

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 9/21/77

Project Title: *Sample Preparation & Introduction for Analytical Atomic Spectroscopy*

Project No: *G-33-628 & E-19-655 (See also sub-account E-16-623)*

Project Director: *Dr. Richard F. Browner and Dr. Michael J. Matteson*

Sponsor: *National Science Foundation; Washington, D. C. 20550*

Agreement Period: From 8/1/77 Until 31 May 80
~~1/31/79*~~
**12 months proposed period plus 6 months for flexibility*

Type Agreement: *Grant No. CHE 77-07618*

Amount: *\$51,000 NSF funds (G-33-628, E-19-655 & E-16-623)*
5,015 GIT Contribution (G-33-314)
\$56,015 Total

Reports Required: *Annual Technical Letters; Summary of Completed Project;
Final Technical Report*

Sponsor Contact Person (s):

Technical Matters

*Dr. Janet Osteryoung, Director
Chemical Analysis Program
Chemical Synthesis & Analysis Section
Division of Chemistry
National Science Foundation
Washington, D. C. 20550*

Contractual Matters

*(thru OCA)
Ms. Mary Frances O'Connell
Grants Administrator
National Science Foundation
Washington, D. C. 20550
(202) 632-2858*

Defense Priority Rating: *none*

Assigned to: *Chemistry & Chemical Engineering* (School/Laboratory)

COPIES TO:

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*Library, Technical Reports Section
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Project File (OCA) (3)
Project Code (GTRI)
Other *Dr. Ducoffe (E-16-623)*
*Dr. Powell (E-16-623)**

SPONSORED PROJECT TERMINATION SHEET

Date 6/13/83

Project Title: Sample Preparation and Introduction for Analytical Atomic Spectroscopy

Project No: G-33-628

Project Director: Dr. Richard F. Browner

Sponsor: National Science Foundation

Effective Termination Date: 5/31/81

Clearance of Accounting Charges: 5/31/81

Grant/Contract Closeout Actions Remaining:

- Final Invoice and Closing Documents
- ^{Accounting} Final ~~Fiscal~~ Report
- Final Report of Inventions
- Govt. Property Inventory & Related Certificate
- Classified Material Certificate
- Other _____

Assigned to: Chemistry (School/Laboratory)

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Research Proposal Submitted to the National Science Foundation

Technical Report on Grant No. CHE-7707618

"Sample Preparation and Introduction for Analytical Atomic Spectroscopy"

Principal Investigator: Richard F. Browner

Co-Principal Investigator: Michael J. Matteson

Georgia Institute of Technology

School of Chemistry

Atlanta, GA 30332

Summary of Accomplishments During Period 3.1.78-9.1.78

1. Characterization of Aerosol Sprays from Nebulizers

A great deal of work has been put into the development and testing of systems for the characterization of aerosol droplets in the size range 0.0032-10 μm . The primary goal has been to obtain truly reliable data without bias introduced by the transfer and measuring process. Many of the systems applicable to airborne aerosols have been found to be unsuitable for atomic spectroscopy nebulizers, as a consequence of the much higher particle density and generally larger droplet sizes of the latter. The two main systems used so far in this work have been the Andersen Cascade Impactor (covering the range 0.4-10 μm) and the Whitby Electrostatic Aerosol Analyzer (covering the range 0.0032-1 μm). The Andersen Impactor has presented little problem and is in use currently routinely for the gathering of particle size data. However, the particle concentrations acceptable to the Whitby Analyzer ($<10^4$ particles/cm³) are approximately two orders of magnitude less than those produced by conventional atomic absorption nebulizers. In order to dilute the primary aerosol flow an entirely novel concentric aerosol diluter has been designed and constructed. Preliminary tests indicate an effective dilution of 250x, with no noticeable disturbance of particle size ratios. If further testing on a wide range of aerosols shows this performance applies uniformly to all aerosol types, then a considerable breakthrough in aerosol dilution techniques will have been achieved, with widespread applicability to environmental monitoring and other problems.

Work with the Whitby Analyzer has indicated that aerosols from a Perkin-Elmer nebulizer have negligible numbers of droplets below 0.136 μm diameter and a total size distribution study indicates a mass median diameter around 1 μm . This is much smaller than has been estimated previously

(typically 8.5 μm), almost certainly due to the improved measurement techniques for smaller particles used in this study. Further studies with a wide range of commercially available nebulizers for both atomic absorption and inductively coupled plasma systems are under investigation. Laser scattering droplet sizing measurements will be implemented as soon as the necessary PDP 11-34 minicomputer arrives (scheduled for November 1978).

2. Development of Improved Nebulizers for AAS and RFICPOES

In parallel with the study of droplet sizes produced by existing nebulizers, work on new improved nebulizers is continuing. A developmental model ultrasonic nebulizer has been designed and constructed in-house and is in the process of final mechanical and electronic testing. When this is complete, the droplet size production will be tested with the previously tested systems, and the analytical performance tested with both atomic absorption flames and radio frequency inductively coupled argon plasmas.

3. Ion Enrichment Properties of Aerosols

A considerable amount of preliminary data has been obtained regarding the differential distribution of salt concentrations between particles of different sizes. A special burner/nebulizer system has been designed which allows the collection of particles as three size groups: $>10 \mu\text{m}$; $1-10 \mu\text{m}$ and $<1 \mu\text{m}$ approximately. It has been shown that when solutions with approximately 3% Na and 0.01% K are sprayed, the ratio of Na/K varies considerably depending on the fraction of droplets considered. A more detailed study is underway to collect droplets with an Andersen Impactor, so that greater resolution of Na/K ratios as a function of droplet size may be found.

4. Sample Introduction into Inductively Coupled Plasmas

A new 2.5 kW Plasma-Therm R.F. Inductively Coupled Plasma system has been added to the equipment available to the project (purchased with

Institutional funds) and an investigation is underway to provide better sample introduction facilities to the plasma. Existing nebulizer/torch configurations are well known to suffer from many limitations and are undoubtedly the weak point in an otherwise excellent elemental analysis facility. At present a variety of new torch designs, incorporating laminar flow as opposed to the universally used tangential turbulent flow systems, are under construction and evaluation. Preliminary studies are very promising, and it is anticipated that the torches will give improved signal-to-noise ratios analytically, by allowing much more uniform and less turbulent sample introduction.

A detailed study on the introduction of organic species into the Ar ICP has also begun and will be pursued in parallel with the torch development, in the hope of improving greatly organic sample introduction capability in ICP work.

Richard F. Browner
Principal Investigator

9.03.78
Date

~~_____~~
Michael J. Matteson
Co-Principal Investigator

9.11.78
Date

Research Proposal Submitted to the National Science Foundation

Technical Report on Grant No. CHE-7707618

SAMPLE PREPARATION AND INTRODUCTION
FOR ANALYTICAL ATOMIC SPECTROSCOPY

Principal Investigator: Richard F. Browner
Co-Principal Investigator: Michael J. Matteson

Georgia Institute of Technology
School of Chemistry
Atlanta, GA 30332

SUMMARY OF ACCOMPLISHMENTS DURING PERIOD 12.01.78-11.30.79

The research program has been directed towards four primary areas: (i) the development of novel droplet sizing techniques, suitable for aerosols used in atomic spectroscopy; (ii) fundamental studies relating to the physical and chemical processes taking place during aerosol formation; (iii) the development of improved pneumatic nebulizers, based on these fundamental studies; and (iv) the development of novel alternate means of direct sample introduction into flames and plasmas, using volatile metal chelates. From this research ten research papers and nine conference presentations have resulted since the last progress report to NSF. These are listed following this section of the report.

A summary of accomplishments in each area follows:

1. Development of Droplet Sizing Techniques Suitable for AAS and ICP Aerosols

There are very real difficulties associated with the determination of droplet size distributions from pneumatic nebulizers operating under realistic conditions. The high particle number densities (approx. 10^6 particles cm^{-3}) and wide particle size distributions can lead to significant measurement errors, even when using sophisticated instrumentation. Unfortunately, much of the previous research in this area has relied upon inadequate techniques, such as low velocity droplet collection on microscope slides, which is not appropriate to particles less than 10 μm diameter.

In this program, two separate aerosol measuring techniques have

been developed, one (A) suitable for low volatility liquids such as dioctylphthalate covering the range 0.03-10 μm , and one (B) suitable for aqueous solutions covering the range 0.3-10 μm .

(A) Dioctylphthalate System. 0.03-10 μm

This system is based upon the series operation of a cascade impactor and an electrical aerosol analyzer. The cascade impactor measures droplets in the range 0.03-10 μm and the electrical aerosol analyzer covers the range 0.03-1 μm , with a useful overlap region. The primary concern with this system was the degree of dilution necessary to obtain reliable data, as the electrical aerosol analyzer in particular cannot tolerate either a high particle number density or any significant number of droplets greater than 1 μm diameter. Consequently, a system of gas dilution and isokinetic sampling was devised which gave no measurable distortion of the primary aerosol. This was checked by comparing data at a controlled very low particle density with and without the dilution system. No significant change in particle size distribution was found. This system was then applied to a wide range of studies of droplet sizing, investigating the influence of various parameters on the droplet size distributions.

(B) Aqueous System. 0.3-10 μm

For a study of pneumatic nebulizers operated with aqueous solutions, the technique described above is unsuitable, for the vapor pressure of water is too high at room temperature and significant evaporation of small

droplets will occur. Our calculations have shown that water droplets of 2 μm or less diameter will be totally evaporated in less than 0.5 seconds in the presence of 100% relative humidity air, because of the pressure difference at the curved surface predicted by the Kelvin equation.

However, we have also calculated that by using a 5-10 mg ml^{-1} solution of sodium chloride, the evaporation of droplets down to $<0.5 \mu\text{m}$ can be neglected. This has led to the development of a procedure in which a 5-10 mg ml^{-1} salt solution is nebulized, and the droplets collected on the plates of a cascade impactor by size range (10.0-9.0, 9.0-5.8, 5.8-4.7, 4.7-3.3, 3.3-2.1, 2.1-1.1, 1.1-0.7 and 0.7-0.32 μm). The plates are then washed with water, and the relative plate loadings found by determining the Na concentration on each, using flame emission spectrometry to determine the Na.

Data obtained with this system has been found to correlate well with data obtained from the previous system over the common range of the two techniques.

2. Fundamental Studies Relating to Physical and Chemical Processes Occurring During Droplet Formation

The droplet size distributions of the nebulized sprays from many types of pneumatic nebulizers have been determined using the techniques described above. The acquisition of these data were necessary as a first step in understanding pneumatic nebulization phenomena, as no droplet size distributions in this range have ever been published previously for systems relevant to analytical atomic spectrometric measurements.

One of the most important initial conclusions to be drawn was that all previous size distributions are greatly weighted towards large droplets, which fits our predictions. Typical droplet distributions for aqueous sprays show a mean droplet diameter around $3.5 \mu\text{m}$, compared to published data indicating values from $8.5\text{-}15 \mu\text{m}$. In practice, our measurements indicate that less than 20% of the spray reaching a flame or plasma is contained in droplets greater than $10 \mu\text{m}$ diameter.

Detailed studies have been made on the influence of the most important variable parameters on droplet size distributions, namely gas and liquid flow rates, surface tension and viscosity of solvents, temperature effects, influence of impact beads and mixer paddles. The validity of the Tanasawa and Nukiyama equation to analytical spectroscopy has been examined, and while qualitatively in agreement with observation, the equation has been shown to be in error when used to predict mean droplet diameters, giving values approximately a factor of $2.4\times$ too high.

An entirely novel process of interference in analytical atomic spectroscopy has been discovered and investigated. This is based upon the ionic redistribution that takes place when binary mixtures of salts are nebulized pneumatically. We have been able to show that on droplet formation from a liquid stream, the relative mobilities of the ions in solution determine the relative concentrations of the ions in the droplets. In other words, in a bulk solution containing a ratio of Li:Mg of 200:1 ($10,000 \mu\text{g ml}^{-1}$ Li and $50 \mu\text{g ml}^{-1}$ Mg), the droplets formed in the range $0.1\text{-}10 \mu\text{m}$ have ratios of Li:Mg varying from 50:1 to 150:1, depending on the droplet size. In all cases, however, there is a net increase in Mg:Li ratio in all the droplets reaching an inductively

coupled plasma and it would be predicted that a positive interference would occur. We have observed this in practice (an enhancement of 200% was observed) and there is therefore good correlation between theory and practice. Furthermore, we have observed this phenomenon with several other ionic species (Na and K, Na and Li, K and Li). This interference effect has been observed by others, but this is the first time that in our experience any valid explanation has been suggested.

3. Development of Improved Nebulizers

Based on the theoretical understanding of nebulization phenomena that has been obtained by our studies, we have been able to design a fixed all-glass crossflow nebulizer with two significant advantages over existing systems: (i) it can be operated with the inductively coupled plasma at sufficiently low gas flow rates that improved detection limits are obtained; (ii) it can be configured such that the waste solution re-cycles in the nebulizer, resulting in a net sample uptake of approximately 0.2 ml min^{-1} , compared to conventional systems using $3\text{-}5 \text{ ml min}^{-1}$. This can be of great advantage when sample volume is limited (e.g., in clinical studies).

4. Development of Alternate Means of Sample Introduction

As a means of avoiding the necessity to ash or otherwise destroy organic matter in biological samples, a preliminary investigation has been made of a technique for the production of volatile metal chelates in situ in the sample, by passing a chelating agent in vapor form over

the sample. The chelating agent, typically H(acac), H(tfa) or H(hfa), is passed into a solution containing the metals of interest, such as blood serum, and reaction takes place. After a few minutes to ensure complete reaction, the reaction vessel is heated, and the metal chelate vaporizes and passes through a heated line to an inductively coupled plasma torch. The process is standardized by a standard additions procedure. Using this process, we have been able to obtain good agreement for analysis of independently analyzed samples, such as NBS Standard Reference Materials (orchard leaves and bovine liver) and independently analyzed blood serum samples.

	<i>10.15.79</i>		<i>10/15/79</i>
Richard F. Browner Principal Investigator	Date	Michael J. Matteson Co-Principal Investigator	Date

RESEARCH PUBLICATIONS DURING CURRENT GRANT PERIOD

1. "A Versatile System for Size Characterization of Droplet Sprays Produced by Pneumatic Nebulizers," John W. Novak, Jr. and Richard F. Browner, *Anal. Chem.*, 1979, submitted.
2. "Observations on the Effects of Impact Beads, Mixer Paddles and Auxiliary Oxidant on Dp Distributions in Analytical Flame Spectroscopy," Malcolm S. Cresser and Richard F. Browner, *Appl. Spectrosc.*, 1979, submitted.
3. "Sample Temperature Effects in Analytical Flame Spectroscopy," Malcolm S. Cresser and Richard F. Browner, *Anal. Chim. Acta*, 1979, in press.
4. "A Method for Investigating Size Distributions of Aqueous Droplets in the Range 0.5-10 μm Produced by Pneumatic Nebulizers," Malcolm S. Cresser and Richard F. Browner, *Spectrochim. Acta B*, 1979, in press.
5. "A Fixed All-Glass Crossflow Nebulizer for Use with Inductively Coupled Plasmas and Flames," John W. Novak, Jr., Donald E. Lillie and Richard F. Browner, *Anal. Chem.*, 1979, submitted.
6. "Aerosol Ionic Redistribution: A Novel Interference Mechanism in Analytical Atomic Spectrometry," J. A. Borowiec, A. Boorn, J. Dillard, M. S. Cresser, R. F. Browner and M. J. Matteson, *Anal. Chem.*, 1979, submitted.
7. "Introduction of Organic Species into the Inductively Coupled Argon Plasma," A. Boorn and R. F. Browner, *Anal. Chem.*, 1979, submitted.
8. "Characterization of Droplet Sprays from Pneumatic Nebulizers," John W. Novak and Richard F. Browner, *Anal. Chem.*, 1979, submitted.
9. "Direct Introduction of Samples into the Inductively Coupled Argon Plasma as Volatile Metal Chelates," Marilyn S. Black and Richard F. Browner, *Anal. Chem.*, 1979, submitted.
10. "Organic Solvent Effects in Analytical Atomic Spectrometry," A. Boorn, M. S. Cresser and R. F. Browner, *Analyst*, 1979, submitted.

JUSTIFICATION OF CAPITAL EQUIPMENT ITEM
GCA McPHERSON 1 M SPECTROMETER

The grant budget includes a proposed sum of \$4,540 to be used towards the purchase of a higher resolution spectrometer. Much of our work centers around the inductively coupled plasma, and the acquisition of a spectrometer of high quality will result in a corresponding improvement in the quality of our ICP data. The School of Chemistry at Georgia Tech will contribute towards the purchase price of the instrument (\$17,500).

**SUMMARY
PROPOSAL BUDGET**

12/1/79

ORGANIZATION AND ADDRESS				FOR NSF USE ONLY		
Georgia Institute of Technology, Atlanta, Ga. 30332				PROPOSAL NO.		
				DURATION (MONTHS)		
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR				PROPOSED	REVISED	
NSF USE	A. SENIOR PERSONNEL (LIST BY NAME; SHOW NUMBERS OF PEOPLE IN BRACKETS; SALARY AMOUNTS MAY BE LISTED ON SEPARATE SCHEDULE) GPM 205.1b			NSF FUNDED MAN MONTHS	FUNDS REQUESTED BY PROPOSER	FUNDS GRANTED BY NSF (IF DIFFERENT)
		CAL.	ACAD.	SUMR.		
	1. P.I./P.D. R.F. Browner			2.0	\$ 4,820	\$
	2. CO P.I./P.D. M. J. Matteson			1.5	\$ 3,800	\$
	3. CO P.I./P.D.				\$	\$
	4. CO P.I./P.D.				\$	\$
	5. CO P.I./P.D.				\$	\$
11115	6. (2) ← SUBTOTALS A1 - A5 →			3.5	\$ 8,620	\$
	FACULTY AND OTHER SENIOR ASSOCIATES (ATTACH EXTRA SHEET IF NECESSARY)					
	7. E. A. Powell	.5			\$ 950	\$
	8.				\$	\$
	9.				\$	\$
	10.				\$	\$
	11.				\$	\$
11117	12. () ← SUBTOTALS A7 - A11 →	.5			\$ 950	\$
	B. OTHER PERSONNEL (LIST NUMBERS IN BRACKETS)					
11141	1. () POSTDOCTORAL ASSOCIATES				\$	\$
11149	2. () OTHER PROFESSIONALS			2.0	\$ 2,200	\$
11150	3. () GRADUATE STUDENTS				\$ 9,000	\$
11152	4. () UNDERGRADUATE STUDENTS				\$	\$
11182	5. () SECRETARIAL - CLERICAL				\$	\$
11183	6. () TECHNICAL, SHOP, OTHER				\$	\$
	TOTAL SALARIES AND WAGES (A+B)				\$20,770	\$
11200	C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) 10.51% of \$11,770				\$ 1,237	\$
	TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)				\$22,007	\$
	D. EQUIPMENT (LIST ITEMS AND DOLLAR AMOUNTS FOR EACH ITEM)					
	1-GAC/McPherson Model 2051 Spectrometer					
23181	TOTAL EQUIPMENT				\$ 4,445	\$
	E. MATERIALS AND SUPPLIES					
32630					\$ 7,920	\$
	F. DOMESTIC TRAVEL					
42111					\$ 2,000	\$
	G. FOREIGN TRAVEL (LIST DESTINATION AND AMOUNT FOR EACH TRIP; GPM 731)					
42112					\$	\$

NOTICE OF RESEARCH PROJECT
SCIENCE INFORMATION EXCHANGE

SMITHSONIAN INSTITUTION
NATIONAL SCIENCE FOUNDATION
PROJECT SUMMARY

PROJECT NO. (Do not use
this space)

NSF AWARD NO.

1. NAME OF INSTITUTION (INCLUDE BRANCH/CAMPUS & SCHOOL OR DIVISION)

2. MAILING ADDRESS

3. PRINCIPAL INVESTIGATOR AND FIELD OF SCIENCE/SPECIALTY

4. TITLE OF PROJECT

5. SUMMARY OF PROPOSED WORK (LIMIT TO 22 PICA OR 18 ELITE TYPEWRITTEN LINES)

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DIVISION (OFFICE) AND DIRECTORATE		PROGRAM	
SECTION	PROPOSAL NO.	F.Y.	

FOR DGC USE ONLY

START AND END DATES	AMOUNT GRANTED
---------------------	----------------

NSF Grant No. CHE-7707618

Statement of Funds Estimated to Remain
at End of Current Grant Period

It is anticipated that no funds will remain unexpended or uncommitted at the end of the current grant period (November 30, 1979).

Current and Pending Support

	<u>Supporting Agencies</u>	<u>Project Title</u>	<u>Award Amount</u>	<u>Period Covered</u>	<u>Man Months Committed to Project</u>		<u>Location of Research</u>
I. <u>Richard F. Browner</u>					ACAD.	SUMM	
A. Current Support	none						
B. Proposals Pending	N.B.S.	Investigations of Smoke Formation by Polymeric Materials: Smoke Reduction Methods and Chemical Characterizations of Smoke Particulates	\$75,000	11/01/79-10/30/80	0.5	0.5	Georgia Tech
II. <u>Michael J. Matteson</u>							
A. Current Support	D.O.E.	Investigation of the Capture of SO ₂ and O ₂ by Condensation of H ₂ O in Droplets	\$38,700	3/1/79-2/29/80	1.8	0.6	Georgia Tech
B. Proposals Pending	none						
<u>Eugene A. Powell</u>							
A. Current Support	none						
B. Proposals Pending	N.B.D.	Investigation of Smoke Formation of Polymeric Materials: Smoke Reduction Methods and Chemical Characterization of Smoke Particulates	\$75,000	11/01/79-10/30/80			
III. Transfer of Support	N/N						
IV. This Proposal has not been and will not be submitted to any other agency.							

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I-PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Georgia Institute of Technology Atlanta, GA 30332	2. NSF Program Chemical Analysis	3. NSF Award Number CHE-7707618
	4. Award Period From 8/1/77 To 5/31/81	5. Cumulative Award Amount \$211,100

6. Project Title
Sample Preparation and Introduction for Analytical Atomic Spectroscopy

PART II-SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

The capability of various techniques for trace elemental analysis, such as flame atomic absorption spectroscopy and inductively coupled plasma emission spectroscopy, to perform reliable analyses at trace levels is often limited by the sample introduction process. Samples most often occur in solid form, which is incompatible with direct introduction to the high temperature devices (flame or plasma) used as atomizing cells in atomic spectroscopy. Consequently, samples must be converted to solution form by dissolution in acid, often after ashing to remove organic material.

This program has been directed towards: (1) Obtaining better fundamental understanding of the processes associated with the solution/atomizing cell interface, with the goal of obtaining more efficient, less interference prone means of sample introduction (2) developing alternate means of sample introduction to obviate the need for sample dissolution prior to analysis. Specifically, techniques have been developed which allow accurate characterization of drop size distributions of pneumatically and ultrasonically generated aerosols. These techniques have been applied to a systematic examination of the primary variables which control the drop size distribution, and the results correlated with the influence of these variables on analytical signals and interferences.

In an examination of various solvents, the evaporation characteristics of organic aerosols have been shown to exert a major influence on analytical signals and the relationship between drop size and evaporation rate derived. These results allow the influence of different organic solvents on the analytical signal to be predicted.

A means of introducing samples, as volatile metal β -diketonates, directly to a high temperature plasma has been developed. This bypasses the normal ashing and acid dissolution procedures and has been applied successfully to the analysis of several trace elements in biological materials, such as skin, bovine liver and blood.

PART III-TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses		X			
b. Publication Citations		X			
c. Data on Scientific Collaborators		X			
d. Information on Inventions	X				
e. Technical Description of Project and Results		X			
f. Other (specify)					
2. Principal Investigator/Project Director Name (Typed) Richard F. Browner	3. Principal Investigator/Project Director Signature			4. Date 8/27/81	

Final Technical Report Submitted to
National Science Foundation

Final Technical Letter Report on Grant No: CHE-7707618

SAMPLE PREPARATION AND INTRODUCTION FOR
ANALYTICAL ATOMIC SPECTROSCOPY

Principal Investigator: Richard F. Browner
Co-Principal Investigator: Michael J. Matteson

Start Date: 8/1/77

Completion Date: 5/31/81

Georgia Institute of Technology
Atlanta, Georgia 30332

I. DESCRIPTION OF RESEARCH AND RESULTS

The following section is a summary of research accomplished during the term of the grant. The majority of this work has been published in the literature, and the references listed refer to grant supported publications described in Section II.

1. Development of Droplet Size Measurement Capabilities.

(a) 0.1-10 μm Dioctylphthalate Method. In order to characterize the aerosol sprays from a wide variety of pneumatic nebulizers, a technique has been developed which permits droplet size measurements to be made in the range 0.1-10 μm . An aerosol spray of dioctylphthalate (DOP) is diluted sequentially in five steps in order to minimize possible diameter-related impaction losses, which might otherwise disturb the particle size distribution. DOP is used because of its high boiling point (384°C) which minimizes vaporization losses of small droplets. Small droplets (0.1-0.5 μm) are measured with an Electrical Aerosol Analyzer and larger droplets (0.5-10 μm) are measured with a Cascade Impactor. The technique has been described in the literature.¹

(b) 0.5-10 μm Aqueous Aerosol Method. A careful study of the theoretical evaporation characteristics of aqueous aerosols² has shown that for pure water, or very dilute solution aerosols, droplets less than 5 μm diameter evaporate rapidly, severely disturbing the size distribution. On the other

hand, the evaporation losses for small droplets in an aerosol produced by nebulizing a concentrated salt solution are greatly reduced. For example, when a $5000 \mu\text{g mL}^{-1}$ NaCl solution is nebulized, evaporation losses of $0.5 \mu\text{m}$ droplets should result in a decrease in droplet diameter of less than 10%.

Apparent droplet size distributions have been measured for a wide range of salt solution concentrations by collection of the generated aerosol on the plates of a cascade impactor. This provides a size fractionation of the aerosol in various stages over the aerodynamic particle diameter range $0.44\text{--}10 \mu\text{m}$. By washing the deposited salt solution off each plate of the impactor, the mass of sodium collected in each size range can be determined. Experimental data have confirmed the theoretical predictions that the droplet size distribution is negligibly disturbed for small droplets, provided that concentrated ($\geq 5000 \mu\text{g mL}^{-1}$) solutions are used. Furthermore, it has been found experimentally that typically 90% of the sample mass reaching analytical flames or plasmas is contained within the droplet size range measured by this technique. Consequently, a technique has been developed which allows simple, rapid characterization of aerosol sprays from most pneumatic or ultrasonic nebulizers. The size range covered is not as wide as with the DOP technique, but is perfectly adequate for most purposes. Full details of the technique have been published.²

(c) Laser Scattering Measurements. By measuring forward scatter at 5° and 15° , produced by shining a He/Ne laser through an aerosol, it is possible to calculate the volume-to-surface area median diameter (d_{32}) of the aerosol. This value will lie close to the mass median diameter. The

laser scattering technique supplements the cascade impactor and electrical aerosol analyzer measurements. The optical system has been assembled and tested with aerosols of known properties and found to be functioning correctly. Software has also been written which allows direct interfacing of the experiment into a PDP 11/34 minicomputer with graphics plotting of d_{32} as a function of time. To date only low speed data acquisition has been attempted, but it is proposed to increase this rate for noise studies to be described later in this proposal. The advantages of the laser measurements are that they allow: (1) non-intrusive droplet size measurements; (2) spatial resolution in examining a physically spread-out aerosol spray; and (3) time-resolved measurements.

2. Fundamental Data on Droplet Size Distributions.

(a) Parametric Investigations of Pneumatic Nebulizers. The DOP and aqueous salt solution techniques described above have both been used to examine parameters of analytical interest, namely: (1) droplet size distributions produced by commercial pneumatic nebulizers; (2) the influence of variations in operating conditions, including gas and liquid flow rates, velocities, liquid surface tension and viscosity, nebulizer design, etc., on these droplet size distributions; and (3) the influence of spray chambers, impact beads and flow spoilers on the droplet size distributions. In addition, the influence of sample temperature on droplet size distributions and hence nebulization efficiencies have also been examined. The results of these studies have been published in a series of papers. 3-5

(b) Evaporation Effects of Organic Solvents. A further area where the particle size distribution of an aerosol is critically important relates to the introduction of organic solvents into flames or plasmas. Organic solvents are used either because the sample is naturally soluble in an organic medium, or because one has been used in a preconcentration/-extraction procedure (e.g. APDC/MIBK extractions). The majority of studies described in the literature note a general enhancement effect on nebulizing an organic rather than an aqueous solution. The enhancement is attributed to the production of a primary aerosol at the nebulizer with a smaller median diameter for the organic solvent than for the aqueous solvent; this effect is a function of surface tension differences between the solvents. However, surface tension effects do not account for differences in nebulization efficiencies between different organic solvents, which may vary from 5% for nitrobenzene to 60% for benzene, in a typical ICP analysis.

We have carried out a detailed theoretical study of droplet evaporation characteristics for a wide range of organic solvents, and have been able to correlate the observed experimental nebulization efficiencies of several selected solvents with the theoretical droplet evaporation curves.⁶

3. Improved ICP Nebulizer.

The ability to monitor droplet size distributions with relative ease has allowed us to develop and test an improved, fixed all-glass crossflow nebulizer design for use with inductively coupled plasmas and flames. The nebulizer overcomes many of the problems of variability and adjustment

difficulty experienced with existing crossflow designs, and does not block readily like present concentric all-glass designs. In addition, a version has been developed which operates at a net sample aspiration rate of 0.2 mL min^{-1} , with no signal degradation from the normal version operating at 3 mL min^{-1} aspiration rate. A full description of this work has been published.⁷

4. Sample Introduction as Volatile Metal Chelates.

Preliminary studies have shown that it is possible to produce β -diketonates of Mn, Co, Fe, Zn and Cr by direct reaction of fluoro- β -diketones with various samples, and then to thermally vaporize the β -diketonate into an ICP. The most successful ligand used to date has been trifluoroacetylacetone, H(tfa). Using this approach, good quantitative agreement has been obtained with certificate data for Fe and Zn in NBS SRM Bovine Liver and independent analyses of Cr in human blood serum and NBS Bovine Liver.⁸

5. Aerosol Ionic Redistribution (AIR) Effects.

We have found, by collecting aerosols of binary salt solutions on the plates of a cascade impactor, that under certain circumstances the concentration ratio of the ions in the collected droplets is greatly different from that in the original bulk solution. This phenomenon, which was observed in ocean sprays as long ago as 1953, is not intuitively obvious to most atomic spectroscopists, which may account for the long delay in seeing its relevance to analytical atomic spectrometry.

The consequence of this effect, which we have termed an Aerosol Ionic Redistribution (AIR) effect, is that the *effective nebulization efficiency* of one cation in a mixed solution may differ from another!⁹ As a consequence, in a typical situation of analytical relevance (i.e. the presence of a high concentration of a matrix ion together with a low concentration of a trace ion to be determined) the signal obtained from the trace ion may be significantly different in the presence of the matrix ion than in its absence. This effect is quite independent of processes which may occur in a flame or plasma, such as possible volatilization or ionization interferences. Consequently, it is possible for a high matrix concentration of an ion to *enhance* the signal from a minor ion, in contradiction to normal experience where the high matrix ion concentration depletes the trace ion atom population by inhibiting its volatilization. Ironically, ICP nebulizers appear to show this effect much more strongly than AAS nebulizers, leading to a situation where there is apparently one interference which is more significant with ICP analysis than with AAS.

II. PUBLICATIONS SUPPORTED BY GRANT

1. "Aerosol Monitoring System for Size Characterization of Droplet Sprays Produced by Pneumatic Nebulizers," John W. Novak, Jr.; Richard F. Browner *Anal. Chem.* 1980, 52, 287.
2. "A Method for Investigating Size Distributions of Aqueous Droplets in the Range 0.5-1.0 μm Produced by Pneumatic Nebulizers," Malcolm S. Cresser; Richard F. Browner *Spectrochim. Acta, Part B* 1980, 35, 73.
3. "Characterization of Droplet Sprays from Pneumatic Nebulizers," John W. Novak, Jr.; Richard F. Browner *Anal. Chem.* 1980, 52, 792.
4. "Observations on the Effects of Impact Beads, Mixer Paddles and Auxiliary Oxidant on Drop Size Distributions in Analytical Flame Spectroscopy," Malcolm S. Cresser; Richard F. Browner *Appl. Spectrosc.* 1980, 34, 364.
5. "Sample Temperature Effects in Analytical Flame Spectroscopy," Malcolm S. Cresser; Richard F. Browner *Anal. Chim. Acta* 1980, 113, 33.
6. "Evaporation Characteristics of Organic Solvent Aerosols Used in Analytical Atomic Spectrometry," Andrew W. Boorn; Malcolm S. Cresser; Richard F. Browner *Spectrochim. Acta, Part B* 1980, 35, 823.
7. "Fixed Crossflow Nebulizer for Use with Inductively Coupled Plasmas and Flames," John W. Novak, Jr.; Donald E. Lillie; Andrew W. Boorn; Richard F. Browner *Anal. Chem.* 1980, 52, 576.
8. "Direct Introduction of Samples into the Inductively Coupled Argon Plasma as Volatile Metal Chelates," Marilyn S. Black; Richard F. Browner *Anal. Chem.* 1981, 53, 249.
9. "Interference Effects from Aerosol Ionic Redistribution (AIR) in Analytical Atomic Spectrometry," James A. Borowiec; Andrew W. Boorn; John H. Dillard; Malcolm S. Cresser; Michael J. Matteson; Richard F. Browner *Anal. Chem.* 1980, 52, 1054.
10. "Recent Studies with Sample Introduction into the RFICP," Richard F. Browner; Marilyn S. Black; Andrew W. Boorn *Developments in Atomic Spectrochemical Analyses*, Heyden, NY, 1981, in press.

III. CONFERENCE PRESENTATIONS OF
MATERIAL SUPPORTED BY GRANT

1. "Sampling Approaches for the Inductively Coupled Plasma in Practical Analyses," R. F. Browner, Eastern Analytical Symposium, New York (1977), invited talk.
2. "Nebulizers for ICPOES and AAS: Aerosol Characterization," John W. Novak, Jr. and Richard F. Browner, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH (1979).
3. "Inductively Coupled Argon Plasma: Introduction of Organic Species," Andrew W. Boorn and Richard F. Browner, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH (1979).
4. "RFICP - Studies with the Introduction of Organics," Andrew W. Boorn and Richard F. Browner, Federation of Analytical Chemistry and Spectroscopy Societies Meeting, Boston (1978).
5. "Characterization of Droplet Sprays from AAS and RFICP Nebulizers," John W. Novak and Richard F. Browner, FACSS Meeting, Boston (1978).
6. "Aerosol Monitoring System for Sprays from AAS and RFICP Nebulizers," John W. Novak, Jr. and Richard F. Browner, 30th Southeastern Regional ACS Meeting, Savannah, GA (1978).
7. "Sample Introduction for Multielement Analysis with the Inductively Coupled Plasma," Richard F. Browner, Andrew W. Boorn, John W. Novak, Jr. and John H. Dillard, 177th ACS National Meeting, Honolulu, HI (1979), invited talk.
8. "Recent Studies with Sample Introduction into the RFICP," Richard F. Browner, Marilyn S. Black and Andrew W. Boorn, Winter Conference on Developments in Plasma Spectrochemical Analysis, San Juan, Puerto Rico (1980), invited talk.
9. "Nebulizers for ICPOES and AAS. The Chemistry of Aerosol Transport and Characterization of Droplet Sizes," Richard F. Browner, Colloquium Spectroscopicum XXI, 8th International Conference on Atomic Spectroscopy, Cambridge, England (1979), invited talk.
10. "The ICP: Organic Compound Interactions and Torch Design," A. W. Boorn and R. F. Browner, CSI XXI and 8th ICAS, Cambridge, England (1979).
11. "An All-Glass, High Efficiency, Crossflow Nebulizer for the Inductively Coupled Argon Plasma," Richard F. Browner, John W. Novak, Donald E. Lillie, Andrew W. Boorn and Malcolm S. Cresser, 6th FACSS Meeting, Philadelphia, PA (1979), invited talk.
12. "Recent Studies with Sample Introduction for the Inductively Coupled Plasma," Richard F. Browner, Southeastern Association of Analytical Chemists' Meeting, Athens, GA (1980).

13. "Inductively Coupled Plasma Sample Introduction of Volatile Metal Chelates," Marilyn S. Black and Richard F. Browner, 179th ACS National Meeting, Houston, TX (1980).
14. "Sample Introduction Studies with the Inductively Coupled Plasma," Andrew W. Boorn and Richard F. Browner, Northeast Regional ACS Meeting, Potsdam, NY (1980), invited talk.
15. "Future Improvements in Sampling and Sample Introduction for Analytical Atomic Spectrometry," 2nd Chemical Congress of the North American Continent, 180th ACS Meeting, Las Vegas, Nevada (1980), invited talk.
16. "Aerosol Ionic Redistribution (AIR) Interferences in ICP Spectrometry," Andrew W. Boorn, Tanya Deal and Richard F. Browner, 7th Annual Federation of Analytical Chemistry and Spectroscopy Societies' (FACSS) Meeting, Philadelphia (1980), invited talk.
17. "Factors Influencing Nebulization Efficiency in ICP and AAS Spectrometry," Richard F. Browner, Malcom S. Cresser and David Smith, 7th Annual FACSS Meeting, Philadelphia (1980), invited talk.
18. "Recent Studies with Nebulization Processes in Atomic Spectrometry," Richard F. Browner, David Smith and Andrew W. Boorn, Expochem 80, Houston, TX (1980), invited talk.
19. "Fundamental Studies with Aerosol Sample Introduction for Atomic Absorption Spectrometry," Richard F. Browner, David Smith and Andrew W. Boorn, Eastern Analytical Symposium, NY (1980), invited talk.

IV. THESES OF STUDENTS WHOLLY OR
PARTIALLY SUPPORTED BY GRANT

PhD:

1. "Improvements in Detection Capabilities in Atomic Spectroscopy," J. W. Novak, Jr., September 1979.
2. "Studies of Sample Introduction for Inductively Coupled Plasma Emission Spectrometry," A. W. Boorn, March 1981.

M.S.:

1. "Ion Enrichment in Aerosols Produced by Conventional Nebulizers Used in Analytical Atomic Spectroscopy," J. H. Dillard, November 1979.
2. "A High Performance Liquid Chromatography/Inductively Coupled Plasma Atomic Emission Spectrometer Interface for Trace Element Speciation and for Analysis of Microliter Samples," K. R. Snable, November 1980.

V. SCIENTIFIC COLLABORATORS
(other than Principal Investigators)

1. Eugene A. Powell, Assistant Professor, Aerospace Engineering.
2. William Bell, Research Engineer, Aerospace Engineering.
3. Malcom S. Cresser, Visiting Faculty Member, Chemistry.
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5. John W. Novak, Graduate Student.
6. John H. Dillard, Graduate Student.
7. Andrew W. Boorn, Graduate Student.
8. Kimberly R. Snable, Graduate Student.
9. Brenda S. Whaley, Graduate Student.
10. David D. Smith, Graduate Student.
11. Ray Kull, Graduate Student.
12. James Borowiecz, Undergraduate Student.
13. Michael Thomas, Undergraduate Student.
14. Tanya Mamantov, Undergraduate Student.

VI. CONTINUATION OF GRANT

A renewal proposal (NSF CHE-8019947) has been submitted to NSF and recommended for funding with effect from 8/1/81.

Richard F. Browner
Principal Investigator

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