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PROGRESS REPORT

In this Report, we summarize our DOE-sponsored research activities over the past three years. Only the most important achievements are included to illustrate our progress and obstacles. Detailed description of our investigations are outlined in the reprints and preprints that accompany this Report.

1. PURPOSE AND SCOPE

In this research, new high temperature plasmas and new sample introduction systems are explored for rapid elemental and isotopic analysis of gases, solutions, and solids using mass spectrometry (MS) and atomic emission spectrometry (AES). These studies 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, new material development, environmental pollution, biomedicine and nutrition. During the period 1990-92, emphasis was placed on:

(a) analytical investigation of atmospheric-pressure helium inductively coupled plasmas (He ICPs) that are suitable for atomization, excitation, and ionization of elements possessing high excitation and ionization energies, for the purpose of enhancing the detecting powers of a number of elements,

(b) simulation and computer modeling of plasma sources that have unique potentials as future tools for spectrochemical analysis, i.e., we are aiming to ease the hunt for new plasmas by predicting their structure and fundamental and analytical properties, without incurring enormous cost for extensive experimental studies,

(c) spectroscopic imaging and diagnostic studies of high-temperature plasmas, particularly new He ICP discharges, to instantly visualize their prevailing structure, to quantify key fundamental properties, and to verify predictions by mathematical models, and

d) development and characterization of new, low-cost sample introduction systems for atomic spectrometry, and examination of new diagnostic techniques suitable for probing the aerosol over a wide range, from 10 nanometer-size particles to droplets having micrometer diameter. Again, these endeavors are designed to ultimately improve analytical performance indices such as detection limits, precision, and the degrees of freedom from interferences.

2. TECHNICAL PROGRESS FROM JANUARY-1990 THROUGH DECEMBER-1992.

Although the studies summarize below represent our DOE-sponsored activities since January 1990, we must inform the readers that our efforts were hampered by two factors. First, during the first two years of this project, a chain of frustrating events surrounding the installation and operation of a newly acquired ICP-MS (Delsi-Nermag Instruments) prevented us from even initiating the studies proposed on He ICP-MS. Briefly, the instrument was delivered four months after the promised delivery date, was installed by the manufacturer three months later, many hardware and software problems had to be overcome for the first two years (for example, the current software, delivered in March 1991, is the ninth version of the original software we received with the instrument), the company filed for bankruptcy in December 1991, and during its reorganization in France and United States, we had no service or parts. Why did we select this instrument in the first place? The funds contributed by DOE ($75,000; 1989 funds) and the University ($35,000) were not sufficient to purchase the widely tested ICP-MS systems, and furthermore, the instrument had an open configuration and was thus suitable for easy interfacing with a variety of plasma sources. On the positive side, the above events educated PI and eight of his associates on the *science and art* of plasma mass spectrometry at the level beyond "normal" graduate research.

The second factor affecting our productivity was the substantial involvement of PI, as a co-author and a co-editor, in the major revision of the book **INDUCTIVELY COUPLED PLASMAS IN ANALYTICAL ATOMIC SPECTROMETRY** (1) published in September 1992 by the VCH Publishers. The first edition of this book, produced in 1987, received numerous accolades in the critical reviews published in major journals on analytical atomic spectrometry, and was widely accepted in the analytical chemistry community. The newest version of this book has been expanded to twenty chapters with contributions of chapter manuscripts by 32 outstanding scientists. PI served as the author or co-authors for six chapters in the second edition. This burden, along with the rigorous editing necessary to influence the content, the style, and the clarity of the new 1000-page book regrettably *delayed the publications* of results for some of the *completed projects*. As the list of our publications shows (Section 5), we have attempted to compensate for the loss of time which was beyond our control. Again, on the positive side, our work on this book will undoubtedly be of value to the community. We are hopeful and confident that the reviewers will accept these statements as a genuine effort on the part of PI for the presentation of his circumstances rather than advertisements for the book or the PI.

Despite the cited difficulties, we have made good progress in all the current projects thanks to the efforts of PI's graduate students and postdoctoral fellows. In terms of human resources, our research has contributed to the preparation of suitably trained scientists to strengthen the research programs in spectrochemical analysis. During the 1990-92 period, three graduate students received their Ph.D degrees based on our DOE research, and three postdoctoral fellows acquired new training and conducted new research. This is indeed a good return for a $71,000/year grant! Also, two graduate students, H. Tan and R. H. Clifford, received the 1991 Gordon F. Kirkbright Bursary Award from the Association of British Spectroscopists, and the 1991-I. L. Barnes Award from the Baltimore-Washington Section of Society for Applied Spectroscopy, respectively. Relatedly, one of our papers (2) has been nominated by the Editors to receive the 1992 Award for best paper published in Spectrochimica Acta, the premier journal of analytical atomic spectrometry. These Awards and nomination recognize the contribution of the graduate students to our DOE-sponsored research during the 1990-92 period.

2.A. Mass Spectrometry of Helium ICP Discharges

Our ICP-MS studies were focused on Ar and He ICP discharges. The work on Ar ICP-MS was essential because our instrumental arrangement for Ar ICP-MS included at least four aspects or features different from the commonly used, commercial ICP-MS instruments (3-5). First, in our study, a crystal-controlled, 41-MHz ICP system is coupled to the mass spectrometer. Second, two quadrupoles are used for ion transmission and mass separation. Third, no photon stops or obstacles are present in the ion trajectory for the mass spectrometer. Fourth, an off-axis, analogue mass detector known as "Coniphot" is used to detect positive ions. In this detector, ions are directed to a dynode where electrons are generated. These electrons then are amplified via a microchannel plate, and are transferred to a scintillator where electromagnetic radiation is produced. The resulting photons pass through a light guide to impinge on the cathode of a standard photomultiplier tube (PMT) held at atmospheric pressure. The signal is amplified at the detector by a current-to-voltage converter and is transferred to an analog-to-digital converter.

Previous work had shown that ion intensities recorded depend in a complicated fashion on instrumental parameters and instrumental arrangement (3-5). For example, different enhancement trends have been observed (6) for ion signals from VG PlasmaQuad and the Sciex Ar ICP-MS systems for the same change in water loading. Because of the cited differences between our ICP-MS system and the widely used commercial instrument (3-5), we acquired a set of data on the effects of experimental parameters on ion signal from the Ar ICP, and complied analytical performance indices for subsequent comparison with results for He ICP-MS(7). During the course of this study, we also explored 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 (7). Note that prior to our work, no extensive studies had been conducted on the analytical potential of the thermospray nebulizer for Ar ICP-MS, particularly when the combination thermospray nebulizer-membrane separator is used for removing solvents from aerosol (8-10). For pneumatic nebulization, such studies have been documented for Ar ICP-MS (3-5,11,12). We obtained parts-per-trillion detection limits for TNMS for the elements tested, superior to the results measured for the PN used with or without a desolvation system. However, the USN provided detection limits which were generally lower than those obtained with the TNMS by a factor of 2 to 5. When cryogenic desolvation was used in tandem with the USN, detection limits generally were degraded by a factor of 2 to 3. 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. Recently, Houk and co-workers (13) also reported substantially reduced oxide levels as the result of cryogenic desolvation.

It is appropriate now to compare our detection limits for Ar ICP-MS to those of the commercial systems for a few elements. This comparison is important for subsequent correlation with results obtained with He ICP-MS. Clearly, our detection limits (Table 1) obtained with an analogue mass detector are approximately one order of magnitude higher than those reported for the commercial instruments that utilize ion counting.

In subsequent experiment, we interfaced the mass spectrometer to the He ICP, reduced the extent of interface-related discharges (see below), and acquired the first analytical results for He ICP-MS using *aqueous* sample injection (14). For the difficult-to-ionize elements such as As, Se, Br, and I, we measure detection limits that are or the order of 50 to 200 pg/mL for the injection of a multielement solution into a 1-kW He ICP (Figure 1). We predict that detection limits of the order 20 pg/mL can be achieved if the He ICP is operated on commercial instruments manufactured, for example, by Perkin-Elmer/Sciex Corporation or Yokogawa Electric Corporation because these instrument use ion counting detection and superior optics. Note that our data were not obtained under critically optimized conditions. For example, due to the problems cited earlier for the mass spectrometer, we have not yet attempted to increase pumping capacity for the interface. Previous work has shown that the pumping capacity required for the ICP-MS interface must be 2 to 5 times higher for helium plasmas (15-19) as compared to the Ar ICP. A second vacuum port must be installed on the interface for connection to an additional vacuum pump. This work will be conducted by December 1992. At any rate, these results for He ICP-MS are encouraging not only due to the low detection limits measured, but because As and Se are subject to strong spectral interferences in Ar ICP-MS. We intend to extend such studies to other difficult-to-ionize elements during the next grant period.

One of the most significant impediment to the use of He ICP as an ion source for mass spectrometry has been the presence of a strong pinch discharge at the sampler cone. Our studies (14,15) and those by Koppenaal and Quinton (16) have shown that the interface-related discharge or the pinch discharge is strikingly stronger in He ICP-MS compared to that reported for Ar ICP-MS (7,11,19-30). Further, we have now established that the approaches used to reduce or eliminate the pinch discharge for Ar ICP-MS are mostly ineffective in the case of the He ICP-MS. We considered five methods for minimizing plasma potential in He ICP-MS. These included the use of: 1) modified

Table I. Detection limit (pg/mL) of various ICP-MS systems for pneumatic nebulization.[1-3]

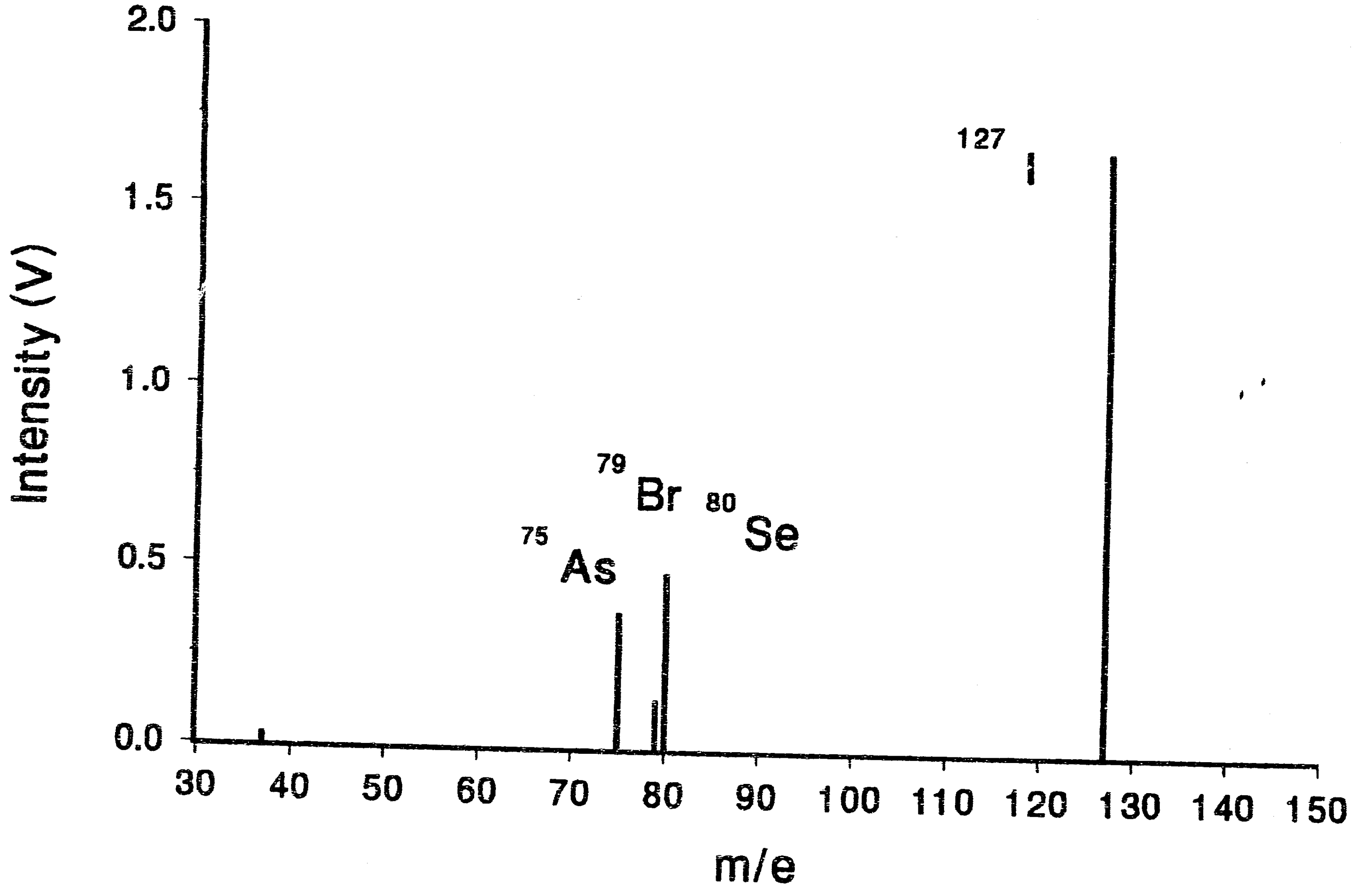
Element	Isotope	This Work	Perkin-Elmer/Sciex	Yokogawa Electric Corp.
Mn	55	2	2	3
Ni	58	9	5	10
Co	59	8	1	2
Cu	64	10	3	8
Zn	65	60	3	10
Cd	114	40	3	2
In	115	5	<0.5	0.5
Cs	113	2	<0.5	0.5
Ba	137	10	<2	0.6
Ce	140	1	0.4	0.4
Nd	144	7	<2	2
Pb	208	2.5	1	0.9
Bi	209	3	<0.5	0.6
Th	232	4	<0.5	0.2
U	238	3	<0.5	0.2

1. The integration time used in this work was 3 s/mass. Results for Perkin-Elmer/Sciex Corporation, and Yokogawa Electric Corporation (Model PMS 2000) have been obtained, respectively, for 3 s/measurement with 3 measurements/mass and 10 s/mass.

2. Ion counting has been used to obtain all results, except for the data obtained in this work.

3. The RF generators were operated at 41 MHz (fixed frequency; this work), 34 MHz (free running; Perkin-Elmer/Sciex Corporation) and 27 MHz (fixed frequency; Yokogawa Electric Corporation).

Figure 1. Spectrum of a 1-μg/mL multielement solution injected in He ICP-MS. These data have been obtained by peak hopping using 3-second integration



induction coils (16,27), 2) electrostatic shields placed between the induction coil and the plasma torch, 3) center-tapped induction coil, 4) 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, and 5) ceramic sampler and oxide-coated samplers. Approaches 1-4 had been successfully used in Ar ICP-MS (19-30). Among the approaches we explored thus far, the use of oxide-coated aluminum sampler has been the most useful for minimizing the pinch discharge for He ICP. Ceramic samplers made (from lava) thus far either cracked during the manufacturing process or they did not survive in the course of experiments as the results of orifice erosion. No useful helium plasma was formed when methods 1-3 were used with crystal-controller generators having an impedance matching network. For example, only a very faint helium plasma was formed when the impedance matching network was modified to use a 3-turn, center-tapped induction coil, even at a forward power of 1.5 kW. With a 5-turn center-tapped induction coil, a faint plasma was formed when 2.5 kW was applied. The fourth approach is yet to be tested for He ICP, but it seems that some degree of capacitive coupling is needed to form an intense He ICP. At the time of writing, our current configuration for analytical sampling of the 41-MHz He ICP is as follows: we use a corner-tapped induction coil with three to five turns, an aluminum sampler coated with aluminum oxide, a grounded ICP-MS interface, and the plasma is sampled off axis to achieve maximum ion signal. This configuration has provided a stable condition for ion sampling. In contrast, if the aluminum sampler is replaced by a nickel or a copper sampler, excessive erosion for the sampler orifice is noted and orifice-originated nickel or copper ions are among the prominent peaks in the mass spectrum.

A number other approaches outlined in our previous proposal remain to be tested. New strategies also are presented in the accompanying proposal. It is appropriate to emphasize, however, that we plan to rely more on mathematical modeling in our future studies. As shown in Section 2.C, our current modeling studies have shown that the magnetic and electric fields in He ICP are approximately one order of magnitude larger than those in Ar plasma for the torch configuration we typically use. The current experimental results have verified these predictions.

2.B. Atomic Emission Spectrometry of He ICP Discharges

During the period 1990-92, we worked on five AES projects: (a) developed methods for improving the detection limit of iodine by two orders of magnitude by Ar and He ICPs (31) and obtained a 10-fold improvement in the detection limits of non-metals for end-on observation of He ICP (32,33); (b) initiated a project for the construction of an imaging spectrometer to record spatially-resolved spectroscopic data for He ICP (34); (c) measured line-width and line-shape of spectral lines excited in He ICP by using the high-resolution Fourier transform spectrometer (FTS) at Los Alamos National Laboratory (35); (d) developed a new, highly versatile C-based algorithm for the calculation of electron number density based on the Stark broadening profile (36); and (e) completed measurement of rotational temperature for argon-nitrogen plasmas using the FTS facility (37). A brief summary of these activities are given below.

The conventional limit of detection for iodine by ICP-AES is inadequate for determining iodine in most samples such as effluents from nuclear production facilities and foods. We combined a preconcentration procedure with an oxidation step to improve detection limit of iodine by He ICP-AES and Ar ICP-AES. Two ionic forms of iodine (I^- and IO_3^-) were studied, and the process was automated with the flow injection technique. The preconcentration medium was a membrane disk containing the AG1-X8 anion-exchange resin within a polypropylene housing. Preconcentration was coupled with chemical conversion of I^- to I_2 to enhance analyte transport to the plasma. The combined technique improved the limit of detection of I^- and IO_3^- in aqueous solution by a factor of 207 (0.75 ng/mL) and 15 (31 ng/mL), respectively. Improvement factors for on-line oxidation of I^- were 33 and 100, respectively, for Ar and He ICP discharges. In a related project (32,33), a 2-kW air-cooled torch was explored for He ICP-AES. Analytical performance of the helium plasmas were compared both for side-on and end-on viewing. For end-on observation, detection limits measured for F, Cl, Br, and S (at the near-IR lines) were improved by factors up to 20 and 50, for gaseous and aqueous nonmetals, respectively. Previous studies have indicated that end-on viewing of the Ar ICP provides 3 to 10-fold improvement in detection limits for approximately 30 elements (38,39). Similarly, helium microwave induced plasma (He MIP) are usually observed end-on to obtain better detection limits (40,41). The detection limits measured at vacuum-ultraviolet lines (VUV) for Ar ICP (42) are by far the best results compared to the data obtained for other plasmas (32,33,38-41). We are unable to conduct a similar study for the He ICP because a vacuum monochromator is not available in our laboratory. We have requested funds from DOE to pursue this project during the next grant period.

We now present some of our diagnostic studies of He ICP using AES. We initiated a project for the construction of an emission imaging spectrometer to instantaneously acquire spectroscopic properties of new He ICPs. This home-made system (34) uses a 0.35-m spectrometer and an inexpensive charge injection detector having 388 by 488 sensor elements. The instrument was used to capture quantitative image maps of the He ICP shown in Figures 2 to 6. These maps will allow us to characterize various region of the plasma more efficiently. Note that our CID detector is not cooled, and therefore, only intense spectral features can be imaged currently. For example, radial distribution of He I 587.5-nm line at 2 kW (Figure 2a) reveals a region of maximum emission intensity on the axial channel at the height of 30 to 35 mm above the induction coil when no water is injected into the plasma. However, similar measurements at 1.5 kW results in noisy profiles, especially at the center of the plasma (maximum error in Abel inversion). Radial distribution of H I 656.3-nm line for the 1.5-kW plasma is shown in Figure 3 for the injection of wet aerosol. In contrast to Figure 2, maximum emission intensity for this line falls off-axis, at a height of 5 to 15 mm above the induction coil. Because of the

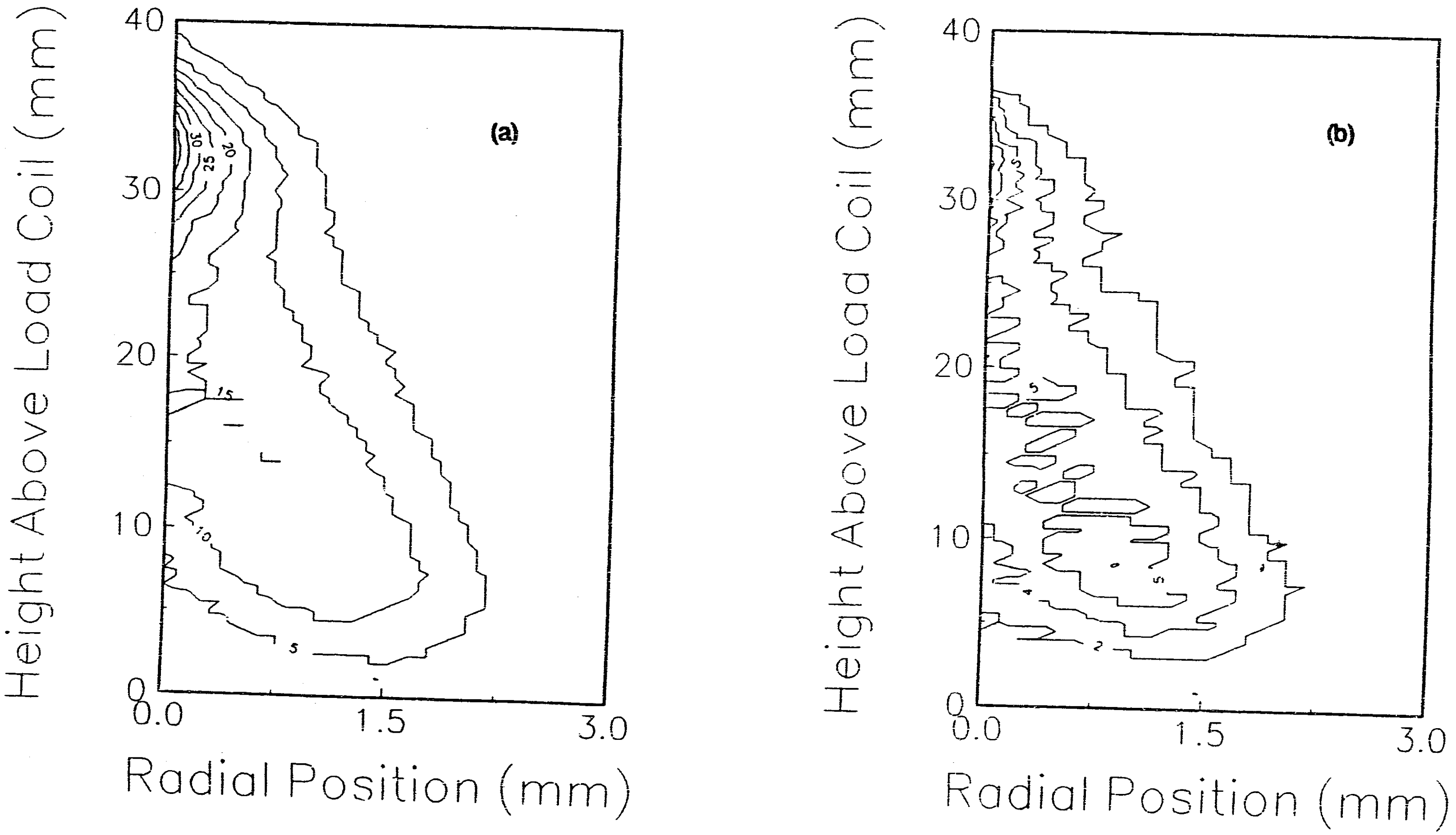


Figure 2. Radial distribution of He I 587.5-nm line excited in He ICP at (a) 2 kW and (b) 1.5 kW forward power without aerosol injection.

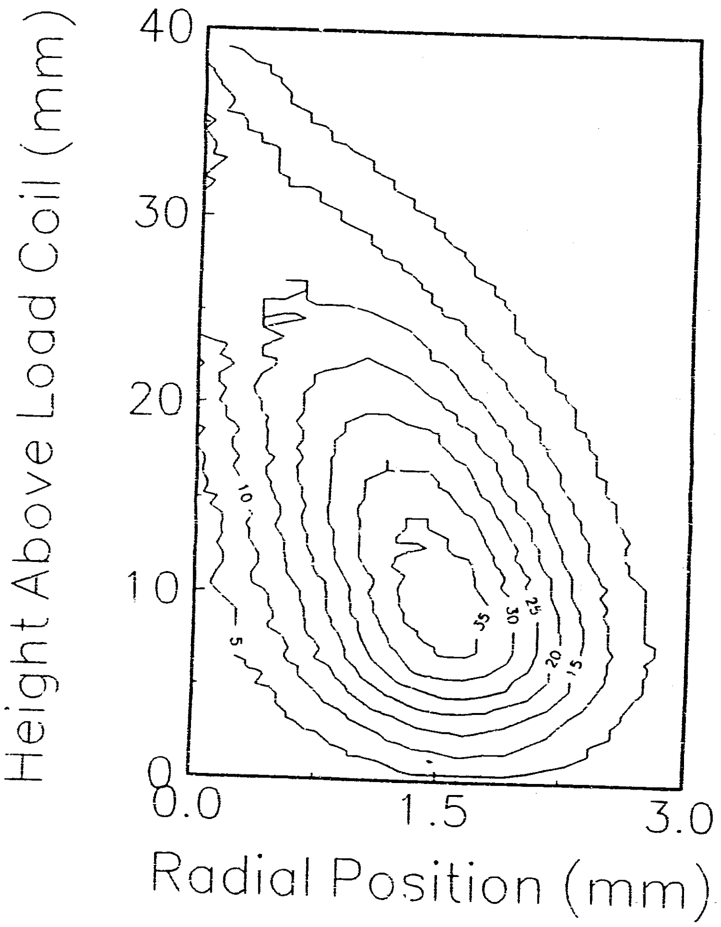


Figure 3. Radial distribution of H I 656.3-nm line excited in He ICP at 1.5 kW forward power for injection of wet aerosol from distilled deionized water.

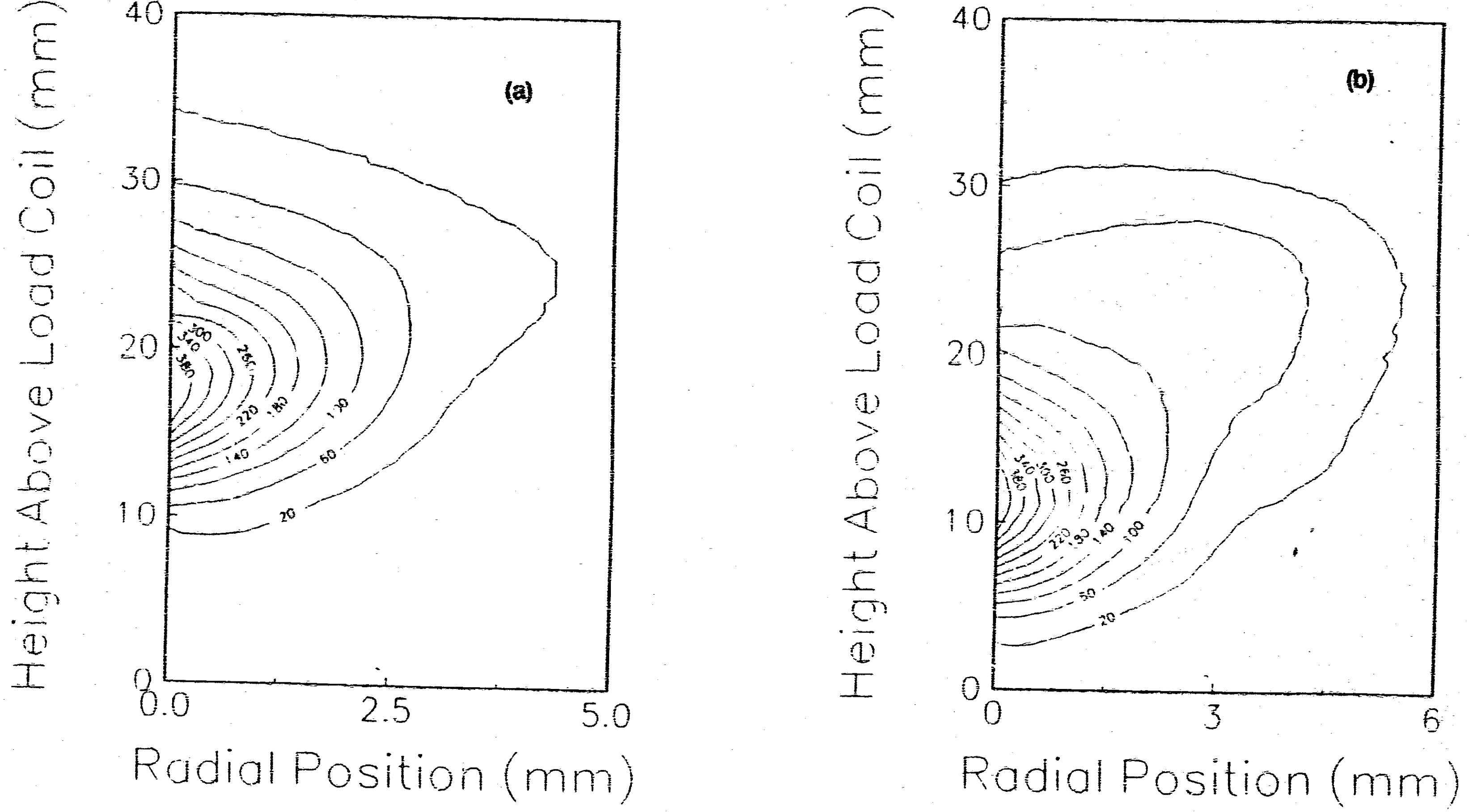


Figure 4. Radial distribution of Na I doublet at 589.0 and 589.6 nm excited in He ICP at (a) 1 kW and (b) 1.5 kW forward power. The concentration of Na (from $NaNO_3$) was 100 $\mu g\ mL^{-1}$.

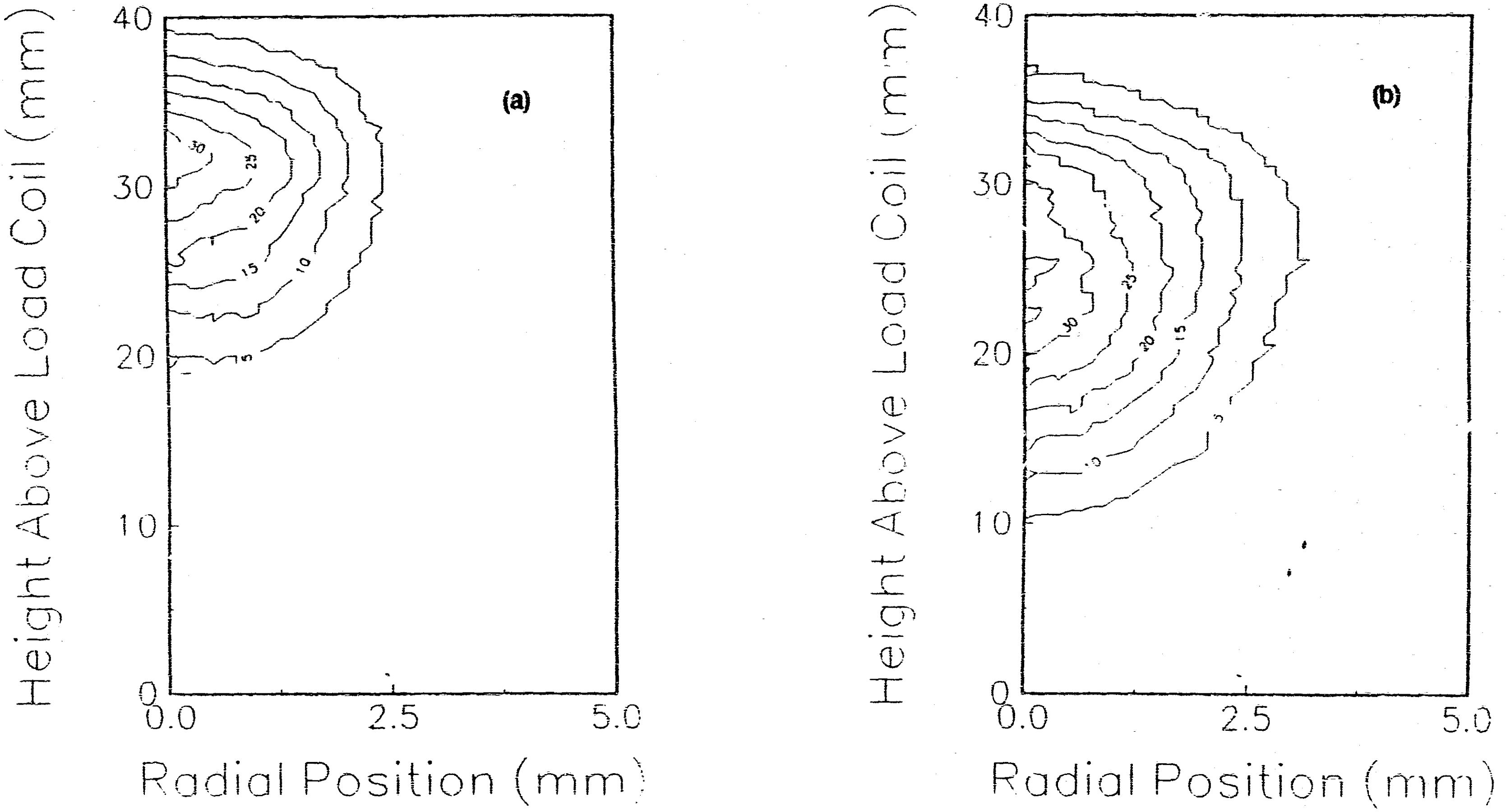


Figure 5. Radial distribution of Ca I 422.7-nm line excited in He ICP at (a) 1 kW and (b) 1.5 kW forward power. The concentration of Ca (from $Ca(NO_3)_2$) was 1000 μg mL^{-1}.

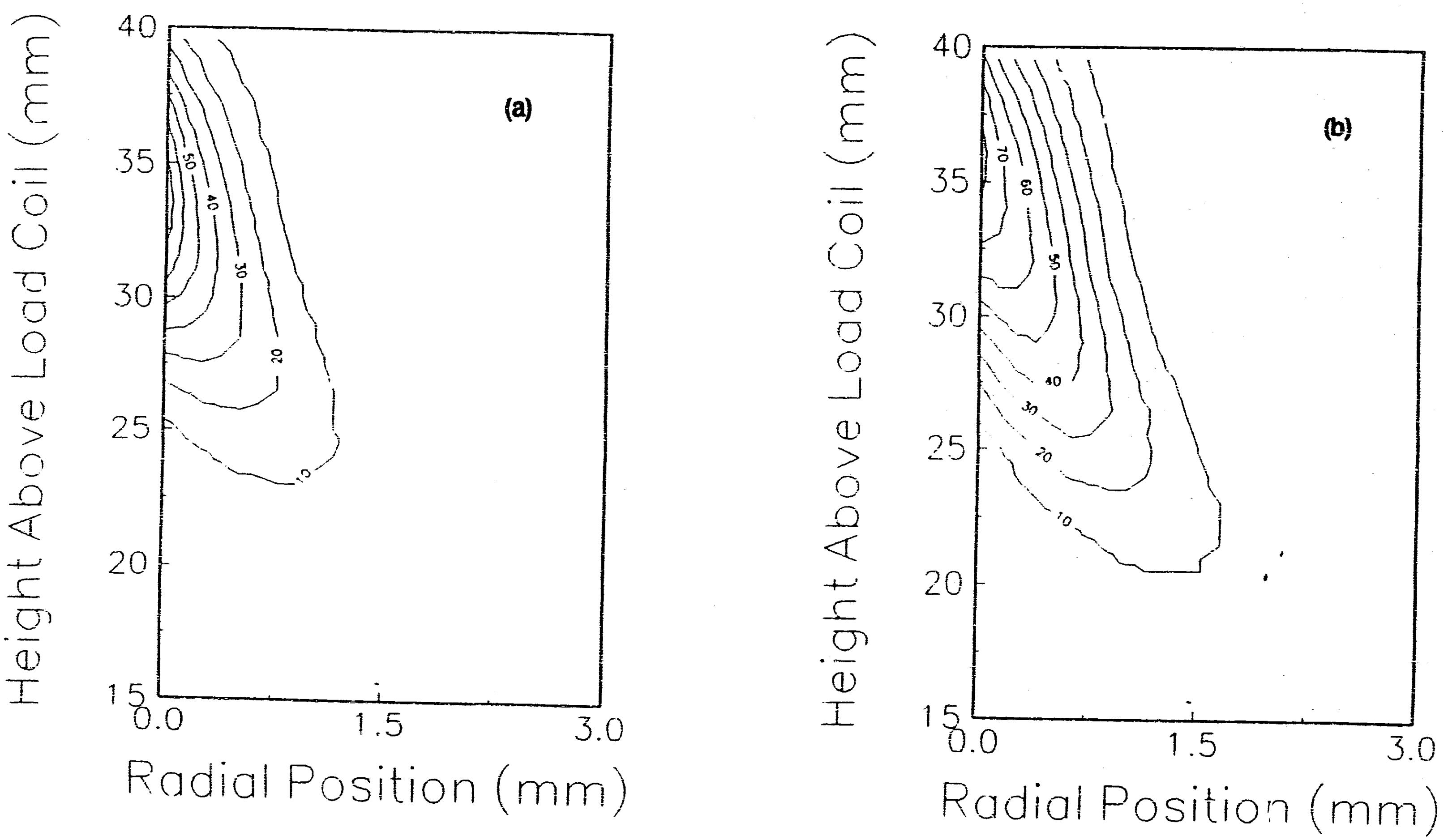


Figure 6. Radial distribution of Cl I 837.6-nm line excited in He ICP at 1500 W forward power for injection of gaseous CF_2Cl_2 at (a) 7 mL min^{-1} and (b) 14 mL min^{-1} flow rate.

limited resolution of our monochromator, the Na I doublet at 589.0 nm and 589.6 nm cannot be resolved (Figure 4), yet these profiles demonstrate the effect of forward power on the atomization and excitation of an easy element in the plasma. In this case, maximum emission occurs on-axis, without a significant increase in emission intensity, as the forward power is changed from 1 to 1.5 kW. The maximum emission profile for Ca I 422.7-nm line occurs on-axis at 25 mm (Figure 5b, 1.5 kW He ICP), above the height noted for Na which is a more volatile element. The data in Figure 6 also show that halogens are excited on-axis, and further, the area of maximum excitation is much narrower compared the results obtained for the excitation of metallic species such as Na and Ca. It is evident that these spatially-resolved images can significantly assist us in identifying zones within the plasma that are interesting and worthy of detailed probing. Also, such data can be used to check the accuracy of the predicted results obtained by mathematical modeling (Section 2.C). We intend to continue this line of work during the next grant period whenever plasmas in new He ICP torches are examined.

In a separate set of diagnostic studies (35-37), we used the high-resolution Fourier transform spectrometer (FTS) of the Los Alamos National Laboratory to conduct diagnostic studies of mixed-gas plasmas and He ICPs. For example, we have recorded high-resolution spectra for a number of analytically useful argon-nitrogen plasmas. These results have been analyzed, and will be ready for publication by December 1992 (37). For the atmospheric-pressure He ICP (35), we measured intensities and widths of atomic spectral lines of He, H, and Fe. These data along with intensities of rotational bands of OH were used to estimate excitation, rotational, and Doppler temperatures and electron number density. Similar to the Ar ICP (1, see Chapter 8), the line width of Fe I lines were 2 to 3 pm in He ICP. Further, the magnitude of the excitation temperature measured from intensities of Fe I lines depended on the excitation energy of the upper level, and ranged from 3000 to 4700 K for dry and wet He ICPs. For the dry He ICP, a temperature of 2200 K was obtained when the $B^2\Sigma_u^+$ --> $X^2\Sigma_g^+$, N_2^+ (0-1) rotational bands were employed , and further, analogous temperatures were obtained for branches P_1, P_2, R_1 and R_2. A substantially different rotational temperature (3000 K) was estimated from branches Q_1, Q_2, P_1 and P_2 of OH $A^2\Sigma^+$ ---> $X^2\Pi_i$ (0-0) rotational bands for dry and wet He ICPs. Note also that the rotational temperature for Ar ICP was 7200 K, as measured from hyperfine structures of $B^2\Sigma_u^+$ ---> $X^2\Sigma_g^+$, N_2^+ (0-0) rotational bands. These data collectively confirm again that He ICP discharges are non-LTE plasmas.

In a related study during the previous grant period (1987-1989), we described an algorithm for the calculation of electron number density (n_e) via least-squares fittings of spectral lines to the theoretical Stark-broadened profiles (43). This copy-righted code was written in BASIC language. It has been used by many prominent investigators worldwide for diagnostic studies of plasmas. A substantially revised version of this program is now prepared in C language for use on an IBM or compatible personal computers (36). The new code provides much greater speed, compared with the BASIC version, is menu-driven, and provides users with versatile tools to: (a) create/edit Vidal profiles,

(b) convert Vidal profiles to Stark profiles, (c) create Doppler profile, (d) create/edit instrumental profiles, (e) create/edit experimental profiles, and (f) calculate electron number density. The calculation of n_e-value is advanced in the following fashion. Both the experimental and the instrumental profiles are background corrected and are both averaged to give symmetric profiles. The averaged experimental profile is area-normalized using the Simpson's rule. The average instrumental profile is convoluted with Doppler profile. This profile is further convoluted with the interpolated Stark profile, from table of theoretical profiles, and is curve-fit to the experimental profiles. In each iteration, a new interpolated, convoluted Stark profile which is closer to the experimental profile is generated. The process is terminated when the squared-sum of residuals reaches a pre-determined criteria. In addition, the user can exclude the center portion of the profile in the curve-fitting procedure. Depending on the situation at hand, accuracy of the n_e-value can be increased if the structured center of Stark profile is avoided. We intend to use this fast code for obtaining images of n_e-values for He ICP discharges. To implement this task, we must utilize a monochromator with resolution far superior to the one used in the present imaging spectrometer.

2.C. Simulation and Modeling of He ICP and Mixed-Gas Plasmas

Another new project started during 1990-92 involved computer simulation of helium ICPs and mixed-gas plasmas. Our overall goal was (and is) to get a look at properties of new plasmas before plasmas are tested experimentally to avoid enormous costs. This effort was partly prompted by our earlier experimental studies concerning the effects of induction frequency and forward power (44) on properties of He ICP. The chief conclusion of this study was that the cited parameters have marginal influence on the analytical and fundamental characteristics of the helium plasma. However, the impacts of many other parameters still were unknown. It was thus desirable to predict plasma properties by simulation. Compared to the experimental approach, computer simulation offers the following advantages: (a) results are obtained rapidly for different sets of operating conditions or different torch designs, (b) resources are saved because a variety of generators operated at different frequencies or many new torches are not needed, and (c) complete information on a given plasma can be acquired rather than measuring parameters at, for example, just one observation height. Indeed, computer modeling has provided (45-62) valuable information on fundamental and analytical properties of Ar ICP and molecular-gas ICPs, but no published work on modeling He ICP, Ar-N_2 and Ar-O_2 plasmas was available prior to our work.

For the studies presented in this section, we collaborated with Professor J. Mostaghimi of University of Toronto. The computer code (63) used was based on a two-dimensional model of an ICP. This code had been used to simulate argon and molecular-gas ICP (45-47,49-53,59-62). Our initial effort was focused on modeling Ar-N_2 and Ar-O_2 plasmas. The effects of many experimental parameters on properties of the plasmas were predicted for comparison to our experimental data. These results are being prepared for publication (64), but two representative data sets are shown in Figures 7 and 8. In these Figures, plasma temperatures obtained through computer simulation are compared to the excitation temperatures we measured earlier (65,66). In general, the simulated temperatures are approximately 2,000 K higher than the radial excitation temperatures measured, except for the axial channel which exhibits a temperature 3,000 K less than the predicted results. This temperature difference is attributed to four factors. First, the excitation temperatures measured were obtained for wet plasmas (65,66), while the plasma was simulated, for simplicity, under dry condition. Second, the power used in experiment represents the forward power as compared to active power utilized in simulation. Third, the length of the outer tube we had to use in simulation was 53 mm instead 23 mm used in experiment. Finally, we assumed an LTE condition for modeling both plasmas. We plan to overcome some of these limitations during the next grant period through the use of improved models.

The simulation studies conducted on He ICP are now summarized (67). Plasma characteristics for He ICP were compared to those of an Ar ICP formed in the same torch. We studied the distributions of heat, temperature, energy dissipation, gas velocity, Lorentzian forces, and electric and magnetic fields in He ICP and in Ar ICP as the function of active power, the number of turns for the induction coil, the gap between the plasma tube and the MACOR insert, the orifice of injector tube, and injector and plasma gas flow rates. Predictions obtained via simulation were also compared to the existing experimental data to examine the validity of the mathematical model. Further, these theoretical predictions were used to interpret analytical results achieved, and to devise new directions for research in He ICP spectrometry.

Predicted contour lines for heat dissipation, temperature distribution, and stream functions for Ar and He ICPs are illustrated in Figure 9. The dissipation of heat in He ICP is concentrated in a small region (3 mm × 12 mm) as compared to the Ar ICP (4 mm × 35 mm). The most focused region for heat dissipation (area surrounded by the 10^9-J/m^3 contour line) in He ICP is located near the center of the induction coil, and it occupies a larger area compared to that in the Ar ICP. Also, the contour lines for heat dissipation in He plasma are much closer to the axial channel, suggesting difficulties for the injection of the sample. In a similar fashion, temperature distribution in He ICP is more constricted than that in Ar ICP. For example, the 2,000-K temperature contour, the outermost contour in Figure 9b, extends approximately from 5 to 40 mm (19 mm above induction coil) above the top of the MACOR insert for the He ICP, and from 0 to 80 mm (59 mm above the induction coil) for the Ar ICP. The same contour also is shifted toward the plasma confinement tube, thus predicting erosion or a melt down if an externally cooled plasma tube is not used for the Ar ICP formed in this torch. Note that the streamlines in He ICP show the presence of the recirculation region near the axial channel in He plasma

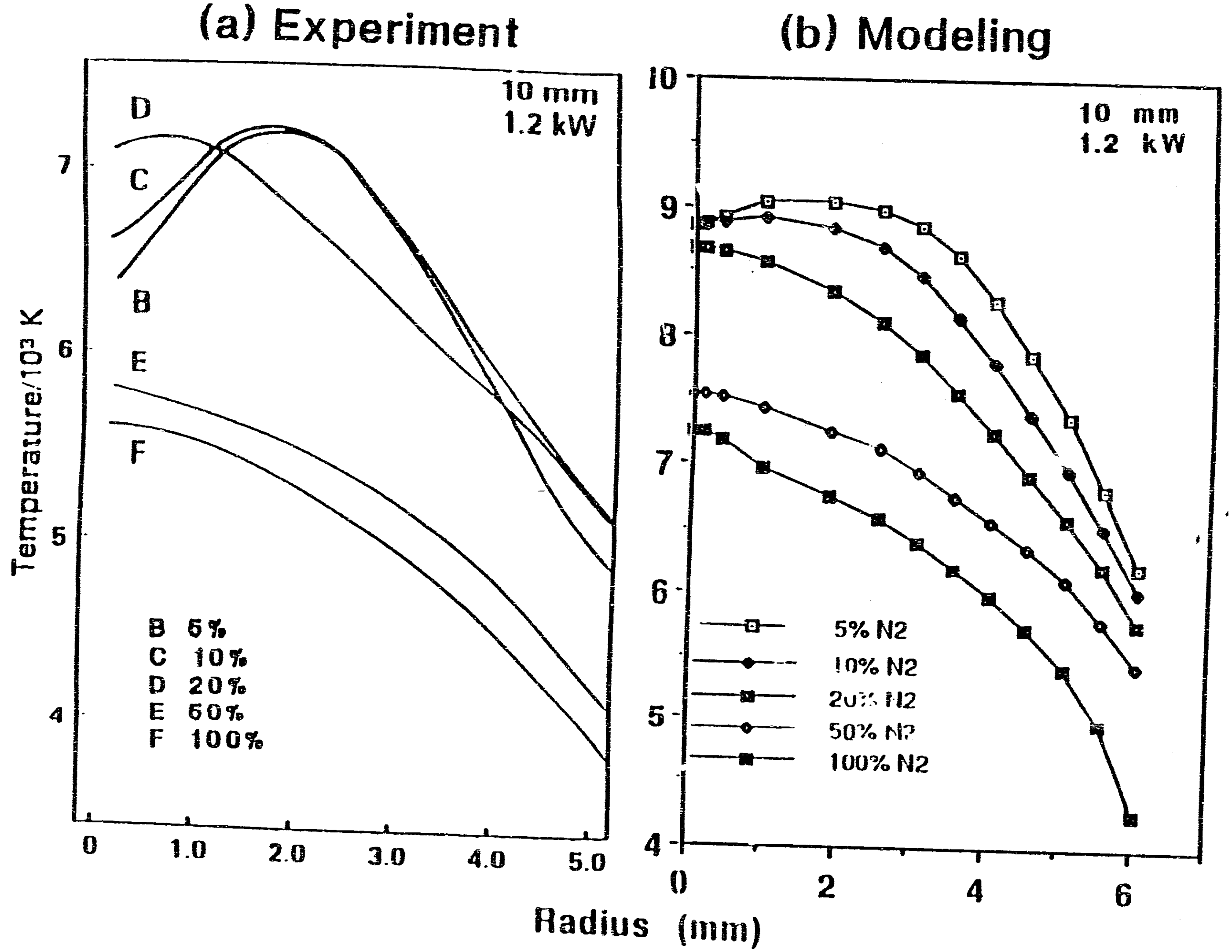
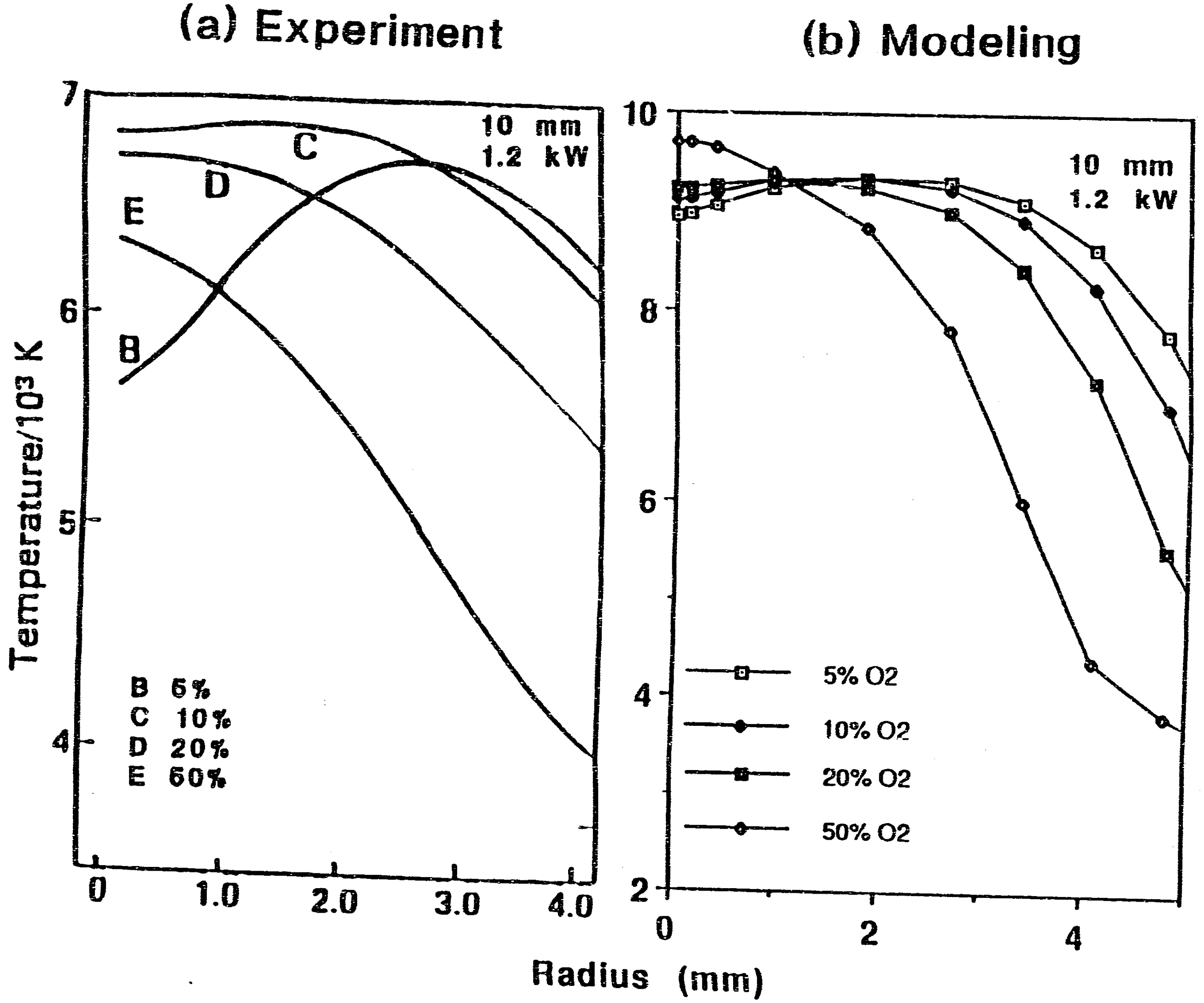


Figure 7.Temperature profiles in Ar-N_2 ICP discharges



(a) Experiment

(b) Modeling

Figure 8.Temperature profiles in Ar-O_2 ICP discharges

while the same region is shifted towards the plasma tube for the Ar plasma.

Axial energy dissipation, temperature and gas velocity distributions for the same plasmas are illustrated in Figure 10. As expected, axial energy distribution (Figure 10, left) in He ICP also is more focused than that in Ar ICP. Accordingly, the maximum axial temperature (Figure 10, right) in He ICP (13,500 K) is predicted to be much higher than that in Ar ICP (8,000 K) for plasmas operated at an active power of 600 W. Two additional points should be noted. First, the position of the maximum temperature is located at height of approximately 12 mm above the MACOR insert (inside the induction coil) in He ICP, as compared to 25 mm for the Ar ICP. Second, axial temperature varies dramatically with observation height in He ICP with steep temperature rise and fall. At the typical observation height, 25 mm above induction coil (44), the He ICP is predicted to have a temperature of approximately 2,000 to 2,500 K, close to the rotational temperatures we measured for the He ICPs (44). For comparison note that the Ar ICP is anticipated to have a temperature of approximately 7,500 K at 15 mm above the induction coil, the height commonly used in Ar ICP spectrometry. These predictions reveal that He ICP is a less efficient atomization source compared to the Ar ICP, particularly because the heat dissipation area in He ICP is not as extensive as the Ar ICP. Obviously, this limitation puts greater demands on sample introduction system, i.e., smaller droplets or particles (with size distribution narrower than that used for the Ar ICP) are needed for He ICP. This stipulation, however, should not distract the reader from one of the important advantages of He ICP with respect to the Ar plasmas, namely, its higher temperature within the induction coil. In short, if the sample can be atomized easily, then He ICP is predicted to be a more efficient excitation-ionization source than the Ar ICP, especially for the difficult-to-excite or ionize elements such as the halogen and other non-metal as proven experimentally (15,44). Because the highest temperature region in He ICP is estimated to be within the induction coil, end-on observation of the plasma should in principle provide lower detection limits compared to the side-on observations. Again, this prediction has been verified experimentally (32,33).

Another interesting prediction by the model is concerned with the strength of the electric and magnetic fields in He ICP. These fields (Figure 11) are approximately one order of magnitude larger than those in the Ar ICP. Experimental results for He ICP-MS (14-16) have documented the validity of this prediction. In short, interface-linked discharges are very strong when the He ICP is used instead of Ar ICP as an ionization source for mass spectrometry. We intend to reduce the strength of the electric field through simulation studies planned for the next grant period.

The reader is refereed to our recent report (67) for the description of other results. The following is a summary of some of these findings. The effects of induction frequency and the orifice size for the injector tube on characteristics of He plasma were insignificant. The principal parameters that govern stability of helium plasma and its properties were: the number of turns for the induction coil, the gap between the plasma tube and the MACOR insert, and the injector and plasma gas flow rates. Because the effective diameter of the He ICP is less than that of an Ar ICP, the simulated results

Figure 9

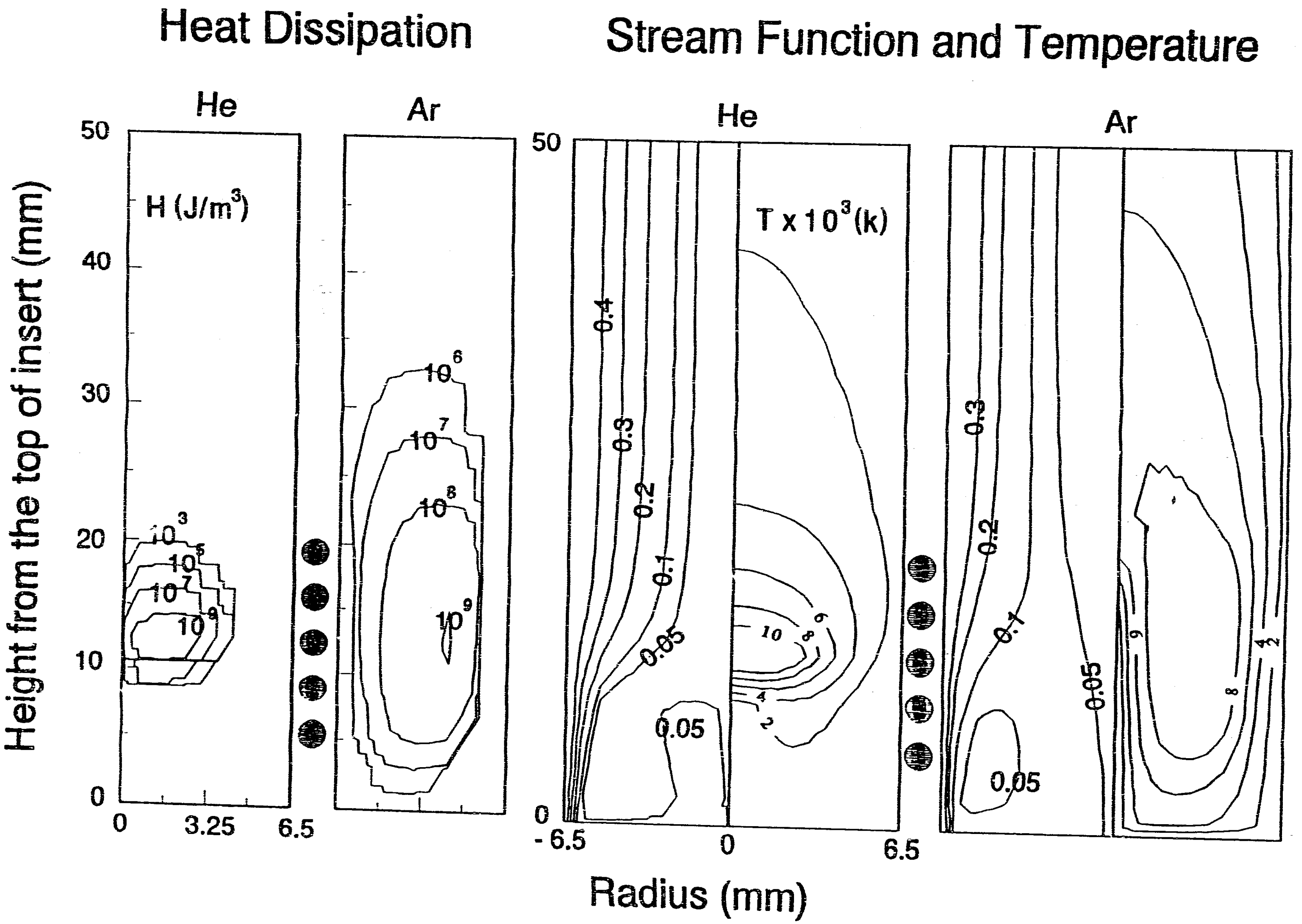

Heat Dissipation
Stream Function and Temperature
He
Ar
He
Ar
Height from the top of insert (mm)
50
40
30
20
10
0
0
3.25
6.5
H (J/m³)
10³
10⁵
10⁷
10⁹
10⁶
10⁷
10⁸
10⁹
50
0
-6.5
0
6.5
T x 10³(k)
0.4
0.3
0.2
0.1
0.05
0.05
10
8
6
4
2
0.3
0.2
0.1
0.05
0.05
6
8
4
2
Radius (mm)

Figure 10

Axial Distribution

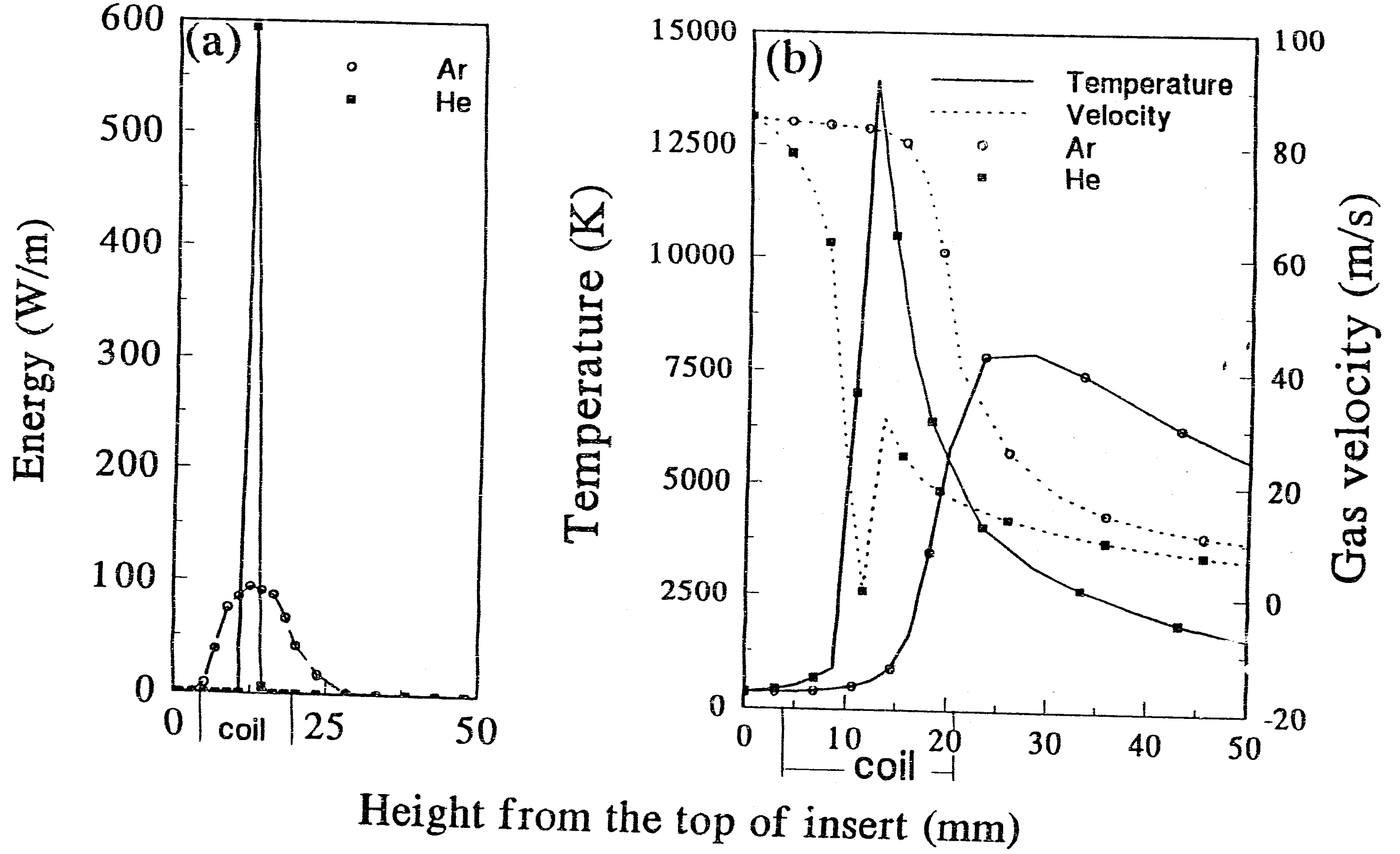
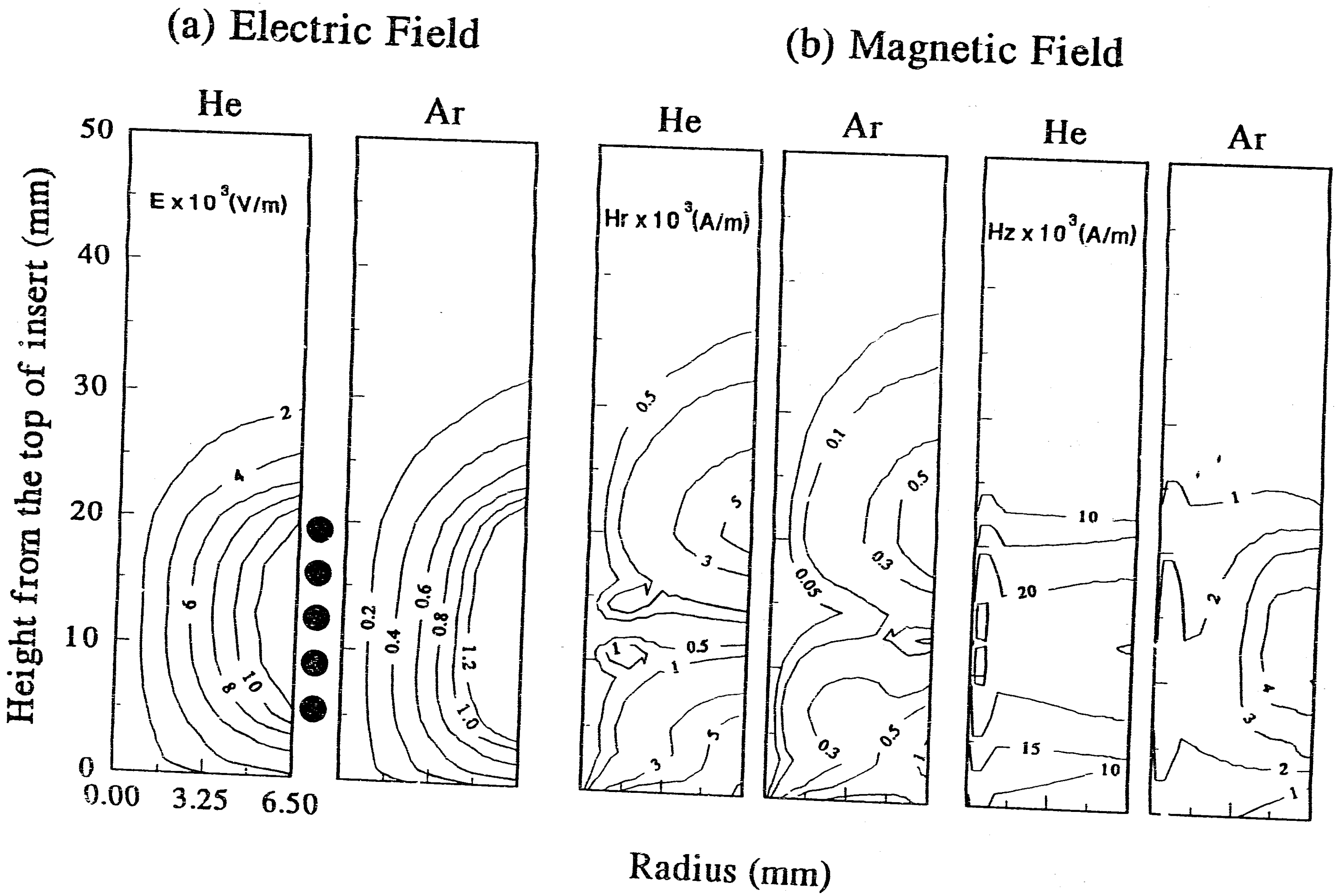


Figure 11


(a) Electric Field
(b) Magnetic Field
He
Ar
He
Ar
He
Ar
E x 10^3 (V/m)
Hr x 10^3 (A/m)
Hz x 10^3 (A/m)
Height from the top of insert (mm)
Radius (mm)
50
40
30
20
10
0
0.00
3.25
6.50
2
4
6
8
10
0.2
0.4
0.6
0.8
1.2
1.0
0.5
5
3
1
0.5
1
5
3
0.1
0.5
0.3
0.05
0.3
0.5
1
10
20
15
10
1
2
4
3
2
1

seem to indicate that a new torch, having an internal diameter smaller than 13 mm, must be used to achieve higher temperatures for He ICP. Such a torch is currently being constructed in our laboratory.

2.D. Studies of Liquid Sample Introduction Systems

Our major studies on liquid sample introduction systems during the period 1990-92 included: (a) development of a low-cost, humidifier-based ultrasonic nebulizer (68) for which one US Patent was issued in 1992; (b) development of a low-cost, disposable thimble-frit nebulizer (69); (c) time-resolved measurements on aerosol prior to injection to the plasma to identify the nature of millisecond-type instabilities in plasma spectrometry (2); (d) comprehensive diagnostic studies on desolvated aerosol from ultrasonic nebulizers (USN) by dual-beam, laser light-scattering interferometry (2); and (e) investigation of differential electromobility technique for aerosol characterization studies (70) in submicron range (0.01 to 1 μm). In Section 2.A, we summarized our studies of membrane separators for reduction of solvent load and oxide ions in ICP-MS (7). Brief description of studies under (a) to (e) are presented below.

The most commonly used solution nebulizers in atomic spectrometry are: (a) pneumatic nebulizers (PN), (b) ultrasonic nebulizers (USN), and (c) glass frit nebulizers (GFN). Most PNs are extremely inefficient because the majority of test solution (98 to 99%) is directed to the drain. Glass frit nebulizers are highly efficient at low uptake rate (50 to 150 μL/min.), but the most glaring disadvantage of the current GFNs is the reduction in aerosol production as the result of repeated usage (71,72). For USNs (68,71-77), efficiency of aerosol production is improved by a factor of approximately 10 compared to PNs if the test solution is not highly viscous. However, the present commercial USNs are quite expensive (approximately $12,000 to $17,000) compared to PNs and GFNs ($100 to $800).

We described (68) the simple conversion of an inexpensive (approximately $50), commercial ultrasonic humidifier to a continuous-type ultrasonic nebulizer suitable for analytical atomic spectrometry. The total cost of the proposed system used in the batch or continuous mode was less than $800. Long-term precision of 1-2% were achieved for 14 elements. For a sample uptake rate of 1 mL/min., detection limits measured with the humidifier-based USN were superior to those obtained with a PN by a factor of 8-50, and equivalent to the commercial USNs. At the present time, this USN suffers from one drawback. The sample cell has a relatively large volume (9 mL). Thus, the time required for a complete sample change-over is approximately 6 minutes, roughly 2-3 times longer than the washout time of the commercial USNs. This limitation is currently being addressed. The main point is that the proposed system can be easily constructed and is quite inexpensive.

In a related study (69), we developed a low-cost, disposable nebulizer (Figure 12) to bypass the main limitation of glass frit nebulizer, i.e., the reduction in aerosol production as a result of repeated usage. As in the past (78), a thimble glass frit is pressurized internally by means of gases such as helium or argon while the sample solution is applied externally to the frit. The pressurized gas exits through the pores of the glass frit and shatters the thin liquid film flowing on the surface of the thimble-shaped device to form small droplets. A small spray chamber surrounds the nebulizer to remove the large droplets. Small droplets then are introduced into the ICP. Long-term stability of this nebulizer over the course of approximately 8 hours (for 13 successive determinations) is illustrated in Figure 13 for the simultaneous measurements of 14 elements by Ar ICP-AES. The fluctuations noted for Co and Pb are due to the corresponding detection channels rather than the nebulizer. Although no degradation in aerosol production is noted for nebulization of standard solutions tested, we expect a gradual reduction in aerosol production for very complex samples. However, an "old" thimble frit can be easily replaced because nebulization system is demountable. Note that the cost of each frit is only $10.

We should emphasize here our main goal in investigating frit-type nebulizers: to understand conditions leading to the degradation of the efficiency of frit for the purpose of prevention. Such a study is important because the internally-pressurized thimble glass frit nebulizer is ten times more efficient in aerosol production (at least for particle size 0.5 to 2.5 μm) when helium is used as the nebulizing gas rather than argon (78). In contrast, the commonly used PNs for Ar ICP are quite inefficient when helium is used (78). Because of time constraints, and the volume of work conducted on other projects, we yet have not been to explore pathways that lead to the gradual loss of sensitivity for a frit. However, the use of demountable frit nebulizer described here along with the clean-out system presented earlier (78) should provide the most practical alternative for the use of frit-type nebulizer at this time.

We now present results of our diagnostic studies. A major component of the noise in ICP spectrometry is contributed by the nebulizer (79-84). To identify the nature of instabilities in plasma spectrometry (2), we conducted time-resolved measurements, in millisecond range, on aerosol prior to injection to the plasma. The technique of dual-beam, laser-scattering interferometry (85) was used for these studies. With this technique, drop-size and velocity distributions of aerosols can be measured simultaneously. During the previous grant period (1987-89), we used this technique to characterize wet tertiary aerosol produced by a pneumatic, an ultrasonic, and three glass frit-type nebulizers (85). For the current grant period (1990-92), we conduct comprehensive diagnostic studies on desolvated aerosol from USN. The instrument (Phase/Doppler Particle Analyzer, Aerometrics Inc., Sunnyvale, CA)) used was similar to a laser Doppler velocimeter, except that scattered light was detected at large angle using three photodetectors placed behind a common aperture at fixed distances. The overall size range of this technique is 0.5 to 10,000 μm as compared to approximately 0.5 to 600 μm for the laser diffraction system (6,77).

We now summarize results of our new diagnostic studies with PDPA (2). The most important

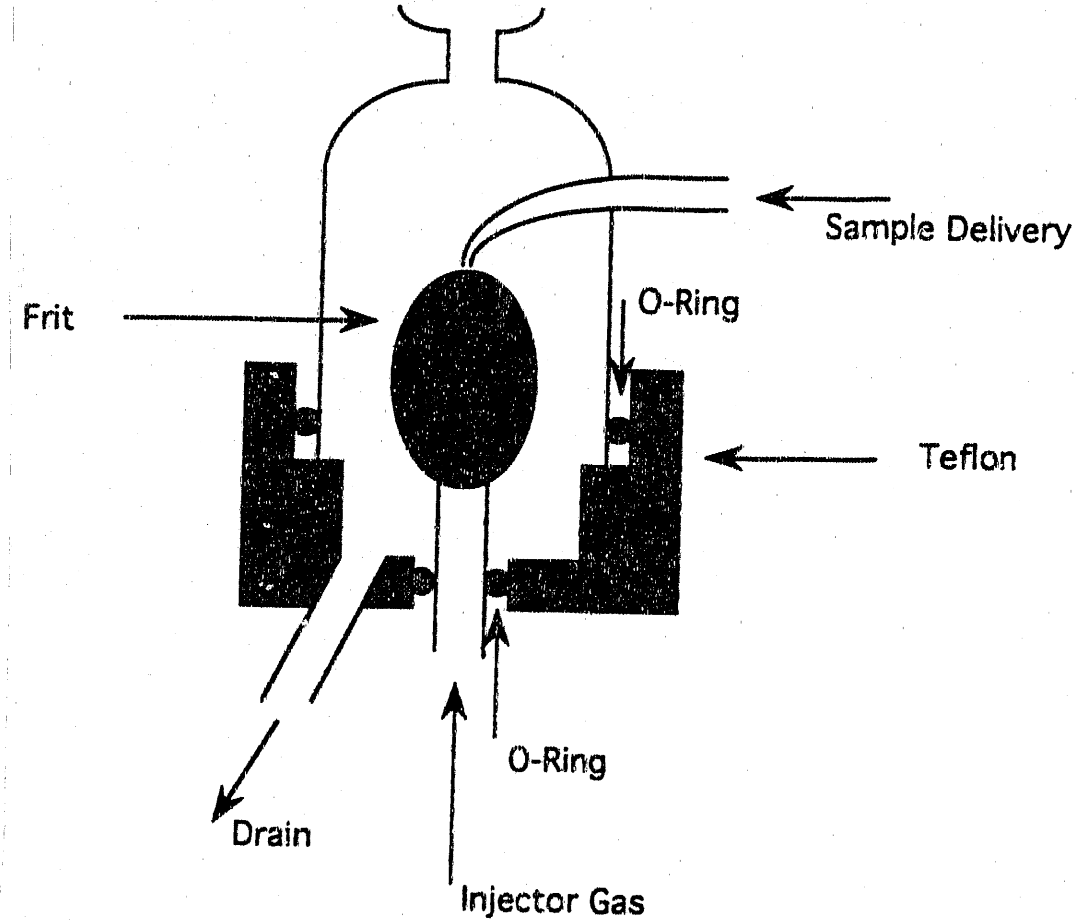
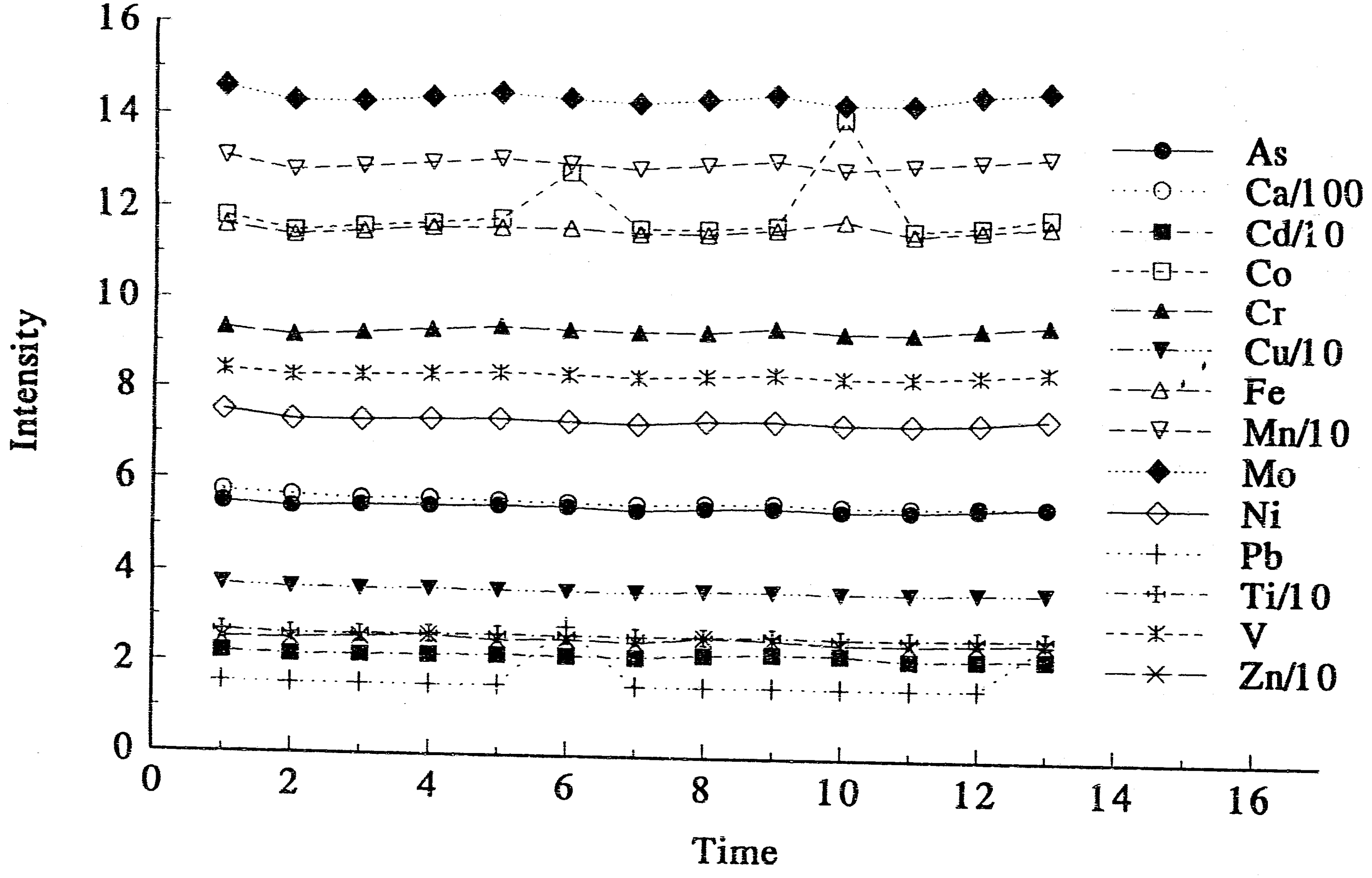


Figure 12. Demountable Thimble Frit Nebulizer

Figure 13. Long-term stability (8 hours) of the thimble frit nebulizer for nebulization of a 10-μg/mL multielement solution. The instabilities noted for Co and Pb are due to the corresponding channels in the direct reader spectrometer.



findings were the following: pulsations and clustering of particles (Figure 14) produced by USNs were observed for the first time by time-resolved measurements on aerosol before injection into an inductively coupled plasma. In certain cases, the local number density of the desolvated particles within the clusters and the diameter of the dry particles varied by a factor of ten on a millisecond time scale. These results are important not only in understanding fundamentals of aerosol generation and transport but in unraveling vaporization-atomization-excitation-ionization processes in high-temperature sources in order to improve analytical performance of atomic spectrometry. In particular, theses findings imply that analytical spectroscopists must devise new sample introduction systems that can provide fine, monodisperse aerosol that exhibits no intermittence for particle arrival. For the next grant period, we plan to devise such devices.

In addition to the cited studies, we conducted simultaneous measurements of particle-size and particle-velocity distributions, size-velocity correlation, particle number density, and volume flux and span of desolvated aerosols. A commercial ultrasonic nebulizer (USN) and our low-cost, humidifier-based USN were used to nebulize pure water, or aqueous solutions containing H_2SO_4, HNO_3, or NaCl. In general, Sauter mean diameter, velocity of particles, and volume flux of desolvated aerosol were larger when Ar was used as the injector gas instead of He. Sauter mean diameter increased with acid concentration, but it was independent from salt concentration. The velocity of desolvated droplets did not change with analyte concentration or the temperature of the heating tube. The implications of these observations in plasma spectrochemical measurements are discussed extensively in our recent report (2). For the next grant period, we plan to extend our diagnostic studies with PDPA to primary aerosol as well. We intend to conduct spatially-resolved measurements on USN and new sample introduction devices suggested in our renewal proposal.

The approaches used to size the primary and tertiary aerosol included the use of cascade impactors, aerosol particle counter based on Mie scattering theory, and laser Fraunhofer diffraction, but these techniques are not suitable for size analysis for droplets and particles smaller than 0.5 μm (71,72). Novak and Browner (86,87) used an electrical aerosol analyzer (EAA) in tandem with a cascade impactor to characterize particles in the 0.03 to 10 μm range from a PN used in atomic spectrometry. In our studies (70), the differential electromobility technique was used for the measurement of particle- and droplet-size distributions in the 0.01 to 1.0-μm range for nebulizers commonly used in atomic and mass spectrometry. This technique is more suitable than EAA (86,87) for particle-size analysis because of its higher resolution (32 versus 8 size channels or classes) and larger linear dynamic range (10^7 vs. $10^{4 \text{ to } 6}$). We described the applications of differential electromobility technique for the characterization of tertiary and desolvated aerosol for a thermospray nebulizer coupled to a membrane separator (TNMS), two USNs, two PNs, and a frit-type nebulizer. In general, volume concentration (volume of droplets or particles per cubic centimeter of injector gas) increased with NaCl concentration, and it was greater for TNMS followed by USNs compared to other nebulizers. For the

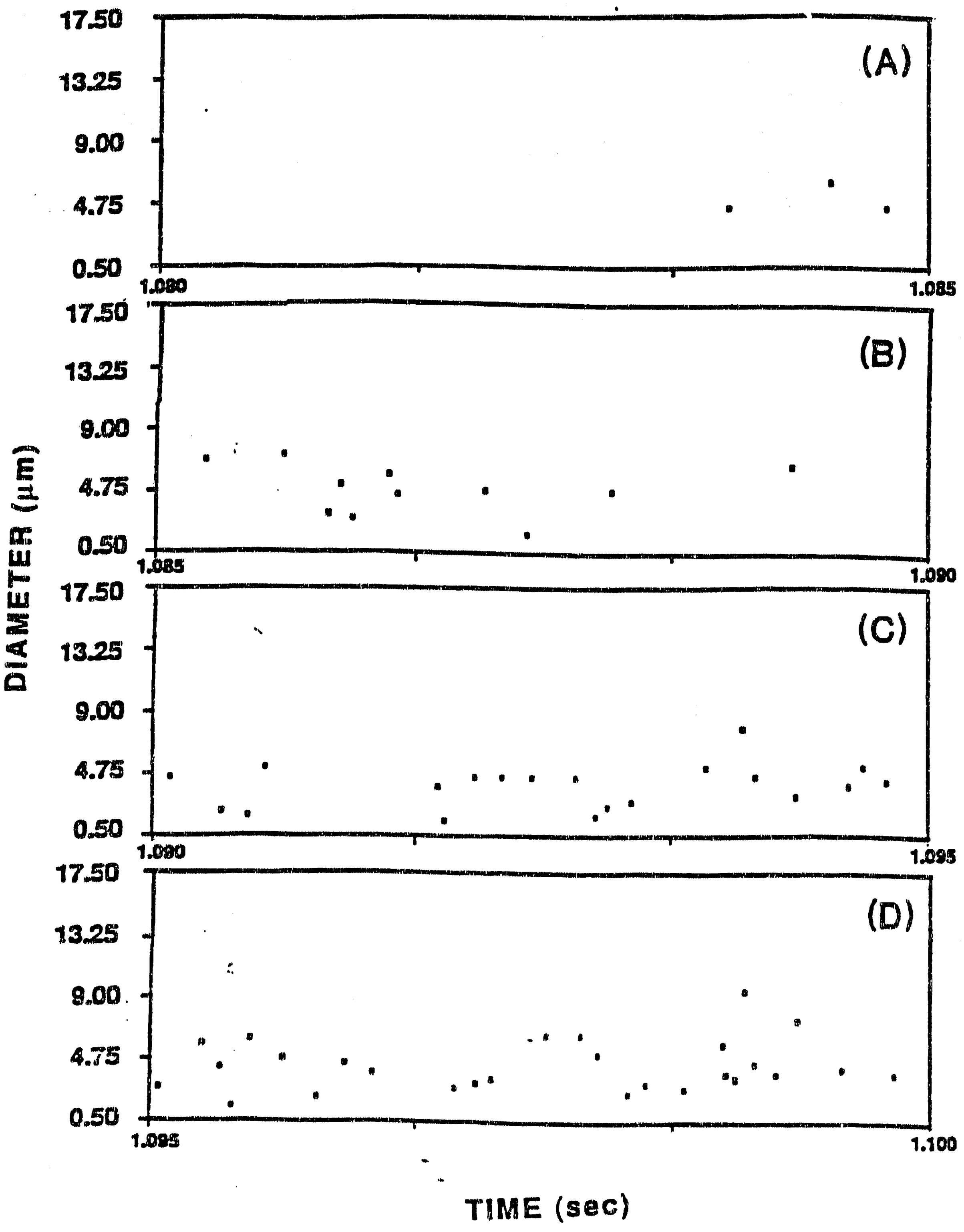


Figure 14. Four consecutive diameter-time traces with a 5-ms time intervals obtained at Ar injector gas of 1 L/min, 140 °C heating tube temperature, and 10% H_2SO_4. The dual-beam, light-scattering interferometry was used to obtain these time-resolved data prior to the injection of aerosol into the ICP.

desolvated aerosol produced by PN and USN, volume concentration was found to be independent of the temperature (140 to 180 °C) of the heating tube for the desolvation device. As the nebulizer tip temperature in thermospray nebulization was varied from 160 to 240 °C, a larger volume concentration of desolvated aerosol was produced. Size distributions shifted towards larger particles with increasing NaCl concentration. Among the nebulization systems investigated, the pneumatic nebulizers and the frit-type nebulizer produced aerosols that exhibited smallest geometric volume mean diameter. Again, the implications of these observations in plasma spectrochemical measurements are discussed in our recent report (70).

2.E. Solid Sampling Spectrometries

The occurrence, distribution, and determination of the platinum group metals (PGMs) in geological materials continues to receive increasing worldwide interest from the mineral exploration and geological research communities. Rising industrial demand for PGMs is depleting the existing major deposits of these elements. Exploration for new reserves requires the development of more sensitive analytical methods. Similar analytical requirements are shared by researchers who continue to use PGMs as indicators of petrogenetic events. For this reason, we developed a new method for the determination of selected platinum group metals in geological samples (88). This work was conducted in collaboration with Anthony Dorrzapf, Jr. of the US Geological Survey, Reston, Virginia. Platinum, palladium, rhodium, and iridium were preconcentrated into gold and silver beads using the classical lead fire assay procedure, and the beads were directly sampled by spark ablation - inductively coupled argon plasma mass spectrometry (spark-ICP-MS). The spark sampling system constructed for this application produced a solid aerosol composed of submicron-sized vapor condensates and small (< 2 μm) spherules. In contrast to solution nebulization, the mass spectrum for spark-ICP-MS was free of potentially interfering metal oxide, polyatomic, and multiply charged ions. The measurement precision ranged from 2 to 4 %RSD for Pt, Pd, and Rh, but a wider range was obtained for Ir due to its heterogeneous distribution in a silver bead. Detection limits based on a 15-g rock sample ranged from 1.0 ng/g (Pt) to 4.0 ng/g (Pd). Calibration curves for these elements were linear up to the highest concentration in the bead studied (2,000 /μg/g). Excellent agreement with certified-values for the SARM-7 geologic standard was found for three of the four elements investigated. For the next grant period, we plan to utilize the spark source for introducing solid samples into He ICP discharges. This work will be initiated when helium plasmas are developed that have higher gas temperature.

Considering the recent surge in glow discharges (89), we plan to evaluate the utility of glow discharge mass spectrometry for sampling gold and silver beads prepared through the fire assay procedure. In fact, we have just initiated an investigation of rf-powered glow discharges for direct sampling of nonconductive solids by atomic and mass spectrometry. These discharges have been traditionally used at 13 MHz (89). Because ICP spectroscopists utilize generators that operate at 27 and 41 MHz, we plan to investigate these devices at the cited frequencies. Our current interest is focussed on detection of halogens and other non-metals. This study complements our current work on He ICP discharges. Thus far, residual funds from non-DOE sources have been used to purchase an rf glow discharge source from Dr. K. Marcus of Clemson University. The source has been coupled to our existing atomic emission and mass spectrometers. We must emphasize here that our studies are not designed or intended to overlap with DOE sponsored studies conducted by Professor W. W. Harrison and co-workers. Similarly, we do not plan to pursue areas that are being explored by Dr. K. Marcus in NSF-sponsored studies. In short, this effort constitutes a minor part of our activities.

3. TECHNICAL PROGRESS EXPECTED FROM JULY TO DECEMBER 1992

We anticipate that the on-going investigations discussed above will continue or expand for the next six months of 1992. The results of these studies are being prepared in 10 publications (see papers number 23 to 32 in Section 5) and will be presented in 8 papers (see presentation number 31 to 38) at the ACS National Meeting, Washington, DC (August 1992) and FACSS Meeting to be held in Philadelphia, PA (September 1992). To prevent repetition of these subjects, the readers are referred to Section 5 of this Progress Report.

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88. R. L. Van Hoven, "Determination of Pt, Pd, Rh, and Ir in Geological Materials by Direct Solid Sampling of Fire Assay Bead Using Spark Ablation - Inductively Coupled Plasma Mass Spectrometry", Ph.D Dissertation, The George Washington University, Washington, DC, September 1992.
89. a) W. W. Harrison, C. M. Barshick, J. A. Klingler, P. H. Ratliff, and Y. Mei, Anal. Chem. 62, 943A (1990); (b) F. L. King and W. W. Harrison, Mass Spec. Rev. 9, 285 (1990); (c) W. W. Harrison and B. L. Bentz, Prog. Anal. Spectrosc. 11, 53 (1988).

5. DOE-SPONSORED PUBLICATIONS AND PAPERS PRESENTED DURING 1990-92

A) List of papers published, in press, submitted, or in preparation:

1. I. Ishii and A. Montaser, "Radial Excitation Temperatures in Argon-Oxygen and Argon-Air Inductively Coupled Plasmas", J. Anal. At. Spectrom. 5, 57 (1990).

2. A. Montaser, I. Ishii, B. A. Palmer, and L. R. Layman,"High-Resolution Fourier Transform Spectroscopy of Ar-Nitrogen ICP Discharges", Spectrochim. Acta 45B, 603 (1990).

3. R. H. Clifford, I. Ishii, A. Montaser, and G. A. Meyer,"Dual-Beam, Laser-Scattering Interferometry for Simultaneous Measurements of Drop-Size and Velocity Distributions of Aerosols From Commonly Used Nebulizers" Anal. Chem. 62, 390 (1990).

4. 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).

5. I. Ishii and A. Montaser, "A Tutorial Discussion on Measurements of Rotational Temperatures in Inductively Coupled Plasmas", Spectrochim. Acta. 46B, 1197 (1991).

6. 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).

7. I. Ishii, H. Tan, S. Chan, and 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).

8. 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., 63, 2660 (1991).

9. S. P. Dolan, R. H. Clifford, S. A. Sinex, and S. G. Capar, "On-Line Preconcentration and Volatilization of Iodine for Inductively Coupled Plasma Atomic Emission Spectrometry", Anal. Chem. 63, 2539 (1991).

10. A. Montaser, Assessment of Potentials and Limitations of Plasmas Sources Compared to ICP Discharges in Analytical Spectrometry, in *Inductively Coupled Plasmas in Analytical Atomic*

Spectrometry, A. Montaser, and D. W. Golightly, Eds, VCH, New York, Second Edition, 1992.

11. 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, VCH, New York, Second Edition, 1992.

12. S. Greenfield and A. Montaser, "Common RF Generators, Torches, and Sample Introduction Systems"; in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser, and D. W. Golightly, Eds, VCH, New York, Second Edition, 1992.

13. 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, VCH, New York, Second Edition, 1992.

14. A. Montaser, K. Ohls, and D. W. Golightly, "Inductively Coupled Plasmas in Gases Other Than Argon"; in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser, and D. W. Golightly, Eds, VCH, New York, Second Edition, 1992.

15. T. Hasegawa, M Umemoto, H. Haraguchi, C. Hsiech and A. Montaser, "Fundamental Properties of Inductively Coupled Plasmas"; ; in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, A. Montaser, and D. W. Golightly, Eds, VCH, New York, Second Edition, 1992.

16. A. Montaser and D. W. Golightly, Eds., *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, VCH, New York, Second Edition, 1992, 1017 pages.

17. "Diagnostic Studies on Desolvated Aerosol from Ultrasonic Nebulizers", (with R. H. Clifford, P. Sohal, and H. Liu), Spectrochim. Acta, in press.

18. "Submicron Particle-Size Measurements with Electromobility Techniques: Comparison of Aerosol from Thermospray, Ultrasonic, Pneumatic, and Frit-Type Nebulizers" (with R. H. Clifford, H. Tan, H. Liu, F. Zarrin, and P. Keady); submitted to Spectrochim. Acta.

19. "Computer Simulation of He ICP Discharges" (with M. Cai and J. Mostaghimi), submitted to Spectrochim. Acta.

20. 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.

21. R. L. Van Hoven, "Determination of Pt, Pd, Rh, and Ir in Geological Materials by Direct Solid Sampling of Fire Assay Bead Using Spark Ablation - Inductively Coupled Plasma Mass Spectrometry", Ph.D Dissertation, The George Washington University, Washington, DC, September 1992.

22. R. H. Clifford, "New Liquid Sample Introduction Systems for Analytical Spectrometry and New Aerosol Diagnostic Techniques", Ph.D Dissertation, George Washington University, Washington, DC 20052, December 1992.

23. M. Cai, A. Montaser, and J. Mostaghimi), "Computer Simulation of Mixed-Gas ICP Discharges", in preparation for Spectrochim. Acta.

24. I. Ishii, A. Montaser, B. A. Palmer, and L. R. Layman, "High-Resolution Fourier Transform Spectroscopy: Line Widths and Line Shapes of Spectral Lines Emitted from Helium Inductively Coupled Plasmas" in preparation for Spectrochim. Acta.

25. I. Ishii, A. Montaser, B. A. Palmer and L. R. Layman; "Rotational Temperatures of Argon-Nitrogen ICP Discharges Measured by High - Resolution Fourier Transform Spectroscopy" in preparation for Spectrochim. Acta.

26. I. Ishii, R. H. Clifford, and A. Montaser, "The Effect of Central Dip of Hydrogen Lines on Electron Number Densities of Ar and He ICPs", in preparation for Spectrochim. Acta.

27. H. Tan and A. Montaser, "An Air-cooled Torch for Helium Inductively Coupled Plasma" in preparation for Spectrochim. Acta.

28. H. Nam, W. Masamba, "Helium Inductively Coupled Plasma-Mass Spectrometry for Analysis of Aqueous Samples", in preparation for publication in Anal. Chem.

29. C. Hsiech, I. Ishii, and A. Montaser;"A Revised, Fast, Flexible Algorithm for Determination of Electron Number Densities in Plasma Discharges in preparation for Spectrochim. Acta Electronica

30. C. Hsiech and A. Montaser, "Imaging He ICP Discharges with a CID-Based Spectrometer"; in preparation for Spectrochim. Acta.

31. H. Liu, S. P. Dolan, and A. Montaser, "A Low-Cost, Disposable Nebulizer for Atomic Spectrometry"; in preparation for Anal. Chem.

32. H. Zhang and A. Montaser, "RF-Powered Glow Discharge Atomic and Mass Spectrometry at 27 and 40 MHz" in preparation for Anal. Chem.

B) List of presentations at scientific meetings:

1. "Recent Advances in Plasma Source Mass Spectrometry", invited talk at the Hampton University, Hampton, VA, April 1990.

2.. "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, paper 191.

3. "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.

4. "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, paper 21.

5. "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, paper 54.

6. "Rotational Temperatures of Argon-Nitrogen ICP Discharges Measured by High-Resolution Fourier Transform Spectroscopy" (with Izumi Ishii, B. A. Palmer and L. R. Layman), presented at the FACSS Meeting, Cleveland, OH, October 1990.

7. "Measurement of Electron Number Densities for Argon and Helium ICP Discharges by Using

Various Hydrogen Lines", (with I. Ishii, R. H. Clifford B. A. Palmer and L. R. Layman), presented at the FACSS Meeting, Cleveland, OH, October 1990.

8. "A Low-Cost Ultrasonic Nebulizer for Plasma Spectrometry: An Update", (with Robert H. Clifford, Scott P. Dolan and Stephen G. Capar, presented at the FACSS Meeting, Cleveland, OH, October 1990.

9. "Solvent-Analyte Separator for Atomic Emission and Mass Spectrometry: An Update" (with Hsiaoming Tan, H. Clifford, S. Nam, and Cai), presented at the FACSS Meeting, Cleveland, OH, October 1990.

10. "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 FACSS Meeting, Cleveland, OH, October 1990.

11. "Line Widths and Temperatures of He ICP Discharges Measured by High-Resolution Fourier Transform Spectroscopy", (with R. H. Clifford, and I. Ishii, B. A. Palmer and L. R. Layman, presented at the FACSS Meeting, Cleveland, OH, October 1990.

12. "Advances in New Sources for Atomic Spectrometry", invited talk at the FACSS Meeting, Cleveland, OH, October 1990.

13. "Dual-Beam, Light-Scattering Interferometry for Simultaneous Measurements of Droplet-Size and Velocity Distributions of Aerosols Produced by New Ultrasonic Nebulizers", (with R. H. Clifford and P. Sohal), invited talk at the 1991 Winter Conference on Plasma Spectrochemistry held in Dortmund, Germany, January, 1991.

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

15. Panel Member for Roundtable Discussion on "Non-Argon and Mixed Gas Plasmas for Spectrochemical Analysis", Chaired by R. M. Barnes at the 1991 Winter Conference on Plasma Spectrochemistry held in Dortmund, Germany, January, 1991.

16. " Advances in Atomic Spectroscopy for Ultratrace Analysis", invited talks at the Department of Chemistry, American University, and Lake Forest University, April 1991.

17. "Spectroscopy of Helium Plasmas", invited talk at the Physics Division of National Institute of Standard and Technology, Gaithersburg, MD, May 1991.

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

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

20. "Computer Simulation of Mixed-Gas ICP Discharges" (with M. Cai and J. Mostaghimi), presented at the XXVII Colloquium Spectroscopicum Internationale, Bergen, Norway, June 1991.

21. "Current Research at the George Washington University on High-Temperature Plasmas", invited

talk at the Perkin-Elmer Corporation, Norwalk, CT, June 1991.

22. "Computer Simulation of Helium Inductively Coupled Plasmas" (with M. Cai and J. Mostaghimi), presented at the FACSS Meeting, Anaheim, October 1991.

23. "Helium Inductively Coupled Plasma-Mass Spectrometry (with S. Nam and H. Tan), presented at the FACSS Meeting, Anaheim, October 1991.

24. "New Sources for Atomic Spectrometry: What Has Happened in the Last Two Years?, invited talk presented at the FACSS Meeting, Anaheim, October 1991.

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

26. "Simplification of Background Spectra in ICP-MS by Ultrasonic Nebulization: Applications in Food Analysis" (with S. Hight, S. G. Capar, H. Tan, and S. Nam, presented at the FACSS Meeting, Anaheim, October 1991.

27. Organized and Chaired Panel Discussion on Critical Needs for Plasma Source Mass Spectrometry at 1992 Winter Conference on Plasma Spectrochemistry, San Diego, CA January 1992.

28. National Tour Speaker for Society for Applied Spectroscopy, " Chemical Analysis Of Things As They Are: Critical Assessment of New and Established Techniques in Elemental Analysis", presented at Niagara Frontiers Section, Buffalo, NY, April 7, 1992.

29. National Tour Speaker for Society for Applied Spectroscopy, "Advances in Plasma Source Mass Spectrometry", presented at New York/Penn Section, Corning, NY, April 8, 1992.

30. National Tour Speaker for Society for Applied Spectroscopy," Chemical Analysis Of Things As They Are: Critical Assessment of New and Established Techniques in Elemental Analysis", presented at New York Section, Murray Hill, NJ, April 9, 1992.

31. "Understanding Processes on the Fundamental Basis: Academic Exercises or Useful Studies for Practical Analytical Spectrometry?" (with M. Cai, C. Hsiech, S. Nam, H. Liu, and H. Zhang); invited talk at the ACS National Meeting, Washington, DC, August 1992

32. "Optical Imaging Studies of Argon and helium Inductively Coupled Plasmas"; (with C. Hsiech), presented at the FACSS Meeting, Philadelphia, September 1992.

33. "Modeling and Simulation of Helium ICPs: Torch Design", (with M. Cai and J. Mostaghimi); presented at the FACSS Meeting, Philadelphia, September 1992.

34. "Recent Studies on Helium Inductively Coupled Plasma Mass Spectrometry" (with S. Nam, W. Masamba, H. Zhang, and C. Hsiech); presented at the FACSS Meeting, Philadelphia, September 1992.

35. "Determination of Pt, Pd, PH, and Ir in Geological Materials by Direct Sampling of Fire Assay Beads Using Spark Ablation ICP-MS" (with R. L. Van Hoven, M. W. Doughten, S. Nam, and A. F. Dorrzapf, Jr.); presented at the FACSS Meeting, Philadelphia, September 1992.

36. "Food Analysis by Inductively Coupled Plasma-Atomic Emission Spectrometry with a Low-Cost Ultrasonic Nebulizer" (with H. Liu); presented at the FACSS Meeting, Philadelphia, September 1992.

37. "Radio Frequency-Powered Glow Discharge Mass Spectrometry at 40 MHz" (with H. Zhang); presented at the FACSS Meeting, Philadelphia, September 1992.

38. "Determination of Total Iodine in Foods by On-Line Volatilization ICP-AES" (with S. P. Dolan); presented at the FACSS Meeting, Philadelphia, September 1992.

6. TIME DEVOTED TO THE PROJECT AND DEVELOPMENT OF HUMAN RESOURCES.

PI devoted 100% of his time during two months of summers 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 postdoctoral fellow and eight graduate students.

During the period 1990-1992, three graduate students (H. Tan, R. L. Van Hoven, and R. H. Clifford) received their Ph.D degree on DOE sponsored research. In addition, three postdoctoral fellows (one per year) acquired new training and conducted new research. Note that the average funding level for this grant has been $71,000/year, less than the national average. Considering the diversity of the projects conducted, this amount is not sufficient to support a research group consisting of eight investigators. During the 1991 summer, PI transferred one month of his DOE summer salary to other accounts to support associates and/or purchase supplies and replacement equipment. We are hopeful that the reviewers will appreciate our circumstances, and encourage DOE to support us at a higher level assuming the accompanying renewal proposal receives favorable review.

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