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Title	**NEW HIGH TEMPERATURE PLASMAS AND SAMPLE INTRODUCTION SYSTEMS FOR ANALYTICAL ATOMIC EMISSION AND MASS SPECTROMETRY**
Subtitle	**Progress Report**
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1. PURPOSE (SCOPE)

In this project, new high temperature plasmas and new sample introduction systems are developed for rapid elemental and isotopic analysis of gases, solutions, and solids using atomic emission spectrometry (AES) and mass spectrometry (MS). These devices offer promise of solving singularly difficult analytical problems that either exist now or are likely to arise in the future in the various fields of energy generation, environmental pollution, nutrition, and biomedicine. Emphasis is being placed on:

a) generation of annular, helium inductively coupled plasmas (He ICPs) that are suitable for atomization, excitation, and ionization of elements possessing high excitation and ionization energies, with the intent of enhancing the detecting powers of a number of elements,

b) computer modelings of ICP discharges to predict the behavior of new and existing plasmas,

c) diagnostic studies of high-temperature plasmas and sample introduction systems to quantify their fundamental properties, with the ultimate aim to improve analytical performance of atomic spectrometry,

d) development and characterization of new, low-cost sample introduction systems that consume microliter or microgram quantities of samples, and

e) investigation of new membrane separators for striping solvent from sample aerosol to reduce various interferences and to enhance sensitivity and selectivity in plasma spectrometry.

2. TECHNICAL PROGRESS FROM JANUARY-1991 THROUGH DECEMBER-1991.

2.A. Computer Modelings of ICP Discharges.

The first computer simulations of He ICPs, $Ar-N_2$ ICPs and $Ar-O_2$ ICPs were initiated this year to predict fundamental properties of these plasmas. No published work on modeling the cited plasmas is available. These discharges are important in spectrochemical analysis because of their greater sensitivity and spectral selectivity (He ICP), superior ability to decompose refractory particles ($Ar-N_2$ ICP), and the capability to operate with higher solvent and analyte loading ($Ar-N_2$ ICP and $Ar-O_2$ ICP) compared to the Ar ICP.

The properties predicted by simulation included temperature and velocity distributions, the magnetic and electric fields, and radial energy dissipation. These results were obtained with a recent computer code developed by Mostaghimi, et al. (1). Professor J. Mostaghimi, University of Toronto, has collaborated with us in these studies.

Results from computer simulations have been presented at three international meetings (2-4) and are being prepared for two publications. Also, predictions obtained by simulation have been compared to our diagnostic data to verify the validity of the mathematical models. Further, these theoretical predictions are being currently used to devise more efficient He ICPs, and for interpreting analytical results achieved in mixed-gas plasma spectrometry.

2.B. Plasma Source Mass Spectrometric Studies.

Last year, we reported on studies with a new instrumental arrangement for ICP-MS (Delsi-Nermag Instruments). It was stated that the software required significant revisions. The current software is the eight version since the instrument has been delivered. Frankly, software-related problems have impeded our studies in the last two years.

The ICP-MS studies this year focused on Ar and He plasmas. In a comprehensive study (5), we examined the utility of the thermospray nebulizer with a membrane separator (TNMS) as compared to the ultrasonic nebulizer (USN) and pneumatic nebulizer (PN) for Ar ICP-MS. Compared to the PN used with or without a desolvation system, respectively, detection limits were improved for TNMS by a factor of up to 20 and 60, but the USN provided detection limits which were generally lower than those obtained with the TNMS by a factor of 2 to 5. Lowest ion kinetic energies (5.0 to 7.7 eV) were obtained when USN-cryogenic desolvation or the TNMS was used. More importantly, lowest oxide levels were measured when: 1) the TNMS approach was used, or 2) cryogenic cooling was applied to the desolvated aerosol from the USN.

Our current work is focused on He ICP-MS. A strong interface-related discharge or a pinch discharge is observed. Four approaches, are being investigated to minimize plasma potential in He ICP-MS. These include the use of: 1) a center-tapped load coil, 2) a symmetrical coil which is capacitively coupled to ground at both ends while rf power is fed to the middle of the coil by a variable capacitor, 3) modified load coils and 4) electrostatic shields placed between the induction coil and the plasma torch. Studies are focused on: 1) understanding the nature of pinch discharge in He as compared to the secondary discharge produced in Ar, 2) the ease of plasma formation when the cited approaches are used to minimize the pinch discharge, 3) effects of operating conditions on ion kinetic energies, 4) and examination of analytical utility of the technique in analysis of aqueous samples of nonmetals. The results of some of these studies are to be presented at the FACSS Meeting (6).

2.C. Diagnostic Studies of Sample Introduction Systems.

Studies of sample introduction systems focused on three projects. In one investigation (7), we utilized dual-beam, light-scattering interferometry to acquire the most comprehensive information yet on the fundamental characteristics of the ultrasonic nebulizers. Simultaneous measurements were conducted on particle-size and particle-velocity distributions, size-velocity correlation, particle number density, and volume flux and span of desolvated aerosols. Also, time-resolved measurements on desolvated aerosol were made. One of the most significant findings that emerged from this study was the observation of intermittence of particle arrival and particle diameter, before injection into the ICP, on a msec-time scale. The local number density and particle diameter varied by one order of magnitude on a msec-time scale. This finding implies that new sample introduction systems must be devised that can provide fine, monodispersive aerosol with minimal or no intermittence for particle arrival.

The smallest particle size that can be measured with the dual-beam, light-scattering technique is approximately 0.5 μm. To measure particle-size distributions in a lower range (0.01- to 1.0-μm), we utilized the differential electromobility technique. The technique was tested in the characterization of aerosols produced by six nebulization systems: one thermospray nebulizer equipped with a membrane separator, two ultrasonic nebulizers, one pneumatic nebulizer used with and without desolvation, and a frit-type nebulizer. Among these devices, the thermospray nebulizer produced the greatest amount of aerosol with particle sizes in the 0.01- to 1.0-μm range. Such studies are important in understanding fundamentals of aerosol generation and transport in order to improve analytical performances of atomic spectrometry. Two papers on this subject have been presented at the FACSS Meeting (8,9), and are being prepared for publication.

2.D. Other Related Projects.

Because of the volume of the work conducted this year, there was no opportunity to complete: 1) evaluation of three types of membrane separators designed last year for removing solvent from aerosol prior to injection into He ICP or ICP-MS systems, 2) the construction of a high-fidelity image transfer optics based on fiber optics to gather spatially resolved fundamental data, and 2) the development of low cost charge injection detector (CID) described in the previous reports. A Research Scientist (postdoctoral fellow) with experience in the cited areas has been hired to assist us effective November 1, 1991.

3. TECHNICAL PROGRESS EXPECTED IN 1992.

We anticipate that the on-going investigations discussed above will continue or expand for the next year. The primary areas of our work will be concerned with: 1) mathematical modeling of He ICPs and mixed-gas ICPs, 2) understanding the nature of interface-related discharges in He ICP-MS, 3) investigation of membrane separators for injection of dry aerosol in He ICP-AES and ICP-MS, 4) studies of a thermospray nebulizer and generation of monodispersive aerosol for He ICP-MS, and 5) the use of spectral-line-width data predicted by the Model Microfield Method for estimation of electron number density in plasma discharges.

4. REFERENCES CITED.

1. M. I. Boulos, J. Mostaghimi, and P. Proulx, "HiFI - Plasma Computer Code", Version 2.0, July 1989 available from M. I. Boulos, Department of Chemical Engineering, University of Sherbrooke, Sherbrooke, Quebec, J1K 2R1, Canada.

2. A. Montaser, "Non-Argon and Mixed Gas Plasmas for Spectrochemical Analysis", presented at the 1991 Winter Conference on Plasma Spectrochemistry, Dortmund, Germany, January, 1991.

3. A. Montaser, M. Cai and J. Mostaghimi, "Computer Simulation of Mixed-Gas ICP Discharges", presented at the XXVII Colloquium Spectroscopicum Internationale, Bergen, Norway, June 1991.

4. M. Cai, A. Montaser, and J. Mostaghimi, "Computer Simulation of Helium Inductively Plasmas", presented at 1991 FACSS Meeting, Anaheim, CA, October 1991.

5. A. Montaser, H. Tan, I. Ishii, S. Nam, and M. Cai, Argon Inductively Coupled Plasma Mass Spectrometry with Thermospray, Ultrasonic, and Pneumatic Nebulization, Anal. Chem., in press.

6. A. Nam, H. Tan, and A. Montaser, "Helium Inductively Coupled Plasma-Mass Spectrometry", presented at 1991 FACSS Meeting, Anaheim, CA, October 1991.

7. R. H. Clifford, P. Sohal, and A. Montaser, Diagnostic Studies on Desolvated Aerosols from Ultrasonic Nebulizers", submitted to Spectrochim. Acta.

8. R. H. Clifford, H. Tan, A. Montaser, F. Zarrin, and P.B. Keady, "Particle Size Measurement in Submicron Range by Differential Electromobility Technique: Comparison of Desolvated Aerosols from Ultrasonic and Pneumatic Nebulizers", presented at 1991 FACSS Meeting, Anaheim, CA, October 1991.

9. H. Tan, R. H. Clifford, A. Montaser, F. Zarrin, and P.B. Keady, "Measurement of Submicron Particles by Differential Mobility Particle Sizer for Thermospray Nebulization", presented at 1991 FACSS Meeting, Anaheim, CA, October 1991.

5. PUBLICATIONS AND PAPERS PRESENTED FROM 12/1990 THROUGH 12/1991.

A) List of DOE-funded papers published, in press, or submitted:

1. R. H. Clifford, A. Montaser, S. P. Dolan, and S. Capar), "Conversion of an Ultrasonic Humidifier to a Continuous-Type Ultrasonic Nebulizer for Atomic Spectrometry", Anal. Chem., 62, 2740 (1990).

2. I. Ishii and A. Montaser, "A Tutorial Discussion on Measurements of

Rotational Temperatures in Inductively Coupled Plasmas", Spectrochim. Acta., 46B, 1197 (1991).

3. H. Tan, I. Ishii, and A. Montaser, "An Extraction Discharge Source for Inductively Coupled Plasma Atomic Emission Spectrometry: Examination of Analytical Potentials in the Detection of a Range of Elements and Fundamental Properties", J. Anal. At. Spectrom., 6, 317 (1991).

4. I. Ishii, H. Tan, and S. Chan, A. Montaser, "Helium ICP-AES: effect of induction frequency and forward power on plasma formation and analytical and fundamental properties", , Spectrochim. Acta., 46B, 901 (1991).

5. A. Montaser, H. Tan, I. Ishii, S. Nam, and S. Cai, "Argon Inductively Coupled Plasma Source Mass Spectrometry with Thermospray, Ultrasonic, and Pneumatic Nebulization", Anal. Chem., in press.

6. S. P. Dolan, S. A. Sinex, and S. G. Capar, R. H. Clifford, and A. Montaser, "On-Line Preconcentration and Volatilization of Iodine for Inductively Coupled Plasma Atomic Emission Spectrometry", Anal. Chem., in press.

7. R. H. Clifford, P. Sohal, and A. Montaser, "Diagnostic Studies on Desolvated Aerosol from Ultrasonic Nebulizers", submitted to Spectrochim. Acta.

8. H. Tan, "Mass Spectrometry and Atomic Spectrometry of Argon and Helium Inductively Coupled Plasmas", Ph.D Dissertation, George Washington University, Washington, DC 20052, September 1991.

9. A. Strasheim and A. Montaser, "Instrumentation for Optical Emission Spectrometry", in Inductively Coupled Plasmas in Analytical Atomic Spectrometry, A. Montaser, and D. W. Golightly, Eds, Second Edition, 1991.

10. D. Demers and A. Montaser, "Analytical Application of the Inductively Coupled Plasma as an Atomization Cell for Atomic Fluorescence Spectrometry", in Inductively Coupled Plasmas in Analytical Atomic Spectrometry, A. Montaser, and D. W. Golightly, Eds, Second Edition, 1991.

B) List of presentations at scientific meetings:

1. A. Montaser, R. H. Clifford, and P. Sohal, "Dual-Beam, Light-Scattering Interferometry for Simultaneous Measurements of Droplet-Size and Velocity Distributions of Aerosols Produced by New Ultrasonic Nebulizers", presented at the 1991 Winter Conference on Plasma Spectrochemistry, Dortmund, Germany, January, 1991.

2. A. Montaser, H. Tan, I. Ishii, and S. Nam, "Analytical and Fundamental Characteristics of the Delsi-Nermag Mass Spectrometer Interfaced to a Versatile ICP System", presented at the 1991 Winter Conference on Plasma Spectrochemistry, Dortmund, Germany, January, 1991.

3. A. Montaser, "Non-Argon and Mixed Gas Plasmas for Spectrochemical Analysis", presented at the 1991 Winter Conference on Plasma

Spectrochemistry, Dortmund, Germany, January, 1991.

4. A. Montaser, R. H. Clifford, and P. Sohal, "Time-Resolved Measurements of Droplet-size and Velocity Distributions of Desolvated Aerosols Produced by Ultrasonic Nebulizers", presented at the XXVII Colloquium Spectroscopicum Internationale, Bergen, Norway, June 1991.

5. A. Montaser, H. Tan, and M. Cai, "Thermospray Nebulizer Coupled with Membrane Separator for Argon Inductively Coupled Plasma Mass Spectrometry", presented at the XXVII Colloquium Spectroscopicum Internationale, Bergen, Norway, June 1991.

6. A. Montaser, M. Cai, and J. Mostaghimi, "Computer Simulation of Mixed-Gas ICP Discharges", presented at the XXVII Colloquium Spectroscopicum Internationale, Bergen, Norway, June 1991.

7. A. Nam, H. Tan, and A. Montaser, "Helium Inductively Coupled Plasma-Mass Spectrometry", presented at 1991 FACSS Meeting, Anaheim, CA, October 1991.

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9. H. Tan, R. H. Clifford, A. Montaser, F. Zarrin, and P.B. Keady, "Measurement of Submicron Particles by Differential Mobility Particle Sizer for Thermospray Nebulization", presented at 1991 FACSS Meeting, Anaheim, CA, October 1991.

10. A. Montaser, "Advances in New Sources in Atomic Spectroscopy: What Has Happened in the Last Two Years", presented at 1991 FACSS Meeting, Anaheim, CA, October 1991.

11. M. Cai, A. Montaser, and J. Mostaghimi, "Computer Simulation of Helium Inductively Plasmas", presented at 1991 FACSS Meeting, Anaheim, CA, October 1991.

6. TIME DEVOTED TO THE PROJECT.

PI devoted 100% of his time during one summer month to this project. During the academic year, PI fulfilled his teaching duties but the remainder of his time was spent on the execution of this project and on the supervision of one research associate, and eight graduate students. Effective November 1, 1991, Dr. Chunming Hsiech will join our research group for one year. Dr. Hsiech received his Ph.D in Analytical Chemistry in October 1991 at Purdue University.

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