below.

(1) Because of the high excitation power and freedom from inter-element interferences, the ICP emission of several elements aspirated simultaneously will result in little, if any, degradation of the detection limits obtained in atomic fluorescence, provided that no spectral interferences will result. Therefore, the use of a programmable slew-scan monochromator would permit the sequential determination of several elements in one sample.
(2) The shape of the "excitation" curve of growth\textsuperscript{72} should allow the possibility of scatter correction by taking advantage of the differences in the source emission intensity and excited-fluorescence intensity dependence on concentration due to self-absorption in the source.

(3) Relatively high concentrations of the element investigated in a given matrix can be analyzed directly by aspirating the sample into the ICP rather than in the flame, while monitoring the fluorescence signal from a standard aspirated into the flame. This avoids the necessary dilution of the sample solution, should the analysis be performed in the conventional manner by AFS.

(4) The system may also prove useful for electrothermal atomization techniques or hydride generation techniques, where the very low emission levels of these atomization cells may further improve detection limits.

(5) To increase the spectral irradiance of the ICP, it is possible to use a double coil system constructed one to two inches in distance apart and then by focusing the volume between them into the flame or any other atom/ion cell for atomic/ionic fluorescence spectrometry. This type of design should produce a higher spectral irradiance than the normal one coil system, and highly stable source of excitation for introduction of very high concentration solutions into the ICP.

(6) Although, in principle, the ICAP could also be advantageously used as a primary source in atomic absorption analysis, especially for elements which exhibit low hollow cathode lamp intensity, this application does not seem to offer any advantage as compared to the emission technique, not even for specific applications as in the case of atomic fluorescence.
In conclusion, it is my opinion that the ICAP-excited AFS technique is an ideal adjunct to an ICAP-emission spectrometer, capable of solving many specific analytical problems. An increase in the collection efficiency of the ICAP-emission focused on the flame should considerably improve the already impressive detection limits.

The results in Chapter 4, show that the atomic fluorescence in the ICP using a cw dye laser source is possible and can be done. However, the system as described is not analytically useful because of the limited wavelength range of the present cw dye laser, the rather high cost of the additional components needed to convert an ICP-AE system into a cw laser excited ICP-AF system, and the rather poor (or not substantially improved) detection limits compared to the ICP-AE system. The use of lower powers (0.5-1 kW) in the ICP is possibly undesirable due to the unknown effects of lower power upon desolvation and vaporization processes for samples more complex than those employed in this study. It was predicted that both the limited wavelength range and the necessity that power be reduced to decrease background radiation could be overcome through the use of a pulsed laser with gated detection. All results from this study support the non-LTE excitation conditions.\textsuperscript{17} The use of fluorescence in the ICP using a laser source should certainly be a practical tool in diagnostic studies (spatial temperatures and densities) of plasmas.

The results presented in this investigation (Chapter 4) have clearly demonstrated the remarkable attractiveness of the laser excited fluorescence technique in modeling directly the relative distribution of species in the ICP discharge with high spatial resolution. As stated in the previous literature,\textsuperscript{106-115} such measurements are compulsory if any attempt is made to understand the complex processes occurring in the plasma.
It is also worth pointing out that the fluorescence intensity depends upon linearity of the quantum efficiency of the transition as long as the fluorescence intensity varies linearly with the excitation intensity. The quantum efficiency may vary locally in the plasma and therefore the measured profiles might be affected by such variations. The measurement of absolute concentration profiles is possible if the laser is able to saturate the observed transition. Preliminary measurements carried out in our laboratory have shown that this can be achieved with our pulsed laser. But the use of an excimer laser would clearly introduce saturation and then the laser-induced fluorescence in ICP would be interesting to take another look from the analytical point of view as a new tool.

While the initial evaluation of laser-excited AFS in the ICP has not indicated the technique to be superior to ICPAES or to LFAFS, the application of multipass optical cells to reflect the laser beam several times through the ICP, as well as the use of more powerful, higher repetition rate laser sources, should improve detection limits enough so that the advantages inherent in the combination of a high-temperature atomic vapor cell with the atomic fluorescence method will be fully realized. Furthermore, laser-excited AFS is still a very powerful tool for diagnostic studies of the ICP.

Metal complexation may be used for the following purposes in gas chromatography with inductively coupled plasma as a detector: (i) to help the separation of certain compounds present in the sample. (In this case complexation is performed by using a stationary phase containing a metal); (ii) to utilize GC-ICP for the calculation of stability constants or other physical/chemical data; (iii) to increase sensitivity for inorganic and organic compounds by forming metal complexes.
The effect of the formation of electron-donor-acceptor complexes (EDA) of transition metal cations with organic molecules containing \( \pi \)-bond(s) or free electron pairs (N, O, S, halogens) may be used for the gas chromatographic separation of these molecules with the ICP as a detector of the metal complexes because of the considerable differences in the retention time of the metal complexes.

In the case of a 1:1 complex formation, GC-ICP is convenient for the determination of the stability constants of the newly formed adducts. The formation of \( \pi \)-complexes with cations of the transition metals are particularly useful in GC-ICP. The thermal stability of these complexes changes in a very broad temperature range depending on the metal and the ligand. The ICP atomic emission spectrometry has been known to be a sensitive technique for metal analysis, thus it will provide a sensitive method for the ligand forming complexes with the metals.

The gas generation technique is known to be effective for the condensation of analyte in solution and minimizing the matrix effect. One could apply this technique to atomic and molecular emission/fluorescence spectrochemical analysis of non-metallic elements, which are difficult to be measured by usual spectrochemical methods. Boron trifluoride can be generated from a specially designed high temperature cuvette, in which boron containing samples are heated with calcium fluoride and sulfuric acid. The gas is carried into a plasma and then atomic emission or fluorescence of boron, emission of boron dioxide, and molecular emission of boron monofluoride can be monitored. Ammonium-N also can be generated as ammonia gas by heating from a strongly alkali solution and then carried into the plasma. This method can also be applicable to the analysis of nitrate-N and nitrite-N by reducing them to ammonia gas with appropriate reducing reagent.
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Later, in 1972, he decided to further his education in the USA. After completing an intensive program of study in an English School in Washington, D.C., he entered the graduate school at the University of Massachusetts. There, he received the Master of Science degree in analytical chemistry in 1975. In September 1976, he then began study on his doctoral degree at the University of Florida in Gainesville, Florida.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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