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NEW HIGH TEMPERATURE PLASMAS AND SAMPLE
INTRODUCTION SYSTEMS FOR ANALYTICAL
ATOMIC EMISSION AND MASS SPECTROMETRY

Progress Report

Akbar Montaser

The George Washington University
Office of Sponsored Research
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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, biomedicine and nutrition. 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) diagnostic studies of high-temperature plasmas to quantify their fundamental properties, with the ultimate aim to improve analytical performance of atomic spectrometry,

c) development and characterization of new sample introduction systems that consume microliter or microgram quantities of samples, and

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

2. TECHNICAL PROGRESS FROM JANUARY-1990 THROUGH DECEMBER-1990.

2.A. Atomic Emission Studies of ICP Discharges.

A number of studies initiated last year on He ICP discharges are still in progress. These include: 1) the use of vacuum ultraviolet (VUV) lines to improve detection limits of iodine and sulfur in aqueous samples by a factor of 50 to 100, 2) investigation of an air-cooled torch for a 2-kW He ICP used in the end-on configuration to improve detection limits of nonmetals by a factor of ten, 3) analytical and fundamental characterization of a 6.8-MHz He ICP for comparison with results obtained for plasmas at 27 and 41 MHz, and 4) high-resolution Fourier transform spectrometry (FTS) of He ICP to calculate rotational temperatures and to estimate line width and line shape of spectral lines from H, He, and Fe for the calculation of electron number density and Doppler temperature. The FTS data were acquired at the FTS Facility of the Los Alamos National Laboratory in collaboration with B. A. Palmer, L. R. Layman, and D. E. Hof, but all data analysis were analyzed by PI's group at the George Washington University. Results of the cited research have been presented at the FACSS Meetings (1-5). Many publications are expected once various aspects of these projects are completed.

In addition to studies discussed above on He ICPs, work continued on other ICP-related projects. In one study, our Copyrighted algorithm (6) for

estimation of electron number density by Stark Broadening was modified to allow the gradual, selective rejection of the line center of the theoretical Stark profile for comparison to the experimental profile. The new algorithm (7) estimates electron number density with accuracy greater than our previous results (6,8). Work is also in progress to test the applicability of the new algorithm to other spectral lines. For the next year, we plan to use spectral-line-width data provided by the Model Microfield Method because these profiles are much closer to the experimental profiles, especially at low densities.

Analysis of high-resolution FTS data is completed for the measurement of rotational temperature in argon-nitrogen plasmas (9). Results have been compared to our previous data for excitation and translational temperatures. These and other experimental data are being used by us to model mixed-gas and He ICPs. Initial results of our modeling studies will be available next year.

2.B. Plasma Source Mass Spectrometric Studies.

Last year, we placed an order for a new ICP-MS instrument manufactured by Delsi-Nermag Instruments. This instrument was selected by us partly because sufficient funds were not available to purchase the widely tested ICP-MS systems manufactured by VG or Perkin Elmer-Sciex. The instrument was delivered in December 1989, four months later than the promised delivery date. It was installed and fine tuned by the manufacturer in late January and March 1990, respectively. Because this instrument was the first ICP-MS in the United States by the Delsi-Nermag Instruments, the software required significant revisions. The current software is the third version of the original software delivered with the instrument.

Our ICP-MS studies are summarized below. We have interfaced the mass spectrometer to a solid state, 41-MHz generator for forming a variety of plasmas on a single ICP facility. For this purpose, we used a versatile impedance matching network as described in our previous work in atomic emission studies (10). Thus far, the ICP-MS system has been tested with the Ar ICP. Analytical results in terms of detection limits, short- and long-term stabilities, ratios of oxide and doubly-charged species to singly-charged ions, ion kinetic energies, and oxide temperatures have been measured for both pneumatic and ultrasonic nebulization as a function of injector gas flow rate, temperature of condenser for the nebulization system, etc. Such data are essential for the conventional Ar ICP before ICP-MS studies of He ICP can be initiated. Results of the cited studies have been presented at three conferences (11-13), and are being prepared for publication by December 1990. Studies of He ICP-MS will begin early next year.

2.D. Studies of Sample Introduction Systems.

Studies of sample introduction systems focused on four projects. In one study, the thimble glass frit (14) introduced last year was further investigated, and the problem of degradation of efficiency as the result of repeated usage was eliminated for continuous runs up to 8 hours. The second project involved conversion of an ultrasonic humidifier to a low-cost ultrasonic nebulizer (15-17). This device can be operated in the batch or

continuous mode. The new system was applied to Ar ICP-AES. Detection limits, signal-to-background ratios (S/B), precision, noise power spectra (NPS), and droplet size distributions measured with the new nebulizer were compared to those of a commonly used pneumatic nebulizer. For the 14 elements tested, precision of 1-2% were achieved. In general, detection limits of the new device were superior to those obtained with the pneumatic nebulizer by a factor of 8 to 50. While detection limits measured with the new device were similar to those reported for the commercial USNs, the proposed system has the advantage of being quite inexpensive. These studies will continue next year.

The third project on sample introduction system focused on the design, fabrication, and evaluation of a momentum separator and three types of membrane separators for removing solvent from aerosol prior to injection into He ICP or ICP-MS systems. The excess solvent is removed either by a purge gas or by the application of a small vacuum used in conjunction with a desolvation system. Initial results on these studies have been reported at conferences (18,19) this year.

Last year, we introduced the technique of dual-beam, light-scattering interferometry (20,21) to measure droplet-size and velocity distributions of aerosols simultaneously. Work in this area continued this year, with greater focus on ultrasonic nebulizers developed in our laboratory and a commercial device. Also, because our current work with membrane separators involves the use of highly efficient thermospray nebulizers, we have just initiated to use scattering interferometry to map droplet size and velocity distribution for the thermospray-based systems. Results of this work was reported at the FACSS Meeting (17,19).

2.G. Other Related Projects.

Because of the volume of the work conducted this year, there was no opportunity to complete 1) 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 report. However, AES studies on extraction discharges formed with a 41-MHz Ar ICP were completed and the results were submitted for publication (22).

3. TECHNICAL PROGRESS EXPECTED IN 1991.

We anticipate that the on-going investigations discussed above will continue or expand for the next year. The primary areas of our work will focus on: 1) interface-related discharges in He ICP-MS, 2) use of membrane separators for injection of dry aerosol in He ICP-AES and ICP-MS, 3) studies of a thermospray nebulizer for ICP-MS, 4) modification of humidifier-based ultrasonic nebulizer for microliter nebulization of highly viscous sample solutions, 5) mathematical modeling of mixed-gas and He ICPs, and 6) the use spectral-line-width data predicted by the Model Microfield Method for estimation of electron number density in plasma discharges.

4. REFERENCES CITED.

1. "Helium Inductively Coupled Plasma: Detection of Halogens in UV and VUV Regions" (with R.H. Clifford, S.A. Sinex and S.G. Capar); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
2. "On-Line Ion Exchange Preconcentration for Detection of Iodine by FIA ICP-AES" (with S. P. Dolan, S. G. Capar, and R. H. Clifford); presented at the 32nd Rocky Mountain Conference, Denver, CO, July 1990.
3. "A Water Cooled-Torch for Helium Inductively Coupled Plasma" (with H. Tan); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
4. "Atomic Emission and Mass Spectrometry of He ICPs Formed at 6 to 41 MHz" (with I. Ishii, H. Tan, and R. H. Clifford); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
5. "Line Widths and Temperatures of He ICP Discharges Measured by High - Resolution Fourier Transform Spectroscopy" (with R. H. Clifford, I. Ishii, B. A. Palmer and L. R. Layman); presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.
6. SCAN, CONVERT, and NE: New Computer Programs for the Determination of Electron Number Density via Stark Broadening (with S. Chan); 1989 US Copyright.
7. "Measurement of Electron Number Densities for Argon and Helium ICP Discharges by Using Various Hydrogen Lines" (I. Ishii, R. H. Clifford, A. Montaser, B. A. Palmer and L. R. Layman); presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.
8. S. Chan and A. Montaser, *Spectrochim. Acta*, 44B, 175 (1989).
9. "Rotational Temperatures of Argon-Nitrogen ICP Discharges Measured by High-Resolution Fourier Transform Spectroscopy" (with I. Ishii, B. A. Palmer and L. R. Layman); presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.
10. A. Montaser, I. Ishii, R. H. Clifford, S. A. Sinex, and S. G. Capar, *Anal. Chem.*, 61, 2589 (1989).
11. "Characterization of the Delsi-Nermag Mass Spectrometer Interfaced to a Versatile ICP System" (with H. Tan, I. Ishii, and S. Nam); presented at the 32nd Rocky Mountain Conference, Denver, CO, July 1990.
12. "Investigation of Helium ICP Discharges and New Sample Introduction Systems for Atomic Spectrometry"; invited talk presented at the 200th ACS National Meeting, Washington, DC August 1990.
13. "Plasma Potential and Ion Kinetic Energies for Delsi-Nermag Mass Spectrometer Interfaced to a Versatile ICP System" (with H. Tan, I. Ishii, S. Nam, and M. Cai); presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.

14. R. H. Clifford, A. Montaser, S. A. Sinex, and S. G. Caper, Anal. Chem., 61, 2777 (1989).
15. "A Low-cost Ultrasonic Nebulizer for Plasma Spectrometry" (with R. H. Clifford); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
16. "Low-Cost Ultrasonic Nebulizer for Atomic Spectrometry" (with R. H. Clifford, S. P. Dolan, and S. Caper), Anal. Chem., in press.
17. "A Low-Cost Ultrasonic Nebulizer for Plasma Spectrometry: An Update" (R.H. Clifford, S. P. Dolan and S. G. Caper); presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.
18. "Solvent-Analyte Separator for Atomic Emission and Mass Spectrometry" (with H. Tan, R. H. Clifford, S. Nam); presented at the 32nd Rocky Mountain Conference, Denver, CO, July 1990, paper 22.
19. "Solvent-Analyte Separator for Atomic Emission and Mass Spectrometry: an Update" (with H. Tan, R. H. Clifford, S. Nam, M. Cai); presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.
20. "Phase Doppler Technique for Simultaneous Measurements of Drop Size and Velocity Distributions of Aerosols Produced by ICP Nebulizers" (with R. H. Clifford, H. Tan, and I. Ishii); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
21. R. H. Clifford, I. Ishii, A. Montaser, and G. A. Meyer, Anal. Chem., 62, 390 (1990).
22. "Characterization of a 15-torr Extraction Discharge Source for Inductively Coupled Plasma-Atomic Emission Spectrometry", (with H. Tan and I. Ishii); Submitted to J. Anal. At. Spectrom.

5. PUBLICATIONS AND PAPERS PRESENTED FROM 9/1989 THROUGH 12/1990.

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

1. "Atomic Emission Detection Powers and Noise Power Spectra of Argon ICP Discharges Sustained in Laminar- and Tangential-Flow Torches" (with R. H. Clifford, S. Sinex, and S. Caper), J. Anal. At. Spectrom., 4, 499 (1989).
2. "Noise Power Spectra Comparing Helium and Argon ICP Discharges" (with I. Ishii, H. Tan, and R. H. Clifford), Spectrochim. Acta, 44B, 1163 (1989).
3. "SCAN, CONVERT, and NE: New Computer Programs for the Determination of Electron Number Density via Stark Broadening" (with S. Chan); 1989 US Copyright.
4. "Thimble Glass Frit Nebulizer for Atomic Spectrometry" (with R. H. Clifford, S. Sinex, and S. Caper), Anal. Chem. 61, 2777 (1989).

5. "Thimble Glass Nebulizer and Method", US Patent Application Serial No. 07/450,761 filed on December 14, 1989 (with R. H. Clifford, S. A. Sinex, and S. G. Capar).
6. "Versatile Impedance Matching Networks for ICP Spectrometry" (with I. Ishii, R. Clifford, S. Sinex, and S. Capar), Anal. Chem., 61, 2589 (1989).
7. "Radial Excitation Temperatures in Argon-Oxygen and Argon-Air Inductively Coupled Plasmas" (with I. Ishii), J. Anal. At. Spectrom., 5, 57 (1990).
8. "High-Resolution Fourier Transform Spectroscopy of Argon-Nitrogen ICP Discharges" (with I. Ishii, B. A. Palmer, and L. R. Layman), Spectrochim. Acta., 45B, 603 (1990).
9. "Dual-Beam, light-Scattering Interferometry for Simultaneous Measurements of Drop-Size and Velocity Distributions of Aerosols From Commonly Used Nebulizers" (with R. H. Clifford, I. Ishii, and G. A. Meyer), Anal. Chem., 62, 390 (1990).
10. "Low-Cost Ultrasonic Nebulizer for Atomic Spectrometry" (with R. H. Clifford, S. P. Dolan, and S. Capar), Anal. Chem., in press.
11. "A Tutorial Discussion on Measurements of Rotational Temperatures in Inductively Coupled Plasmas", (with I. Ishii), Submitted to Spectrochim. Acta.
12. "Characterization of a 15-torr Extraction Discharge Source for Inductively Coupled Plasma-Atomic Emission Spectrometry", (with H. Tan and I. Ishii); Submitted to J. Anal. At. Spectrom.

B) List of presentations at scientific meetings:

1. "Recent Studies on Extraction Discharge Sources for Argon and Helium Inductively Coupled Plasma Atomic Emission Spectrometry" (with H. Tan); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
2. "A Water Cooled-Torch for Helium Inductively Coupled Plasma" (with H. Tan); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
3. "Helium Inductively Coupled Plasma: Detection of Halogens in UV and VUV Regions" (with R.H. Clifford, S.A. Sinex and S.G. Capar); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
4. "A Low-cost Ultrasonic Nebulizer for Plasma Spectrometry" (with R. H. Clifford); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
5. "Enhancement Techniques for Detection of Iodine in Foods by ICP Spectrometry" (with S. A. Sinex, S. G. Capar, and R. H. Clifford); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
6. "Phase Doppler Technique for Simultaneous Measurements of Drop Size and Velocity Distributions of Aerosols Produced by ICP Nebulizers" (with R. H. Clifford, H. Tan, and I. Ishii); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.

7. "Applications of High-Resolution Fourier Transform Spectroscopy in Diagnostic Studies of Non-Argon ICP Discharges" (with I. Ishii, B. A. Palmer, L. R. Layman, and D. E. Hof); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
8. "Atomic Emission and Mass Spectrometry of He ICPs Formed at 6 to 41 MHz" (with I. Ishii, H. Tan, and R. H. Clifford); presented at the 1989 FACSS Meeting, Chicago, IL, October 1989.
9. "Rotational Temperatures of Argon-Nitrogen ICP Discharges Measured by High-Resolution Fourier Transform Spectroscopy" (with I. Ishii, B. A. Palmer and L. R. Layman); presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.
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13. "Investigation of Helium ICP Discharges and New Sample Introduction Systems for Atomic Spectrometry"; invited talk presented at the 200 th ACS National Meeting, Washington, DC August 1990.
14. "Measurement of Electron Number Densities for Argon and Helium ICP Discharges by Using Various Hydrogen Lines" (I. Ishii, R. H. Clifford, A. Montaser, B. A. Palmer and L. R. Layman); presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.
15. "A Low-Cost Ultrasonic Nebulizer for Plasma Spectrometry: An Update" (R.H. Clifford, S. P. Dolan and S. G. Capar); presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.
16. "Solvent-Analyte Separator for Atomic Emission and Mass Spectrometry: an Update" (with H. Tan, R. H. Clifford, S. Nam, M. Cai); presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.
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18. "Line Widths and Temperatures of He ICP Discharges Measured by High - Resolution Fourier Transform Spectroscopy" (with R. H. Clifford, I. Ishii, B. A. Palmer and L. R. Layman); presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.
19. "Advances in New Sources for Atomic Spectroscopy"; presented at the 1990 FACSS Meeting, Cleveland, OH, October 1990.

6. TIME DEVOTED TO THE PROJECT.

PI devoted 100% of his time during two summer months 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.

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