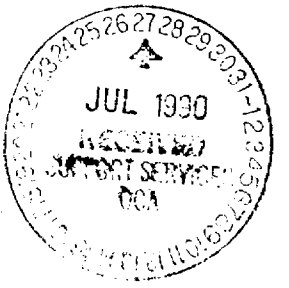
Active

Project #: G-33-627 Cost share #: G-33-334 Rev #: 6
Center # : R6562-0A0 Center shr #: F6562-0A0 OCA file #:
Work type : RES
Contract#: CHE-8808183 Mod #: BUD REV (AMD 3) Document : GRANT
Prime #: Contract entity: GTRC

Subprojects ? : N
Main project #:

Project unit: CHEMISTRY Unit code: 02.010.136
Project director(s):
BROWNER R F CHEMISTRY (404)894-4020



Sponsor/division names: NATL SCIENCE FOUNDATION / GENERAL
Sponsor/division codes: 107 / 000

Award period: 880715 to 911231 (performance) 920331 (reports)

Sponsor amount	New this change	Total to date
Contract value	0.00	358,200.00
Funded	0.00	358,200.00
Cost sharing amount		80,901.00

Does subcontracting plan apply ?: N

Title: SAMPLE INTRODUCTION FOR INDUCTIVELY COUPLED ATOMIC EMISSION SPECTROMETRY...

PROJECT ADMINISTRATION DATA

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Security class (U,C,S,TS) : U ONR resident rep. is ACO (Y/N): N
Defense priority rating : N/A NSF supplemental sheet
Equipment title vests with: Sponsor GIT X
EQUIPMENT PROPOSED, BUT NOT FUNDED IN THE FIRST YEAR. SEPARATE FUNDING IN 89.
Administrative comments -
REVISION ISSUED TO CORRECT BUDGET FROM AMENDMENT # 3; FUNDS ($88200)
ORIGINALLY BUDGETED IN EQUIP. ONLY IN ERROR; THIS REVISION REDISTRIBUTES;

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 05/04/92

Project No. G-33-627 Center No. R6562-0A0

Project Director BROWNER R F School/Lab CHEMISTRY

Sponsor NATL SCIENCE FOUNDATION/GENERAL

Contract/Grant No. CHE-8808183 Contract Entity GTRC

Prime Contract No. _____

Title SAMPLE INTRODUCTION FOR INDUCTIVELY COUPLED ATOMIC EMISSION SPECTROMETRY.

Effective Completion Date 911231 (Performance) 920331 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	N	
Final Report of Inventions and/or Subcontracts	N	
Government Property Inventory & Related Certificate	N	
Classified Material Certificate	N	
Release and Assignment	N	
Other _____	N	

Comments"BILLING" VIA LINE-OF-CREDIT; 98A SATISFIES PATENT REPORTING REQUIREMENT.

Subproject Under Main Project No. _____

Continues Project No. _____

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

Annual Progress rpt. 6-33-627

Research Proposal Submitted to the National Science Foundation

Technical Report on Grant No. CHE-8808183

SAMPLE INTRODUCTION FOR INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY AND INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Principal Investigator: Richard F. Browner

Georgia Institute of Technology
School of Chemistry
Atlanta, GA 30332-0400

SUMMARY OF ACCOMPLISHMENTS UNDER CURRENT GRANT DURING PERIOD 7.15.88 to 4.12.89

The program in the current year has resulted in a total of three publications, one patent, and one paper in press. Additionally, seven conference presentations have been made, including the Benedetti-Pichler Award presentation, one keynote talk and five invited talks. Details of publications are given on page 5 of this report.

1. Study of Water Loading Effects in ICP Atomic Emission Spectrometry (ICPAES)

Goals of Sample Introduction

One of the primary purposes of studies with sample introduction in atomic spectrometry is to attempt to produce an aerosol with the optimum properties for introduction to a plasma. The factors necessary to control in this situation are: (1) the aerosol drop size (2) the aerosol drop size distribution (3) the analyte mass transport loading and (4) the solvent mass transport loading. This last term may also be subdivided into components of solvent *aerosol* and solvent *vapor* loading.

In this particular project, the focus is on the roles of analyte and solvent mass loadings in influencing plasma properties, and the drop size is (temporarily) removed as a variable from the studies.

One of the most intriguing aspects of recent work we have carried out with ICPAES has been a series of systematic studies on the influence of water loading on plasma properties. This is a topic that we have pursued for several years, from a variety of aspects, and one which we have increasingly become convinced offers a key to making major improvements in ICPAES performance. We have recently published two papers describing fundamental background work in this area *(2, 3)*, but the implications of these studies are really much broader than might be inferred from these studies alone. Consequently, we are currently examining several areas in which the effect of solvent loading has a very major practical effect on plasma properties.

One area that we have studied extensively in ICPAES is the influence of changes in water vapor and aerosol loading on atomic and ionic signals and their spatial emission profiles. Our research has used two basic configurations to study these effects. In the first, a standard pneumatic nebulizer passes into an empty cylindrical chamber, whose temperature is controlled by means of external heating. The effluent from the chamber, which includes analytical aerosol and solvent vapor, then passes through a condenser before it reaches the plasma. The temperature of the spray chamber is used to control the extent of solvent evaporation from the aerosol drops. This moves the equilibrium towards higher solvent vapor loading in the gas stream, and results in a corresponding downwards shift in the drop size distribution of the aerosol.

When the system is set up with a heated spray chamber, in sequence with a cooled condenser, the following effects are observed: (1) the analyte-containing aerosol evaporates, to an extent which is determined totally by the chamber temperature (2) the drop size distribution of the evaporating aerosol shifts to a lower value, as the chamber temperature is raised (3) the *analyte* mass transport, W_{tot}, increases as the drop size decreases (4) the total combined *solvent* loading of vapor and aerosol remains constant, whatever temperature the evaporation chamber temperature reaches.

In the second experiment, aerosol is generated in a single chamber, whose temperature is controlled with a heated/cooled water jacket. In this system, the effect of raising the chamber temperature is to *increase* the net solvent loading, S_{tot}, to the plasma. This increase is made up entirely of increased solvent *vapor*, and the solvent aerosol remains essentially constant. This is in clear contrast to the experiment described previously.

Influence of Heated Chamber/Condenser on Emission Signals

A detailed study has been made of the influence of increased analyte loading, resulting from higher spray chamber temperatures and constant condenser temperatures, on plasma properties for a series of test elements. Height profile studies were also carried out, using a photodiode array system with the diode array arranged vertically along the exit slit. It was observed that the emission intensities increased substantially, but non-linearly, with desolvation chamber temperature. The increase in intensities was greater for the atomic than for the ionic lines, but was substantial for both. This clearly indicates that there is a direct relationship between analyte mass transport to the plasma and analyte emission signal.

The influence of spray chamber temperature on height profiles was much as anticipated. With the ionic lines, there is very little shift in height profile with spray chamber temperature. With the atomic lines, by contrast, there is a shift to higher positions in the plasma for higher desolvation temperatures.

The conclusion from these preliminary studies is that it is possible to increase the net signal intensities for a number of elements substantially (typically by a factor of ≥ 3) by increasing the analyte total mass transport, W_{tot}, without regard for aerosol drop size. This has important implications for improving detection limits in ICPAES, and practical means of accomplishing this simply are currently being pursued.

Interference Effects

It is of great importance to examine the effect of potentially interfering species on the improved signals observed through heating the spray chamber. Two suitable species, representing two distinct types of interfering mechanism, K^+ and PO_4^{3-}, were tested. K^+ represents a typical easily ionized element (EIE) and PO_4^{3-} represents a typical species giving rise to a vaporization interference. The influence of both species on signal intensities and signal height profiles was examined. With the PO_4^{3-} interference, there was no detectable effect on height profiles for either the atomic or ionic species. However, there was a 40% signal loss at a high spray chamber temperature (90 °C), when 2,000 p.p.m. of PO_4^{3-} was added to the solution.

The K^+ interference, as anticipated, exhibited some height profile effects, which were much more noticeable for the atomic lines than for the ionic lines. As a marked contrast with the PO_4^{3-} interference, the interference effect was as noticeable at low spray chamber temperatures a it was at high temperatures. This indicates clearly that the interference of K^+ is almost entirely a plasma excitation condition effect, whereas the interference observed with PO_4^{3-} is a particle-size related effect. This is, to the best of our knowledge, the first time that the onset of vaporization interferences in the ICP has been related directly to drop size effects.

2. Study of Water Loading Effects in ICP Mass Spectrometry (ICP/MS)

Our previous studies with ICP/MS have demonstrated that changes in plasma conditions induced by varying sample introduction parameters are often quite different for ICP/MS compared to ICPAES. Consequently, we have also carried out a series of experiments with a heated spraychamber and condenser, varying the temperatures of both in order to vary the analyte mass transport and the solvent loading, in parallel with the ICPAES experiments.

The most noticeable feature of the experiments in which the spraychamber was heated to approximately 90 °C, and the condenser was maintained at approximately 10 °C, was that there was a significant increase in signal across a wide range of element masses, ranging from Li to Pb. While there were no detectable mass-related trends, there was some variation from element to element. The average increase in signal-to-background ration was approximately a factor of 10, and the range was from 7 to 20.

This increase in signal-to-background ratio converts directly into a improvement in detection limit, as the increase in analyte mass transport does not result in any noticeable increase in background count level. These improvements in detection limits are very significant, and can be anticipated to make a major contribution to low level detection for difficult trace and ultra-trace elements in a variety of sample types. The effect of interfering ions, carried out at comparable concentration excesses to the ICPAES studies, showed much less significant effects. This is probably because the ICP/MS studies take place at much lower absolute concentrations than the ICPAES studies, and consequently the concentrations of the interfering ions are much lower in absolute terms in the plasma.

We are currently carrying out extensive diagnostic tests to determine fundamental parameters of the plasma in the two cases of ICPAES and ICP/MS, in order to determine what the key factors may be. We hope that this study will lead to greater understanding of the processes involved, and consequently to further improvements in performance.

3. Characterization of Key Aerosol Parameters

In earlier work *(1)*, we have derived an empirical relationship to predict the mean drop size and breadth of the distribution of aerosols produced by typical ICP pneumatic nebulizers. This relationship has been demonstrated to be far more accurate and reliable than the previously accepted equation of Nukiyama and Tanasawa. As a continuation of this work, and in an attempt to probe deeper into the precise mechanisms that dominate the pneumatic aerosol generation process, we have carried out many systematic studies of the influence of nebulizer parameters on aerosol properties. From this work, we have attempted to derive some basic models which can be used to describe the processes leading to the breakdown of liquid jets, and the subsequent formation of analytically important aerosols. This work should lead to a major improvement in our understanding of many key processes in aerosol generation, and hopefully in our ability to control them.

RESEARCH PUBLICATIONS

1. "Empirical Model for Estimating Drop Size Distributions of Aerosols Generated by Inductively Coupled Plasma Nebulizers," Antonio Canals, Janet Wagner, Vicente Hernandis and Richard F. Browner, Spectrochim. Acta, Part B, *43*, 1321 (1988).
2. "Study of the Influence of Water Vapor Loading and Interface Pressure in Inductively Coupled Plasma/Mass Spectrometry," Guangxuan Zhu and Richard F. Browner, J. Anal. Atom. Spectrosc., *3*, 781 (1988).
3. "The Influence of Water on the Inductively Coupled Argon Plasma," Stephen E. Long and Richard F. Browner, Spectrochim. Acta B, *43*, 1461 (1988).
4. "Interfacing with Aerosols: Concept, Place and Time," Richard F. Browner, Microchem. J., in press (1989).
5. "Monodisperse Aerosol Generator," US Patent No. 4,762,994 issued Aug. 9, 1988.

CONFERENCE PRESENTATIONS

1. "Sample Introduction Strategies for Inductively Coupled Plasma Mass Spectrometry," Rocky Mountain Conference, Denver, CO, August 1988, ***keynote lecture.***
2. "Interactions of Liquid and Dry Aerosols in ICP/MS: in Search of the Perfect Aerosol," Guangxuan Zhu, Edison Becerra, Vincent Nwogu and Richard F. Browner, Eastern Analytical Symposium, New York, October 1988, **invited talk.**
3. "Interfacing with Aerosols: Concept, Place and Time," Richard F. Browner, Eastern Analytical Symposium, New York, October 1988, **Benedetti-Pichler Award Presentation.**
4. "Samples and Plasmas: Interactions of Particles, Solvents and Vapors," Richard F. Browner, Federation of Analytical Chemistry and Spectroscopy Societies Meeting, Boston, MA, November 1988, **invited talk.**
5. "Measurement and Prediction of Aerosol Characteristics for ICP Nebulizers," Ntombioyomusa Msimanga, Antonio Canals, Vicente Hernandis and Richard F. Browner, Federation of Analytical Chemistry and Spectroscopy Societies Meeting, Boston, MA, November 1988.
6. "Aerosols for Interfacing in Atomic and Molecular Analysis," Richard F. Browner, Indiana University, School of Chemistry, November 1988, **invited talk.**
7. "Aerosol MAGIC for Interfacing Analytical Instruments," Richard F. Browner, Emory University, Department of Chemistry, November 1988, **invited talk.**

SUMMARY OF CURRENT AND PENDING RESEARCH SUPPORT

A	B	C	D	E		F
Source	Title	Amount	Period	Person Months Acad	Summ	Location
I. Richard F. Browner						
A. Current Support						
NSF	1	$270,000	7/15/88 6/14/90	___	1	Ga Tech
DOE	2	$293,250	9/1/85-11/30/89	___	2	Ga Tech
EPA	3	$157,097	7/15/86-7/14/89	1	___	Ga Tech
NIH	4	$354,000	7/1/88-6/30/90	1	___	Ga Tech
B. Proposals Pending						
1. This proposal NSF	1	$ 90,000	7/15/89-6/14/90	___	___	Ga Tech
2. Other proposals pending NSF	5	$ 85,000	7/1/89-6/30/90	___	___	Ga Tech
3. Proposals to be submitted in the near future	None					
III. Transfer of Support	None					
IV. Other agencies to which this proposal will be submitted	None					

Proposal Titles

1. Sample Introduction for Inductively Coupled Plasma Atomic Emission Spectrometry and Inductively Coupled Plasma Mass Spectrometry
2. Fundamental Studies with a Monodisperse Aerosol-Based Liquid Chromatography/Mass Spectrometry Interface (MAGIC-LC/MS)
3. Mass Spectrometric Analysis of Pollutants Using the MAGIC-LC/MS Interface
4. Fundamental Studies With A MAGIC-LC/FT-IR Interface
5. Sample Introduction for Inductively Coupled Plasma Atomic Emission Spectrometry and Inductively Coupled Plasma Mass Spectrometry (Supplementary request for Inductively Coupled Plasma Mass Spectrometer instrumentation).

Statement of Funds Remaining at End of Current Grant Period

It is anticipated that no funds will remain unexpended at the end of the current grant period (7.14.89).

SEE INSTRUCTIONS ON REVERSE BEFORE COMPLETING)

SUMMARY PROPOSAL BUDGET

FOR NSF USE ONLY		
PROPOSAL NO.	DURATION (MONTHS) Proposed	Granted
AWARD NO.		

ORGANIZATION: Georgia Institute of Technology

PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR: Richard F. Browner, Principal Investigator

A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title; A.6. show number in brackets)	NSF FUNDED PERSON-MOS. CAL.	ACAD	SUMR	FUNDS REQUESTED BY PROPOSER	FUNDS GRANTED BY NSF (IF DIFFERENT)
1. Richard F. Browner			1	$ 6,200	$
2.					
3.					
4.					
5. ( ) OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)					
6. (1) TOTAL SENIOR PERSONNEL (1-5)			1	6,200	
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1. (1) POST DOCTORAL ASSOCIATES	12			22,000	
2. ( ) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)					
3. (1.5) GRADUATE STUDENTS @ $11,400 for 47% time				17,100	
4. ( ) UNDERGRADUATE STUDENTS					
5. ( ) SECRETARIAL-CLERICAL					
6. ( ) OTHER					
TOTAL SALARIES AND WAGES (A+B)				45,300	
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) (25.5% of 6200=1581, 8.2% of 22,000=1804, FB=3,385)				3,385	
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)				48,685	
D. PERMANENT EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $1,000:)					
TOTAL PERMANENT EQUIPMENT					
E. TRAVEL 1. DOMESTIC (INCL. CANADA AND U.S. POSSESSIONS)				1,500	
2. FOREIGN					
F. PARTICIPANT SUPPORT COSTS					
1. STIPENDS $					
2. TRAVEL					
3. SUBSISTENCE					
4. OTHER					
TOTAL PARTICIPANT COSTS					
G. OTHER DIRECT COSTS					
1. MATERIALS AND SUPPLIES				6,739	
2. PUBLICATION COSTS/PAGE CHARGES				1,000	
3. CONSULTANT SERVICES					
4. COMPUTER (ADPE) SERVICES					
5. SUBCONTRACTS					
6. OTHER					
TOTAL OTHER DIRECT COSTS					
H. TOTAL DIRECT COSTS (A THROUGH G)				56,812	
I. INDIRECT COSTS (SPECIFY) 60.0% of TMDC ($55,312)					
TOTAL INDIRECT COSTS				33,188	
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)				90,000	
K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPM 252 AND 253)					
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				$ 90,000	$

PI/PD TYPED NAME & SIGNATURE*	DATE	FOR NSF USE ONLY
Richard F. Browner	4.23.89	INDIRECT COST RATE VERIFICATION
INST. REP. TYPED NAME & SIGNATURE*	DATE	Date Checked / Date of Rate Sheet / Initials - DGC / Program

*SIGNATURES REQUIRED ONLY FOR REVISED

THIS PAGE MUST BE SUBMITTED AS PART OF THE PROPOSAL

This certification is required for an award of a Federal contract, grant, or cooperative agreement exceeding $100,000 and for an award of a Federal loan or a commitment providing for the United States to insure or guarantee a loan exceeding $150,000.

CERTIFICATION REGARDING LOBBYING

Certification for Contracts, Grants, Loans, and Cooperative Agreements

The undersigned* certifies, to the best of his or her knowledge and belief, that:

(1) No Federal appropriated funds have been paid or will be paid, by or on behalf of the undersigned,* to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with the awarding of any federal contract, the making of any Federal grant, the making of any Federal loan, the entering into of any cooperative agreement, and the extension, continuation, renewal, amendment, or modification of any Federal contract, grant, loan, or cooperative agreement.

(2) If any funds other than Federal appropriated funds have been paid or will be paid to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with this Federal contract, grant, loan, or cooperative agreement, the undersigned* shall complete and submit Standard Form-LLL, "Disclosure Form to Report Lobbying," in accordance with its instructions.

(3) The undersigned* shall require that the language of this certification be included in the award documents for all subawards at all tiers (including subcontracts, subgrants, and contracts under grants, loans, and cooperative agreements) and that all subrecipients shall certify and disclose accordingly.

This certification is a material representation of fact upon which reliance was placed when this transaction was made or entered into. Submission of this certification is a prerequisite for making or entering into this transaction imposed by section 1352, title 31, U.S. Code. Any person who fails to file the required certification shall be subject to a civil penalty of not less than $10,000 and not more than $100,000 for each such failure.

Statement for Loan Guarantees and Loan Insurance

The undersigned* states, to the best of his or her knowledge and belief, that:

If any funds have been paid or will be paid to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with this commitment providing for the United States to insure or guarantee a loan, the undersigned* shall complete and submit Standard Form-LLL, "Disclosure Form to Report Lobbying," in accordance with its instructions.

Submission of this statement is a prerequisite for making or entering into this transaction imposed by section 1352, title 31, U.S. Code. Any person who fails to file the required statement shall be subject to a civil penalty of not less than $10,000 and not more than $100,000 for each such failure.

*By signing the Cover Sheet and submitting this page as part of the proposal, the applicant is providing Certification Regarding Lobbying.

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SUMMARY

Improved interfacing capabilities will be developed for coupling various chromatographic systems to atomic emission and mass spectrometric detectors. The study will focus on developing a greater understanding of several key processes which control the overall transfer of eluting bands from the chromatograph to the detector. Factors to be optimized will include analyte transport, eluent band broadening and solvent removal. The control of these factors will give rise both to improved detection limits and chromatographic efficiency in the analysis of complex environmental and biochemical samples. The development of several novel interfacing options will be studied. As part of the studies, use will be made of specialized particle velocimetry and particle sizing instrumentation which will be developed as part of the project.

Various atomic emission and mass spectrometric sources will be studied, including atmospheric pressure argon inductively coupled plasma and reduced pressure helium microwave plasma sources. The nebulization systems to be studied include promising variations of monodisperse and ultrasonic nebulizers. Interfacing options will include studies with a unique solvent removal interface, the particle beam system. As part of the project, mechanisms of aerosol formation and transport with each system will be studied, and models developed to describe the basic processes.

INTRODUCTION

The demand for trace and ultratrace elemental analysis of environmentally and biochemically important species grows substantially each year. However, even state-of-the-art instrumentation often does not provide the *sensitivity*, *selectivity* and *accuracy* needed for elemental analysis in such complex matrices. Additionally, *speciation* information is of great value in many biological and environmental studies, as a means to assess mechanisms of biochemical action or to follow the fate and distribution of pollutants in the environment. Monitoring the levels of many species as they occur naturally, without using heroic preconcentration procedures, requires significantly lower *limits of detection* for many elements than are presently available using either ICP/MS or electrothermal vaporization AAS. In particular, real world samples generally occur in quite hostile matrices, which makes direct analysis very difficult at any acceptable level of accuracy.

Most commercial instrumentation available for elemental analysis, using either atomic spectrometry or mass spectrometry, takes relatively little account of the diverse and demanding sample introduction needs of real world analysis. In general, commercial instruments provide basically a facility to inject a relatively matrix-free sample into the system, and to provide an estimate of its elemental concentration. Information on the oxidation state of the sample or the nature of its organic component, if an organometallic complex, are not provided. As a consequence, many important avenues for research into biological pathways of, for instance, enzyme interactions in brain neurochemistry, the role of trace elements in crossing cell boundaries and their influence on the spread of malignant tumors, cannot be considered from the simple elemental perspective, but can only be followed through monitoring the action of the element, rather than the complete organometallic species. The inability to address these issues effectively is a real limitation for present day trace element analysis. Many other instances exist where there is a real need for lower detection limits, combined with freedom from interference and additionally some degree of speciation. Important examples exist in environmental monitoring, such as in the detection of As and Se in their various forms at very low levels, and in nutritional biochemistry, where many elements, such as Mn and V, lack reliable information on normal human levels.

A number of workers have attempted, with varying degrees of success, to interface separations techniques, such as liquid chromatography and ion chromatography, with ICPAES[1-2]. However, it is generally accepted that the detection limits possible with conventional pneumatic nebulizer ICPAES are more often than not inadequate for determining many compounds at normal levels without extensive pre-concentration.[3] This then defeats the purpose of providing the rapid, on-line analysis which is necessary with the types of screening studies often necessary in speciation work. The use of more efficient nebulizers, such as Thermospray[3,4] and direct injection nebulizers[5] has, however, improved this situation considerably.

The advent of ICP/MS has made speciation studies at realistic levels much more feasible for many real-world problems. In fact, the exceptionally low detection limits provided by ICP/MS, typically two orders of magnitude lower than those possible with ICPAES, have re-invigorated speciation investigations.[6,7] However, even ICP/MS does not by any means provide all the necessary answers to the problems of ultratrace detection of inorganic and organometallic species, and it is becoming clear that one major limitation in the process is provided not by the mass spectrometry instrumentation, but by the inadequacies of present sample introduction techniques.

Sample introduction processes have become much better understood over the last decade. Advances in basic knowledge of the fundamental processes which control aerosol formation, solvent vaporization, and particle and solvent interactions in plasmas have been very significant. In the last three to four years, there has been a strongly renewed focus on the importance of the sample introduction process, and in determining how it may be improved in order to enhance the performance of ICPAES and ICP/MS instruments. This has led to some real breakthroughs in the level of understanding of important interactions that occur in aerosol generation, transport and in aerosol interactions in the plasma. Some particularly noteworthy efforts are the organic solvent studies of Blades *et al.*[8] and of Maessen *et al.*[9],the nebulizer and plasma studies of Houk *et al.*[10], the particle sizing and nebulizer studies of Koropchak *et al.*[11], the particle sizing and velocity measurements of Montaser *et al.*[12], the slurry/plasma interaction studies of Broekaert *et al.*[13], the particle/plasma interaction studies of Olesik *et al.*[14] and the nebulizer and interfacing studies of Caruso *et al.*[15]. The common factor which unites these studies, and also provides the driving force for the work of our own group, is the underlying conviction that it is only by achieving a more complete understanding of fundamental sample introduction processes that the much needed additional breakthroughs in this area will be achieved.

In some regards, progress in the area of sample introduction may have an appearance of *evolution-*

ary, rather than *revolutionary* development. However, this appearance is deceptive, because it is the *ultimate* prospects for advance in this area which are important, rather than simply the instantaneous rate of progress. In the area of sample introduction it has often proved necessary to first probe deeply into existing fundamental knowledge and mechanistic models, which have turned out to be either inappropriate or inaccurate when applied to present systems. In consequence, many well established reference points and concepts have proven on closer experimental study to be erroneous, and have needed replacement with more accurate and reliable models.

A few instances of this type are: (1) the misuse of the Nukiyama and Tanasawa equation for predicting mean aerosol diameters for pneumatic nebulizers. This had long served as the *only* model for predicting the performance of the pneumatic nebulizers used in almost all ICPAES and ICP/MS studies. We have recently demonstrated that the predictions of this equation are in error by factors ranging from 2.5x to 40x. (2) The observation that the interactions of solvent vapor and solvent aerosol in the plasma are totally different in kind, a fact first noted by Long and Browner,[16] and since studied in far greater depth by Olesik *et al.*[17] This has far-reaching implications for understanding how atoms and ions are formed in plasmas, and will probably require a re-evaluation of much existing thermodynamic plasma data which has been based on the postulate of a homogeneous analyte/plasma model (3) The operating mechanisms of current ultrasonic nebulizers, which probably provide the best state-of-the-art detection limit performance for ICPAES and ICP/MS, are significantly different from the predictions of the Kelvin and Lang models. The aerosol produced by such nebulizers actually has a very wide drop size range, extending to >100 μm diameter, in spite of the assumption of most workers that ultrasonically generated aerosols are all small and monodisperse. Again, the culprit is the combination of an inadequate historical model for predicting ultrasonic nebulizer operation, combined with a misunderstanding of basic aerosol processes. Many other instances of this type could be cited.

The thrust of the present proposal is: (1) to justify the need to carry out basic research in various aspects of sample introduction for elemental analysis using ICPAES, ICP/MS, microwave/AES and microwave/MS (2) to describe research projects designed to develop fundamental knowledge in these techniques and (3) to direct this knowledge towards the development of really effective chromatographic and flow injection coupling for ICPAES, ICP/MS, microwave/AES and microwave/MS.

In spite of a renewed focus on sample introduction issues, much of the published research in this area still uses an approach which ranges from semi- to wholly empirical. While empirical research in this area has historically led to some worthwhile advances, the benefits are often short term and limited. Additionally, very few untried empirical possibilities remain at this time. Consequently, major progress will probably come only from a deeper understanding of the *fundamental phenomena* underlying the conversion of condensed phase atoms to vapor phase atoms and ions.

The need for continued basic research on sample introduction in atomic and mass spectrometry may be justified on several grounds. Most important is the need to improve the *quality* of measurements possible by plasma emission and plasma mass spectrometry. In this proposal, the focus is on ICPAES, microwave/AES, ICP/MS and microwave/-MS, although the potential for development in other areas such as glow discharge and other unique discharges is clearly significant.

It is probably fair to say that, with some notable exceptions, researchers in the atomic spectrometry and mass spectrometry communities have only recently begun to realize the need for understanding on a *truly rigorous basis* the basic physical and chemical processes involved with the introduction of samples to plasmas. While our research program has attempted to explore a number of avenues in the sample introduction field over a number of years, the work has in many instances served to make us acutely aware of the present limitations in our knowledge, and to emphasize just how many new areas worthy of exploration still remain. There is really still an amazing dearth of fundamental information in many critically important areas. Examples of situations where the lack of information is particularly acute include the ***microscopic processes*** associated with **aerosol formation, aerosol transport, aerosol charging, aerosol solvent evaporation** and **aerosol vaporization in the plasma.** The strong emphasis here, and one which will be echoed many times throughout this proposal is on the basic importance of examining and understanding processes on a *microscopic* level.

Recent research[14,16,17,18] has indicated that the ability to make that kind of distinction is crucial to really making progress in understanding a number of basic processes occurring in ICPAES, ICP/MS microwave/AES and microwave/MS. In fact, the mechanisms of microscopic interaction of solvents with plasmas are clearly of major importance in understanding sample introduction processes using solvents.

GENERAL RESEARCH NEEDS

1. IMPROVED ANALYTICAL BENCHMARKS FOR ICPAES AND ICP/MS

The three prime areas of opportunity for improving analytical performance are those of: (1) improved detection limits (2) increased accuracy (3) better precision. While these are certainly not new themes, the need to accomplish these goals remains absolutely central to research in the field. The lowering of detection limits, especially in the context of improved transport efficiency, also plays a key role in improving the utility of liquid chromatography or capillary zone electrophoresis coupled to elemental detectors. This aspect is also discussed in Section 2 below.

Developments with sample introduction on these fronts will be possible only through the precise control of sample introduction processes which in turn depends on developing a deeper understanding of basic mechanisms. The possibilities for truly novel developments in this area appear to be quite considerable at the present time, and will probably come through the development of a better knowledge and understanding of the fundamental parameters of analyte aerosol properties, and the manner in which they actually influence the magnitudes of signals in ICPAES and ICP/MS.

If one considers, from a simple perspective, that the analytical signal resulting from the presence of atoms or ions in a high temperature plasma is directly due to the instantaneous population of such species in the sampled spatial zone, then the importance of being able to both control and predict these populations becomes obvious. Such a level of control can only come about through the development of a better knowledge of how these populations arise.

2. DEVELOPMENT OF IMPROVED INTERFACES FOR LC, IC AND CZE WITH ICPAES, ICP/MS, MICROWAVE/AES AND MICROWAVE/MS

The primary needs for effective chromatographic interfacing involve the following key attributes: (1) highly efficient transfer of analyte from the sample injection point to the detection cell (2) maintenance of narrow bands for eluting compounds as they pass through the interface (3) effective solvent removal in conjunction with the efficient transfer of analyte, in order to maintain good excitation and/or ionization conditions in the plasma (4) minimization of memory effects associated with the solvent removal process. In practice, all of the above four attributes are closely interrelated. Solvent removal, if approached in such a way as to reduce the fraction of overly large droplets in the primary aerosol can greatly increase the analyte mass transport to the plasma, and so significantly enhance the efficiency of analyte mass transport. While increased analyte mass transport is always an important factor in the optimization of ICPAES and ICP/MS, it becomes particularly critical in the case of chromatographic interfacing. This is apparent when one considers that a single chromatographic peak may contain only a few pg of analyte, eluting in a matter of a few seconds. Any significant peak broadening will reduce the instantaneous analyte concentration in the plasma accordingly, based on the dilution of the eluting band which takes place in the LC-ICP interface. This will reduce the analytical signal proportional to the aerosol dispersion occurring in the interface.

Capillary Zone Electrophoresis (CE or CZE) is a powerful new separation technique with great possibilities for complex mixtures of ionic metallic and organometallic species. Column efficiencies up to 500,000 theoretical plates can often be achieved in approximately 30 mins. The ability to interface this technique effectively with inorganic emission or mass spectrometry depends, however, on the ability to operate with the very low mass loadings ($\leq$pg) and flow rates ($<$20 μL/min) possible with the technique.

Further, in a typical pneumatic nebulizer interface, with 1-2 % transport efficiency, the few ng-pg of analyte present in the original band eluting from the chromatographic column will become only a few fg by the time it reaches the plasma. This will oftentimes take the level of analyte reaching the plasma below the detection limit of the system, and so make the analysis impossible. While the greatly improved detection limits of ICP/MS over ICPAES have improved this situation, in many real practical analytical situations, such as with clinical samples, and with marine and surface waters, detection limits still remain below what is needed for practical use of LC-ICP/MS.

Ultrasonic nebulizers, which currently provide some of the best detection limits for ICPAES and ICP/MS also suffer from severe band broadening, making them of limited value for chromatographic coupling. Frit-type nebulizers, which also provide finer aerosols than conventional pneumatic types, suffer from similar aerosol dispersion and washout time limitations. Experiments aimed at alleviating this problem will be discussed later in the proposal.

A very useful contribution to LC interfacing is the direct injection nebulizer, which addresses many of the key issues of interfacing by directing the entire effluent from an LC micro-column as an aerosol into the base of an ICP. This both minimizes band broadening and provides effectively 100% transport efficiency. Unfortunately, it is not possible to desolvate the aerosol with this device, which restricts its use to low flows (≤100 μL/min), and gives a lower improvement in detection limit (approx 2x) than might otherwise be possible.

The problems of LC interfacing with plasmas are not new, and a number of innovative approaches have been tried over the years with varying degrees of success. In this work, however, we will propose both some radically different approaches to solving the problem, as well as some novel variations of more established approaches. These will be discussed under the Proposed Research section.

3. IMPROVED UNDERSTANDING OF BASIC NEBULIZATION-TRANSPORT-PLASMA INTERACTIONS

In spite of all the work which has been applied to developing models for the mechanisms of pneumatic and ultrasonic nebulization, remarkably few major improvements have been accomplished in the key benchmark parameters of detection limits, accuracy and precision over the last twenty years. In the last few years, however, there have been significant accomplishments made in some areas of sample introduction, which have resulted in the lowering of detection limits by approximately one order of magnitude. For example, recent work with ultrasonic nebulizers[19] has shown the capability to achieve across-the-board improvements in detection limits while still retaining a good level of reliability of the system. Also, work with desolvation in the present author's laboratories has shown the capability to enhance detection limits, especially in ICP/MS, by up to an order of magnitude even when using conventional pneumatic nebulization[20].

The current state of knowledge in the area of aerosol generation and aerosol transport has recently been extensively reviewed by Sharp,[21,22] who describes, largely from an engineering perspective, the principles under which aerosols are both generated and transported to plasmas. From the viewpoint of the present author, this monumental and in many respects excellent review suffers from the fatal flaw that it fails to step back in order to look at the broader picture and ask the fundamental questions: "(1) What are the properties of the optimum aerosol that would be used by choice for introduction to ICPAES, ICP/MS, microwave/AES and microwave/MS and (2) how is it possible to generate this aerosol?" Based on the experimental data available to date, it appears clear that the basic properties of an optimum aerosol for ICP-AES differ markedly from that of an optimum aerosol for ICP/MS, which in turn differs significantly from that of an optimum aerosol for microwave/AES *etc.* The relevant aerosol properties for each type of spectrometric detector differ in terms of both aerosol particle size and of solvent loadings (clearly differentiating between condensed phase and vapor phase loading) associated with the transported aerosol. If chromatographic or flow injection interfacing is considered in comparison with normal continuous introduction, the amount of acceptable dispersion is also an important variable to be considered.

To the extent that a knowledge base of criteria for aerosol-based sample introduction in ICPAES exists at all, and what exists presently is very fragmentary, that knowledge base has been transferred essentially intact from the ICPAES environment to the ICP/MS environment. This expedient solution to a practical problem will certainly limit the future development potential for ICP/MS *unless* appropriate new criteria for sample introduction for ICP/MS are established within a reasonable period of time.

TECHNICAL REPORT OF ACCOMPLISHMENTS UNDER CURRENT NSF GRANT NO. CHE88-08183 "Sample Introduction for Inductively Coupled Plasma Atomic Emission Spectrometry and Inductively Coupled Plasma Mass Spectrometry" 7/15/88 - 7/14/91

A summary of progress under current NSF support is included here so that it may also serve as an introduction to the following Proposed Research section.

Research which has been carried out under current NSF support falls under three basic categories: (1) Studies with aerosol generation (2) studies with aerosol transport and evaporation (3) studies with aerosol and vapor interactions with plasmas.

1. FUNDAMENTAL ASPECTS OF AEROSOL GENERATION AND TRANSPORT WITH PNEUMATIC NEBULIZATION

1.1. *Drop Size Distributions.* It is important to characterize the processes which take place when

aerosols pass through spray chambers and also when they enter plasmas. We have studied the aerosol generation process in some depth, and from this work some surprising results have emerged. These may be summarized as follows: (1) the mean drop sizes of all aerosols generated pneumatically are *much* smaller than is predicted from calculations using the classical Nukiyama and Tanasawa equation. The difference may be as much as a factor of 20x, and is particularly noticeable for low surface tension organic solvents. For example, under typical operating conditions (1.9 mL/min liquid flow and 1.1 L/min gas flow) the Nukiyama and Tanasawa equation predicts a primary Sauter mean diameter (D3.2) of 79.7 μm for H_2O and 147.1 μm for n-butanol.[23] The actual experimental data, obtained with Fraunhofer laser diffraction, are 11.1 μm and 7.4 μm respectively. Not only are the experimental values much lower than the Nukiyama and Tanasawa predictions, but the Nukiyama and Tanasawa equation also predicts that the organic solvent will produce an aerosol with a mean drop size *substantially greater than* that of the aqueous aerosol, which contradicts both experience and common sense.

1.2. *Aerosol Modelling.* Based on a series of extensive studies with pneumatically generated aerosols, we have begun the development of various modelling exercises. Our initial studies have allowed us to produce an empirical equation, which gives a quite good fit to experimental data generated with Meinhard-type nebulizers, and so allows both Sauter mean aerosol spread (*i.e.* size distribution) data to be estimated with a knowledge of the nebulizer nozzle dimensions. We are also in the process of developing a potentially much more useful, and more generally applicable, model which allows for differences in nebulizer type, and which includes variable parameters such as gas and liquid flows and solvent surface tension directly in the equation, and not buried in empirical constants as in our earlier work.[23]

1.3. *Aerosol Evaporation.* The value of desolvation for improving detection limits has long been known, especially when applied to ultrasonic nebulization. However, it has rarely been applied *except* for use with ultrasonic nebulization. Furthermore, the precise mechanisms of solvent vapor and aerosol interactions with plasmas have not been rigorously examined until recent years. When an ultrasonic nebulizer is used without a desolvation system, an additional solvent loading is placed on the plasma because the solvent transport increases by a factor similar to that of the analyte, which is typically of the order of 10-30x. The need for the plasma to dissociate the increased solvent mass places a much greater energy absorption load on the plasma, with a consequent reduction in plasma excitation and ionization temperature.

We have carried out detailed studies with various desolvation systems, involving both the direct cooling of the spray chamber and the combination of a heated spray chamber and cooled condenser and observed the changes in signal response for both ICPAES and ICP/MS. In these studies, we have measured the signals under conditions where the *solvent* transport properties of the system are also carefully measured, so that detailed correlations can be made between solvent loading and analytical response. We have correlated these studies with measurements of fundamental plasma properties, such as electron densities and excitation and ionization temperatures.

In ICP/MS, the particular value of highly efficient desolvation, involving both a heated spray chamber and a double chamber condenser is clear, where the BaO^+/Ba^+ ratio is reduced to <0.04% and the CeO^+/Ce^+ ratio is reduced to <0.08%, which are excellent values for the reduction of isobaric interferences.

1.4. *Transport Processes and Particle Velocities.* The ability to understand the nature of processes which limit the transport of aerosol through spray chambers is still of utmost importance to analytical ICPAES, ICP/MS, microwave/AES and microwave/-MS. As yet the models are not quite clear, although there has been ongoing discussion from various groups for a number of years.[22,24] The ability to deliver a clear picture of what occurs in aerosol transport is largely limited by our present ability to characterize the *size distribution* and the *velocities* of the aerosol particles flowing through a spray chamber and into an ICP torch or a microwave torch. We have carried out some preliminary studies of particle velocity profiles measured with a photon correlation anemometer (phase Doppler velocimetry system) which have shown some extremely interesting data on aerosol velocities a few cm away from the tip of a pneumatic nebulizer. The high velocities of the particles (approx. 40 m/s) are noteworthy, but even more interesting is the rather narrow range of velocities of the particles in the aerosol stream, and the very sharp velocity cutoff which occurs outside the relatively tight aerosol beam. This is of particular importance for *chromatographic interfacing*, as it will directly influence chromatographic band broadening.

2. ULTRASONIC NEBULIZATION.

2.1 *Drop Size Distributions.* We have carried out recently a detailed study of the basic characteristics of ultrasonic nebulizers. Our recent work has been aimed at: (1) attempting to discover exactly what the aerosol characteristics of ultrasonic nebulizers are (2) seeing if the data fit any of the pre-existing models for ultrasonic nebulizers and (3) attempting to overcome the weaknesses of the nebulizers based on this knowledge.

Our work has shown a number of interesting and unexpected phenomena. We have found that the relationship of Lang[25] used to predict the primary numerical mean drop size, D_n, for ultrasonic nebulizers:

$$D_n = 0.34\,(\pi\sigma/\delta F^2)^{0.33} \qquad \text{-------- (1)}$$

where σ = surface tension, F = frequency and δ = density, fits quite well with experimental data. That unremarkable fact leads, however, directly to some important insights on the performance of ultrasonically generated aerosols. The values predicted using the Lang equation are *numerical mean diameters*, rather than the analytically much more relevant Sauter or mass mean diameters. By contrast, the mass mean and Sauter mean diameters *do* change substantially as liquid flow and rf power to the crystal are changed.

Our studies have also shown that, most interestingly, the drop size distribution of a typical ultrasonic aerosol is by no means monodisperse, as has implicitly been assumed through the use of the Lang Equation. In fact, the *primary aerosol* (*i.e.* aerosol at the face of the ultrasonic nebulizer) may have a higher percentage of large drops than does a typical aerosol generated pneumatically with a Meinhard nebulizer. Our work has led us to believe that two key factors for successful operation of an ultrasonic nebulizer are: (1) ensure a highly uniform liquid loading on the transducer face (2) disperse the aerosol drops rapidly when formed, to avoid the agglomeration which will otherwise occur close to the crystal face. These two issues have now been addressed, in a preliminary fashion, by forcing the analyte onto the face of the crystal as a very fine (25 μm diameter), high velocity (approx. 20 m/s) liquid jet, running at 0.5 mL/min. The use of this jet, in place of the usual stream of liquid flowing onto the crystal face produces a quite dramatic change in the operation of the transducer. The very fine, uniform film which is formed as the jet strikes the crystal surface immediately forms into a visually quite striking, stable, standing wave pattern, quite unlike any normal system where the liquid runs directly onto the surface of the transducer from a larger bore tube. The liquid film at the antinodal points of the standing wave pattern immediately forms aerosol, whereas the liquid at the nodes never leaves the transducer face. If the liquid jet is stopped, the nodes remain unchanged for an extended period of time.

The stability of the aerosol generation process, and of the rf loading (and hence the surface power density coupling to the liquid film) is also markedly improved compared to normal sample injection. Another significant improvement in the ultrasonic nebulizer operation has been obtained through directing an Ar gas dispersal jet tangentially across the crystal face, very close to the surface. This substantially reduces the agglomeration of drops which initially leave the transducer surface at high velocity, and which would otherwise collide with one another to form multiple drops. The use of dispersion gas therefore appears to produce an aerosol with an improved drop size distribution compared to the conventional ultrasonic nebulizer. Additionally, the *band width* and *noise level* of flow injection or chromatographic peaks with the liquid jet/dispersion gas system are dramatically improved over conventional drip introduction. The band width is improved by approximately a factor of 3x and the noise by 2x. This translates directly to improved detection limits and enhanced chromatographic resolution. *(This is discussed further in the Proposed Research Section 3.7, p. 17).*

2.3 *Aerosol Evaporation.* The higher *analyte* transport found with USN as also associated with higher *solvent* transport. To produce a major improvement in detection limits, therefore, ultrasonically generated aerosols require desolvation.[26] The memory effects and aerosol dilution effects which typically accompany heated spraychamber/condenser systems make them problematical for normal practical analysis, and even less ideal for chromatographic coupling. We are currently investigating various alternative means to circumvent these limitations.

2.4 *Particle Velocities.* The velocities of the aerosol drops as they leave the surface of the ultrasonic transducer are presently unknown. However, it is clear that close to the transducer surface the particle velocities must be quite high. Our preliminary work has indicated that without aerosol dispersion close to the transducer surface, using a gas jet, agglomeration readily occurs, with a consequent increase (degradation) in the aerosol drop size. There is therefore a need to measure the particle velocities just above the transducer face in order to determine what effect operating parameters have on these particle velocities, as a means of minimizing droplet agglomeration.

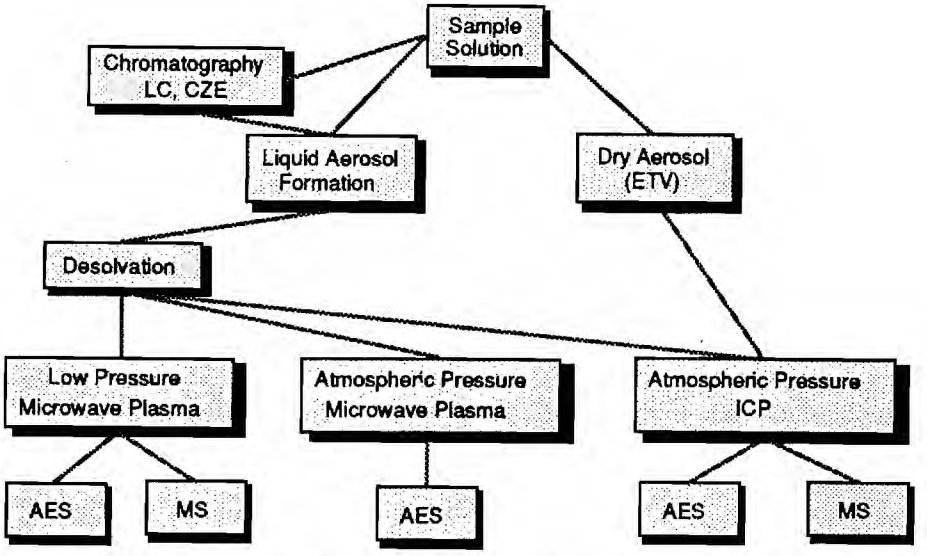

Fig. 2 Sample Introduction Paths Discussed in This Proposal

influence analyte transport by up to a factor of five. However, with proper flow and pressure control, the interface can be made to function quite effectively with a 1-3 torr He or Ar MIP.

7.3 *Particle beam enrichment; skimmer geometry.* The spacing and orifice diameters of the skimmer components are very important in determining both the efficiency with which particles move through the system, and also the pressures in the various parts of the system. We have carried out preliminary studies with the various options of nozzle/skimmer and skimmer/skimmer spacings, and also with skimmer diameters. From these studies, we have been able to develop an interface design which works quite effectively with the microwave discharge.

PUBLICATIONS ARISING FROM CURRENT NSF SUPPORT

Publications and conference presentations arising from this work are listed on page 21.

PROPOSED RESEARCH PLAN

Goals. Our research goals are the following: (1) improve the accuracy and detection limits of ICP-AES, ICP/MS, microwave/AES and microwave/MS through control of analyte aerosol properties (2) develop highly efficient, solvent removal interfaces for coupling LC and CZE with ICPAES, ICP/MS, microwave/AES and microwave/MS (3) improve basic understanding of processes taking place during nebulization, transport and aerosol-plasma interactions (4) develop highly efficient low-flow nebulizers for use in LC and CZE interfacing. The areas covered by this proposal are shown in Figure 2.

Particle Size and Solvent Loading. In this research an attempt will be made to think first in terms of the specific and individual sample introduction needs of a particular plasma type, such as an atmospheric Ar plasma for ICP/MS use, or a low pressure He plasma for use as an elemental detector for LC. Then, bearing in mind the thermal, excitation and ionization capabilities of each plasma, to determine the optimum analyte mass flow, mean particle size and particle size distribution for each plasma type. Finally, the development of appropriate sample delivery systems which will provide suitable aerosols for each plasma will be attempted.

Clearly, the present level of understanding of plasmas and their interactions with aerosols is not well enough developed to allow a very precise set of criteria to be defined for each sample delivery system. However, some generalizations may be made for various plasma types which will be useful as guidelines. For example, it now appears reasonably clear that sample delivery systems for atmospheric pressure Ar ICPs have been empirically optimized as a balance between the rate of analyte delivery, W_{tot}, and the rate of solvent delivery, S_{tot}. In a typical Ar ICP, doubling the solvent aerosol loading (from 10 to 20 mg/min) causes a 1,000 K drop in ionization temperature (from 8,000 to 7,000 K). Increasing W_{tot} by allowing more large diameter aerosol drops to reach the plasma will also result in a proportional increase in S_{tot}. Consequently, while the number of atoms reaching the plasma per unit time will increase, the instantaneous ionic population may actually *decrease*, due to the low-

ered temperature of the plasma. The size of the analyte particles remaining in an ICP after solvent evaporation is almost certainly largely a chance factor resulting from the size range of the primary aerosol which remained after passage through a spray chamber designed to pass a certain mass of solvent aerosol to the plasma. The maximum size of *dry* particles capable of efficient vaporization by an Ar ICP is unknown, although it has been suggested that Al_2O_3 slurry particles as large as 5 μm may be vaporized with reasonable efficiently. With present ICPAES and ICP/MS systems, which deliver *wet* aerosol with a mean diameter of approximately 2 μm to the plasma, the dry particle size remaining after solvent evaporation from a 1 ppm solution would be approximately 20 nm. When comparing an upper limit of possibly 5 μm with a present usage of typically 20 nm, it seems that dry particle size is not presently a real limitation of analyte vaporization in the ICP. Of course, particle size also plays an important role in determining the *precision* of measurements, and signal noise will generally increase with increasing particle size.

In contrast to the atmospheric pressure Ar ICP, which has been well studied for a number of years, low pressure He microwave plasmas (MIP) have been much less studied. As will be discussed in more detail later (see Section 5 below), there are many reasons for favoring use of the low pressure MIP. However, the thermal energy available from such a plasma, which runs with a typical maximum input power of 150 W, is so limited that almost any solvent loading has a serious, negative effect on the plasma. It is very probable also that particle size limitations will be much more severe with this type of source, making it particularly prone to matrix interferences. For these reasons, it will be essential to introduce analyte to the plasma only as a stream of *very small, solvent-free* particles. The extent of desolvation necessary, and determination of the maximum permissible particle size will also be discussed later.

We propose to do this predominantly using liquid sample introduction, as this will remain undoubtedly the most convenient and effective means of sample introduction for the foreseeable future, but we intend also to develop the microsampling capabilities of ETV introduction to a point where it will provide a useful adjunct to routine liquid sample introduction.

As a general approach, we intend to focus on the basic, underlying phenomena of each component of the sample introduction process. For liquid aerosol studies key issues include: (1) generating aerosols of controlled particle size (2) evaporating solvent efficiently from these aerosols (3) removing the evaporated solvent vapor from the dry aerosol and (4) vaporizing the solvent-free analyte particles rapidly and completely in the plasma. For dry aerosol (ETV) studies this will involve: (1) generating small, uniform and *reproducibly* sized particles suitable for direct introduction to plasmas (2) controlling the particle size, primarily through control of the temperature environment of the furnace and the residence time of the element on the surface (3) ensuring efficient transport of these particles to the plasma.

We believe that the likelihood of this program yielding tangible benefits is enhanced by its focus on achieving more *precise* and *intentional* control over aerosol generation and transport processes than has been possible previously. With our present knowledge of the influence of solvent and nebulizer parameters on the formation of primary aerosols by various types of pneumatic, ultrasonic and MAG-type nebulizers, we should be able to achieve a level of control over aerosol formation which has not been possible before. The experiments to be carried out under each of the above headings will be of several types, dependent on the type of plasma to be used (*e.g.* atmospheric pressure Ar ICP, low pressure or atmospheric pressure He or Ar microwave plasma). Although many nebulizers and interfaces are equally suitable for several types of plasma, there are some restrictions. For example, the MAG-particle beam interface only works efficiently at present with reduced pressure plasmas.

1. IMPROVEMENT OF DETECTION LIMITS, ACCURACY AND PRECISION THROUGH CONTROL OF AEROSOL PROPERTIES

1.1 *Fundamental Aspects*. For a plasma in LTE at a given temperature, the major factors which influence detection limits are: (1) the net rate of analyte mass transport to the plasma, W_{tot} (2) the mean particle size, D3.2, of the tertiary aerosol reaching the plasma (3) the breadth (Span) of the particle size distribution of the tertiary aerosol (2) the mass of solvent aerosol, S_{liq}, reaching the plasma (3) the amount of solvent vapor, S_{vap}, reaching the plasma, and (4) the lifetime, t_p, of the evaporating analyte particle in the plasma.

Proposed experiments are aimed at improving detection limits through both an increase in analytical signal and a decease in background noise. Typically, the rate of analyte mass delivery to the plasma, W_{tot}, is around 1% of the injected mass. An clear example of how increasing the rate of analyte transport to the plasma may improve detection limits is shown by the use of ultrasonic nebulizers. An ultrasonic nebulizer generally produces a higher percentage of small drops in the primary aerosol than does a pneumatic nebulizer, and consequently

a higher percentage of the primary aerosol passes through the spray chamber and reaches the plasma. Typically, W_{tot} increases by 10x. With reasonably efficient solvent removal, the plasma temperature can be kept reasonably constant during this process, and so detection limits also improve, and do so approximately in proportion to the increase in W_{tot}.

There is no fundamental reason why the analyte transport efficiency, ε_n should not approach 100%. In fact values approaching 100% ε_n have been reported for frit nebulizers. However, ε_n comparisons may be deceptive when flow rates also differ substantially, and this is the case with frit nebulizers, which operate at very low flow rates. In fact the W_{tot} values for frit nebulizers are generally not very much greater than those from pneumatic nebulizers, and are lower than those from ultrasonic nebulizers. What should give rise to major improvements in detection limits is to increase ε_n to close to 100%, while still operating at normal (0.5-2 mL/min) flow rates. In this case, the W_{tot} values should increase by approximately 100x compared with normal pneumatic nebulization.

1.2 *Aerosol Size.* A direct correlation exists between signal noise and particle size,[38] as one would expect from a consideration of statistical factors. It should therefore be possible to improve detection limits by approximately 5x through a reduction in *sample introduction signal noise.* A primary source of this noise is liquid aerosol entering, and interacting with, the plasma. This causes local variations in plasma temperature through the interaction of evaporating solvent drops with the plasma. We believe that this noise is directly related to both the *size* and *size distribution* of evaporating solvent aerosol drops in the plasma. An aerosol with a finer size distribution and a smaller mean particle size should lead to a direct reduction of this noise. This improvement may be partly canceled out through the presence of high matrix concentrations, through an increase in background, through influencing the plasma conditions and by adding statistical noise to the analytical signal. However, there now exists a relatively straightforward and highly effective solution to problems of this type through the use of ion exchange pre-columns, of the type recently developed by Dionex, which strip out matrix elements such as Ca and Na from the solution with very high efficiency, and so essentially eliminate matrix problems of this type.

In our experiments, we propose to use developments of three approaches that have shown considerable promise for this type of highly controlled aerosol generation. These are: (1) a modified MAG nebulizer, such as those now used routinely in organic particle beam LC/MS interface (2) a new type of ultrasonic nebulizer, the Jet Ultrasonic Nebulizer (JUSN) and (3) the Supercritical Fluid MAG nebulizer.

1.3 *MAG Aerosol Generator.* The particle beam interface used in our organic LC/MS work incorporates a MAG (Monodisperse Aerosol Generator).[39] Although the size distribution of the aerosol which the commercial versions of this device produce is no longer truly monodisperse, the acronym has remained. In fact, when used correctly in its original form, the MAG is still capable of producing a *highly uniform* aerosol, with a mean drop size which may be controlled in the range from 10-100 μm, with a spread of approximately ±20%. We are presently carrying out a detailed study of the operation of the MAG under conditions relevant to normal sample introduction conditions (0.5-2.0 mL/min), and also characteristic low-flow conditions (10-100 μL/min). The MAG has the great advantage over a conventional pneumatic nebulizer that it can operate very readily at low flows. Its principle of operation relies on the energy contained in the liquid, rather than in the gas jet. In fact, a highly uniform stream of drops may be formed just purely by spraying the liquid jet directly into the laboratory air, or into a reduced pressure chamber, without any gas enhancement or surface impaction. The only requirement is that a stable liquid jet be maintained from the capillary tip, which means that for low liquid flows a tapered capillary tip with an orifice size of 5-7μm is ideal.

From our experiments it appears that a good initial drop size for optimum analyte transport through the interface is approximately 20 μm, although this is somewhat dependent on solvent type and solvent flow. The rate of solvent evaporation is maximized by operating the chamber at 100-200 torr, which ensures that the rate limiting step in the evaporation is thermal transfer from the surrounding gas to the evaporating drop. The evaporation rate can be enhanced significantly through the use of He dispersion gas, due to its high thermal conductivity.

It might be considered, from comparison with the mean drop size of tertiary aerosols currently used in ICPAES and ICP/MS that these drops would be too large for introduction to the ICP. However, as discussed earlier, solvated drops of this size will, after desolvation give rise to dry particles in the 10-100 nm range, which lie well within the vaporization capabilities of the ICP.

1.3.1 *Particle Velocities.* A knowledge of the lifetimes, velocities and directions of the particles in various parts of the interface is of great importance

in understanding important processes which occur in the interface. The transport efficiency of the interface and its effect on peak broadening are two parameters of great interest, especially in chromatographic interfacing studies. Using a current model particle beam interface with a MAG aerosol generator results in a typical analyte transport efficiency of 15%, at 0.4 mL/min solvent flow. It is also of great importance to track the particles through the interface, to know their paths as well as their speeds. In the free-jet expansion region of the first chamber of the momentum separator they will experience velocities up to sonic and also have the opportunity to be entrained in highly turbulent gas flows. This will have a major impact on peak broadening, and becomes absolutely critical for low-flow situations, where any significant increase in external variance (*i.e.* variance in addition to that of the column) may exert a drastic (negative) effect on the chromatographic resolution of the system.

Preliminary studies have been carried out for velocities measured across a stream of primary (predesolvation) drops in the evaporation chamber. This showed that their velocities, measured with the laser Doppler system, were close to 40 m/s, and remarkably uniform in a direction orthogonal to the aerosol flow.[40] This indicates: (1) that an average drop lifetime in the evaporation chamber is ≤10 ms and (2) that very little turbulence and hence band broadening, should occur in this part of the system. The extremely short drop lifetime in the chamber also illustrates clearly the need for highly efficient energy transfer from the surrounding atmosphere to the drop surface.

After evaporation, the remaining solvent vapor and He gas are removed in a differentially pumped two-stage momentum separator. The dried particles have mostly sufficient momentum to travel with reasonable efficiency through the momentum beam separator (Fig. 1).

It is possible to make aerosols with a mean diameter substantially smaller than 20 μm by using a smaller capillary orifice. We have prepared tapered orifices from fused silica capillary with diameters down to 5 μm diameter with little difficulty, and these are capable of generating a stable jet at pump back pressures of ≤100 psi, which is quite acceptable for the zero dead volume fittings used to hold the capillary tube. The aerosols produced by such a nebulizer are of very low mean particle size, and quite uniform. Furthermore, as the aerosol generation process relies primarily on Rayleigh jet breakup, the interaction point of liquid jet and dispersing gas stream occurs 4-5 mm beyond the end of the liquid capillary tip. As a consequence, these nebulizers are quite remarkably free from blockage due to the deposition of solids on the capillary tip. We can routinely nebulize solutions containing 1% dissolved solids for many hours without blockage. If blockage should occur, the capillary tube can be replaced with a fresh tube in 1-2 minutes.

We propose with this system to make particle velocity measurements using a Malvern laser Doppler velocimeter (photon correlation anemometer). This system has a high power (3W Ar ion) laser and uses autocorrelation to obtain extremely high signal-to-noise values for small particles traveling at velocities up to and including sonic velocities. This system, which we have only had available for a few months, was custom designed to provide measurement capabilities for our specific type of interface, and so is uniquely suited to allow us to follow the complex, but very important particle dynamics of the particle beam interface as applied to LC-microwave/AES and LC-microwave/MS. More general discussion of these interfaces will follow in Section 5 below.

1.4 *Ultrasonic Nebulizer.* Present ultrasonic nebulizers (USN) typically provide 15-20% transport efficiency, and give overall a ten-to-twentyfold improvement in detection limits compared to conventional pneumatic nebulization.[19,26] In theory, USN should be capable of providing a 4-500x improvement (100x from improved analyte transport, 4-5x from noise reduction). This leaves a potential improvement factor of 20x available by USN through control of aerosol properties which is not currently achieved. This improvement should apply equally to ICPAES and ICP/MS.

Our recent studies with ultrasonic nebulizers have shown some very interesting and promising trends for their practical development as aerosol generators of small diameters aerosol drops. As mentioned earlier, the aerosol generated by typical commercial USN are far different from the popular conception, and actually possess a much wider particle size distribution than that produced by Meinhard type nebulizers. In fact standard design nebulizers produce aerosols with a substantial fraction of drops around 100 μm. However, our recent work with high velocity capillary jet interaction onto a piezoelectric transducer, combined with transverse gas dispersion of the aerosol close to the crystal face, has shown some very interesting effects. As shown in Fig. 3, there is a significant fraction of drops formed in the primary aerosol with diameters around 1 μm, and another group centered around 10 μm. We believe that it should be possible, by careful experimental design, to enhance this mode of aerosol formation, and produce an aerosol with a narrow distribution < 5 μm. As part of this

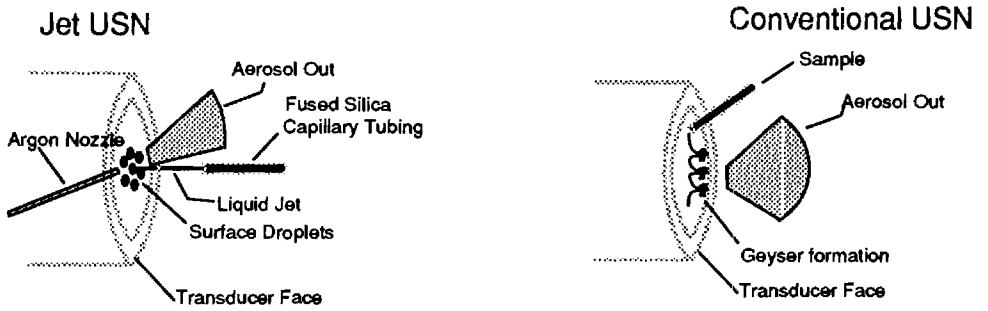

Fig. 4 Jet and Conventional Ultrasonic Nebulizer Operating Modes

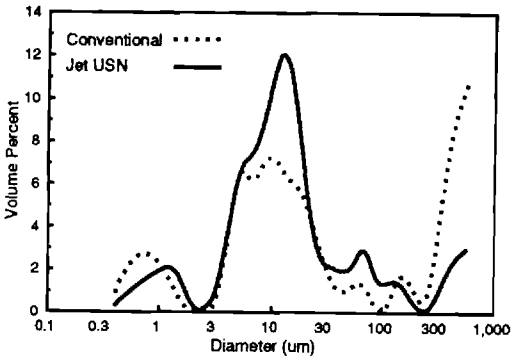

Fig. 3 Primary distributions from Ultrasonic Nebulizer

experimental design, we plan to construct transducer systems with much higher frequencies of oscillation than those presently used (which are generally around 1.2 MHz). By extending the frequency range to 2-10 MHz, we hope that the standing wave pattern on the transducer face may be reduced in size so as to enhance the formation of the very small droplets at the expense of the larger drops. This type of effect would not be observable with the traditional method of dripping the liquid onto the crystal face, as the film thickness is much greater in this case, and probably results in at least a partial undesirable "geyser" formation mode of nebulization (Fig. 4). Although the precise mechanism of aerosol formation in the jet impact mode of operation has not yet been clarified, as part of this work we intend to develop a model based on the experimental data obtained at several frequencies. With the jet impact mode, we do not anticipate any problems with the necessary scaling down of the crystal size at higher frequencies, as aerosol formation in the jet impact mode occurs in a space on the crystal surface only 3-4 mm in diameter, and so a thin, small diameter crystal should present no practical problem. We already have available a 2 MHz crystal, and 5 and 10 MHz crystals can be readily fabricated. Suitable rf power supplies will be fabricated in house.

1.5 *Supercritical Fluid/MAG Aerosol Generator (SFC/MAG).* In recent studies with (organic) supercritical fluid chromatography-LC/MS interfacing, using a particle beam LC/MS interface, we have joined the SFC effluent to the LC line with a low-dead-volume T-connector (Fig. 5) The aerosol

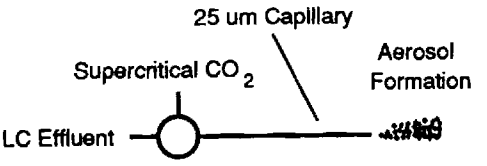

Fig. 5 Supercritical Fluid/MAG Aerosol Generator

resulting from this *internal* addition of gas to the liquid line has proven to have an exceptionally small drop size, actually below the measurement range of our Malvern system (*e.g.* <1.2 μm in diameter). This is much finer than any aerosol that we have previously generated by either pneumatic or ultrasonic means, and appears to be even finer than that produced by the fritted disk type of nebulizer. Ironically, this aerosol has turned out to be *not* very useful for its original intended purpose, which was for use with an organic particle beam LC/MS interface. The aerosol produced is so fine that most of the dry particles left after desolvation are pumped away in the momentum separator unit of the particle beam LC/MS interface. In order to make this nebulizer useful with a particle beam-type interface will require re-design of the momentum separator in order to work efficiently with the smaller drops. We have not yet been able to characterize the aerosol drop size, but propose to use SEM images of collected particles to generate data on the original aerosol distribution. We propose also to use an on-line size characterization system (see section 2.2 below) to confirm these results.

Unlike the fritted disk nebulizer, which is restricted to low liquid flow rates (<100 µL/min) and has major washout problems, the new nebulizer system appears to operate well over a wide range of flow rates, from normal (0.4-2 mL/min) liquid flows to very low liquid flows (<50 µL/min) and suffers from no apparent washout problems. Sample blockage is also not a problem, even for high solids content solutions up to 1% dissolved solids.

To the best of our knowledge, this is the first nebulizer to use gas and liquid flows *combined in the same actual stream*, as compared to co-axial flows of gas and liquid. In essence, the nebulizer provides many of the features of a Thermospray nebulizer, without the need to boil the solvent. The Thermospray nebulizer is an excellent device for interfacing to chromatographic separations, because it causes relatively little band broadening. However, one of the major limitations of the Thermospray nebulizer is that its very mode of operation may cause salting-out on the capillary tip, with often rapid and complete nebulizer blockage.

We propose to further evaluate the use of the SFC/MAG nebulizer, and examine both its basic aerosol size characteristics and its practical analytical properties. This device could be of considerable use for both normal atmospheric pressure nebulization in ICPAES and ICP/MS, as well as for interfacing with the low pressure microwave plasma. This device could have major implications for sample introduction by providing an aerosol with a much smaller drop size than is possible with either pneumatic nebulizers or with ultrasonic nebulizers. This could improve both analyte transport and detection limits quite considerably. At present, we propose to use the nebulizer to enhance the operation of normal *liquid flow pneumatic nebulization*, and *not* as a means to interface with SFC systems. This nebulizer would be of great value to *speciation* studies with LC and CZE, and also to flow injection introduction.

1.6 *Aerosol Modeling Studies for Pneumatic, Ultrasonic and MAG Nebulizers.* One of the most notable deficiencies in sample introduction for ICPAES and ICP/MS is the lack of useful models for describing the properties of aerosols and their transport from the point of generation to the plasma. The most critical lack is of a reliable model to describe primary aerosol generation from various classes of nebulizer. We have previously developed an empirical model to describe aerosols from certain solvents (H_2O, MeOH, n-BuOH) using concentric (Meinhard-type) pneumatic nebulizers. We are currently working to develop a more general model, based on physical parameters of solvents and nebulizers, in order to characterize pneumatic nebulizers more accurately than the Nukiyama and Tanasawa equation.

We have also begun preliminary studies for developing models to describe aerosols generated by ultrasonic nebulizers and MAG-type nebulizers. The work involves the generation and analysis of a great deal of data from different nebulizer types, operated under a wide range of conditions and with many solvent of different surface tension and viscosities. We propose to continue to gather data of this type and subject it to analysis using various computational approaches, including non-linear curve fitting routines and optimization procedures. This type of approach both helps with the generation of appropriate mathematical models and also indicates clearly which are the critical variables that influence the main parameters of mean drop size and drop size distribution. We feel that we are close to having some really practically useful models that will allow workers to *predict* the key properties of their aerosols, without the need to make any but some simple physical measurements of their systems.

2. ON-LINE PARTICLE CHARACTERIZATION OF SUBMICRON PARTICLES.

2.1 *Fundamental Aspects.* One of the major limitations of many of our present studies is our inability to size small particles efficiently. Laser scattering systems suitable for aerosol studies are unsuitable for particles <0.5-1.2 µm. Our only present option for particles below 1.2 µm diameter is to desolvate a salt solution, collect by impaction on a Cu surface and to measure particle sizes by scanning (SEM) or transmission (TEM) electron microscopy. This is a time consuming and tedious process, although for some of our work the ability to size particles microscopically will be very important, as when shape factors need to be considered.

2.2 *On-line Particle Size Characterization.* For many of our studies, the capability for on-line submicron particle sizing would be of great value. We propose, therefore, to develop an electrostatic sub-micron particle size analyzer for deriving particle size distributions for particles below the range currently possible. For many of the aerosols of real interest, such as those remaining after desolvation and those initially below the measurement range of the Malvern laser Fraunhofer system used in many of our studies (*e.g.* <1.2 µm diameter), such a system would be invaluable. The system will charge particles <1 µm with a unit charge, by passage through a corona discharge, apply a fixed and known velocity to the particle stream, and then deflect particles with an electrostatic field, as a function of their mass-to-charge-ratio (somewhat

akin to a mass spectrometer) by a voltage ramp applied to a deflection rod. The current (μA) carried by the remaining particles will be measured by collection on a silver-plated filter disk, which indicates the number of particles of a certain mass range removed from the system. As the probability of achieving a unit charge on small particles decreases non-linearly as the particle size falls much below 1 μm, a correction factor must be applied to compensate for this. However, the theory for this correction is well established. The particle size range open to the system should be approximately 0.01-1.0 μm.

In our work, we propose to develop an on-line sizing system (Fig. 6) as part of our low-pressure particle collection chamber, taking as our starting point commercially available hardware and software.

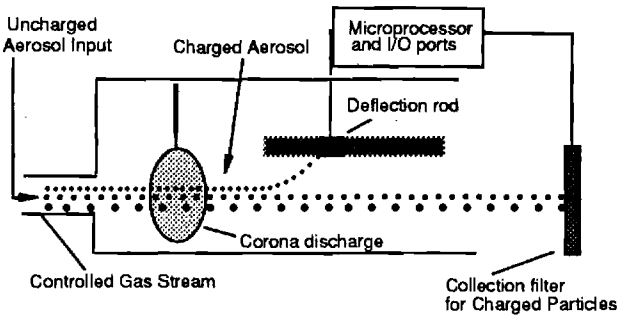

Fig. 6 On-line Sub-micron Particle Sizer

This equipment allow us to carry out on-line measurements of the size distribution of particles generated in various experiments, ranging from normal pneumatic nebulization to the novel SFC/MAG nebulizer described earlier. Using the system, we intend to investigate the effects of variations in gas and liquid flows, solvent types and analyte types on particle sizes. This type of measurement will only be applicable to stable (*e.g.* post evaporation) particles, which means that it will be effective for either salt crystals remaining after solvent evaporation, suspensions of monodisperse latex particles, or for highly involatile liquids such as dioctylphthalate (DOP). Unfortunately, it will not be suitable for kinetic measurements of rapidly evaporating droplets, a measurement of great interest in our work.

In order to calibrate this system against reference data, we will both use latex particle size standards and comparison with SEM photomicrographs, using the microscopic data analysis module for accurate size distribution estimates.

2.3 *Particle Velocity Measurements.* A major unexplored avenue in aerosol generation and transport is the measurement of particle velocities in the operation of nebulizers and aerosol interfaces, including both simple spray chambers and more complex solvent removal interfaces, such as the particle beam interface. Monitoring particle motion has profound implications for the understanding of basic aerosol phenomena and so subsequently for the design of improved systems. The aspects of particle velocity which exert a direct influence on important aerosol properties include: (1) the tendency of high velocity drops, close to the moment of formation, to agglomerate or coalesce so as to increase the population of larger particles in the aerosol stream. An instance where this has been observed is with the ultrasonic nebulizer, mentioned in Section 1.4, where conventional USN produce >60% of the aerosol mass in drops ≥100 μm diameter. All this aerosol is useless, and passes to waste. By dispersing the aerosol close to its point of formation, and so minimizing collisions between drops close to the transducer surface, it is possible to reduce these large drops by approximately a factor of 3x, so enhancing the percentage of useful drops in the range <30 μm nearly twofold. This first experiment, to prove the value of aerosol dispersion with a USN indicates that considerable progress could be made if more precise data were available of the aerosol properties close to the transducer surface. Non-invasive laser Doppler velocimetry provides a nearly ideal tool to explore this region of the USN where clearly very important processes take place. With our present laser Doppler system, it is possible to achieve spatial resolution better than 500 μm, which should provide an excellent opportunity for characterizing and controlling this important, and hitherto undetected, process of particle agglomeration.

Another situation where particle velocity, and turbulence characterization measurements would be of great value is in the operation of chromatographic interfaces. In this situation, an ideal flow profile for the aerosol is a rectangular profile, so that no dispersion will occur in the interface. Either turbulent gas mixing or laminar flow velocity profiles can give rise to significant band broadening, which will result in loss of both signal and chromatographic resolution. As mentioned earlier, some preliminary measurements with Doppler velocimetry have indicated that in the initial aerosol generated by a conventional pneumatic nebulizer, there is a relatively rectangular velocity profile, as one would wish.[40] This profile remains intact up until a critical gas flow is reached, when the particle flow stream suddenly becomes highly turbulent. This point would correspond to a condition of considerable band broadening in an interface. We have not as yet characterized any other places in the particle or gas flow, nor have we as yet examined other types of nebulizer or any of the particle beam-type inter-

faces. Typical particle flow profiles for different systems are shown in Fig. 7. The narrow velocity profile of the MAG-type system is very noticeable, compared to normal pneumatic nebulizers, as is its very narrow spatial spread within the chamber. Whereas normal nebulizers and spraychambers produce extensive aerosol wetting of the walls, the MAG-type system has negligible aerosol/wall interaction.

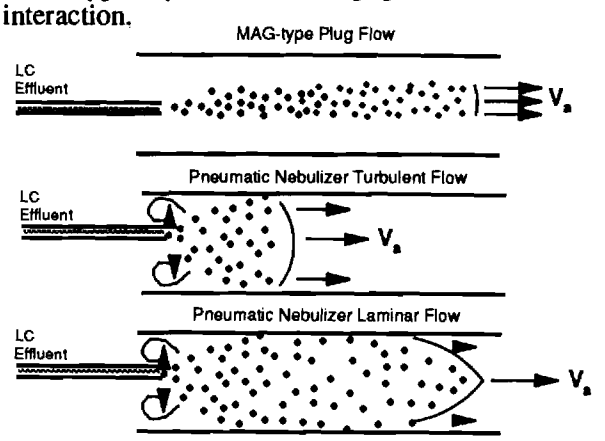

Fig. 7 Flow Profiles Through different Nebulizers

We propose to carry out extensive studies of this type using the laser Doppler system, in order to gain insights into the nature of aerosol loss processes and aerosol band broadening processes which occur in various nebulizer/interface combinations. The experiments will involve the tracking of aerosol streams at different distances from the point of generation for a number of nebulizer types, including pneumatic, ultrasonic and MAG-type nebulizers.

2.4. *On-line Mass Transport Measurements.* Another parameter of great importance to our measurements is the ability to measure rapidly the mass transport of μg or less quantities of analyte transmitted through various interfaces. It is necessary to work at such low mass loadings in order to simulate the aerodynamic properties of micro-crystalline particles moving through various environments, particularly following evaporation of solvent from the original aerosol. We propose to develop, therefore, an on-line quartz-microbalance detection system for rapid measurements of analyte mass transport rates through various interfaces. At present, such measurements require a tedious collection process, followed by washing off the analyte into a volumetric flask and subsequent determination by ICPAES or ICP/MS. With an on-line quartz microbalance approach, we could obtain much more rapid mass transport data. The microbalance detector would be positioned in a low pressure collection chamber, such as the one we use now SEM particle collection. This would eliminate the need to compensate for gas pressure effects on the face of the quartz surface. Of course, the particle flow would need to be stopped for the duration of the actual signal recording, as the momentum of the impacted particles would distort the true mass of particles collected.

3. INTERFACING LC, FIA AND CZE WITH AES AND MS

3.1 *Fundamental aspects of process.* In an ideal LC interface, the following key criteria would be satisfied: (1) analyte would be transported with nearly 100% efficiency from the column to the detector (2) chromatographic integrity would be maintained, with minimal peak broadening or peak tailing (3) all solvents and buffer systems would work equally well (4) all solvent aerosol would be removed, and solvent vapor would held at a very low level.

3.2 *Optimum analyte aerosol characteristics.* The optimum properties of an analyte for introduction to a plasma are: (1) The analyte will be in the form of microscopic particles, of the order of ≤500 nm, so that they will vaporize extremely rapidly in the plasma, free from matrix interferences (2) the particles will be essentially solvent free. This will allow their evaporation in the plasma to take place in an atmosphere of pure argon, and not be adversely influenced by a surrounding sphere of water vapor.

3.3 *Optimum solvent characteristics.* In an ideal LC interface, the solvent will not in any way influence the analytical signal. This means that it must not influence either the initial drop size distribution or the transport properties of the aerosol. With any pneumatic aerosol generator, the primary aerosol drop size will be heavily influenced by the surface tension of the solvent, so that a gradient elution separation (*e.g.* 70:30 H_2O:MeOH to 100% H_2O) will result in a significant change in transport efficiency of the eluting chromatographic bands, by approximately a factor of five in the quoted case. The evaporation of volatile organic solvents will be much more rapid than that of water, which again will cause a relative enhancement of bands eluting at this solvent composition and so lead to non-uniform transport characteristics of the interface.

3.4 *Desolvation.* The ability to remove solvent efficiently from the aerosol is highly advantageous for a number of reasons: (1) it addresses the non-uniformity of analyte transport discussed above (2) it enhances the analytical response by increasing the analyte mass transport to the plasma (3) it enhances the analytical response by reducing the solvent

loading in the plasma. This is particularly important in the case of solvent *aerosol*, as discussed earlier (4) in the case of MS detection, it will also decrease the magnitude of MO^+ and MOH^+ isobaric interferences to insignificantly low levels. For all these reasons, desolvation of LC effluent streams is highly desirable in the context of LC, FIA and CZE interfacing.

The primary limitations with current thermal desolvation systems (*e.g.* heated spray chambers) is the considerable dead volume they possess, together with the tendency of the liquid aerosol to impact on the chamber walls, and become a subsequent source of background signal and ghost peaks. The problem here is not the thermal process, but *the physical spread of the expanding aerosol spray.* In the particle beam interface, these factors are negligible, because *the aerosol does not at any stage touch the evaporation chamber walls.* In order for this to apply generally to evaporation chamber requires work on the design of the *aerosol*, rather than of the chamber and heater.

We believe that our present work with examining the spatial properties of expanding aerosols, using the laser Doppler system, have given us some very valuable insights into spray patterns, and the factors which influence them. We propose, therefore to apply studies of this type to the aerosol generation patterns of several of the more promising nebulizer types we have already examined, and to see of the lack of band broadening, memory effects and general aerosol loss processes which are so remarkably absent with the particle beam (MAG) system cannot be developed for other types of nebulizers, such as the ultrasonic nebulizer.

3.5 *Analyte transport.* The efficiency of the interface, and so ultimately its detection capabilities, will depend directly on the efficiency of analyte transport. However, the transport efficiency, ε_n, is a deceptive benchmark, because the magnitude of the analytical signal does not depend on the value of ε_n *unless the solvent flow rate is kept constant.* Unless this condition is met, ε_n may increase and the signal decrease simultaneously. The analyte mass transport, W_{tot}, is the number which should directly correlate with analytical signal and detection limit, at least in the absence of solvent interaction effects.

The analyte transport efficiency is critically tied in with the drop size distribution of the primary aerosol and the lack of impaction on spraychamber surfaces, as discussed above. Experiments in this area will therefore be closely allied with those to be carried out under the topic covered in Section 4.

3.6 *Chromatographic Considerations*

3.6.1 **Band broadening.** One of the key issues in chromatographic interfacing is the ability to maintain adequate resolution through the column/detector interface.[1] In AAS this presents little problem, as washout times are rapid (≤1 s). With typical pneumatic nebulizer/spraychamber systems, washout times are typically 40s, and band broadening becomes a significant problem. The use of ultrasonic nebulization with LC coupling is effectively impossible because of the excessive band broadening. When low flow (<500 μL/min) chromatography is used, these problems are compounded. For CZE (with flows in the range 10-50 μL/min), there is at present no established way to generate an aerosol other than to place a very high voltage (>10 kV) on the effluent and generate an electrospray aerosol. Unfortunately, this type of aerosol is not very useful for atomic spectrometry, because its high surface charge makes it likely to stick firmly to any grounded surface (*i.e.* spraychamber walls, plasma torch) in its path. The development of solvent removal interfaces which produce little band broadening is therefore a key requirement for effective LC and CZE interfacing.

3.6.2 **Flow rates.** As mentioned above, it is extremely difficult to generate a useful aerosol at very low flow rates. One of our major interests is to interface micro-column LC and CZE to ICPAES, ICP/MS, microwave/AES and microwave/MS detectors. Here, the flow rate is typically in the range of 10-100 μL/min, which is incompatible with normal pneumatic nebulization. The development of efficient, very low flow nebulizers is therefore an important goal of this research. Transport efficiencies close to 100% will also be essential, because of the very low masses of analyte present in the eluting peaks.

3.6.3 **Solvent types.** Although most elemental analysis is carried out in aqueous solvents, much chromatography is carried out in solvents containing various percentages of organic solvents, such as MeOH or CH_3CN, any many separations also require the use of gradients. As signal response in both ICPAES and ICP/MS varies greatly in the presence of organic solvents, this makes the role of an efficient desolvation interface even more important. This should then eliminate variable solvent/-plasma interactions that would otherwise vary during the course of the gradient separation.

3.7 *Nebulization and Desolvation Options.* Two issues which are vital to the success of chromatographic interfacing are: (1) maximize analyte trans-

port efficiency and (2) minimize band broadening. At very low flow rates (approx. 1 μL/min), the solvent loading in the plasma for a (hypothetical) 100% transport efficiency will be close to that with normal (1-2 mL/min) flow rates and low (1%) transport efficiencies, and so will not cause a reduction in plasma performance below normal levels, although it will also not allow for any enhancements. At intermediate flow rates (approx. 5-50 μL/min), solvent elimination will enhance analytical performance substantially, and at higher flows (≥50 μL/min), solvent removal is essential in order to maintain plasma stability. Solvent removal is generally desirable at all solvent flow rates, in order to maintain optimum plasma excitation temperatures (for ICPAES) and ion populations (for ICP/MS), and also to minimize isobaric MO^+ and MOH^+ isobaric interferences in ICP/MS.

In our experiments, we propose to develop low dead-volume, solvent removal systems which will combine high analyte transport efficiency with high solvent removal efficiency. This will be based on our work with jet ultrasonic and MAG-type nebulizers, in which the system will be designed to minimize solvent and analyte interaction with the chamber walls, and so minimize band broadening and memory effects. Although our work is in its early stages, and many factors need to be improved, including the need to optimize both the noise levels and the dispersion of the peaks, nevertheless, the jet USN shows some real promise as a low-flow aerosol generator for LC and CZE interfacing. The narrowness of the dispersion bandwidth of the Jet USN compared with a conventional USN is shown in Fig. 8.

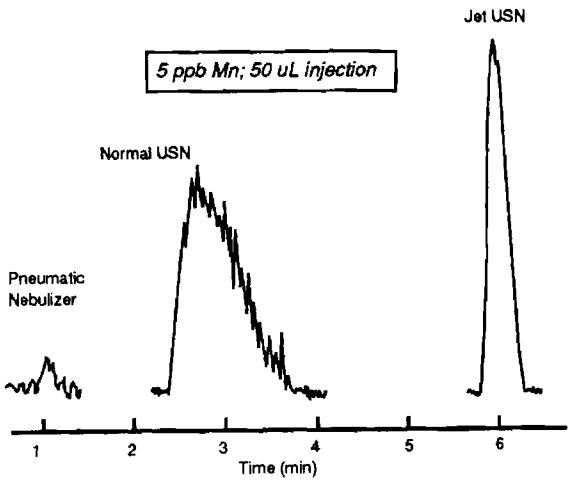

Fig. 8 Dispersion Profiles for Flow Injection Peaks Using Pneumatic and Ultrasonic Nebulizers With Desolvation

4. DEVELOPMENT OF LOW-FLOW LC AND CZE INTERFACES

One of the most difficult things to accomplish in nebulization is the efficient nebulization of very low liquid flows (1-100 μL/min) without causing extreme band broadening of eluting peaks. Possibly the most effective approach to date is the direct injection nebulizer (DIN), which as mentioned earlier, suffers from an inability to desolvate. A Thermospray approach has also been applied successfully to LC[41] and micro-LC[42] interfacing. We propose to study two basic options for low flow nebulization, both linked to low-flow and ultra-low-flow chromatographic techniques, such as micro-LC and CZE separations. The micro-LC situation is in principle the simplest, because it is readily possible to lead the column effluent through a 25 μm diameter or less tube to either a jet ultrasonic nebulizer, or to a MAG-type nebulizer. Both should be highly effective, with future developments in their performance, in generating a very fine aerosol which will be readily suitable for rapid desolvation and very high transport efficiency to the plasma.

5. PARTICLE BEAM/LOW PRESSURE MICROWAVE LC AND CZE INTERFACING FOR AES AND MS

5.1 *Basic considerations.* It is known that low pressure microwave induced plasmas (MIP) are capable of achieving very high excitation and ionization temperatures, and electron densities in excess of 10^{11} cm^{-3}. However, it is also known that these discharges are far from LTE, and so the thermal energy available for solvent and particle vaporization is very limited. For this reason, workers have tended recently to move away from these plasmas and concentrate instead on atmospheric pressure microwave plasmas. However, the analytical properties of microwave atmospheric pressure plasmas can never realistically approach those of higher power Ar ICPs, however efficiently the microwave field is applied. For this reason, the primary application of atmospheric pressure microwave plasmas has been as reasonable cost, highly effective elemental detectors for gas chromatography of either metal chelates or for C, P, S *etc.* monitoring of normal GC organic separations.

The reasons for the present neglect of the reduced pressure (1-10 torr) MIP are quite logical, but pre-date either: (1) the present level of understanding and control over sample introduction processes and (2) the advent of Surfatron microwave couplers. For these reasons, we believe that the low pressure MIP has excellent future prospects as an analytical source. We propose to focus on its

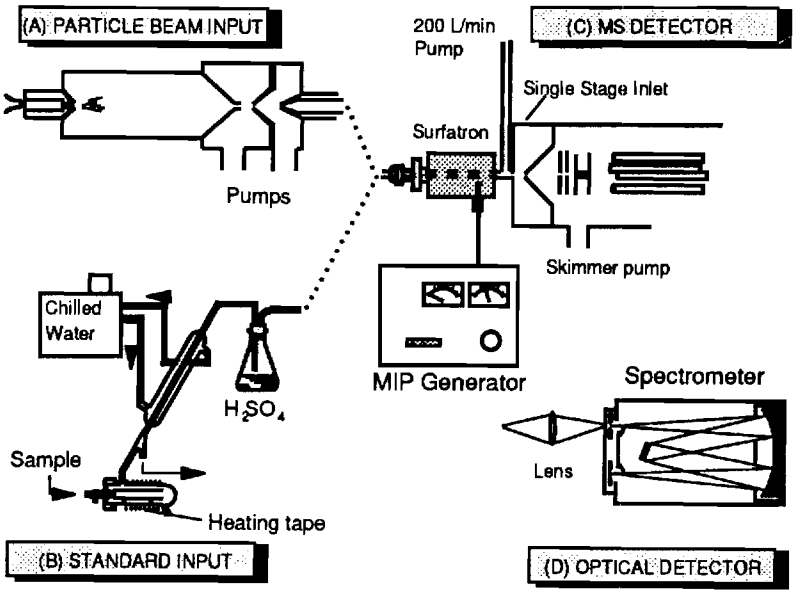

Fig. 9 Reduced Pressure Microwave Plasma Input and Detector Options

excellent excitation and ionization properties, and to allow it to function primarily in an excitation and ionization mode, not in a vaporization mode, by ensuring that analyte reaches it only on the form of *very small, dry* particles. In order for the energy of the discharge (<200 W) to be sufficient to vaporize and ionize the analyte, it is essential that the analyte aerosol be presented to the plasma as *solvent-free, nanometer-size* particles. The most successful attempts to introduce sample in this form to the low pressure MIP were the MINDAP experiments carried out several years ago by Hieftje *et al.*,[43] using an electrothermal wire vaporizer to introduce a solvent-free aerosol to the plasma. This device, which produced excellent detection limits, had the limitation of being a discrete system, not allowing the continuous sample introduction necessary for chromatographic interfacing, and also suffering from matrix interferences at high matrix loadings. In the light of recent studies with ETV sample introduction to plasmas in ours, and others laboratories, problems of matrix variations with ETV sample introduction are to be expected, especially when a heated filament, rather than a graphite furnace is used. Additionally, the more efficient and stable Surfatron source was not available to the MINDAP studies.

We therefore believe that the reduced pressure He MIP is a most valuable source for atomic emission and inorganic mass spectrometry purposes. It appears that the main limitation has been in the sample introduction stage. It is hoped that present sample delivery systems will allow analyte to be delivered to the plasma in a sufficiently small and sufficiently reproducible size range that it will be able to achieve its potential as a versatile analytical source. Possible applications include its use as an elemental detector for on-line LC work (by analogy to the highly efficient GC atomic emission detector now commercially available). Our recent work with the atmospheric pressure MIP has demonstrated that detection limits for a wide range of elements may be improved by up to an order of magnitude *simply by removing the last traces of water* from the desolvated aerosol introduced to the plasma. In every other regard, the system was as previous experiments, and used conventional nebulization.

5.2 *System design.* Our current low pressure microwave plasma system is shown schematically in Fig. 9. The system has options of either particle beam or other (*e.g.* ultrasonic desolvation system) sample introduction. Presently, the system is configured for as an emission spectrometric source, but removal of the optical window would allow configuration as a replacement for the source in our ICP/MS system.

We propose to develop this source both for AES and for MS use. Although we believe that AES can be a very powerful detector for such an interface we feel that the most attractive aspect of the source is its ability to interface very readily with the low pressure ion optics of the Perkin-Elmer Sciex Elan mass spectrometer. The low pressure nature of the source would allow the sampling cone stage of the current mass spectrometer to be removed, needing

only one additional stage of pressure reduction before entry into the quadrupole region of the mass spectrometer. We hope that by this means the sampling efficiency of the entire system may be improved significantly over the present arrangement. With present systems, only approximately 1% of analyte actually reaches the plasma, several percent are ionized in the plasma, again only a few percent are sampled into the first sampling cone, and again only a few percent pass through the second skimmer cone. In total, maybe 1 ion arising from 10^5 atoms originally introduced to the system actually reaches the quadrupole region of the mass spectrometer. With the proposed interface, net analyte transport efficiency should be capable of improvement by approximately 500x (50x analyte transport to plasma, 10x skimmer sampling), with the hope that this would lead to a comparable lowering of detection limits.

We propose to carry out experiments with several solvent removal interfaces for this plasma. We have achieved initially very promising results using both a conventional nebulizer/heated spray-chamber/condenser interface, and a MAG particle beam interface. In the conventional nebulizer system, a single-stage pressure reduction approach, essentially a single-stage momentum separator from the particle beam system, was found to be highly effective for pressure reduction with efficient analyte transport. We propose to test both MAG and jet ultrasonic nebulizers for this study.

5.3 *Use As Elemental Detector for LC and CZE.* The system described in section 6.3 will be further refined for operation as a detection system for both normal (4.6 mm) bore LC, micro-column LC and CZE separations. With the LC systems, the column effluent will pass directly to a 25 μm fused silica capillary under pressure, and the jet produced will then be used either with a jet ultrasonic nebulizer or a MAG nebulizer. By using small-bore tubes and zero-dead-volume connectors, system dead volume will be kept to very low levels. With CZE, the chromatographic effluent will not naturally form a jet, as the osmotic column pressure is too low to do this. Consequently, we propose to use a hybrid form of LC/CZE, as proposed recently by Niessen[44] for LC/MS use, in which a high pressure solvent flow can be switched into the CZE column flow, causing temporary pressure increase and the formation of a jet. After pressure release, the separation returns to its normal mode, and so diffusional band broadening does not become a dominant factor as with normal LC separations, and good separation efficiency is maintained.

6. ELECTROTHERMAL AES AND MS SAMPLE INTRODUCTION

The utility of electrothermal sample introduction is still of considerable interest for ICPAES, and particularly for ICP/MS sample introduction of micro samples. Our work will concentrate on the precise nature of vapor and particle interactions which take place soon after the vaporization step. We will attempt to determine with greater accuracy the precise nature of the crystalline solids which result when elements are vaporized from different matrices, and how the particle sizes of these agglomerates may influence particle transport to the plasma. We will carry out collection experiments with these species, taking SEM photomicrographs, and carry out a detailed analysis of particle size distributions, in an attempt to relate these properties to the vaporization characteristics of material from the furnace surface. The ability of various furnace surface treatments, such as Mo and Ta, to generate a more uniform particle size from the different matrix types will be investigated. It will be a goal to produce an operating environment which will allow particles with much more uniform sizes to be generated, as we believe that this will remove the interference effects previously observed, and allow ETV sample introduction take its place as a valuable adjunct to the other sample introduction techniques currently found useful.

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PUBLICATIONS FROM CURRENT NSF SUPPORT: CHE88-08183

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2. "Reply to "Comments on Influence of Water on ICP," by L. de Galan," Richard F. Browner and Stephen E. Long, *Spectrochim. Acta, Part B,* **1989**, *44*, 831.

3. "Evolution of Drop Size Distributions for Pneumatically Generated in Inductively Coupled Plasma Atomic Emission Spectrometry," Antonio Canals, Vicente Hernandis and Richard F. Browner, *Spectrochim. Acta, Part B*, **1990**, *44*, 8.

4. "Experimental Evaluation of the Nukiyama-Tanasawa Equation for Pneumatic Nebulizers Used in Plasma Atomic Emission Spectrometry," Antonio Canals,Vicente Hernandis and Richard F. Browner, *J. Analyt. Atom. Spectrosc.*, **1990**, *5*, 61.

5. "Comparison of Desolvation Effects with Aqueous and Organic (CCl_4) Sample Introduction for Inductively Coupled Plasma Atomic Emission Spectrometry," Chankang Pan, Guangxuan Zhu and Richard F. Browner, *J. Analyt. Atom. Spectrosc.*, **1990**, *5*, 537.

6. "Fundamental Studies with an Ultrasonic Nebulizer," Matthew A. Tarr, Guangxuan Zhu and Richard F. Browner, *Appl. Spectrosc.*, **1991**, in press.

7. "Effect of Solvent and Transport Variables on Signal Intensities in Inductively Coupled Plasma Atomic Emission Spectrometry," Richard F. Browner, Antonio Canals and Vicente Hernandis, *Spectrochim. Acta, Part B*, **1991**, in press.

8. "Influence of Auxiliary Gas Flow Rate on Excitation Conditions in the Inductively Coupled Plasma," Chankang Pan, Guangxuan Zhu and Richard F.Browner, *Spectrochim. Acta, Part B*, **1991**, submitted for publication.

9. "Differences in Aerosol and Vapor Loading Characteristics for Organic Sample ICPAES," Chankang Pan, Guangxuan Zhu and Richard F. Browner, *J. Analyt. Atom. Spectrosc.*, **1991**, submitted for publication.

10. "Influence of Desolvation on Emission Features in ICPAES," Chankang Pan, Guangxuan Zhu and Richard F. Browner, *J. Analyt. Atom. Spectrosc.*, **1991**, submitted for publication.

11. "Flow Injection Characteristics for ICP/MS," Guangxuan Zhu, Chankang Pan and Richard F. Browner, *Spectrochim. Acta, Part B*, **1991**, submitted for publication.

DEVELOPMENT OF HUMAN RESOURCES

Listed below are the students, postdoctoral associates and visiting scientists who have participated in the present research program.

Graduate Students:

1. Chankang Pan, Ph.D. 1991
2. Ntombioyumsa Msimanga, 4th year Ph.D.
3. Vincent Nwogu, 4th year Ph.D.
4. Matthew Tarr, 3rd year Ph.D.
5. Annia Ruiz, 4rd year Ph.D.
6. Hanqi Zhang, visiting Ph.D. student from Jilin University, PRC.

Undergraduate Students:

1. Kevin Goodner, Summer U.R.P. student 1991
2. Brian Williams, Summer student 1991
3. Elaine Powers, Summer U.R.P student 1990

Postdoctoral and Visiting Scientists:

1. Dr. Guangxuan Zhu, Dalien Institute of Chemical Physics, P.R.C.
2. Dr. Antonio Canals, University of Alicante, Spain
3. Dr. Neal Barnett, Deakin University, Australia

TALKS PRESENTED BY STUDENTS AT NATIONAL MEETINGS

"Interactions of Liquid and Dry Aerosols in ICP/-MS: in Search of the Perfect Aerosol," Guangxuan Zhu, Edison Becerra, Vincent Nwogu and Richard F. Browner, Eastern Analytical Symposium, New York, October 1988, invited talk.

"Measurement and Prediction of Aerosol Characteristics for ICP Nebulizers,"Ntombioyomusa Msimanga, Antonio Canals, Vicente Hernandis and Richard F.Browner, FACSS Meeting, Boston, MA, November 1988.

"Interactions of Solids, Liquids and Vapors in ICP/MS: Potential for Advances," Guangxuan Zhu, Changkang Pan and Richard F. Browner, American-Society for Mass Spectrometry Annual Meeting, Miami Beach, FL, May 1989, invited talk.

"Sample Introduction Characteristics of Flow Injection with ICP/MS," Guangxuan Zhu, Changkang Pan and Richard F. Browner, American Society for Mass Spectrometry Annual Meeting, Miami Beach, FL, May 1989.

"Analytical Studies of Oxygen Addition in ICPAES and ICP/MS with Organic Solvent Introduction," Chankang Pan, Guangxuan Zhu and Richard F. Browner, FCASS Meeting, Cleveland, OH, October 1990.

"An Evaluation of the MAGIC Interface for Aqueous Sample Introdcution in Low Pressure Microwave Induced Plasma Emission Spectrometry," Annia Ruiz, Hanqi Zhang, Guangxuan Zhu and Richard F. Browner, FACSS Meeting, Cleveland, OH, October 1990.

"Particle Size Distributions and Transport Data of Ultrasonic Nebulizers Used for ICPAES and ICP/-MS," Matthew A. Tarr, Guangxuan Zhu and Richard F. Browner, FACSS Meeting, Cleveland, OH, 1990.

"The Effects of Solvent and Liquid Flow on a Proposed Model for Pneumatic Nebulizers," Ntombiyomusa D. Msimanga and Richard F. Browner, Pittsburgh Conference, Chicago, IL, 1991.

"Studies on Electrothermal Vaporization (ETV) Samle Introduction for ICPAES," Vincent Nwogu, Guangxuan Zhu and Richard F. Browner, Pittsburgh Conference, Chicago, IL, 1991.

CURRICULUM VITAE

Richard F. Browner ..... Regents Professor, School of Chemistry and Biochemistry, Georgia Institute of Technology

onal Data: Born 3/10/44, London, U.K. U.S. Citizen.

:ational Background:
B.Sc. University of London, Chelsea College, Chemistry - 1967
D.I.C. University of London, Imperial College, Analytical Chemistry - 1970
Ph.D. University of London, Imperial College, Analytical Chemistry - 1970

loyment History:

Postdoctoral Research Fellow Chemistry Department, University of Florida	1970-1972
Senior Scientific Officer Laboratory of the Government Chemist, London, U.K.	1972-1976
Assistant Professor School of Chemistry and Biochemistry Georgia Institute of Technology	1976-1980
Associate Professor School of Chemistry and Biochemistry Georgia Institute of Technology	1980-1984
Professor School of Chemistry and Biochemistry Georgia Institute of Technology	1984-1989
Regents Professor School of Chemistry and Biochemistry Georgia Institute of Technology	1989-present
Visiting Professor University of Manchester Institute of Science and Technology	May-July 1984

'nt Fields of Interest

element analysis: Atomic spectrometry; inductively coupled plasma mass spectrometry

organic analysis: Liquid chromatography/mass spectrometry interfacing; liquid chromatography/infrared spectrometry

ol characterization: Particle sizing, aerodynamic and kinetic properties of aerosols

's, Awards and Recognitions

:r Fassel Lecturer, Department of Chemistry, Iowa State University, Ames, Iowa (1990)

'y Research Author Award, Georgia Institute of Technology (1989)

letti-Pichler Award of the American Micro-chemical Society (1988).

ent - Society for Applied Spectroscopy (1988).

iate Editor - Applied Spectroscopy (1986-).

Foundation Faculty Grant Awardee (1983).

y for Applied Spectroscopy: National Tour Speaker (1983).

Society of Chemistry: 10th SAC Silver Medal Award for Analytical Chemistry (1982).

COLLABORATORS WITHIN PAST 48 MONTHS

1. Professor James A. de Haseth, Department of Chemistry University of Georgia
2. Professor Vicente Hernandez, Department of Analytical Chemistry, University of Alicante, Spain
3. Dr. Antonio Canals, Department of Analytical Chemistry, University of Alicante, Spain
4. Professor Neal Barnett, Department of Chemistry, Deakin University, Australia

GRADUATE ADVISOR

Professor Thomas S. West, Secretary General, IUPAC

POSTDOCTORAL ADVISOR

Professor James D. Winefordner, Department of Chemistry, University of Florida

MANAGEMENT PLAN

The following personnel in the School of Chemistry and Biochemistry will actively participate in the proposed research programs: (1) Richard F. Browner, Principal Investigator (2) Dr. Guangxuan Zhu, visiting faculty member from the Dalien Institute of Chemical Physics, Peoples Republic of China and (3) two graduate research assistants.

The principal investigator will be responsible for overall administration, planning and supervision of the proposed research activities and will contribute approximately 33% of his time (3 man months) to the project during the academic year. During the summer, the principal investigator will also devote 33% of his time (one man month) to the proposed research. Dr. Zhu, postdoctoral associate, will devote 100% of his time during the calendar year to the project.

JUSTIFICATION OF BUDGET ITEMS

1. PERSONNEL

Requested funds will support two full-year RA positions, one full-year postdoctoral position and one month of the P.I.'s summer salary. The RA positions, at 47% time, correspond to a total of 0.94 FTE positions. Additionaly, it is anticipated that there will be participation from several visiting scientists, including Dr. Antonio Canals (University of Alicante, Spain), who will participate with scholarship funds, or who are partly supported with our own limited discretionary funds available through the Georgia Tech Foundation.

2. PERMANENT EQUIPMENT

(i) *TSI SUB-MICRON PARTICLE SIZER*

As outlined in the proposal, a major need in our research program is to have the ability to monitor particles much smaller than is possible with our present, invaluable, Malvern laser Fraunhofer system (*e.g.* <1.2 μm). The Malvern system works admirably with the larger, solvated, primary aersol particles, but cannot monitor the sizes of *desolvated* aerosols. The Thermo-Systems (TSI) sub-micron particle sizing system is a well proven instrument, widely and reliably used in monitoring airborne particulates for pollution control, which covers the range 0.01 - 1.0 μm. The ability to monitor *rapidly* the particle size range below 1 μm is very important for our proposed research, because it is largely in this range that desolvated analyte particles lie.

We propose to use the basic components of the system and re-engineer it to provide on-line measurement capabilities for many of the small particle systems, such as the desolvated aerosols remaining after ultrasonic or MAG nebulization, which are presently inaccessible to on-line measurements. This will provide very useful information when system variables are altered in systematic investigations of the properties of these nebulizers and desolvation systems, such as gas and liquid flow, nebulizer physical dimensions *etc.*.

We believe that many of the really important properties of aerosols used in emission and mass spectrometry are heavily dependent on the size characteristics of the tertiary desolvated aerosols, which at present we can only monitor off-line, using SEM and TEM techniques. The sub-micron particle analyzer will give us small-particle capabilities comparable to our present large particle capabilities provided by the Malvern system.

(ii) *OLYMPUS MICROSCOPE, IMAGING AND SIZING SYSTEM*

A frequent need in our work is to obtain actual visual images of small particles. While the TSI small-particle analyzer will provide valuable information on aerosol properties, there is still the need for further particle characterization, including important factors such as *shape factors*. When particles dry, they often assume non-spherical shapes, and there all-important aerodynamic properties are determined significantly by their shape. Microscopic evidence of particle shape is very important to evaluate many parameters of the

important to evaluate many parameters of the aerosols which are generated by the electrothermal (ETV) and the MAG de-solvation interface. We propose to purchase a high quality optical microscope for the examination of collected particles, either directly, or as SEM photomicrographs. Additionally, the microscope would be invaluable for the accurate measurement of physical nebulizer and capillary dimensions. At present we have a relatively poor quality microscope that we use for semi-quantitative measurements, and have occasional access to another higher quality microscope with suitable depth of field in the School of Physics.

It would be of great advantage to us to be able to carry out much more frequent microscopic examinations in-house. Additionally, we request the purchase of a computer coupled video-image analysis detector to use with the microscope. This will allow us to obtain fast, accurate, quantitative image analysis data on a wide range of particles collected in various experiments. Again, the SEM images will be analyzed quantitatively for particle size distributions, which at present is essentially impossible, except by using some very subjective and semi-quantitative approaches. We also propose to use the image analysis system to obtain quasi real-time images of aerosols at the moment of generation from various nebulizers. This type of information is sadly lacking at present, and is difficult to acquire except by photographic means, which is slow and non-interactive. While the scan rate of the detector (25 ms) is much too slow to follow aerosol *formation* processes, which occur on a μs time scale, it should be fast enough to follow secondary aerosol transport patterns in various spray chambers and desolvation systems. This could be invaluable to help us with the precise measurements of velocity we propose to make using the laser Doppler system.

(iii) *RAININ MODEL HDX ACID-RESISTANT LC PUMP*

A major focus of our studies is the coupling of liquid chromatography with various emission and mass detectors. At present our pumps are all conventional LC pumps, not intended for use with strongly acidic solutions. We therefore request a pump with titanium and non-metallic wetted parts, suitable for pumping acidic solutions without either damaging the pump or contaminating the very dilute solutions used.

3. TRAVEL

(i) *DOMESTIC*

Travel funds are requested to attend and present the findings of this research at two major meetings (*e.g.* from FACSS, national ACS meetings and the Pittsburgh Conference) for each year of the grant.

(ii) *FOREIGN*

Travel funds are requested to attend and present a paper at the biennial Colloquium Spectroscopicum Internationale, to be held in York, U.K. in the summer of 1993. This is the premier international meeting in the field of atomic and inorganic mass spectrometry.

4. SUPPLIES

The research carried out by our group requires a substantial supplies budget. Costs included under this category include support for general electronic, optical and machining costs for our research, as well as the cost of argon to run our ICPAES and ICP/MS instruments. Additional needs are for photo- and electron-multipliers, torches, nebulizers and sample cones for the ICP/MS instrument, optical components, chemicals and mechanical parts. In recent years, these costs have risen substantially, and our budget often runs short in this category. The requested sum reflects recent operating costs of our research.

5. PUBLICATION CHARGES

Publication of our research in international journals is a high priority and the requested sum reflects typical expenses for page charges.

633-627

OMB Number 3145-0058

NATIONAL SCIENCE FOUNDATION
1800 G STREET, NW
WASHINGTON, DC 20550

PI/PD Name and Address

Richard F. Browner
Department of Chemistry
GA Tech Res Corp - GIT
Atlanta GA 30332

NATIONAL SCIENCE FOUNDATION
FINAL PROJECT REPORT

PART I - PROJECT IDENTIFICATION INFORMATION

1. Program Official/Org.	Henry N. Blount, III - CHE
2. Program Name	ANALYTICAL & SURFACE CHEMISTRY PROGRAM
3. Award Dates (MM/YY)	From: 07/88 To: 12/91
4. Institution and Address	GA Tech Res Corp - GIT Administration Building Atlanta GA 30332
5. Award Number	8808183
6. Project Title	Sample Introduction for Inductively Coupled Plasma Atomic Emission Spectrometry and Inductively Coupled Plasma Mass Spectrometry

This Packet Contains
NSF Form 98A
And 1 Return Envelope

NSF Grant Conditions (Article 17, GC-1, and Article 9, FDP-II) require submission of a Final Projec Report (NSF Form 98A) to the NSF program officer no later than 90 days after the expiration of the award. Final Project Reports for expired awards must be received before new awards can be made (NSF Grant Policy Manual Section 677).

Below, or on a separate page attached to this form, provide a summary of the completed project and technical information. Be sure to include your name and award number on each separate page. See below for more instructions.

PART II - SUMMARY OF COMPLETED PROJECT (for public use)

The summary (about 200 words) must be self-contained and intelligible to a scientifically literate reader. Without restating th project title, it should begin with a topic sentence stating the project's major thesis. The summary should include, if pertiner to the project being described, the following items:

- **The primary objectives and scope of the project**
- **The techniques or approaches used only to the degree necessary for comprehension**
- **The findings and implications stated as concisely and informatively as possible**

PART III - TECHNICAL INFORMATION (for program management use)

List references to publications resulting from this award and briefly describe primary data, samples, physical collections inventions, software, etc. created or gathered in the course of the research and, if appropriate, how they are being made availabl to the research community. Provide the NSF Invention Disclosure number for any invention.

	April 20, 1992
Principal Investigator/Project Director Signature	**Date**

IMPORTANT:
MAILING INSTRUCTIONS
Return this *entire* packet plus all attachments in the envelope attached to the back of this form. Please copy the information from Part I, Block I to the *Attention block* on the envelope.

PART IV — FINAL PROJECT REPORT — SUMMARY DATA ON PROJECT PERSONNEL

(To be submitted to cognizant Program Officer upon completion of project)

The data requested below are important for the development of a statistical profile on the personnel supported by Federal grants. The information on this part is solicited in response to Public Law 99-383 and 42 USC 1885C. All information provided will be treated as confidential and will be safeguarded in accordance with the provisions of the Privacy Act of 1974. You should submit a single copy of this part with each final project report. However, submission of the requested information is not mandatory and is not a precondition of future award(s). Check the "Decline to Provide Information" box below if you do not wish to provide the information.

Please enter the numbers of individuals supported under this grant.
Do not enter information for individuals working less than 40 hours in any calendar year.

	Senior Staff		Post-Doctorals		Graduate Students		Under-Graduates		Other Participants[1]	
	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.
A. Total, U.S. Citizens					1	1				
B. Total, Permanent Residents			1		2	1				
U.S. Citizens or Permanent Residents[2]:										
American Indian or Alaskan Native ...										
Asian			1		1					
Black, Not of Hispanic Origin					1	1				
Hispanic						1				
Pacific Islander										
White, Not of Hispanic Origin					1					
C. Total, Other Non-U.S. Citizens										
Specify Country 1.										
2.										
3.										
D. Total, All participants (A + B + C)			1		3	2				
Disabled[3]										

☐ Decline to Provide Information: Check box if you do not wish to provide this information (you are still required to return this page along with Parts I-III).

[1]Category includes, for example, college and precollege teachers, conference and workshop participants.

[2]Use the category that best describes the ethnic/racial status for all U.S. Citizens and Non-citizens with Permanent Residency. *(If more than one category applies, use the one category that most closely reflects the person's recognition in the community.)*

[3]A person having a physical or mental impairment that substantially limits one or more major life activities; who has a record of such impairment; or who is regarded as having such impairment. *(Disabled individuals also should be counted under the appropriate ethnic/racial group unless they are classified as "Other Non-U.S. Citizens.")*

AMERICAN INDIAN OR ALASKAN NATIVE: A person having origins in any of the original peoples of North America, and who maintain cultural identification through tribal affiliation or community recognition.

ASIAN: A person having origins in any of the original peoples of East Asia, Southeast Asia and the Indian subcontinent. This area includes, for example, China, India, Indonesia, Japan, Korea and Vietnam.

BLACK, NOT OF HISPANIC ORIGIN: A person having origins in any of the black racial groups of Africa.

HISPANIC: A person of Mexican, Puerto Rican, Cuban, Central or South American or other Spanish culture or origin, regardless of race.

PACIFIC ISLANDER: A person having origins in any of the original peoples of Hawaii; the U.S. Pacific Territories of Guam, American Samoa, or the Northern Marianas; the U.S. Trust Territory of Palau; the islands of Micronesia or Melanesia; or the Philippines.

WHITE, NOT OF HISPANIC ORIGIN: A person having origins in any of the original peoples of Europe, North Africa, or the Middle East.

1.3. *Aerosol Evaporation.* The value of desolvation for improving detection limits has long been known, especially when applied to ultrasonic nebulization. However, it has rarely been applied *except* for use with ultrasonic nebulization. Furthermore, the precise mechanisms of solvent vapor and aerosol interactions with plasmas have not been rigorously examined until recent years. When an ultrasonic nebulizer is used without a desolvation system, an additional solvent loading is placed on the plasma because the solvent transport increases by a factor similar to that of the analyte, which is typically of the order of 10-30x. The need for the plasma to dissociate the increased solvent mass places a much greater energy absorption load on the plasma, with a consequent reduction in plasma excitation and ionization temperature.

We have carried out detailed studies with various desolvation systems, involving both the direct cooling of the spray chamber and the combination of a heated spray chamber and cooled condenser and observed the changes in signal response for both ICPAES and ICP/MS. In these studies, we have measured the signals under conditions where the *solvent* transport properties of the system are also carefully measured, so that detailed correlations can be made between solvent loading and analytical response. We have correlated these studies with measurements of fundamental plasma properties, such as electron densities and excitation and ionization temperatures.

In ICP/MS, the particular value of highly efficient desolvation, involving both a heated spray chamber and a double chamber condenser is clear, where the BaO^+/Ba^+ ratio is reduced to <0.04% and the CeO^+/Ce^+ ratio is reduced to <0.08%, which are excellent values for the reduction of isobaric interferences.

1.4. *Transport Processes and Particle Velocities.* The ability to understand the nature of processes which limit the transport of aerosol through spray chambers is still of utmost importance to analytical ICPAES, ICP/MS, microwave/AES and microwave/MS. As yet the models are not quite clear, although there has been ongoing discussion from various groups for a number of years. The ability to deliver a clear picture of what occurs in aerosol transport is largely limited by our present ability to characterize the *size distribution* and the *velocities* of the aerosol particles flowing through a spray chamber and into an ICP torch or a microwave torch. We have carried out some preliminary studies of particle velocity profiles measured with a photon correlation anemometer (phase Doppler velocimetry system) which have shown some extremely interesting data on aerosol velocities a few cm away from the tip of a pneumatic nebulizer. The high velocities of the particles (approx. 40 m/s) are noteworthy, but even more interesting is the rather narrow range of velocities of the particles in the aerosol stream, and the very sharp velocity cutoff which occurs outside the relatively tight aerosol beam. This is of particular importance for *chromatographic interfacing*, as it will directly influence chromatographic band broadening.

2. ULTRASONIC NEBULIZATION.

2.1 *Drop Size Distributions.* We have carried out recently a detailed study of the basic characteristics of ultrasonic nebulizers. Our recent work has been aimed at: (1) attempting to discover exactly what the aerosol characteristics of ultrasonic nebulizers are (2) seeing if the data fit any of the pre-existing models for ultrasonic nebulizers and (3) attempting to overcome the weaknesses of the nebulizers based on this knowledge.

Our work has shown a number of interesting and unexpected phenomena. We have found that the relationship of Lang[25] used to predict the primary numerical mean drop size, D_n, for ultrasonic nebulizers:

$$D_n = 0.34\,(\pi\sigma/\delta F^2)^{0.33} \qquad \text{-------- (1)}$$

where σ = surface tension, F = frequency and δ = density, fits quite well with experimental data. That unremarkable fact leads, however, directly to some important insights on the performance of ultrasonically

PART II - SUMMARY OF COMPLETED PROJECT FOR NSF GRANT NO. CHE88-08183 "Sample Introduction for Inductively Coupled Plasma Atomic Emission Spectrometry and Inductively Coupled Plasma Mass Spectrometry" P.I. Richard F. Browner

Injecting sample into a high temperature argon plasma as a fine, uniform-sized aerosol produces lower detection limits, greater accuracy, and improved precision in inductively coupled plasma atomic emission and inductively coupled plasma mass spectrometry. The fundamental premise of this research has been to discover practical approaches to the generation of such ideal aerosols, both in liquid and in solid form. Studies have been made of the fundamental processes of aerosol formation, aerosol desolvation, and aerosol transport through complex interfaces. Empirical models have been derived to describe the process of pneumatic nebulization using concentric nebulizers, and additionally the processes of desolvation and transport using a unique particle beam interface have been investigated. A considerable new body of information describing aerosol characteristics has been developed, which indicates that much previous data on drop size and particle interaction processes is erroneous, often by factors varying between 4 and 10 fold. Based on improved aerosol treatment approaches, improvements in detection limits of between 4 and 8 times have been made for most elements. The overall conclusions of the work are that a base of knowledge has been established which will allow progress in sample introduction processes to be made in the future, resulting in valuable improvements in analytical benchmarks.

PART III - TECHNICAL INFORMATION ON NSF GRANT NO. CHE88-08183

Research which has been carried out under NSF support falls under three basic categories: (1) Studies with aerosol generation (2) studies with aerosol transport and evaporation (3) studies with aerosol and vapor interactions with plasmas.

1. FUNDAMENTAL ASPECTS OF AEROSOL GENERATION AND TRANSPORT WITH PNEUMATIC NEBULIZATION

1.1. *Drop Size Distributions.* It is important to characterize the processes which take place when aerosols pass through spray chambers and also when they enter plasmas. We have studied the aerosol generation process in some depth, and from this work some surprising results have emerged. These may be summarized as follows: (1) the mean drop sizes of all aerosols generated pneumatically are *much* smaller than is predicted from calculations using the classical Nukiyama and Tanasawa equation. The difference may be as much as a factor of 20x, and is particularly noticeable for low surface tension organic solvents. For example, under typical operating conditions (1.9 mL/min liquid flow and 1.1 L/min gas flow) the Nukiyama and Tanasawa equation predicts a primary Sauter mean diameter (D3.2) of 79.7 μm for H_2O and 147.1 μm for n-butanol.[23] The actual experimental data, obtained with Fraunhofer laser diffraction, are 11.1 μm and 7.4 μm respectively. Not only are the experimental values much lower than the Nukiyama and Tanasawa predictions, but the Nukiyama and Tanasawa equation also predicts that the organic solvent will produce an aerosol with a mean drop size *substantially greater than* that of the aqueous aerosol, which contradicts both experience and common sense.

1.2. *Aerosol Modelling.* Based on a series of extensive studies with pneumatically generated aerosols, we have begun the development of various modelling exercises. Our initial studies have allowed us to produce an empirical equation, which gives a quite good fit to experimental data generated with Meinhard-type nebulizers, and so allows both Sauter mean aerosol spread (*i.e.* size distribution) data to be estimated with a knowledge of the nebulizer nozzle dimensions. We are also in the process of developing a potentially much more useful, and more generally applicable, model which allows for differences in nebulizer type, and which includes variable parameters such as gas and liquid flows and solvent surface tension directly in the equation, and not buried in empirical constants as in our earlier work.

generated aerosols. The values predicted using the Lang equation are *numerical mean diameters*, rather than the analytically much more relevant Sauter or mass mean diameters. By contrast, the mass mean and Sauter mean diameters *do* change substantially as liquid flow and rf power to the crystal are changed.

Our studies have also shown that, most interestingly, the drop size distribution of a typical ultrasonic aerosol is by no means monodisperse, as has implicitly been assumed through the use of the Lang Equation. In fact, the *primary aerosol* (*i.e.* aerosol at the face of the ultrasonic nebulizer) may have a higher percentage of large drops than does a typical aerosol generated pneumatically with a Meinhard nebulizer. Our work has led us to believe that two key factors for successful operation of an ultrasonic nebulizer are: (1) ensure a highly uniform liquid loading on the transducer face (2) disperse the aerosol drops rapidly when formed, to avoid the agglomeration which will otherwise occur close to the crystal face. These two issues have now been addressed, in a preliminary fashion, by forcing the analyte onto the face of the crystal as a very fine (25 μm diameter), high velocity (approx. 20 m/s) liquid jet, running at 0.5 mL/min. The use of this jet, in place of the usual stream of liquid flowing onto the crystal face produces a quite dramatic change in the operation of the transducer. The very fine, uniform film which is formed as the jet strikes the crystal surface immediately forms into a visually quite striking, stable, standing wave pattern, quite unlike any normal system where the liquid runs directly onto the surface of the transducer from a larger bore tube. The liquid film at the anti-nodal points of the standing wave pattern immediately forms aerosol, whereas the liquid at the nodes never leaves the transducer face. If the liquid jet is stopped, the nodes remain unchanged for an extended period of time.

The stability of the aerosol generation process, and of the rf loading (and hence the surface power density coupling to the liquid film) is also markedly improved compared to normal sample injection. Another significant improvement in the ultrasonic nebulizer operation has been obtained through directing an Ar gas dispersal jet tangentially across the crystal face, very close to the surface. This substantially reduces the agglomeration of drops which initially leave the transducer surface at high velocity, and which would otherwise collide with one another to form multiple drops. The use of dispersion gas therefore appears to produce an aerosol with an improved drop size distribution compared to the conventional ultrasonic nebulizer. Additionally, the *band width* and *noise level* of flow injection or chromatographic peaks with the liquid jet/-dispersion gas system are dramatically improved over conventional drip introduction. The band width is improved by approximately a factor of 3x and the noise by 2x. This translates directly to improved detection limits and enhanced chromatographic resolution.

2.3 *Aerosol Evaporation.* The higher *analyte* transport found with USN as also associated with higher *solvent* transport. To produce a major improvement in detection limits, therefore, ultrasonically generated aerosols require desolvation. The memory effects and aerosol dilution effects which typically accompany heated spraychamber/condenser systems make them problematical for normal practical analysis, and even less ideal for chromatographic coupling. We are currently investigating various alternative means to circumvent these limitations.

2.4 *Particle Velocities.* The velocities of the aerosol drops as they leave the surface of the ultrasonic transducer are presently unknown. However, it is clear that close to the transducer surface the particle velocities must be quite high. Our preliminary work has indicated that without aerosol dispersion close to the transducer surface, using a gas jet, agglomeration readily occurs, with a consequent increase (degradation) in the aerosol drop size. There is therefore a need to measure the particle velocities just above the transducer face in order to determine what effect operating parameters have on these particle velocities, as a means of minimizing droplet agglomeration.

3. PARTICLE BEAM NEBULIZATION AND INTERFACING

3.1 *General Concepts.* Various versions of the particle beam interface, each suitable for particular situations, have been developed. All versions of the particle beam interface discussed here are based on the original particle beam concept developed for use in organic LC/MS interfacing. However, the specific needs of atomic and inorganic mass spectrometry differ significantly from those experienced in organic LC/MS interfacing, where pressure reduction and solvent removal needs are the key factors to allow the production of true electron impact mass spectra. The use of direct injection, low flow nebulizers, as developed by LaFreniere *et al.* is a highly efficient way to inject LC column effluent directly into a plasma. However, the full benefit of the increased sample transfer is not accomplished with this innovative approach because it is not possible to *enrich* the analyte with respect to solvent before it enters the plasma. Consequently, there still remains a major need to be able to inject LC effluent into a plasma with both high analyte transport efficiency *and* low solvent transport efficiency.

The particle beam interface has a well established base of proven performance in its use for organic LC/MS interfacing, and our goal is to make it equally applicable to the fields of *inorganic* LC/MS, LC/ICP-AES, LC/microwave/AES and LC/microwave/MS.

3.2 *Drop Size Distributions.* In contrast to pneumatic nebulizers, with a particle beam nebulizer the primary source of energy comes form the liquid jet. As the jet, typically ranging in diameter between 5 μm and 50 μm emerges from the capillary, surface instabilities form through frictional interaction between the liquid jet and the surrounding gas. While initially all frequencies are present, mathematical analysis (due to Lord Rayleigh) using Lagrange functions shows that one frequency of instability soon dominates, and the amplitude of this frequency becomes sufficient to cause the jet to shatter into individual drops with a remarkably narrow size range. Other workers have maintained that Rayleigh's analysis is incomplete, as harmonics may form on the jet, with the subsequent formation of satellite drops (*cf.* Plateau's spherules).

Our experimental studies have confirmed the accuracy of Rayleigh's predictions *when the jet diameter is of the order of 50 μm or less.*

3.3 *Aerosol Evaporation.* One of the most powerful attributes of the particle beam system is its ability to generate an aerosol which is sufficiently uniform in size, laminar in flow pattern and narrowly directional to allow rapid solvent evaporation at room temperature and somewhat below atmospheric pressure (*e.g.* 100-200 torr). The particle beam desolvation process has a number of advantages when compared to heated chamber desolvation processes, particularly its almost total freedom from memory effects.

4. ELECTROTHERMAL VAPORIZER SAMPLE INTRODUCTION

4.1 *Basic factors.* Electrothermal vaporization (ETV) provides, in concept, a nearly ideal sample introduction device for ICPAES and ICP/MS, providing low absolute detection limits along with freedom from solvent/plasma interactions. In principle, may of the interelement vaporization and light scattering interferences which hinder AAS measurements should be absent when the vaporizer is used only for sample introduction and not as an atom and ion source. Unfortunately, ETV as a means of sample introduction for ICPAES and ICP/MS suffers from its own interference problems, as has been reported by a number of workers. For example, Cd (as $CdNO_3$) in the presence of Se undergoes a substantial signal enhancement, which appears to be due to the agglomeration of the Cd micro-crystals into larger units, which reduces their condensation loss on intermediate surfaces, and so actually *enhances* their transport to the plasma. With less volatile species, such as Fe, the effect of particulate agglomeration may be to *de*crease particle transport to the plasma. We have also found that the use of surface modification treatments, such as Ta and Mo

coatings for the furnace surface, reduces many of these interferences significantly, holding back the element on the furnace wall and causing its release in a particulate form which seems to be more readily transported to the plasma. We have made extensive transport measurements with ETV introduction, and correlated this with SEM photographic information.

5. DESOLVATION AND SOLVENT INTERACTIONS WITH PLASMAS

5.1 *Solvent effects on plasma.* Solvents generally absorb substantial rf or microwave energy from discharges, causing the discharge to behave as a highly expensive solvent removal system. In extreme cases, such as with high water loadings or with even small amounts of highly volatile solvents such as hexane, even a 1.5 kW atmospheric pressure ICP will be extinguished.

5.2 *Techniques for solvent removal.* To date, solvent removal techniques have been based on either: (1) heated spraychamber/condenser type systems, as used extensively for ultrasonic nebulizers and (2) heated spraychamber/membrane vapor removal devices, as described by Gustavsson. Both of these types have many limitations, such as substantial memory effects and limited solvent removal efficiency. The need for efficient solvent removal in both normal sample introduction and in chromatographic interfacing is clear, especially for ICP/MS, microwave/AES and microwave/MS.

5.3 *Solvent effects on analyte transport and on signal.* The efficiency of transport of analyte from the nebulizer to the plasma is determined by the particle size distribution of the aerosol. Several models to describe this process have been presented, notably by Sharp, Browner, Boorn and Smith and Gustavsson. In our recent studies, we have made an number of analyte and solvent transport measurements, in order to correlate analytical ICPAES and ICP/MS signals with the transport properties of various organic solvents. We have demonstrated how important these effects may be in influencing analytical signals, have examined the use of various means to overcame these interferences through desolvation and O_2 addition to the plasma gas, and believe that we have developed a reasonably thorough basic working model of how the transport properties of analyte, solvent aerosol and solvent vapor interact to give rise to signal magnitudes for a number of elements and solvents.

6. ATMOSPHERIC PRESSURE MICROWAVE PLASMA SAMPLE INTRODUCTION

6.1 *Desolvation effects.* The atmospheric pressure microwave plasma has long been suggested as an excellent emission source, especially as a detector for LC separations. However, the two key issues in sample introduction to the atmospheric pressure microwave plasma are: (1) particle size and volatility of the sample and matrix, and (2) solvent loading in the plasma.

6.2 *Aerosol transport and solvent transport.* While we have not as yet investigated the first of these parameters, we have studied the second extensively. During the course of our studies, we have developed a highly efficient solvent removal system, using a special heated spray chamber and condenser, with a solvent "polishing" trap of concentrated H_2SO_4, which reduces water vapor loading to < 10 ppm.

6.3 *Detection limits.* Using our system, with a 60 W power input, system, we have been able to produce detection limits comparable or superior to the best data yet reported for such a low power plasma. In fact, for a wide range of elements the detection limits are comparable or superior to those produced by *any microwave plasma emission technique.* The data are very close to that from the 510 W plasma system of Haas and Caruso. The prime difference with our system seems to be the scrupulous removal of water from

the system, demonstrating once more the key importance of solvent as a factor influencing performance, even in atmospheric pressure plasmas.

7. PARTICLE BEAM SAMPLE INTRODUCTION FOR LOW PRESSURE MICROWAVE PLASMA

7.1 *Aerosol generation.* Aerosols for this system have been generated using both conventional nebulizers and the MAG nebulizer. In the early experiments, the focus has been on the optimization of the plasma itself, and of the pressure reduction interface between the aerosol generation/desolvation part of the system and the low pressure discharge. Consequently, to this point several types of nebulizer have been used, including conventional pneumatic nebulizers and MAG-type nebulizers.

7.2 *Desolvation.* Desolvation has been carried out with either: (1) a heated spraychamber and cooled condenser, or (2) the particle beam desolvation system. Both systems function well. The operation of the particle beam interface has required extensive system re-optimization compared to the normal (LC/MS) type of operation, largely because the pressure of the discharge (1-10 torr) is substantially greater than that of a mass spectrometer ion source area (10^{-5} torr). This has required a number of careful studies in which the efficiency of the interface has been measured by collection of analyte in a low pressure collection chamber, while controlling the intermediate pressures of the two stages of the momentum beam separator. This study has demonstrated that these intermediate pressures have a marked effect on the performance of the interface by changing the efficiency of analyte transport. Pressure variations of a few torr in these chambers can influence analyte transport by up to a factor of five. However, with proper flow and pressure control, the interface can be made to function quite effectively with a 1-3 torr He or Ar MIP.

7.3 *Particle beam enrichment; skimmer geometry.* The spacing and orifice diameters of the skimmer components are very important in determining both the efficiency with which particles move through the system, and also the pressures in the various parts of the system. We have carried out preliminary studies with the various options of nozzle/skimmer and skimmer/skimmer spacings, and also with skimmer diameters. From these studies, we have been able to develop an interface design which works quite effectively with the microwave discharge.

PUBLICATIONS ARISING FROM CURRENT NSF SUPPORT: CHE88-08183

1. "Interfacing with Aerosols: Concept, Place and Time," Richard F. Browner, *Microchem. J.* **1989**, *40*, 4.

2. "Reply to "Comments on Influence of Water on ICP," by L. de Galan," Richard F. Browner and Stephen E. Long, *Spectrochim. Acta, Part B*, **1989**, *44*, 831.

3. "Evolution of Drop Size Distributions for Pneumatically Generated in Inductively Coupled Plasma Atomic Emission Spectrometry," Antonio Canals, Vicente Hernandis and Richard F. Browner, *Spectrochim. Acta, Part B*, **1990**, *44*, 8.

4. "Experimental Evaluation of the Nukiyama-Tanasawa Equation for Pneumatic Nebulizers Used in Plasma Atomic Emission Spectrometry," Antonio Canals,Vicente Hernandis and Richard F. Browner, *J. Analyt. Atom. Spectrosc.*, **1990**, *5*, 61.

5. "Comparison of Desolvation Effects with Aqueous and Organic (CCl_4) Sample Introduction for Inductively Coupled Plasma Atomic Emission Spectrometry," Chankang Pan, Guangxuan Zhu and Richard F. Browner, *J. Analyt. Atom. Spectrosc.*, **1990**, *5*, 537.

6. "Fundamental Studies with an Ultrasonic Nebulizer," Matthew A. Tarr, Guangxuan Zhu and Richard F. Browner, *Appl. Spectrosc.*, **1992**, *45*, 1424.

7. "Effect of Solvent and Transport Variables on Signal Intensities in Inductively Coupled Plasma Atomic Emission Spectrometry," Richard F. Browner, Antonio Canals and Vicente Hernandis, *Spectrochim. Acta, Part B*, **1992**, in press.

8. "Influence of Auxiliary Gas Flow Rate on Excitation Conditions in the Inductively Coupled Plasma," Chankang Pan, Guangxuan Zhu and Richard F.Browner, *J. Analyt. Atom. Spectrosc.*, **1992**, in press.

9. "Differences in Aerosol and Vapor Loading Characteristics for Organic Sample ICPAES," Chankang Pan, Guangxuan Zhu and Richard F. Browner,, **1992**, in press.

10. "Influence of Desolvation on Emission Features in ICPAES," Chankang Pan, Guangxuan Zhu and Richard F. Browner, *J. Analyt. Atom. Spectrosc.*, **1992**, in press.

11. "Flow Injection Characteristics for ICP/MS," Guangxuan Zhu, Chankang Pan and Richard F. Browner, *Spectrochim. Acta, Part B*, **1992**, submitted for publication.

TALKS PRESENTED BY STUDENTS AT NATIONAL MEETINGS

"Interactions of Liquid and Dry Aerosols in ICP/MS: in Search of the Perfect Aerosol," Guangxuan Zhu, Edison Becerra, Vincent Nwogu and Richard F. Browner, Eastern Analytical Symposium, New York, October 1988, invited talk.

"Measurement and Prediction of Aerosol Characteristics for ICP Nebulizers,"Ntombioyomusa Msimanga, Antonio Canals, Vicente Hernandis and Richard F.Browner, FACSS Meeting, Boston, MA, November 1988.

"Interactions of Solids, Liquids and Vapors in ICP/MS: Potential for Advances," Guangxuan Zhu, Changkang Pan and Richard F. Browner, American Society for Mass Spectrometry Annual Meeting, Miami Beach, FL, May 1989, invited talk.

"Sample Introduction Characteristics of Flow Injection with ICP/MS," Guangxuan Zhu, Changkang Pan and Richard F. Browner, American Society for Mass Spectrometry Annual Meeting, Miami Beach, FL, May 1989.

"Analytical Studies of Oxygen Addition in ICPAES and ICP/MS with Organic Solvent Introduction," Chankang Pan, Guangxuan Zhu and Richard F. Browner, FACSS Meeting, Cleveland, OH, October 1990.

"An Evaluation of the MAGIC Interface for Aqueous Sample Introduction in Low Pressure Microwave Induced Plasma Emission Spectrometry," Annia Ruiz, Hanqi Zhang, Guangxuan Zhu and Richard F. Browner, FACSS Meeting, Cleveland, OH, October 1990.

"Particle Size Distributions and Transport Data of Ultrasonic Nebulizers Used for ICPAES and ICP/MS," Matthew A. Tarr, Guangxuan Zhu and Richard F. Browner, FACSS Meeting, Cleveland, OH, 1990.

"The Effects of Solvent and Liquid Flow on a Proposed Model for Pneumatic Nebulizers," Ntombiyomusa D. Msimanga and Richard F. Browner, Pittsburgh Conference, Chicago, IL, 1991.

"Studies on Electrothermal Vaporization (ETV) Sample Introduction for ICPAES," Vincent Nwogu, Guangxuan Zhu and Richard F. Browner, Pittsburgh Conference, Chicago, IL, 1991.