EFFECTS OF ORGANIC ACIDS IN INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY

By

TERRANCE DAYAKANTHA HETTIPATHIRANA

B. Sc. (Hons.), University of Colombo, Sri Lanka, 1984

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ABSTRACT

The effects of organic acids in an inductively coupled plasma (ICP) have been studied with reference to solvent introduction and plasma excitation conditions. When compared with water, an increase in emission intensity for Mg, Cd, and Zn atom and ion lines is observed when organic acids are present in the sample solution. The presence of organic acids causes an increase in both the efficiency of nebulization and the temperature in the lower region of the central aerosol channel.

The feasibility of using a semi-automated flow injection (FI) method to investigate the interference effects of acetic acid over a wide range of analyte and interferent concentration has been studied. This FI-ICP procedure makes use of the concentration gradient formed by the analyte in the FI system. Using this method, a response surface can be constructed quickly and with the preparation of relatively few solutions. The response surface shows the system response (for example, emission intensity) as a function of analyte and interference surface prevalent under any set of experimental conditions.

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PART ONE

EFFECTS OF ORGANIC ACIDS IN LOW POWER INDUCTIVELY COUPLED ARGON PLASMA OPTICAL EMISSION SPECTROSCOPY

Chapter 1

INTRODUCTION

1.1 Objective

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) has been widely used to analyze major, minor and trace quantities of elements in a wide variety of sample matrices. Although early reports described the ICP as being almost free from interference effects [1,2], it is now clear that this is not the case. Much of the early confusion has been attributed to the inconsistency of the data due to different operating conditions and a lack of understanding of the ICP at a fundamental level [3,4].

The majority of samples analyzed by ICP are aqueous, frequently acidic, solutions. The transport properties of these solutions have been studied by a number of investigators. For a nitrogen-cooled, high power ICP, Greenfield *et al.* [5] reported a reduction of emission intensity with inorganic acids and an enhancement effect when organic acid solutions were introduced. The predicted decrease in emission intensity based on reduced uptake rates for organic acid solutions was contrary to this observation and they concluded that the physical properties of the solvent play a major role in nebulization and aerosol transport processes. Jinrui Xu *et al.* [6] studied some effects of organic acids and solvents and Belchamber *et al.* [7] used simplex optimization to find operating conditions which would minimize the effects of acetic acid in a multi-element mixture. In the latter study, it was found that optimization of rf power, nebulizer, intermediate and outer gas flow rates led to removal of a matrix effect for five elements (Mn, Ni, Cu, Fe, and Cr) and a substantially reduced matrix effect for the other (Zr). Recently, Farino *et al.* [8] reported a detailed investigation of transport properties of representative inorganic acid solutions.

The observed emission intensity depends on two major factors: the analyte mass transport rate to the plasma and the degree of vaporization, dissociation, ionization and excitation in the plasma. The analyte mass transport rate depends on the efficiency of the nebulizer and the physical properties of the solvent. The introduction of solvent into the plasma also changes the discharge characteristics and these changes are solvent dependent. Energy is absorbed from the plasma during the solvent vaporization, and dissociation and thus analyte atom and ion populations as well as electron number densities are dependent on the solvent aspirated. Also the solvent and its decomposition products determine the total heat capacity of the plasma. In an equilibrium plasma, the balance between thermal conduction and power dissipation determines the plasma temperature and excitation conditions [9]. Therefore, the product of the analyte mass transport rate and the plasma excitation conditions determines the excited state atom or ion population in plasma, which in turn determines the observed emission intensity for any element in any particular solvent. Thus, studying both the transport properties and excitation conditions enables one to understand poorly perceived interference mechanisms.

In an effort to understand interference mechanisms of organic acids, a study based on spatially resolved vertical emission intensity profiles of Mg, Cd and Zn was undertaken. Part One of this thesis presents the results of this study and discusses the mechanism of interference in the plasma with reference to solvent introduction and plasma excitation conditions^{*§}.

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1.2 History of the ICP

Of all the various plasma devices used for elemental analysis during the past 25 years, the inductively coupled plasma (ICP) has had the most significant impact on the field of atomic spectroscopy. Other plasmas, such as the direct current plasma (DCP), the microwave induced plasma (MIP), the capacitively coupled plasma (CCP) and glow discharges, have been found to be useful for spectrochemical analysis; however, the ICP is the primary source used for trace multi-element analysis.

The seed for the development of the ICP can be traced back to 1947 when Babat [10] described the operation of a low pressure induction coupled discharge. The development lay fallow until 1961 when Reed [11] described an ICP operating at atmospheric pressure supported by flowing argon gas.

Although it was originally designed for growing highly purified crystals [12], this device displayed certain advantages for spectrochemical analysis. In 1964, Greenfield *et al.*[1] described the use of an ICP for spectroscopic analysis. The torch design was similar to that used in present day, commercially available ICP instruments. It consisted of two quartz tubes with tangential gas inlets and a central pyrex tube to introduce sample into the plasma. A number of advantages over existing atomic emission methods were observed. These included a lack of electrode contact which gave freedom from contamination and a simple spectral background. A year later, Wendt and Fassel [13] described a laminar flow ICP torch for producing a toroidal shaped plasma. However, Fassel's group eventually converted to tangential gas inlets, favouring Reed's approach of vortex stabilization [14,15] to keep the torch cool.

Over the next ten years after these two independent studies by Greenfield *et al.* and Wendt and Fassel, work proceeded slowly. In the mid 1970's, the ICP was still very much a research tool. Results were sufficiently promising to merit additional research and development. Basic research was confined to a limited number of academic, government and industrial laboratories and significant advances emerged. In 1974, the revival of atomic emission was heralded in a number of ways, for example, by provocative titles in several scientific communications. Boumans [16] used the title "Multi-elemental Analysis by Optical Emission Spectroscopy-Rise and Fall of an Empire ? " and Fassel [17] used the title " Optical Emission Spectroscopy : Stagnant or Pregnant ? ". Both these titles predicted that emission spectroscopy would soon regain its appeal and again become a mainstay analytical technique.

Since 1975, further developments and applications of the ICP have been truly amazing. In the ten years following the introduction of the first commercial ICP spectrometer in the mid 1970's, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) has matured and promises to play a leading role during the next decade. It is a rapid, multielement technique with a wide dynamic range, which enables analysis of concentrations from minor to trace levels. There are approximately 30 manufacturers internationally and more than 6000 installed units [18]. Applications are numerous, including geological, industrial, agricultural, clinical and environmental [19].

The success of ICP-OES as an analytical method has led to the use of the ICP as an excitation source for other analytical methods. The ICP has been used as an atomization cell for atomic fluorescence spectrometry (ICP-AFS) [20]. More recently, it has been incorporated as an ion source for mass spectrometry (ICP-MS) [21].

A more complete review of the historical development of the ICP has been published by Fassel [22]. The historical development of high-energy excitation sources for emission spectroscopy has been reviewed by Schrenk [23].

1.3 The Inductively Coupled Plasma

Historically, the ICP has been composed of a " torch " which contains the plasma and some means to sustain the plasma inside the torch. The plasma is generated by inducing a magnetic field in a flowing, conducting gas, usually argon, which flows through the quartz confinement tubes. Radio frequency power of approximately 0.5-3 kW is transferred to the plasma using three or four turns of a water-cooled copper induction coil connected to the radio frequency generator. The standard rf frequency of operation in North America is 27.12 MHz. The high frequency currents flowing in the induction coil generate an oscillating magnetic field whose lines of force are oriented inside the tube and follow elliptical closed paths outside the coil as provided in the Fig 1.1. The induced magnetic field causes the electrons and ions to flow in closed annular paths inside the quartz tube space. This interaction (or inductive coupling) of the oscillating magnetic field with free electrons in the flowing gas generates the plasma. Since the argon that sustains the plasma is initially neutral and non-conducting, the argon must be made conductive using "seed" electrons generated by a Tesla coil before a self-sustained plasma results. The entire process of formation and stabilization of an inductively coupled plasma takes several milliseconds. An argon ICP, when operating, is about 1 % ionized with a temperature of approximately 4000-8000 K.

The torch typically consists of three concentric quartz tubes through which the plasma gases flow. Exact dimensions and details of design differ among different users. The nomenclature of gas flows is confusing in the literature. To avoid the confusion, this thesis uses unambiguous terms. The "outer gas " (also called plasma or coolant gas) which flows at a relatively high rate (8 - 15 L/min) sustains the plasma and also cools the quartz tubes. The next flow inward is the "intermediate gas " (also called auxiliary or



Fig. 1.1. Schematic diagram of the ICP discharge and the torch. (adapted from reference [19].)

plasma gas) which is merely used to lift the plasma, thus preventing contact with the top of the aerosol tube. This gas flows at a lower rate (0 to 0.5 L/min). The outer and intermediate gas flows are introduced tangentially, a feature which has been widely adopted. These tangential flows stream upward, cooling the inside walls of the outermost quartz tube and centering the plasma axially in the tube. The central flow is the " nebulizer gas " (also called the aerosol gas) and is used to transport the sample to the plasma. This gas may also be called the inner gas, but the terms nebulizer or aerosol gas have become common.

The rather flat-bottomed, " tear drop " shaped plasma formed by the outer and intermediate gas is of no analytical use until a channel is formed in it by the nebulizer gas. This forms an annular shape often described as a " doughnut " when observed from the bottom.

The analyte, most commonly in solution form, is converted to a fine aerosol by the nebulizer and is transported to the plasma by the nebulizer gas flow. The aerosol progresses up through the plasma to form the "central aerosol channel ", where the processes of desolvation, vaporization, dissociation, excitation and ionization take place. The process of excitation followed by radiative emission is the basis of Optical Emission Spectroscopy (OES).

1.4 Aerosol Generation and Transport

1.4.1 Introduction

Referred to by Browner and Boorn [24] as the "Achilles heel of atomic spectrometry", sample introduction presents one of the biggest challenges in atomic 8

spectrometry. In spite of the wealth of studies available in the literature, there are relatively few studies which examine the fundamentals of aerosol formation and its relation to analytical performance. The current state of the art is probably the limit of empirical development, and major advances will come only when a sound framework of fundamental knowledge is in place.

Research on sample introduction into the ICP has yielded a diversity of methods. These can be summarized as follows: pneumatic, ultrasonic, electrothermal, thermospray, direct insertion, heated wire, arc or laser vaporization, powder suspension and hydride generation. Nebulization of a solution to form an aerosol is the method used for all the measurements described in this thesis. Details of other methods of sample introduction are available in reference [25] and the references therein.

The nebulizer is used in conjunction with the spray chamber to form a fine mist of aerosol. This aerosol is transported into the plasma by the nebulizer gas flow. Efficiency of these devices varies between 1 and 3 % of the total solution. The remainder of the sample goes to waste. For an optimized sample introduction method, the following parameters must be known.

(1) aerosol droplet size

(2) maximum solvent loading, for both aerosol and vapour

Important practical implications of the above are; first, there is an upper limit to the size of droplets which can be vaporized within the residence time of analyte in the plasma (typically 1-2 ms). Also, droplet size may have a marked effect on the transport efficiency. On the other hand, the nebulizer/spray chamber combination has an important effect on the droplet size that reaches the plasma. Second, the solvent load to the plasma should be quantified and characterized. Above a certain limit, for example, alcohols readily extinguish the plasma under normal operating conditions. It has been shown that the tolerance of the ICP to organic solvents is greatly improved when a large fraction of the solvent is removed from the gas stream passing to the plasma.

1.4.2 Pneumatic Nebulization

The method liquid sample introduction using pneumatic nebulizers was already established through work with flame atomic absorption spectrometry and was quickly adapted for use with the ICP. Currently, the most important pneumatic nebulizer designs are the cross-flow [26] and the concentric configurations [27]. In a cross-flow nebulizer, the gas and liquid streams interact at right angles to one another whereas in a concentric nebulizer, the gas and liquid streams interact coaxially (Fig. 1.2). The precise microscopic processes by which pneumatic nebulizers operate are not well understood. In simple terms, a liquid jet is shattered by interaction with the high velocity gas jet. This process may be described by successive removal of thin surface films of liquid followed by spontaneous collapse under surface tension forces to produce the aerosol droplets.

The introduction of the concentric nebulizer by Meinhard [27] proved extremely successful. It is widely used as an ICP nebulizer and is the type used for all the measurements described in this thesis. Currently, a number of different tip designs are available. Specifications vary, but a typical nebulizer with a nebulizer gas flow of 0.6-1.3 L/min and a line pressure of 200-300 kP will take up 0.5-3.0 mL/min solution. Concentric nebulizers are self-actuating and self-priming, in that solutions are drawn up by the low pressure generated as the nebulizer gas passes through the orifice.

For many years, the main alternative to a concentric nebulizer in ICP has been the crossflow systems. In this, a horizontal jet of gas passes across the top of a vertical narrow tube. The reduced pressure so generated draws solution up the vertical tube, and at the top,



Fig. 1.2. Schematic diagram of a nebulizer. (a) concentric, (b) cross flow. (adapted from reference [19].)

it is disrupted into fine droplets. A typical cross-flow nebulizer is the MAK^R which was developed by Anderson *et al.* [28].

1.4.3 Spray Chamber

The aerosol produced by the nebulizer contains a broad distribution of droplet sizes known as the primary distribution. The larger droplets are not completely dissociated under normal plasma conditions, and contribute only noise to the emission signal. It is the function of the spray chamber to remove these droplets, which condense and go to waste. This is achieved by sharp changes in the direction of the gas flow and direct collisions of the aerosol with the internal surfaces of the spray chamber. In carrying this out, the spray chamber has a marked effect on the efficiency of the sample introduction system as a whole.

One of the earliest systems, the double-pass system described by Scott *et al.* [29], is still used today. It was optimized to reduce dead space, as aerosol circulating within the spray chamber is a major contributing factor to signal stabilization and clean out time. This is the type of spray chamber used for all the measurements described in this thesis.

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1.4.4 Aerosol Transport

The processes which occur in aerosol generation and transport can be divided into three categories as outlined in Fig. 1.3. In primary aerosol generation, the solution stream is initially shattered by nebulization into an aerosol resulting in a polydisperse droplet distribution. The corresponding droplet distribution is described as the "primary " distribution. The secondary process is the one in which the relatively high velocity droplet stream impinges on an impact surface (*e.g.*, spray chamber surfaces). Large droplets, on striking the impact surface, will generally adhere and run into the waste, whereas small droplets will tend to follow the air stream around the surface without destruction. Intermediate droplets with sufficiently high velocity may shatter and generate small droplets. The impact surface, therefore, modifies the primary droplet size distribution by shifting it to a smaller mean diameter and as a result the aerosol assumes its " secondary " droplet size distribution.

Impact, turbulent and centrifugal loss, gravitational setting and evaporation occur in the tertiary stage. These modify the droplet size distribution in the region between impact surface and plasma. This process further shifts the aerosol size distribution to smaller droplets. Following these steps, the aerosol has a distribution which may be called a "tertiary " or a pre-atomization droplet size distribution. It is the interaction of all these stages in the generation and transport process which determines the transport efficiency and analyte mass transport rate to the plasma.

A more complete description of the aerosol transport model for atomic spectrometry has been published by Browner *et al.* [30].



Fig. 1.3. Stages in aerosol generation and modification from nebulizer to plasma.

1.4.5 Aerosol Characterization

The mechanism of primary aerosol formation is not well understood and no exact theoretical treatment is available. One can only be guided by the results of various empirical investigations and theoretical explanations that have been proposed. Traditionally, the equation proposed by Nukiyama and Tanasawa [31] is used to estimate the mean droplet size distribution. The transport efficiency may change with median droplet diameter d_s , as estimated by Nukiyama and Tanasawa equation,

$$d_{s} = \frac{585}{V} \left(\frac{\sigma}{\rho}\right)^{0.5} + 597 \left(\frac{\eta}{(\sigma\rho)^{0.5}}\right)^{0.45} \left(10\frac{3Q_{L}}{Q_{G}}\right)$$

where d_s is the Sauter mean diameter (μm), V is the difference between gas and liquid velocities to the nebulizer (m/s), σ is the surface tension of the liquid (dyn/cm), ρ is the liquid density (g/cm³), η is the liquid viscosity (P), and Q_L and Q_G are the volumetric flow rates of liquid and gas (cm³/s), respectively.

This equation was developed for a specific nebulizer design using subsonic gas velocities and a range of solvents covering the surface tension range of 30 to 70 dyn/cm and viscosities of 1 to 3 cP. However, it should be noted that the equation is dimensionally inconsistent and is said to predict too high a proportion of large droplets [32]. Another serious misconception in the literature is the frequent use of the Nukiyama and Tanasawa equation for directly estimating the effect of tertiary droplet size [30]. In reality, the Nukiyama and Tanasawa equation provides data only on the primary droplet size distribution and the influences of the secondary and tertiary aerosol modifying process must also be considered in order to derive the pre-atomization aerosol formation. In spite of all these limitations, the Nukiyama and Tanasawa equation provides the only empirical model of aerosol formation of direct value to atomic spectroscopy.

1.5 Analyte Excitation and Ionization

It is beyond the scope of this thesis to go into details of various excitation and ionization mechanisms in the ICP, yet a brief discussion is warranted.

A plasma can be simply described as an ionized gas. In a plasma sustained by argon, the principal species present are neutral argon atoms, singly charged argon ions and unbound or free electrons. The total energy of this three component system is distributed in internal electronic states of the atoms and ions and in translational degrees of freedom of the atoms, ions and electrons. The plasma is sustained in a flowing argon stream and there is a net transport of all species away from the energy addition region. It is spatially nonhomogeneous and therefore characterized by concentration and temperature gradients. It is into this environment that analyte species, solvent aerosol and its vapour are introduced. Provided with sufficient energy from the plasma, desolvation, vaporization, dissociation, excitation and ionization of the analyte species occur. In addition, the presence of solvent and its decomposition products introduces a further complexity.

In a plasma such as an ICP, the collisional and radiative process are assumed to be important among the variety of mechanisms through which energy exchange occurs. In an electron collision, kinetic energy is lost to excite or ionize the analyte particles. Conversely, the energy stored in an excited state of the analyte may be transferred to kinetic energy of the electrons. Stored energy may also be released radiatively in the form of a photon. A more detailed discussion of the current interpretation of excitation mechanisms was published by Blades *et al.* [33]. 16

1.6 Plasma Temperature

1.6.1 Introduction

One of the most striking features of the ICP and one which makes it particularly suitable for emission spectrometry is its relatively high temperature. Spectroscopic methods are the most popular for the measurement of plasma temperature and for very high temperatures, this may be the only applicable method. The emission intensity of one or more spectral lines are measured and substituted into the appropriate distribution function to yield the plasma temperature. The interpretation of what is meant by temperature is briefly discussed here. A more detailed account of the recent developments of the subject has been published by Blades [34].

1.6.2 Thermodynamic Equilibrium

For a partially ionized gas in a closed system at temperature T, the macroscopic state of the gas may be described by parameters such as pressure, temperature, concentration and so forth. Statistical methods describe the microscopic state using macroscopic parameters (pressure, temperature and concentration *etc.*). This microscopic state of the plasma can be completely characterized by a number of distribution functions that are functions of the temperature T. These distribution functions are provided in Appendix A.

This leads to several different definitions of temperatures in the plasma. These are the electron temperature (T_e , from Maxwell distribution), gas kinetic temperature (T_g , from Maxwell distribution), excitation temperature (T_{exc} , from Boltzmann distribution) and ionization temperature (T_{ion} , from Saha distribution). In a system which is in complete thermodynamic equilibrium, the condition

$$T_e = T_g = T_{exc} = T_{ion} = T_{rad}$$

holds. This description of a plasma in thermodynamic equilibrium is simple. If the plasma is in thermodynamic equilibrium, it can be characterized by the same temperature. The presence of thermodynamic equilibrium defines the plasma as a static state entity at the macroscopic level. But this is not the case at the microscopic level.

1.6.3 Departures from Thermodynamic Equilibrium

Laboratory plasmas are limited in spatial dimensions - large temperature and concentration gradients exist and matter and radiation are escaping from the plasma boundaries. Under these conditions thermal equilibrium is rarely established. Since the photons are more likely to escape than particles, the radiation field can deviate from the equilibrium distribution described by Planck's law. However, the energy exchange between particles can remain locally effective so that the Boltzmann, Saha, and Maxwell distributions are retained. Thus, atoms, ions and electrons have the same temperature. Plasmas in which equilibrium is maintained for all distributions (except the Planck's law) at any spatial point are said to be in Local Thermodynamic Equilibrium (LTE). Essential features of LTE are that matter and radiation cannot be described by the same temperature and possibly different plasma temperatures exist at different spatial positions. The matter and radiation are said to be "decoupled".

Many authors have measured various temperatures and electron concentrations in the ICP in an effort to demonstrate the presence or absence of LTE. It has been shown that measured electron density cannot be reconciled with spectroscopically measured excitation and ionization temperatures which vary with the thermometric species used for the

measurement [35]. Kornblum and de Galan [36] summarized the results of spectroscopic measurements with the following relationships:

$$T_g < T_{exc} < T_{ion}$$

 $T_{exc} = f(E_{exc})$
 $T_{ion} = f(E_{ion})$

This is considered to be sufficient evidence to show that the ICP is not in LTE.

Chapter 2

EXPERIMENTAL

2.1 Instrumentation

A block diagram of the instrument used is provided in Fig. 2.1. The ICP consisted of a Plasma-Therm (Kreeson, NJ) HFP-2500E rf generator, an AMN 2500E automatic matching network and an APCS-1 automatic power control unit. The generator operating frequency was 27.12 MHz and the maximum output power to the load coil was 2.5 kW. The rf powers used in this study were 0.75, 1.00 and 1.25 kW. The following gas flow rates were used for all measurements : outer gas - 10 L/min, intermediate gas - 0.2 L/min and nebulizer - 1 L/min.

The ICP torch used in this study was constructed at the UBC glass shop from quartz tubing. A concentric nebulizer (Meinhard type) constructed at the UBC glass shop was used to introduce the sample into the plasma. The uptake rate was varied by a peristaltic pump (model - Alitea C4V, Seattle, WA) The free uptake rate was used unless otherwise stated. The spray chamber was a Scott type (Plasma- Therm, model SC-5037). Fig. 2.2 provides the diagram of the nebulizer, spray chamber and torch assembly.

A 1 m Czerny-Tuner monochromator (Schoeffel-McPherson, Acton, MA) model 2061 was used. This was equipped with a holographic grating with 1200 line/mm (Schoeffel, McPherson, Model AH-3264). The image of the plasma was formed at the entrance slit of the monochromator by a 150 mm focal length, 50 mm diameter, planoconvex fused silica lens. The imaging distance was adjusted to provide an image with a magnification of 1. The viewing height was changed by moving the lens vertically. The entrance slit was 50 mµ wide and 2 mm high.







Fig. 2.3. Schematic diagram of the nebulizer, spray chamber and the torch assembly.

The detector used was Reticon RL-4096/20 (Reticon, Sunnyvale, CA) photodiode array. This array consisted of 4096 discrete photodiodes, 7.5 μ m wide and mounted on 15 μ m centres. The dimensions of the light sensing area were 0.5 mm in height and 61 mm in length. This provided the simultaneous measurement of a wavelength window of 40 nm. A Melcor (Trinton, NJ) model CP14-71-10L thermoelectric cooler allowed the photodiode array to be cooled down to -15 ⁰C. The photodiode array was continuously purged with nitrogen to prevent the build up of ice on it. The array readout was provided by a RL- 4096SS-3 evaluation board. Further details of the system are available in reference [37].

Analog-to-digital conversion was provided by a fast A/D converter card (model ISC-16, R.C. electronics, Santa Barbara, CA). The digital output was acquired with a PC/AT^{R} compatible microcomputer (Telex, model-1280, Tulsa, OK). This was used to control the operation, data acquisition and data processing (signal averaging, background subtraction etc.).

2.2 Data Acquisition

The following procedure was used for measurement of emission intensities. For each of the three analytes (Mg, Cd and Zn), three different " wavelength windows ", 40 nm in width, were chosen. Analytes selected along with their spectral data are listed in table I. Analyte lines of interest were centred in the wavelength window. Net emission intensities were obtained by aspirating the analyte solution and then subtracting the intensity obtained with the solvent alone. Integration times were chosen so as to provide reasonable signal-to-background ratios without saturating the diodes. Emission intensities were averaged at least 50 times to give an averaged emission intensity.
Species	λ(nm)	E _q (eV)	$E_i(eV)$
Mg(I)	285.21	4.35	7.644
Mg(II)	279.55	4.43	
Cd(I)	228.80	5.42	8.911
Cd(II)	226.50	5.47	
Zn(I)	213.85	5.80	9.391
Zn(II)	202.54	6.13	

Table I.	Wavelengths (λ), Excitation energies (E_q), and
	Ionization energies (E_i) for Mg, Cd, and Zn.

2.3 Transport Efficiency Measurements

A small glass column was fitted with approximately 5 g of self-indicating, 6-20 mesh silica gel (laboratory reagent, BDH, Toronto) and was fitted to the spray chamber. Fig. 2.3 provides the schematic of the column used. Solutions were aspirated and the uptake rate was changed by the use of a peristaltic pump. The solvent load to the plasma was measured by collecting aerosol that is absorbed on to the silica column over a 30 min period and weighing by difference of the column. A similar method was previously used by Ripson and de Galan [38] to measure transport efficiencies for nebulizer-spray chamber combinations. Physical properties of water, formic acid and acetic acid are provided in Table II.

2.4 Measurement of Excitation Temperatures

The excitation temperature of the plasma was measured using iron as the thermometric species using seven emission lines in the 370-377 nm region. The lines that were selected along with their spectral characteristics (λ_{pq} = wavelength of the emission line, g_p = degeneracy of the upper level (p), f_{pq} = oscillator strength value and E_q = excitation energy of the lower level (q) with respect to the ground state) are listed in Table III. The background subtracted emission intensities (I_{pq}) were substituted in Boltzmann distribution from which the slope log(2.303KT)⁻¹ was evaluated from the regression of ($I_{pq}\lambda^3_{pq}/g_pf_{pq}$) vs E_q . The excitation temperature T was evaluated from the slope. A detailed description of this method was published by Blades and Caughlin [39].





Solvent	Density (g/cm ³)	Boling point (⁰ C)	Surface tension (dyn/cm)	Vicosity (cP)
water	1.00	100	72.8	1.0
formic acid	1.15	101	43.4	1.5
acetic acid	1.05	118	34.3	2.6

Table II. Physical data of water, formic acid and acetic acid.

Wavelength (nm)	$(\lambda^{3}_{pq}/g_{p}f_{pq})$	$E_{\rm q}$ (cm ⁻¹)
371.99	1.38550e-13	26875
372.25	9.82936e-13	27560
373.48	2.55167e-14	33695
373.71	1.93916e-13	27167
375.82	5.30828e-14	34329
376.37	8.25802e-14	34547
375.19	1.16964e-13	34692

Table III. Fe (I) lines used for temperature measurement and relevant spectral data

2.5 Reagents

All analyte solutions were prepared in water and in 70 % (v/v) acid solutions. The concentration used was 100 ppm for both Mg and Cd. Mg solution was prepared by dissolving MgO (analytical reagent, MCB, Norwood, Ohio) in a minimum quantity of 1M HCl (analytical reagent, BDH, Toronto). Cd solution was prepared from CdCl₂ (laboratory grade, Fisher, NJ). The concentration used for Zn was 250 ppm. Zn solution was prepared from ZnCl₂ (analytical reagent, BDH, Toronto). 70 % (v/v) acid solutions were prepared using formic (general purpose, MCB, Norwood, Ohio), acetic (analytical reagent, BDH, Toronto) and propionic (general purpose, BDH, Toronto) acids.

Chapter 3

RESULTS AND DISCUSSION

3.1. Transport Efficiency Measurements

The introduction of solution into the plasma as a finely dispersed aerosol is the most common procedure for sample introduction in ICP-OES. The relative performance of various nebulizer/spray chamber configurations is assessed through comparison of analyte transport efficiency (defined as the percentage ratio of the amount of analyte reaching the plasma per unit time to the amount of analyte aspirated per unit time). Alternatively, efficiency of the same combination can be assessed by solvent transport efficiency (defined as percentage ratio of the amount of solvent reaching the plasma per unit time to the amount of solvent reaching the plasma per unit time to amount of solvent aspirated per unit time). Whether or not both of these approaches give the same value has been a controversy [40,41]. In order to avoid the ambiguity, in this thesis, measurement of efficiency of nebulization is simply called " transport efficiency ". A comparison of various methods of measuring of aerosol transport efficiency in atomic spectrometry has been published by Smith and Browner [42].

One approach to the measurement of transport efficiencies involves collection on silica gel [38,42]. In this procedure, the aerosol which is normally passed into the plasma is instead passed directly into a column packed with silica. The silica gel traps the solvent component of the aerosol with high efficiency, and weighing the column before and after the run gives the mass of aerosol reaching the plasma. This gives the solvent load (defined as the amount of solvent reaching the plasma per unit time) to the plasma because silica gel collects both aerosol and solvent vapour passing to the plasma. Provided that the amount of solution aspirated is measured, the transport efficiency can be calculated.

The measured transport efficiency for water and acetic and formic acids as a function of solution uptake rate is plotted in Fig. 3.1. According to the mean droplet diameters (Fig. 3.2) estimated by the Nukiyama and Tanasawa equation [31], for a given uptake rate, we would expect a decrease in transport efficiency for the acid solutions compared with water due to an increase in the mean droplet diameter. This is contrary to the increase in transport efficiency observed in the experimental data. Current understanding is that the Nukiyama and Tanasawa equation is only an empirical model for aerosol formation and has limited use in atomic spectroscopy nebulization systems [43]. In reality, primary droplets undergo modifying processes once formed and will have different properties from those arriving at the plasma. Fig. 3.3 is a plot of the solvent load reaching the plasma as a function of the solution uptake rate. The solvent load is significantly higher for formic and acetic acid relative to water. The data contained in Fig. 3.1 and Fig. 3.3 suggests that, at a fixed delivery rate, the mean droplet diameter is smaller for organic acids relative to water.

The droplet diameter or size may affect the emission intensity in two ways. The smaller the primary droplets, the higher will be the analyte and solvent load to the plasma. Any increase in analyte load (mass of analyte reaching the plasma per unit time) increases the emission intensity. The effect of an increase in solvent load (mass of solvent reaching the plasma per unit time) may either act to enhance the emission signal or depress it depending on the nature of the interaction of the solvent with the discharge. An increase in solvent load often has the effect of lowering the plasma excitation temperature in the aerosol channel [44-46]. Also, in low power plasmas larger droplets may not be completely desolvated during passage through the plasma.



Fig. 3.1. Transport efficiency as a function of uptake rate. • water, ● formic acid, □ acetic acid.



Fig. 3.2. Calculated primary median droplet diameter (d_s) as a function of uptake rate. \circ water, \bullet formic acid, \Box acetic acid.

Ξ.



Fig. 3.3. Solvent load as a function of uptake rate. O water, ● formic acid, □ acetic acid.

Both inorganic and organic acids have higher viscosities which result in lower free uptake rates than water. For the work reported in this thesis, the free uptake rate for water for was 0.8 mL/min compared with 0.5 mL/min for acetic acid. Inorganic acids show a reduction of analyte emission intensity relative to pure water. This result has been attributed to reduced analyte mass transport [5,8]. There must also be a change in the median droplet size since the interference cannot be eliminated by pumping the solutions at uptake rates the same as water [8]. In this study, it was found that organic acids enhance the analyte emission intensity compared with water. At a fixed delivery rate, organic acids produce smaller droplets compared with water, increasing the transport efficiency and creating a positive interference effect in the plasma. This observation is in agreement with Greenfield *et al.* [5]. However, the mechanism of interference due to organic acids is complex and is not simply a function of the analyte transport rate. The nature of the solvent and the solvent load play an important role in changing the plasma excitation conditions.

3.2. Vertical Emission Intensity Profiles

The effect of aspirating organic acid aerosols into the ICP on the emission intensities on atomic and ionic emission from Mg, Cd, and Zn has been studied. Since spatial effects have been shown to be important for interference effect studies on the ICP [3,4], the spatially resolved measurements were made along the plasma axis from 6 to 20 mm above the load coil. Fig. 3.4 (a-c) is a plot of the net emission intensity of Mg(I) as a function of height above the load coil for water and three organic acids. Figs. (a), (b) and (c) are for rf input powers of 0.75, 1.00 and 1.25 kW respectively. Fig. 3.5 (a-c) is that of Mg(II) for water and three organic acids. Figs. 3.7 (a-c) are the plots of net emission intensity of both atom and ion lines as a function of height above the load coil for water and three as a function of for cd and Zn in water and acetic acid respectively.



Fig. 3.4. Emission intensity of Mg (I) as a function of height above the load coil. o in water, o in formic acid, □ in acetic acid, ▲ in propionic acid. (a) rf power: 0.75kW, (b) rf power: 1.00kW, (c) rf power: 1.25kW.



Fig. 3.5. Emission intensity of Mg (II) as a function of height above the load coil. o in water, o in formic acid, □ in acetic acid, ▲ in propionic acid. (a) rf power: 0.75kW, (b) rf power: 1.00kW, (c) rf power: 1.25kW.



Fig. 3.6. Emission intensity of Cd (I) and Cd (II) as a function of height above the load coil. O Cd (I) in water, O Cd (II) in water, Cd (II) in acetic acid, ▲ Cd (II) in acetic acid. (a) rf power: 0.75kW, (b) rf power: 1.00kW, (c) rf power: 1.25kW.



Fig. 3.7. Emission intensity of Zn (I) and Zn (II) as a function of height above the load coil. O Zn (I) in water, ● Zn (II) in water, □ Zn (I) in acetic acid, ▲ Zn (II) in acetic acid. (a) rf power: 0.75kW, (b) rf power: 1.00kW, (c) rf power: 1.25kW.

Fig. 3.8 (a-c) is a graph of the interference (defined as the ratio between emission intensity in acid to that in water) for Mg in formic acid plotted as a function of height above the load coil. Fig. 3.9 (a-c) and Fig. 3.10 (a-c) are plots of the interference for Mg in acetic and propionic acid as a function of height above the load coil. Figs (a), (b) and (c) are for rf power of 0.75, 1.00 and 1.25 kW respectively. This shows that all three acids behave similarly. Fig. 3.11 (a-c) is a plot of the interference for Cd in acetic acid and Fig. 3.12 (a-c) is a plot of that for Zn.

Several observations can be made on the basis of the data presented in these plots. In general, ion lines are subject to a higher level of interference than atom lines. The interference tends to decrease for the ion lines as the rf power is increased; for atom lines the interference is relatively unchanged. There is some spatial dependence to the interference effect. The interference is larger at lower heights above the load coil. As a first approximation, changes in nebulization affect only the mass of analyte reaching the plasma per unit time. If the excitation conditions are not changed due to an increase in solvent load, we would expect the same magnitude of interference for atom and ion lines. The different magnitude of the interference for atom and ion lines shows that excitation conditions in the plasma changé.

As aerosol droplets enter the plasma discharge and progress through the aerosol channel, a variety of processes take place. First, droplets desolvate to yield solid salt particles. At the same time, these vaporizing droplets produce a large vapor load to the plasma and consequently undergo decomposition in the hot plasma environment. The presence of this vapor and its decomposition products can change the excitation conditions. Second, once desolvated, salt particles are vaporized and then dissociated producing atoms which are then ionized and excited in the aerosol channel. Atoms are ionized predominantly by electron collisions and should the presence of an organic acid change the



Fig. 3.8. Interference for Mg in formic acid as a function of height above the load coil. o Mg (I), ● Mg (II). (a) rf power: 0.75 kW, (b) rf power: 1.00 kW, (c) rf power: 1.25kW.



Fig. 3.9. Interference for Mg in acetic acid as a function of height above the load coil. O Mg (I), ● Mg (II). (a) rf power: 0.75 kW, (b) rf power: 1.00 kW. (c) rf power: 1.25kW.



Fig. 3.10. Interference for Mg in propionic acid as a function of height above the load coil. O Mg (I), ● Mg (II). (a) rf power: 0.75 kW, (b) rf power: 1.00 kW, (c) rf power: 1.25kW.



Fig. 3.11. Interference for Cd in acetic acid as a function of height above the load coil. O Cd (I), ● Cd (II). (a) rf power: 0.75 kW, (b) rf power: 1.00 kW, (c) rf power 1.25 kW.



Fig. 3.12. Interference for Zn in acetic acid as a function of height above the load coil. o Zn (I), ● Zn (II). (a) rf power: 0.75 kW, (b) rf power: 1.00 kW, (c) rf power 1.25 kW.

electron density or temperature, the ionization process will be changed. Therefore any changes in excitation conditions will lead to changes in both atom and ion populations in the plasma.

Several investigators have studied excitation temperatures with organic solvent introduction. In general, organic sample introduction requires an rf power increase of about 0.5kW to achieve similar performance to that found with aqueous sample introduction [47,48]. Blades and Caughlin [39] found that at a fixed power and height, the excitation temperature in the plasma is lowered when an organic aerosol is aspirated compared with an aqueous aerosol; an increase of power by approximately 0.5 kW is required to simulate the temperature reached in the aqueous ICP. Boorn and Browner [46] studied the effect of organic solvents on analyte emission and explained the emission characteristics when organic solvents are used compared with aqueous ones by a lowering of the temperature in the plasma. From that study, it is interesting to note that butanol and nitrobenzene which contain oxygen show a different behavior compared to hydrocarbons. However, a general feature of organic solvents is that they lower the plasma temperature. In flame atomic absorption spectrometry, an enhancement of signal is observed when organic solvents are used to introduce samples; this effect is attributed to an increase in temperature of the flame. For ICP-OES, however, solvent load control (aerosol thermostatting) is necessary to increase plasma stability and signal to background ratios [49]. In general, for organic solvents, a decrease in emission intensity is observed in the absence of solvent load control.

As has been observed, there is a difference in the interference for atom and ion lines and this suggests that excitation conditions in the plasma for organic acids are different from both water and other organics. One sensitive method for observing changes in excitation conditions in the ICP discharge is to measure ion-to-atom emission intensity ratios [35,50].

In this study, ion-to-atom ratios were chosen because they are independent of the aerosol generation and transport process. The ion-to-atom ratios can also be used to follow the plasma temperature based upon a relative scale without measuring the electron densities. Qualitatively, any increase of temperature results in an increase in ion-to-atom ratio for any analyte.

Fig. 3.13 (a-c) is a plot of the ion-to-atom emission intensity ratio for Mg in aqueous and formic acid solution for rf power of (a) 0.75, (b) 1.00 and (c) 1.25 kW. Fig. 3.14 (a-c) and Fig. 3.15 (a-c) are those for acetic and propionic acids respectively. Fig. 3.16 (a-c) is a plot of the ion-to-atom ratio for Cd and Fig. 3.17 (a-c) is plot of that for Zn. Ion-to-atom emission intensity ratios in organic acid aerosols are greater than those measured for water aerosols. This implies that the temperature is higher for organic acids than that in water. As power increases, ion-to-atom ratios in water increase. In contrast, the ion-to-atom ratios for organic acids remain relatively unchanged. Possible explanations for this behavior are that the aqueous droplets require a higher rf power to vaporize and dissociate compared with that of acid droplets or that the dissociation products from acid decomposition are less "energy absorbing" than those for water. Regardless, these ion-toatom ratio measurements further demonstrate that an increase in the temperature of the central aerosol channel is found when organic acids are aspirated.

3.3 Temperatures

Several workers have measured the temperature when alcohols are introduced. Huang [51] reported an increase in excitation temperature at 15 mm above the load coil compared to an aqueous plasma when a 50 % (v/v) ethanol-water mixture was aspirated. Kreuning and Maessen [52] reported a similar behavior for ethanol and methanol. They



Fig. 3.13. Ion-to-Atom ratio for Mg as a function of height above the load coil.
o in water,

in formic acid.
(a) rf power: 0.75 kW, (b) rf power:
1.00 kW, (c) rf power 1.25 kW.



Fig. 3.14. Ion-to-Atom ratio for Mg as a function of height above the load coil.
○ in water, ● in acetic acid. (a) rf power: 0.75 kW, (b) rf power: 1.00 kW, (c) rf power 1.25 kW.



Fig. 3.15. Ion-to-Atom ratio for Mg as a function of height above the load coil.
o in water,

in propionic acid.
(a) rf power: 0.75 kW, (b) rf power: 1.00 kW, (c) rf power 1.25 kW.



Fig. 3.16. Ion-to-Atom ratio for Cd as a function of height above the load coil.
o in water, ● in acetic acid. (a) rf power: 0.75 kW, (b) rf power: 1.00 kW, (c) rf power 1.25 kW.



Fig. 3.17. Ion-to-Atom ratio for Zn as a function of height above the load coil.
o in water,

in acetic acid.
(a) rf power: 0.75 kW, (b) rf power: 1.00 kW, (c) rf power 1.25 kW.

explained the observed behavior as due to the difference in solvent load for water, methanol and ethanol.

Plasma background results from continuum emission which is a consequence of radiative recombination; it is related to both the electron number density and the electron temperature [36]. Fig. 3.18 (a-c) is a plot of the background emission as a function of height above the load coil for water and formic, acetic and propionic acids at rf powers of 0.75, 1.00 and 1.25 kW respectively. Background emission was monitored in the wavelength region between 430 and 450 nm and was corrected for dark current in the diode array. 70% (v/v) acid solutions were used and aspirated at 0.8 mL/min uptake rate. For the three rf powers studied, there was an enhancement of background between 4-10 mm above the load coil and decreased with increasing height above the load coil. This suggests that the aerosol from organic acids increases either the electron density or temperature, or both, lower in the plasma.

Molecular band heads due to organic solvents in plasma have been reported by several investigators [46,53,54]. Only three very weak, C_2 bands were found in the wavelength region between 430 and 450 nm and the possibility of any spectral overlap is excluded due to (i) the observed enhancement of background for formic acid (ii) the observed increase in background as power increases (iii) propionic acid (with relatively high carbon percentage) shows almost the same background emission as formic acid.

The results of excitation temperature measurements using aqueous and acid sample introduction are given in Fig. 3.19. At lower than 12 mm above the load coil, using 0.75 kW input power, there is an apparent increase in excitation temperature for organic acids compared with aqueous sample introduction. There is no significant difference at higher powers. This behavior is in general agreement with ion-to-atom emission intensity ratios found for analytes studied. Fig. 3.19 suggests that acid introduction results in



Fig. 3.18. Background emission intensity as a function of height above the load coil.
o in water, ● in formic acid, □ in acetic acid, ▲ in propionic acid.
(a) rf power: 0.75 kW, (b) rf power: 1.00 kW, (c) rf power 1.25 kW.



Fig. 3.19. Fe (I) excitation temperatures as a function of height above the load coil.
(a) rf power: 0.75 kW, O in water, ● in acetic acid. (b) rf power:
1.25 kW, □ in water, ▲ in acetic acid.

a decrease in temperature beyond 12 mm above the load coil. This observation is in contrast to the observation that appreciable differences in ion-to-atom ratios (with and without organic acids) are still found beyond 12 mm above the load coil. It should be noted that it has been demonstrated that the ICP is not in LTE so that the ionization temperature and excitation temperature can be at different values. In this case, the ion-to-atom ratios are a measure of the ionization temperature. It is possible that the excited state distribution is less affected by acid introduction than the ionization equilibrium. Detailed measurements of electron number densities should be carried out.

Spectral observations have indicated that the efficiency of nebulization and the chemical make-up of the central aerosol channel are different when organic acids are introduced as compared with aqueous introduction. The increase in efficiency of nebulization leads to an enhancement of emission intensity and an increase in solvent load to the plasma for the organic acid compared with water. The increase in efficiency of nebulization is due to the physical properties of organic acids, such as the surface tension, which play an important role in the nebulization. The nature and amount of solvent introduced into the plasma changes the plasma excitation conditions. In the plasma with aqueous aerosol, the most abundant molecular constituent between 0-10 mm above the load coil is OH [39]. In a plasma with organic aerosol, the most abundant molecular constituent is probably C_2 [55]. In general, a so called "organic aerosol" represents the hydrocarbons (aliphatic or aromatic), halogenated hydrocarbons and other compounds with high carbon percentage. During the process of dissociation, these molecular carbon species absorb energy from the plasma and affect the thermal conductivity of the plasma. The total thermal conductivity [9] of the aerosol channel is composed of conductivity due to:

(i) the motion of atoms, molecules, and electrons.

(ii) transport of energy via molecular dissociation and ionization.and, (iii) thermal diffusion.

It is the second factor that leads to a reduction in temperature and electron density in the central aerosol channel for the organic plasma [9]. For organic compounds containing relatively large amounts of oxygen, molecular C_2 is not the most abundant species in the plasma. Kreuning and Maessen have [52] have reported that the maximum C_2 emission for chloroform is about twenty times greater than that for methanol for the same carbon load. They explained this observed intensity difference as due to the formation of stable carbon monoxide. Carbon monoxide formation has been reported by several other investigators [54-56] when oxygen was added to the nebulizer gas flow. Organic sample introduction is more critical in low power argon plasmas, but the effects can be mitigated by adding 5-15 % oxygen to the coolant gas [48].

Chapter 4

CONCLUSIONS

Previously, it has been reported that the interference effect of organic acids is mainly due to changes in transport properties. Measurement of transport properties, vertical intensity profiles of analytes and excitation temperatures for organic acids shows that it is not only the transport properties but also the nature of solvent and its decomposition products that contributes to the emission characteristics of the analytes. First, organic acids increase the aerosol transport efficiency to the plasma . Second, organic acid aerosols do not modify the plasma temperature as much as a water aerosol does, thus the temperature (and electron number density) is slightly higher in the central aerosol channel, leading to a differential behavior for ion and atom lines and higher ion-to-atom emission intensity ratios than are observed for water aerosols. This is contrary to the reported observation with so called "organic solvents".

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PART TWO

SEMI-AUTOMATED STUDY OF THE EFFECTS OF ANALYTE AND INTERFERENT CONCENTRATION IN ICP-OES BY FLOW INJECTION ANALYSIS

Chapter 5

INTRODUCTION

5.1 Objective

The usual methodology of Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) is continuous input of sample for a certain time and measurement of an averaged emission intensity. This approach can be considered a static or steady state measurement process. In recent years, use of ICP for dynamic measurements has rapidly increased. An example is "microliter sample introduction", for which the input is not a continuous stream of sample, but a pulsed injection of a limited amount of sample. The response of the ICP is then not a static intensity level, but a dynamic peak-shaped signal. A similar process is flow injection analysis [1].

It is apparent from most Flow Injection Analysis (FIA) publications that analytical readouts are overwhelmingly derived from measurement of peak height at the peak maximum, possibly because this is the easiest to identify, but perhaps also for lack of realization of the enormous potential of the concept in hand. Flow injection creates a well defined concentration gradient of the injected sample plug within the carrier stream containing a virtually infinite number of different concentrations. However with peak maximum measurement only one of them is exploited.

Part two of this thesis presents a study of the feasibility of using FIA to investigate the interference effects of acetic acid over a wide range of analyte and interferent concentrations in a semi-automated fashion^{*}. This FI-ICP procedure makes use of the concentration gradient formed by the analyte in the FI system. Use of concentration gradients formed by flow injection is described and discussed.

^{*} Part of this work was presented by the author at Fifteenth Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACCS), Boston, Massachusetts, October 30-November 4, 1988.

5.2 History of Flow Injection Analysis

In 1957, Skeggs's [2] concept of a continuous, air segmented flow gave rise to the widespread use of continuous flow systems for performing discrete chemical analysis. Thus, it became generally assumed that air segmentation and the attainment of the "steady state " signal were essential prerequisites for performing continuous flow analysis.

In 1958, Spackman *et al.* [3] described the first semi-automated amino acid analyzer. This apparatus was the prototype of the modern high-performance liquid chromatograph. As the effluent stream came off of an ion exchange column, it was mixed with ninhydrin reagent (also pumped) to form Ruhemann's purple. This mixture then flowed through small-bore tubing which was immersed in a boiling water bath. After emerging from the reaction bath, the solution entered the flow-cell of a colorimeter, the output of which was recorded on a strip chart recorder. The concentrations of the amino acids were determined by measuring the area under the peak on the chart recorder trace. This was the first use of unsegmented continuously flowing streams for analysis of discrete samples. Very little work was done to further develop the continuous flow analysis until the beginning of 1970.

In 1970, Nagy *et al.* [4] reported the use of graphite electrodes for the voltammetric measurement of samples injected into a continuously flowing stream. Their system involved injecting samples into an unsegmented continuously flowing carrier stream and passage of the sample zone through a magnetically stirred mixing chamber, followed by a silicone-rubber-based graphite electrode. The resulting analytical readouts were in the form of transient peaks. There is no doubt that this paper described an early version of the flow injection analytical technique.

In 1972, several papers appeared which provided critical concepts for flow injection analysis. These include a method for enzymatic analysis by Bermeyer and Hagan [5] and determination of ascorbic acid by the photobleaching of the ascorbic acid-methylene blue complex by White and Fitzgerald [6]. Gerding *et al.* [7] devised a sensitive detector system for peptides and proteins in column effluents. These workers developed an unsegmented continuous-flow system using small-bore tubing, very slow delivery syringe pumps and a valving system with two sample loops to transfer samples from chromatographic effluents to a reaction stream while maintaining a flow in each stream. The most interesting feature of this paper was their discussion of dispersion in small-bore tubing. They found that when the internal diameter of the tubing used is very small and very low flow rates used, no segmentation is necessary.

In 1973, Frantz and Hare [8] described a system for the determination of silica at submicrogram levels by use of an unsegmented continuous-flow system. In 1974, Feher and Pangor [9] continued their work on the use of the system they described in 1970 [4].

In 1974, Ruzicka and Hansen [1] in Copenhagen, Denmark and Stewart *et al.* [10,11] in Washington, D.C., United States independently performed similar experiments of injecting samples directly into an unsegmented carrier stream, and they proved that analysis without air segmentation is not only possible but also advantageous. Ruzicka's paper was the first to use the term " flow injection analysis ".

A U.S. patent granted to Ruzicka and Hansen [1] described the injection of discrete samples into a continuously flowing carrier stream for subsequent reaction and detection. The patent makes several claims about turbulent flow in flow injection analysis, which have since been questioned and refuted [12-15].

65[·]

A number of requirements must be met to accept a new technique. The pioneers in the field must publish their findings, an appropriate theory must be established and commercial instruments must be developed and sold. Advocates of the system must talk and write about the system at every opportunity. Many of these requirements were well on the way to fulfillment by the end of 1977. The number of papers on FIA was increasing and new workers were entering the field. Work on the theory had been started and several manufacturers entered the field. A number of early researchers were lecturing extensively, especially Ruzicka and his co-workers.

Since 1977, hundreds of variations and applications have been reported in the literature, with an exponential growth in recent years [16]. The majority of papers have dealt with spectrophotometric techniques. A significant fraction of the applications to atomic spectroscopy are in atomic absorption. Only recently have applications to plasma spectroscopy appeared. This is further discussed in section 5.7.

The sole reason for automation of chemical analysis is the need to analyse a large number of samples rapidly and reliably with a minimum expense of labour and chemical reagents. This is indeed so in most clinical and many industrial laboratories. The versality and simplicity of the FI system led to high sampling throughput and instant availability of the analytical readout with minimum expense. Therefore, FIA became increasingly accepted as an automated or semi-automated method in agricultural, clinical, pharmaceutical industrial and environment analyses [16].

5.3 Flow Injection Analysis

The term " flow injection analysis " was coined over a decade ago [1] to describe the technique of injecting a small liquid sample plug into an unsegmented carrier stream. The



Fig. 5.1. Schematic diagram of a single line flow injection (FI) manifold with corresponding recorded FI peak. S = sample injection, D = detector, t = residence time.

simplest single line FI system (Fig. 5.1) consists of a tubular channel connecting a reservoir of liquid (to form a carrier stream) with a flow-through detector. The carrier stream is driven at a constant flow rate through the channel by means of a peristaltic pump (syringe pumps, gravity feeds or gas pressure have been used as well). A volume of sample (S) is injected into the carrier stream by means of a valve. From the point of injection, this well-defined sample plug moves through the channel and undergoes some dispersion and mixing with the carrier on its way towards the detector (D). Therefore, the detector senses the concentration gradient formed by the mutual dispersion of sample and carrier stream solutions as a transient signal - a peak. The channel dimensions, injected sample volume, and flow rates are selected in a such a way that a sampling cycle lasts typically 15-30s.

The technique of FIA is rigorous and dependent on two primary factors:

1. Sample injection

2. Reproducible timing

The amount of sample injected need not be accurately known but it has to be injected with high precision so that the volume and length of the sample zone at the point of injection is reproducible. Injected volumes may vary from a microliter or so to a milliliter. Also, depending on the application, FI systems may be designed to dilute or to preconcentrate the analyte on-line so that its concentration falls within the dynamic range of the detector used.

. Timing has to be reproducible because the chemical reactions employed are very seldom allowed to reach equilibrium. Therefore, any imprecision in residence time of the sample on its way to the detector will be reflected in the readout. It is obvious that in a simple case where a dye is injected, an increase in dispersion will cause a decrease in peak

height. However, in a case where a reaction is developed as a result of the mixing effected by dispersion, the peak height will increase as the reaction proceeds towards completion. The maximum response will be attained when an optimum balance is reached between dispersion and reaction time. Therefore, only when the rate of decrease in response due to dispersion exceeds the rate of increase in response due to reaction will the signal begin to decrease.

Qualitatively, dispersion may be considered as being limited, medium or large. Limited dispersion conditions can be chosen to feed detectors such as electrodes and atomic spectrometers to effect high sampling throughput. Limited dispersion is also used in atomic spectrometry to analyse samples with a very high salt content, which, when aspirated continuously in a traditional manner, would block the nebulizer. In the FI mode, the sample zone is preceded and followed by carrier stream which provides effective rinsing. Medium dispersion can be applied to attain a wide variety of reaction conditions to develop some detectable entity such as color, fluorescence or an electro-reactive product. Finally, large dispersion can be utilized to develop a substantial degree of mixing between sample and carrier stream to form a well develop concentration gradient. This is necessary when performing continuous flow titrations or investigating the chemistry of the concentration gradient in the stream.

A more detailed account of the FIA and associated analytical procedures is available in an excellent book by Ruzicka and Hansen [16].

5.4 Dispersion in FIA

It is beyond the scope of this thesis to go into detail on the theory of flow conditions in FIA, yet a brief discussion is warranted.

The actual flow conditions obtained in FIA have been the subject of much investigation. While it was originally thought that turbulent flow is present [1,17], it was subsequently determined that FIA operates under laminar flow conditions [14,15]. The dispersion is brought about partly by convection (axial dispersion) and radial diffusion. The relative importance of these processes depends upon the sample volume, the tubing length and radius, flow rate, time of the analysis and magnitude of the diffusion coefficient. All of these will be reflected in the height, width and shape of the peak observed. Some guidelines that assist in method development of new FI procedures have been given by Ruzicka and Hansen [15]. However, their suggestions are valid only for cases where either diffusion or convection is dominant in the dispersion process.

In reality, the flow conditions under which most FI systems operate cause dispersion through both diffusion and convection. Vanderslice *et al.* [18] have demonstrated that FI systems can be described in terms of a convection-diffusion equation. These are related to the diffusion and convection processes which operate in the laminar flow region where FI experiments are generally carried out. They also confirmed that it is radial rather than axial dispersion that determines the sample band spreading. Radial dispersion operates to move the fluid both toward and away from the tubing walls and thus serves as an efficient scrubbing mechanism. This concept is critical in understanding the low carryover and cross-contamination exhibited between samples proceeding in an unsegmented stream.

Since the radial dispersion occuring in the time frame of an FI experiment is not sufficient to offset the axial dispersion initially formed during sample introduction, the peak shape observed in FI are typically Gaussian or skewed Gaussian. Thus, some peak tailing is normally observed.

Although it has been pointed out that "..... the comprehensive theory of the flow injection method will eventually combine the theory of mixing of liquids in continuously moving stream with the theory of chemical kinetics " [15], the effects of chemical kinetics have been largely ignored and most attention has been given to dispersion alone. The occurrence of chemical reactions, however, can alter the spontaneous process of concentration equalization (described by diffusion) and the mass transfer by movement of the system as a whole (known as convection). Chemical reactions can alter the concentration profile which in turn leads to changes in diffusion and convection and these then alter the collisional frequency that governs the chemical reaction. This interdependence defines the complexity of the description of dispersion in FI in purely physical terms, since in the unsegmented flow systems, all measurements are made under non-equilibrium (kinetic) conditions.

5.5 Repeatable Concentration Gradients

One of the fundamental principles of FI methodology is repeatable dispersion of the sample in the carrier stream as the sample moves from the injection point to the detector. The factors which influence dispersion are flow rates, injected sample volume, viscosity, temperature, tube dimensions, manifold design (confluences, splits, coiling *etc.*) together with detector characteristics and injection method. For time-based FI procedures, reproducible measurement of a selected portion of the dispersed sample zone can only be achieved if all operating parameters remain constant and synchronization of injection with data acquisition has been arranged.

When a flow injection procedure is based on peak-height measurements, one may imagine that the selected signal represents a continuum of concentration between zero and C_{max} as given in Fig. 5.2 (concentration is represented by the height of the peak). Since dispersion of the sample zone can be strictly controlled and reproduced from one measuring cycle to the next with high precision, any element of fluid along the gradient corresponds to a fixed dispersion value, D. Thus the dispersion coefficient (D_t) of the injected sample at any time delay (t) is equal to $C_s/C_{s(t)}$, where C_s is the initial sample concentration and $C_{s(t)}$ is the concentration after time t. D_t is not called a dilution factor because the dispersed sample zone is nonhomogeneous, since it is a portion of a continuous gradient. It is also imaginary since its concentration is obtained via a detector readout, which in turn depends on the characteristics of the detector.

The principle of gradient dilution [19] is based on selection of any point other than the peak maximum (C_{max}). Each point along the dispersion sample zone will be characterized by a fixed D_t value, corresponding to a fixed delay time t (Fig. 5.2). The response and the calibration curves obtained from data collected at fixed delay times are linear, provided the analytical readouts are always taken at exactly the same time after the point of injection. This method is illustrated in Fig. 5.3. To a borate carrier stream, 160 μ L of bromothymol blue (BTB) solutions at four different concentrations were injected, giving the highest peak, described as 100 %. Four injected dye samples give a set of straight lines with the slope decreasing with increasing delay time. This means that the readout, which is usually obtained from maximum peak height, may be replaced by the readouts collected at any other point of the peak, provided that they are always taken using exactly the same delay after the time of injection.



Fig. 5.2. Dispersed sample zone of initial concentration C_s at time t_0 , and the corresponding recorder output. (For details, see text.)



Fig. 5.3. The principle of the gradient dilution technique. The recorder output for a series of injected dye (BTB) solutions - the most concentrated one being denoted by 100 % - and the corresponding calibration curves obtained at different delay times (Reprinted with permission from S. Olsen, J. Ruzicka and E.H. Hansen, "Gradient Technique in Flow Injection Analysis ", Anal. Chim. Acta, 136, 101 (1982). Copyright (1982), Elsevier Science Publishers, Amsterdam).

The gradient calibration technique [19] depends on the same phenomenon: reproducible dispersion. Its main goal is repetitive calibration using serially injected solutions, as the information sought is in fact already contained within segments of the sample zone of the most concentrated sample material. This is illustrated in Fig. 5.4. The highest concentration value (C_{max}) can be supplemented by a series of sequential C values spaced along the gradient and identified through increasing delay time. For each peak height obtained in the conventional way, a certain delay time can be identified on the tail section of the single recorded peak. This can be done most conveniently by describing the relationship of concentration as a function of delay time and is obtained from normal calibration and stored by a computer. Both gradient dilution and gradient calibration are practical only with the aid of a computer, which acquires data, identifies the t values and constructs and checks the calibration from a single injection.

5.7 Use in Emission Spectrometry

In 1980, Ito *et al.* [20] published the first application of FIA to ICP spectroscopy. A line sample injector was attached to a coventional glass concentric nebulizer, into which 40 μ L of sample solution was injected with a microsyringe. In order to prevent the sample being diluted with carrier stream, the sample was injected into an approximately 50 μ L air bubble, formed by lifting the end of the carrier tubing above the water for a short time. Peak intensities were about 65 % of the intensities obtained by continuous nebulization, but detection limits were five times higher than that of those conventional methods. Jacintho *et al.* [21] examined some fundamental considerations of FIA-ICP. They determined that the peak profiles measured with the spetrophotometer correspond closely with the true sample zone distribution near the inlet of the spectrometer, estimated by a zone sampling process, illustrating that the plasma is not a limiting factor in signal distortion.



Fig. 5.4. The principle of the gradient calibration technique. The recorder output for a triplicate injection of four different concentrations (25 to 100 % of a stock solution) of dye (BTB) solution and shown as a calibration run on the left-hand side. The recorder output of a single injection of the 100 % BTB stock solution is reproduced on the right-hand side, the four concentration levels corresponding to delay time t₁ to t₄. (Reprinted with permission from S. Olsen, J. Ruzicka and E.H. Hansen, "Gradient Technique in Flow Injection Analysis ", Anal. Chim. Acta, 136, 101 (1982). Copyright (1982), Elsevier Science Publishers, Amsterdam).

Greenfield [22] published a detailed account of the properties and advantages of the transient emission signal as achieved in FIA, and applied the technique to an analysis of Portland cement. Lawrence *et al.* [23] studied the efficiency limitations which have been attributed to the large dead volume and sample losses associated with conventional nebulizers and peak broadening from FI tubings. La Frieniere *et al.* [24] performed a critical comparison of direct injection with conventional pneumatic and ultrasonic nebulizers and concluded that under optimized FIA conditions, the direct injection nebulizer is comparable to or better than the others with respect to detection limits and reproducibility. Horner *et al.* [25] studied the interference effect of easily ionizable elements in theICP in a semi-automated fashion, using a gradient-based technique developed in this laboratory.

Applications of ICP coupled with FIA are becoming more numerous. Multi-element analysis [26,27], hydride generation [19,27-29], separation and preconcentrations [30-32], have all been recently reported.

Chapter 6

EXPERIMENTAL

6.1 Instrumentation

The flow injection manifold used was constructed as given in Fig. 6.1. This manifold consists of a peristaltic pump (model C4V, Alitea, Seatle, WA) and six port sample introduction valve (model 5020P, Rheodyne, Cotati, CA) with pneumatic actuator (model 5701, Rheodyne, Cotati, CA) driven by solenoid valve (model 7163, Rheodyne, Cotati, CA). The sample introduction valve was interfaced with the data acquisition system. This was done by using Port C of the 8255-IC of PXB 721 parallel expansion boad (Qua Tech, Akron, Ohio) of the data acquisition system. Acidflex flow rated pump tubing (Technicon, Tarrytown, NY), 0.8 mm i.d. Teflon^R tubing and 1/4 inch low pressure chromatography fittings (Omnifit, Atlantic Beach, NY) were used throughout.

Analyte, carrier and interferent were pumped at 0.8 mL/min and the total flow rate to the nebulizer was 1.6 mL/min. 70 μ L of analyte was injected with a fill time of 60 s and an inject time of 60 s. The tubing length from the valve to the mixing tee and from the tee to the nebulizer were 50 cm and 4.5 cm respectively. The length of the nebulizer used was 6.5 cm.

A complete description of the ICP is given in the section 2.1 in Chapter 2. Only the experimental parameters used are given here. For all experiments, an rf power of 1.00 kW was used. The outer gas flow rate was 10 L/min, the inner gas flow rate was 0.2 L/min and the nebulizer gas flow rate was 1.3 L/min. The emission wavelengths monitored were 325.03 nm for Cu(I) and 279.55 nm for Mg(II). The plasma was viewed at a height of 8 mm above the load coil. The entrance slit used was 50 µm wide and 2 mm high. The





imaging distances for Cu and Mg were 28.9 and 28.1 cm respectively. The integration time used were 50 and 60 units (1 unit is equal to 0.0089 s) for Cu and Mg respectively.

6.2 Method

The first step in setting up this system (FI-ICP) was synchronization of the timing of the FI system with the data acquisition system (ICP). Fig. 6.2 gives the relationship between these two systems. The first time selected was the " fill time " (the time taken to fill the sample loop of the sample introduction valve). During this, the carrier stream bypasses the valve and preflushes the ICP while the sample loop is filled. The second time selected was the " inject time " (the time taken to introduce the sample into the carrier stream). During this, the sample stream bypasses the valve and goes to waste. Computer data acquisition was synchronized with a manually triggered injector valve. Therefore, computer data aquisition was simultaneous with injection of the sample. The third time selected was the " data acquisition time ". The transient signal generated by a 60 s inject time requires at least a 60 s time window, so as to accommodate band broadening caused by dispersion of the sample zone between the point of injection to the tip of the nebulizer. After a 60 s inject time, the valve was turned back to the fill position. After the data acquisition was completed, the data were stored on a 5.25 inch floppy disk.

A 100 ppm analyte solution was injected into the water carrier stream. Analyte then merged with the interferent stream which contained 0-99 % (v/v) acetic acid. The resulting mixture then entered the ICP. When interferent was absent (*i.e.*, 0 % acetic acid), the experiment was called the "reference experiment". When any finite concentration of interferent was present, then it was called the " interferent experiment ". Seven to ten replicate injections were done for each of different interferent concentrations. Finally, the



Fig. 6.2. Synchronization of the flow injection system with ICP.

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dispersion of the flow injection system was characterized. This was done by filling the entire flow injection manifold with analyte standards of 0, 10, 20, 30, 40 and 50 ppm and measuring the steady state emission intensity.

6.3 Data Acquisition

Operating software written in Turbo Pascal (Borland International, Scotts Valley, CA) was available and was modified to interface with the injector valve. Diode numbers were chosen which best represented the analytical lines of interest. This was done by aspirating the analyte sample and solvent separately. Thus, background subtracted emission intensities were due to analyte emission only. The ICP system allows one to observe a 40 nm wavelength window, spread over 4096 diodes (see section 2.1). One FI peak (one injection) was stored in one data file. Each data file contained a maximum of 200 data points per diode to represent the data acquisition time, to a maximum of 50 diodes out of 4096 diodes. In addition to analyte lines of interest, several diodes were selected for measurement of background.

6.4 Data Processing

An overview of the data processing stages is given in Fig. 6.3. Data averaging software was written in MicroSoft QuickBasic, Ver 3.0 (MicroSoft, Mississuga, ON, Canada). The output files were produced in simple ASCII format with the diode number, data point number and averaged emission intensity for each data point. Diode selecting software was also written in QuickBasic. This allows several diodes to be summed or averaged together to produce a single higher precision data file for further processing. Data averaging and diode selecting programs are provided in Appendix B.



Fig. 6.3. Overview of the data processing stages.

Data processing software written in MicroSoft QuickBasic, Ver. 3.0 was available [25]. All QuickBasic programs were run on a 12 MHz PC/AT^R compatible microcomputer (NORA systems, Vancouver, B.C.). A calibration curve for analyte concentration was obtained from the emission intensities observed for the analyte standards in the absence of interferent. The averaged peak obtained by replicate injection of 100 ppm without interferent (the reference experiment) was then calibrated to represent the concentration gradient formed by the dispersion of the sample. Therefore, the analyte concentration and emission intensity were known at any time after the start of the data acquisition.

Since all the operating parameters remained constant throughout the experiment and data acquisition was synchronized with the injection, dispersion of the analyte in the FI manifold with and without interferent was assumed to be constant. Correlation of the file from each interferent experiment with that from the reference experiment was used to obtain the emission intensity observed for each analyte concentration at each interferent concentration. The program then gives the following options of data files to be displayed:

1. The absolute response (no transform): $R = I_E$

2. The deviation from the response when interferent is present: $R = I_E - I_A$

where I_E is the emission intensity of analyte with interferent and I_A is the emission intensity of analyte without interferent. The program then produces an output file for display using SURFER^R (Golden Software, Golden, CO) 3D graphics/plotting package.

6.5 Reagents

A 1000 ppm Cu stock solution was prepared by dissolving $CuSO_4$. $5H_2O$ (analytical reagent, BDH, Toronto, Canada) in deionized water. Analyte standard solutions of 0, 10,

20, 30, 40, and 50 ppm were obtained by appropriate dilution with deionized water. A 1000 ppm Mg stock solution was prepared by dissolving MgO (analytical reagent, MCB, Norwood, Ohio) in a minimum quantity of 1M HCl (analytical reagent, BDH, Toronto, Canada) and making up to the volume by deionized water. Mg standard solutions were prepared as described for Cu. The sample carrier stream was deionized water. Solutions containing 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 99 % (v/v) of acetic acid (analytical reagent, BDH, Toronto, Canada) were prepared by appropriate dilution with deionized water.

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Chapter 7

RESULTS AND DISCUSSION

All gradient techniques in FI procedures are based on the reproducible dispersion from the injection point to the detector. The factors which control dispersion are flow rates, volume injected, tube dimensions, manifold design, together with detector characteristics and injection method. Physical properties of the sample and carrier stream solutions such as viscosity, diffusion coefficient, temperature *etc*. of liquids also play a role. As all experimental parameters and physical properties of liquids remained constant from one injection to another, dispersion is repeatable.

In order to improve precision and to minimize the effect of noise originating from the peristaltic pump and diode array system, replicate injections were made. Fig. 7.1 (a-f) is the plot of an averaged peak corresponding to ten injections of 100 ppm Cu as an analyte at six different interferent concentrations. Fig. 7.2 (a-k) is the plot of an averaged peak corresponding to seven injections of 100 ppm Mg as an analyte at eleven different interferent concentrations. Ideally for any detector, the FI response should be a smooth function of time. Some noise is still visible even after averaging several peaks as can be seen from Fig. 7.1 and Fig. 7.2.

Maintaining a constant flow rate to the nebulizer is important in conventional FI-ICP procedures. In the usual methodology of ICP, the effect of imprecision of liquid flow rate to the nebulizer can be minimized by signal averaging. In FI-ICP, the detector senses the concentration gradient formed by the sample plug as a transient signal. In a such a situation use of a long integration time and/or signal averaging within one sample injection is not possible. Therefore, use of a pulse free pump such as a syringe pump may be an





Fig. 7.1 (continued). The FI averaged peak corresponding to ten injections of 100 ppm Cu as an analyte at different acetic acid concentrations: (a) 0 % HOAc, (b) 20 % HOAc, (c) 40 % HOAc, (d) 60 % HOAc, (e) 80 % HOAc and (f) 99 % HOAc.











Fig. 7.2 (continued). The FI averaged peak corresponding to seven injections of 100 ppm Mg as an analyte at different concentrations of acetic acid: (a) 0 % HOAc, (b) 10 % HOAc, (c) 20 % HOAc, (d) 30 % HOAc, (e) 40 % HOAc, (f) 50 % HOAc, (g) 60 % HOAc, (h) 70 % HOAc, (i) 80 % HOAc, (j) 90 % HOAc and (k) 99 % HOAc.

alternative. Another alternative would be to connect the speed control of the peristaltic pump to a very accurate and precise flow rate meter in a sample feed back loop.

Constant dispersion of the sample with and without interferent was maintained by the FI manifold design. The length of tubing from injection point to the mixing tee is ten times the length of the tubing from the mixing tee to the tip of the nebulizer. In a such a situation, dispersion predominantly occurs in the length of tubing before the mixing tee rather than after the mixing tee. An investigation was made to determine if any change in dispersion characteristics of sample zone from mixing tee to the nebulizer was caused by the presence of interferent. Fig. 7.3 (a-e) is the plot of normalized emission intensity with and without interferent for Cu. Fig. 7.4 (a-j) is the normalized peak emission intensity with and without interferent for Mg. Fig. 7.3 and Fig. 7.4 show that, for both analytes, there is a slight shift in the peak maximum as interferent concentration increases. The maximum shift in peak maximum is four data points corresponding to a delay of 1.8 s for Cu and three data points corresponding to a delay of 1.6 s for Mg at 99 % (v/v) acetic acid. One possible explanation for this is a decrease in flow rate of the carrier stream due to an increase in viscosity and/or changes in the dispersion characteristics of the sample zone when higher concentrations of acetic acid are present. The flow rate drop in the sample carrier stream can be minimized by use of two independent pumps for each channel and flow rate calibration by weight loss of the carrier reservoir rather than by measuring the weight passed to waste. This change in dispersion characteristics can be further minimized by reducing the length of the nebulizer. As the length of the nebulizer was fixed, this would need a change in the nebulizer design.

Fig. 7.5 gives normalized FI peak profiles with (99% acetic acid) and without interferent. The peak without interferent is shifted so that the peak maxima will coincide. For Cu as an analyte (Fig. 7.5 (a)), there is an apparent broadness of the peak





Fig. 7.3 (continued). The normalized FI peak with and without acetic acid for Cu as an analyte: _____ in water, - - - in acetic acid. (a) 20 % HOAc, (b) 40 % HOAc, (c) 60 % HOAc, (d) 80 % HOAc and (e) 99 % HOAc.






Fig. 7.4 (d-f). (continued)







Fig. 7.4 (continued). The normalized FI peak with and without acetic acid for Mg as an analyte: _____ in water, - - - in acetic acid. (a) 10 % HOAc, (b) 20 % HOAc, (c) 30 % HOAc, (d) 40 % HOAc, (e) 50 % HOAc, (f) 60 % HOAc, (g) 70 % HOAc, (h) 80 % HOAc, (i) 90 % HOAc and (j) 99 % HOAc.



Fig. 7.5 The FI peak corrected for viscosity effects of interferent in flow injection manifold. _____ in water, - - - in 99 % (v/v) acetic acid. (a) Cu emission intensity (b) Mg emission intensity.

with interferent compared to that without interferent. But, for Mg as an analyte (Fig. 7.5 (b)), there is no apparent broadness of the peak with intereferent compared to that without interferent. These observations may be attributed to the changes in the plasma conditions and/or changes in dispersion characteristics of the FI manifold in the presence of acetic acid.

Fig. 7.6 is a plot of the background subtracted emission intensity as a function of interferent and analyte concentration for Cu and Fig 7.7 is that for Mg. Fig. 7.8 is a plot of the net emission enhancement as a function of interferent and analyte concentration for Cu and Fig. 7.9 is that for Mg. Dispersion of the Cu and Mg samples in the FI system was such that the injected 100 ppm analyte standards reached the ICP as maximum concentrations of approximately 30 and 21 ppm of Cu and Mg respectively. It is apparent from the above plots that interference effect increases with increasing interferent concentration and is non-linear. The effect of the analyte concentration is linear.

These interferences are due to combined effects of variation in nebulizer performance produced by the physical properties of the sample solution and the changes in the excitation conditions in the plasma caused by acetic acid. Such interference effects from organic acids are discussed in Chapter 3. In addition, further complications are observed which arise from changes in dispersion characteristics in the F1 manifold in the presence of viscous interferent. These interferences can be characterized by the mathematical modelling of the interference surface which is beyond the scope of this thesis.

Several improvements over the previously described FI-ICP system [25] merit comment. The new FI-ICP system described in this thesis makes use of a minimum of 150 data points per FI peak (one data file) compared to a maximum of 200 points containing 5 to 10 peaks (one data file). The synchronization of injector valve with data acquisition gives better signal-to-noise ratios by peak averaging. The use of multiple diodes eliminates the noise originating from diode shifts observed over the course of a long run.

Full automation of whole procedure is needed. This will facilitate computer controlled dilution of the analyte and interferent stock solutions and result in the need for manual preparation of just two solutions to carry out the entire set of experiments described above. In a such an experiment, the computer should be able to introduce known quantities of interferent by controlling the liquid flow rates. Then it should be able to inject the sample and acquire the data for user defined time intervals, and average the FI profiles for one set of interferent concentrations.



Cu as an analyte.



.

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for Mg as an analyte.





Fig. 7.9. Plot of emission enhancement as a function of interferent and analyte for Mg as an analyte.

Chapter 8

CONCLUSIONS

The flow injection gradient techniques can be considered as "solution robotics " since they effectively carry out the preparation and automated introduction of many analyte concentrations from one injected concentration of the sample. In an interference study such as this, the effect of analyte concentration can be determined by a minimum preparation of analyte solutions. It reduces the amount of time spent on the collection of the data since far fewer than the n * m solutions containing varying concentrations of analyte (n levels) and interferent (m levels) are required.

This work has shown that FI process may be used to study effectively interference effects over a wide range of analyte and interferent concentrations in a semi-automated manner. Precise controlling of flow rates is recommended if carrier and interferent streams of widely different viscosities are to be used. The interference increases with increasing concentration of acetic acid, the interferent studied and the effect of analyte is linear.

The FI-ICP procedure developed can be used to map the interference surface prevalent under any set of experimental conditions, for example, different viewing heights above the load coil or rf input powers. As such, it represents a significant new source of multidimensional data. It is hoped that future studies will be able to use this procedure to unravel the interference mechanisms present in inductively coupled plasmas.

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Appendix A

(1) Velocity of Particles - Maxwell Distribution

The Maxwell velocity distribution for a particle i is described by

$$F_i(v) = 4\pi v^2 \left(\frac{m_i}{2\pi kT_i}\right)^{3/2} \exp\left(\frac{-m_i v^2}{2kT_i}\right)$$

where $m_i = \text{masss of the particle}$

v = velocity of the particle *i*

k = Boltzmann constant

 T_i = kinetic temperature of the particle *i*

Thus the electron temperature T_e is the kinetic temperature of the free electrons and the gas temperature T_g is the kinetic temperature of the neutral atoms. For complete thermodynamic equilibrium, the velocities of all kinds of free particles (molecules, atoms, ions and electrons) in all energy levels obey the Maxwell distribution and the temperature T_i in the distribution function is the same for all particles and energy levels.

(2) Population Distribution of Bound States - Boltzmann Distribution The ratio of number densities of particles in energetically different bound states p and q is given by

$$\frac{n_p}{n_q} = \left(\frac{g_p}{g_q}\right) \exp\left[-(E_p - E_q) / kT_{exc}\right]$$

where n_q, n_p = population of particles in a state q and p respectively g_p, g_q = statistical weights E_p, E_q = excitation energy with respect to ground state T_{exc} = excitation temperature

For complete thermodynamic equilibrium, $T_{exc} = T$, the plasma temperature for each type of particles and all energy levels.

(3) Population Distribution of Ionization Products - Saha Distribution For each species, the number density of singly ionized positive ions in the ground state and the corresponding number density of neutral particles in a level p are related to the free electron number density by the Saha equation

$$\frac{n_e n_p^+}{n_q} = 2(g_p^+/g_q)(2\pi m_e kT/h^2)^{3/2} \exp(-(E_i + E_p^+ - E_q)/kT_{ion})$$

where n_q , n_p^+ = number density of the ground state ion and excited state atom respectively.

 $n_e =$ free electron number density

 $g_{\rm p}^+$, $g_{\rm p}$ = statistical weights of the two levels

 $m_e =$ electron mass

h = Planck's constant

 E_i = ionization energy of the level p

 $E_{\rm p}^+$ = excitation energy of the ionic state p

 E_q = excitation energy of the atomic state p

 T_{ion} = ionization temperature

For complete thermodynamic $T_{ion} = T$, the plasma temperature for all ionization stages of species and for all species.

(4) Distribution of Dissociation Products - Guldberg-Waage Distribution

Distribution of species and their dissociation products should follow the mass action law of Guldberg and Waage. For thermal equilibrium, the dissociation temperature T_d must be equal to the plasma temperature for all species.

(5) Distribution of Radiation - Planck's law

The radiation density within a closed system is given by Planck's law for black body radiations. The back body temperature is called T_{rad} .

Appendix B.

'________

PROGRAM ICPAVG

['] Program to average FIA files collected from the ICP. The program can handle upto ten files in a series and produces an averaged file. It assumes a consistent root name and extension for all of the files and adds a the 'strings '01' to '10' to the root name. The input files are assumed to be standard as produced by the ICP software. The output files are produced in simple ASCII format with the diode number, point number, and averaged response on each line. Since the number of points per file, and the number and identity of the diodes used may change between files, the final file contains each unique set specified. Averaging will only be overt hose files which contain the particular data. The limit on the total number of different diodes, however, is 50, and the maximum number of points in any file is 500.

'Initialization section

DIM SIGNL%(51, 500), DIODNO%(51), BINCNT%(51, 500), PTCNT%(51) DIM BINPNTR%(51)

MAXFIL% = 10	'Maximum number of files
MAXPTS% = 500	'Maximum number of pts/diode
MAXDID% = 50	'Max no. of different diodes

DIDCNT% = 0

'Current no. of diodes

'Get the file information.

CLS

INPUT "File name root (1-6 chars., no ext)"; FROOT\$

INPUT "Extension (3 characters)"; FEXT\$

FEXT\$ = "." + LEFT\$(FEXT\$, 3)

NFIL: INPUT "Number of files (1-10)"; NUMFIL% IF NUMFIL% < 1 OR NUMFIL% > MAXFIL% THEN GOTO NFIL

'Now loop to process each file

FOR I% = 1 TO MAXDID% DIODNO%(I%) = 0 FOR J% = 1 TO MAXFIL% SIGNL%(I%, J%) = 0 BINCNT%(I%, J%) = 0 NEXT J% NEXT I%

FOR I% = 1 TO NUMFIL% TMP = "0" + RIGHT\$(STR\$(I%), 1) IF I% > 9 THEN TMP\$ = RIGHT\$(STR\$(I%), 2) FILNAM\$ = FROOT\$ + TMP\$ + FEXT\$ PRINT "Working on file "; FILNAM\$ **OPEN FILNAM\$ FOR APPEND AS #1** IF LOF(1) = 0 THEN PRINT "File not found - skipped." CLOSE #1 **KILL FILNAM\$ GOTO NXTFIL** END IF CLOSE #1 **OPEN FILNAM\$ FOR INPUT AS #1** INPUT #1, NDIOD%, DUMMY% INPUT #1, NPTS%, DUMMY% FOR J% = 1 TO 5INPUT #1, TMP\$ NEXT J% FOR J% = 1 TO NDIOD%

INPUT #1, DIOD%

```
IF J% <= MAXDID% THEN
 DIDFLG\% = 0
 FOR K\% = 1 TO DIDCNT%
  IF DIODNO%(K%) = DIOD% THEN
    DIDFLG\% = -1
    BINPNTR\%(J\%) = K\%
 NEXT K%
 IF DIDFLG\% = 0 THEN
  IF DIDCNT% < MAXDID% THEN
```

DIDCNT% = DIDCNT% + 1

DIODNO%(K%) = DIOD%

BINPNTR%(J%) = DIDCNT%

ELSE

END IF

BINPNTR%(J%) = MAXDID% + 1

END IF

END IF

END IF

NEXT J%

```
IF NDIOD% > MAXDID% THEN NDIOD% = MAXDID%
```

FOR J% = 1 TO NDIOD%

INPUT #1, TMP\$

INPUT #1, TMP\$

INDX% = BINPNTR%(J%)

IF PTCNT%(INDX%) < NPTS% THEN PTCNT%(INDX%) = NPTS%

IF PTCNT%(INDX%) > MAXPTS% THEN PTCNT%(INDX%) = MAXPTS%

FOR K% = 1 TO NPTS%

INPUT #1. Y

IF K% <= MAXPTS% THEN

SIGNL%(INDX%, K%) = SIGNL%(INDX%, K%) + CINT(Y)

```
BINCNT%(INDX%, K%) = BINCNT%(INDX%, K%) + 1
```

END IF

NEXT K%

NEXT J%

NXTFIL: CLOSE #1

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NEXT I%

PRINT

OFIL\$ = UCASE\$(FROOT\$) + ".AVG" PRINT "Output file name <"; OFIL\$; ">"; INPUT A\$ IF LEN(A\$) <> 0 THEN OFIL\$ = A\$

PRINT "Writing file "; OFIL\$

OPEN OFIL\$ FOR OUTPUT AS #1

FOR I% = 1 TO DIDCNT%

FOR J% = 1 TO PTCNT%(I%)

Y = CSNG(SIGNL%(I%, J%)) / CSNG(BINCNT%(I%, J%))

PRINT #1, DIODNO%(I%), J%, Y

NEXT J%

NEXT I%

CLOSE #1

PRINT "Done."

END

'Program to process data generated by ICPAVG. This program finds the diode with maximum emission intensity. Allows several diodes to be summed or averaged together to produce a single set of data. The output file is prodused in simple ASCII format with data set number, point number and response on each set of data.

'Initialization

DIM DIODNO%(50), SIGNL(50, 300), PTCNT%(50) DIM DNUM%(50), IPNTR%(50) MAXDID% = 50 MASPTS% = 300

'Get file info

CLS

INPUT "Input file name (including extension)"; INFIL\$ PRINT "Reading file "; INFIL\$

'Read the file

```
OPEN INFIL$ FOR INPUT AS #1
ICNT% = 0
WHILE NOT EOF(1)
INPUT #1, DIOD%, X, Y
IF ICNT% = 0 OR DIOD% <> DIODNO%(ICNT%) THEN
IF INCT% > MAXDID% THEN
PRINT " TOO MANY DIODES "
STOP
END IF
ICNT% = ICNT% + 1
```

```
PTCNT%(ICNT%) = 0
DIODNO%(ICNT%) = DIOD%
END IF
PTCNT%(ICNT%) = PTCNT%(ICNT%) + 1
IF PTCN%(INCT%) > MAXPTS% THEN
PRINT " TOO MANY POINTS "
STOP
END IF
SIGNL(ICNT%, PTCNT%(ICNT%)) = Y
WEND
CLOSE #1
NDIODES% = ICNT%
```

'Find the diode with the largest intensity.

```
MAXSIG = SIGNL(1, 1)

BIGDID% = 1

FOR I% = 1 TO NDIODES%

FOR J% = 1 TO PTCNT%(I%)

IF SIGNL(I%, J%) > MAXSIG THEN

MAXSIG = SIGNL(I%, J%)

BIGDID% = I%

END IF

NEXT J%

NEXT I%
```

'Now get info on diodes to be averaged and output file name.

```
INPUT "Output file name (include ext)"; OUTFIL$

OPEN OUTFIL$ FOR OUTPUT AS #1

ISIG% = 1

DIODES: PRINT : PRINT

PRINT "The diodes available are:"

FOR I% = 1 TO NDIODES%

PRINT , DIODNO%(I%);

IF I% = BIGDID% THEN PRINT " <";
```

PRINT

NEXT I%

PRINT

GETND: PRINT "How many diodes do you wish to use (1 -"; NDIODES%;

PRINT ") for signal"; ISIG%; " (0 to exit)";

INPUT NAVG%

IF NAVG% = 0 THEN GOTO DONE

IF NAVG% < 1 OR NAVG% > NDIODES% THEN GOTO GETND

FOR I% = 1 TO NAVG%

GETDN: PRINT "Diode number for diode"; I%;

INPUT DNUM%(I%)

DFLG% = 0

FOR J% = 1 TO NDIODES%

IF DNUM%(I%) = DIODNO%(J%) THEN

DFLG% = -1

IPNTR%(I%) = J%

END IF

NEXT J%

```
IF DFLG\% = 0 THEN
```

PRINT "Illegal diode number."

GOTO GETDN

END IF

NEXT I%

PRINT

PRINT "With what integer do you want to label this signal <"; ISIG%;

INPUT ">"; A\$

ILABEL% = VAL(A\$)

IF LEN(A) = 0 THEN ILABEL% = ISIG%

GETMOD: INPUT "Do you want averaged (A) or summed (S) signal <A>"; SIGMOD\$

IF LEN(SIGMOD\$) = 0 THEN SIGMOD\$ = "A"

SIGMOD\$ = UCASE\$(LEFT\$(SIGMOD\$, 1))

IF SIGMOD\$ <> "A" AND SIGMOD\$ <> "S" THEN GOTO GETMOD

'Send signal to the output file

```
PRINT

PRINT "Working."

ICNT% = 0

MAXPTS% = 0

FOR I% = 1 TO NAVG%

IF PTCNT%(IPNTR%(I%)) > MAXPTS% THEN MAXPTS% =

PTCNT%(IPNTR%(I%))
```

NEXT I%

```
FOR I\% = 1 TO MAXPTS%
```

SIGAVG = 0

BINCNT% = 0

FOR J% = 1 TO NAVG%

IF PTCNT%(IPNTR%(J%)) >= I% THEN

SIGAVG = SIGAVG + SIGNL(IPNTR%(J%), I%)

BINCNT% = BINCNT% + 1

END IF

NEXT J%

```
IF SIGMOD$ = "A" THEN SIGAVG = SIGAVG / CSNG(BINCNT%)
PRINT #1, ILABEL%, I%, SIGAVG
```

NEXT I%

ISIG% = ISIG% + 1 GOTO DIODES

DONE: CLOSE #1

END