Plasma sources with multiple electrodes have been developed and characterized in this research for atomic emission spectroscopy. Multi-electrode plasma sources use electrodes to shape the plasma in order to continuously entrain a sample stream in the center of hot plasma, in a manner similar to an inductively coupled plasma (ICP) source. By changing the electrode spacings, the residence time can be readily adjusted even during plasma operation. For a 25-mm plasma length, a relatively long residence time of the analyte species (23 msec) in the plasma was calculated, indicating sufficient time for desolvation, vaporization, and atomization of the sample.

For a 30-mm plasma length, the interference effect of either phosphate or aluminum on calcium emission at 393.37 nm is insignificant over the entire vertical region of the plasma. The effect of an easily ionized element (EIE) is to generally enhance Ca(II) emission in the lower regions, and to depress the emission in
the higher regions in the plasma, which is in general agreement with observations in an ICP. Under an assumption of local thermal equilibrium (LTE), the Fe excitation temperature and the electron number density in the center of the plasma at 8 mm above the top of the quartz tube are 5000 K and $1.0 \times 10^{15}$ cm$^{-3}$ for a 30-mm plasma.

When current, gas flow rate, and plasma length are varied, the spatial emission profiles reflect many of the characteristics associated with an ICP. The short term stability of the plasma with a blank solution is better than 2% (relative standard deviation). A total of less than 6 L/min of argon gas is required to operate the plasma. With the vertical 4-electrode plasma source, 4 to 5 orders of magnitude of linear dynamic range are obtained and detection limits for 12 elements are comparable to those obtained with an ICP.
SAMPLE ENTRAINING MULTI-ELECTRODE PLASMA SOURCES
FOR ATOMIC EMISSION SPECTROSCOPY

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# TABLE OF CONTENTS

I. INTRODUCTION .................................................. 1

II. HISTORICAL DEVELOPMENT ...................................... 5

1. Inductively Coupled Plasma (ICP) ............................... 5
2. Direct Current Plasma (DCP) .................................... 9

III. INSTRUMENTATION .............................................. 14

1. Introduction .................................................. 14
2. System Components ........................................... 18
   2.1. Plasma Tube Arrangements ............................... 18
       2.1.1 Horizontal 4-Electrode Plasma .................... 18
       2.1.2 Vertical 4-Electrode Plasma ....................... 20
       2.1.3 Vertical 6-Electrode Plasma ....................... 21
2.2 Electrical Power System .................................... 23
   2.2.1 Power Supply ........................................ 23
   2.2.2 Electrical Circuit ................................... 28
   2.2.3 Electrode and Electrode Holder ...................... 28
2.3 Gas Flows and Operating Arcs ............................... 34
   2.3.1 Horizontal 4-Electrode plasma ...................... 34
   2.3.2 Vertical 4- and 6-Electrode plasma ................. 36
2.4. Sample Introduction ...................................... 39
   2.4.1 Aerosol Generation .................................. 39
   2.4.2 Performance of Multi-electrode plasma sources .... 41
2.5. Spectroscopic Measurement Systems ....................... 44
   2.5.1 Introduction ........................................ 44
   2.5.2 Dispersive Device ................................... 46
   2.5.3 Signal Measurement and Detection System ......... 50
   2.5.4 Operation Modes and Computer Control System .... 52

IV. ANALYTICAL CHARACTERIZATION OF SAMPLE ENTRAINING
   MULTI-ELECTRODE PLASMA SOURCES FOR ATOMIC EMISSION
   SPECTROSCOPY : PART I. PRELIMINARY STUDIES ............... 55

1. Abstract .................................................. 56
2. Introduction ................................................ 57
3. Experimental ............................................... 60
   3.1 Plasma Tube Arrangements .............................. 60
       3.1.1 Horizontal 4-Electrode Plasma .................... 60
       3.1.2 Vertical 4-Electrode Plasma ....................... 62
       3.1.3 Vertical 6-Electrode Plasma ....................... 63
   3.2 Electrical Power System ................................ 63
IV. ANALYTICAL CHARACTERIZATION OF SAMPLE ENTRAINING
MULTI-ELECTRODE PLASMA SOURCES FOR ATOMIC EMISSION
SPECTROSCOPY: PART I. PRELIMINARY STUDIES (continued)

3.3 Electrodes and Electrode Holders 64
   3.3.1 Horizontal 4-Electrode Plasma 64
   3.3.2 Vertical Multi-Electrode Plasma 65
3.4 Gas Flows 66
3.5 Sample Introduction System 67
3.6 Operating the Multi-Electrode Plasma Sources 69
3.7 Echelle Spectrometer 69
3.8 Standards Preparation 71

4. Results and Discussions 71
   4.1 Performance of the Multi-Electrode
      Plasma Sources 71
   4.2 Sample Introduction System 74
   4.3 Dependence of the Emission Profiles on the
      Experimental Parameters 76
   4.3.1 Influence of Observation Height 77
   4.3.2 Influence of Plasma Length 82
   4.3.3 Influence of Current 92
   4.3.4 Influence of Position of the Tip
      of the Sample Introduction Tube 112
   4.3.5 Influence of Plasma Gas Flow Rate 120
   4.3.6 Influence of Sample Carrier Gas
      Flow Rate 122
   4.4 Stability of Plasma 126
   4.5 Residence Time of Analyte Species in Plasma 129
   4.6 Analytical Curves and Detection Limits 130

5. Conclusion 135

V. SIMPLEX OPTIMIZATION OF THE VERTICAL 4-ELECTRODE PLASMA
SOURCE FOR ATOMIC EMISSION SPECTROSCOPY 138

1. Abstract 139

2. Introduction 139

3. Experimental 141
   3.1 Instrumentation 141
   3.2 Experimental Variables and Response
      Functions 141
   3.3 Boundaries for the Experimental Variables 143
   3.4 Operation of the Modified Sequential
      Simplex Optimization 146

4. Results and Discussions 147
<table>
<thead>
<tr>
<th>Figures</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Schematic diagram of the horizontal 4-electrode plasma source: a) top view b) side view.</td>
<td>19</td>
</tr>
<tr>
<td>2. Schematic diagram of the vertical 4-electrode plasma source: a) side view b) top view.</td>
<td>22</td>
</tr>
<tr>
<td>3. Schematic diagram of the vertical 6-electrode plasma source (top view).</td>
<td>22</td>
</tr>
<tr>
<td>4. Pin connection for normal mode operation in the TCR 40S45 power supply.</td>
<td>27</td>
</tr>
<tr>
<td>5. Electrical circuit for the horizontal 4-electrode plasma source.</td>
<td>29</td>
</tr>
<tr>
<td>6. Schematic diagram of upper electrode holder for the vertical multi-electrode plasma sources.</td>
<td>32</td>
</tr>
<tr>
<td>7. Formation of two vertical columns of plasma with the sample stream in the vertical 4-electrode plasma source. (Without sample stream, the plasma appears as a vertical sheath.)</td>
<td>38</td>
</tr>
<tr>
<td>8. Influence of sample carrier gas flow rate on the shape of the plasma columns in the horizontal 4-electrode plasma source. (a) slow flow rate (b) fast flow rate</td>
<td>42</td>
</tr>
<tr>
<td>9. Spectrum indicating excellent resolution for the Plasma-Spec Echelle Spectrometer: a) 1 ppm Sn, using a line at 235.48 nm, is resolved from strong lines from 1000 ppm Ti at 235.46 and 235.51 nm. b) Strong Al interference 0.04 nm from V at 309.31 nm.</td>
<td>47</td>
</tr>
<tr>
<td>10. Influence of I.D. of the tip of sample introduction tube on the shape of the plasma columns in the vertical 6-electrode plasma source. a) small I.D. b) large I.D.</td>
<td>73</td>
</tr>
<tr>
<td>11. Horizontal-vertical spatial emission profile for the Mg neutral atom line at 285.21 nm. (Maximum intensity is at 6 mm above the quartz tube.)</td>
<td>78</td>
</tr>
<tr>
<td>12. Horizontal-vertical spatial emission profile for the Mg ion line at 280.27 nm. (Maximum intensity is at 8 mm above the quartz tube.)</td>
<td>79</td>
</tr>
<tr>
<td>13. Emission profile for the Mg ion line at 280.27 nm as a function of current at different observation heights. (○) 2 mm; (+) 4 mm; (◇) 6 mm; (△) 8 mm; (×) 10 mm above the quartz tube.</td>
<td>80</td>
</tr>
</tbody>
</table>
14. Emission profile for the Mg ion line at 280.27 nm as a function of length of plasma at different observation heights. (○) 2 mm; (+) 4 mm; (○) 6 mm; (△) 8 mm; (×) 10 mm above the quartz tube.

15. Horizontal distribution of Mg neutral atom line emission intensity at 285.21 nm with three different lengths of plasma. (○) 15 mm; (+) 20 mm; (○) 25 mm. (The center of the plasma is located at 3.7 mm on the horizontal axis; the emission intensities were observed at 8 mm above the quartz tube; A current of 19 A for each pair of electrodes was used.)

16. Horizontal distribution of Mg ion line emission intensity at 280.27 nm with three different lengths of plasma. (○) 15 mm; (+) 20 mm; (○) 25 mm. (The center of the plasma is located at 3.7 mm on the horizontal axis; the emission intensities were observed at 8 mm above the quartz tube; A current of 19 A for each pair of electrodes was used.)

17. Vertical distribution of Mg neutral atom line emission intensity at 285.21 nm with three different lengths of plasma. A current of 19 A for each pair of electrodes was used. (○) 15 mm; (+) 20 mm; (○) 25 mm.

18. Vertical distribution of Mg ion line emission intensity at 280.27 nm with three different lengths of plasma. A current of 19 A for each pair of electrodes was used. (○) 15 mm; (+) 20 mm; (○) 25 mm.

19. Horizontal distribution of line to background ratios for the Mg ion line at 280.27 nm with three different lengths of plasma. (○) 15 mm; (+) 20 mm; (○) 25 mm. (The observation height is 8 mm above the quartz tube; A current of 19 A for each pair of electrodes was used.)

20. Vertical distribution of line to background ratios for the Mg ion line at 280.27 nm with three different lengths of plasma. A current of 19 A for each pair of electrodes was used. (○) 15 mm; (+) 20 mm; (○) 25 mm.

21. Horizontal distribution of the Mg neutral atom line emission intensity at 285.21 nm as a function of current for a 25-mm plasma length at an observation height of 8 mm above the quartz tube. (○) 19 A; (+) 18 A; (○) 17 A; (△) 16 A.

22. Horizontal distribution of the Mg ion line emission intensity at 280.27 nm as a function of current for a 25-mm plasma length at an observation height of 8 mm above the quartz tube. (○) 19 A; (+) 18 A; (○) 17 A; (△) 16 A.
Figure

23. Horizontal distribution of the line to background ratios for the Mg ion line at 280.27 nm as a function of current. The length of the plasma is 25 mm and the observation height is 8 mm above the quartz tube. (○) 19 A; (△) 16 A.

24. Vertical distribution of the 285.21-nm Mg neutral atom line emission intensity at the center of the plasma as a function of current. The length of the plasma is 25 mm. (○) 19 A; (+) 18 A; (○) 17 A; (△) 16 A.

25. Vertical distribution of the 280.27-nm Mg ion line emission intensity at the center of the plasma as a function of current. The length of the plasma is 25 mm. (○) 19 A; (+) 18 A; (○) 17 A; (△) 16 A.

26. Horizontal distribution of the 285.21-nm Mg neutral atom line emission intensity at the center of plasma as a function of current. The length of the plasma is 20 mm and the observation height is 8 mm above the quartz tube. (○) 19 A; (+) 18 A; (○) 17 A; (△) 16 A; (x) 15 A.

27. Horizontal distribution of the Mg ion line emission intensity at 280.27 nm as a function of current for a 20-mm plasma length at an observation height of 8 mm above the quartz tube. (○) 19 A; (+) 18 A; (○) 17 A; (△) 16 A; (x) 15 A.

28. Horizontal distribution of the line to background ratios for the Mg ion line at 280.27 nm as a function of current. The length of the plasma is 20 mm and the observation height is 8 mm above the quartz tube. (○) 19 A; (+) 18 A; (○) 17 A; (△) 16 A; (x) 15 A.

29. Vertical distribution of the 285.27-nm Mg neutral atom line emission intensity at the center of the plasma as a function of current. The length of the plasma is 20 mm. (○) 19 A; (+) 18 A; (○) 17 A; (△) 16 A; (x) 15 A.

30. Vertical distribution of the 280.27-nm Mg ion line emission intensity at the center of the plasma as a function of current. The length of the plasma is 20 mm. (○) 19 A; (+) 18 A; (○) 17 A; (△) 16 A; (x) 15 A.

31. Vertical distribution of the line-to-background ratios for the Mg ion line at 280.27 nm as a function of current for a 20-mm plasma length. (○) 19 A; (+) 18 A; (○) 17 A; (△) 16 A; (x) 15 A.

32. Horizontal distribution of Mg neutral atom line emission intensity at 285.21 nm as a function of current for a 15-mm length of plasma. (○) 21 A; (+) 20 A; (○) 19 A; (△) 18 A.
33. Horizontal distribution of Mg ion line emission intensity at 280.27 nm as a function of current for a 15-mm length of plasma. (□) 21 A; (+) 20 A; (○) 19 A; (△) 18 A.

34. Influences of length of plasma and current on the line-to-background ratios of the Mg ion line at 280.27 nm. (□) 25 mm; (+) 20 mm; (○) 15 mm.

35. Influences of length of plasma and current on the line-to-background ratios of the Mg neutral atom line 285.21 nm. (□) 25 mm; (+) 20 mm; (○) 15 mm.

36. Horizontal distribution of Mg ion line emission intensity at 280.27 nm for several positions of the tip of the sample introduction tube. The position of the tip of the sample introduction tube is expressed with respect to the end of inner electrode. A current of 17 A for each pair of electrodes was used. (□) 2 mm; (+) 4 mm; (○) 6 mm; (△) 8 mm; (×) 10 mm.

37. Horizontal distribution of Mg neutral atom line emission intensity at 285.21 nm for several positions of the tip of the sample introduction tube. The position of the tip of the sample introduction tube is expressed with respect to the end of inner electrode. A current of 17 A for each pair of electrodes was used. (□) 2 mm; (+) 4 mm; (○) 6 mm; (△) 8 mm; (×) 10 mm.

38. Vertical distribution of Mg neutral atom line emission intensity at 285.21 nm for several positions of the tip of the sample introduction tube. The position of the tip of the sample introduction tube is expressed with respect to the end of inner electrode. A current of 17 A for each pair of electrodes was used. (□) 2 mm; (+) 4 mm; (○) 6 mm; (△) 8 mm; (×) 10 mm.

39. Vertical distribution of Mg ion line emission intensity at 280.27 nm for several positions of the tip of the sample introduction tube. The position of the tip of the sample introduction tube is expressed with respect to the end of inner electrode. A current of 17 A for each pair of electrodes was used. (□) 2 mm; (+) 4 mm; (○) 6 mm; (△) 8 mm; (×) 10 mm.

40. Horizontal distribution of line-to-background ratios for the Mg ion line at 280.27 nm for several positions of the tip of the sample introduction tube. A current of 17 A for each pair of electrodes was used. (□) 2 mm; (+) 4 mm; (○) 6 mm; (△) 8 mm; (×) 10 mm.
Figure 41. Influences of the plasma gas flow rate on the Mg ion and neutral atom line intensities. (○) Mg neutral atom line at 285.21 nm; (+) Mg ion line at 280.27 nm.

42. Vertical distribution of the Mg ion line emission intensity at 280.27 nm as a function of plasma gas flow rate. (○) 2.92 L/min; (+) 2.74 L/min; (○) 2.56 L/min; (Δ) 2.38 L/min; (x) 2.19 L/min; (V) 2.01 L/min.

43. Horizontal distribution of the Mg neutral atom line emission intensity at 285.21 nm for several sample carrier gas flow rates. Observation height is 8 mm above the quartz tube. (○) 0.7 L/min; (+) 0.8 L/min; (○) 0.9 L/min.

44. Horizontal distribution of the Mg ion line emission intensity at 280.27 nm for several sample carrier gas flow rates. Observation height is 8 mm above the quartz tube. (○) 0.7 L/min; (+) 0.8 L/min; (○) 0.9 L/min.

45. Vertical distribution of the Mg ion line emission intensity at 280.27 nm for several sample carrier gas flow rates. (○) 0.7 L/min; (+) 0.8 L/min; (○) 0.9 L/min.

46. Stability of the plasma as expressed by the relative standard deviation (RSD) of the Fe neutral atom line emission intensity at 371.9 nm for plasma operation of one hour. Each point in the plot represents the RSD of 32 measurements each a with 1-s integration time.

47. Movement of the L/B ratio as a function of the simplex vertex number. (The L/B ratio for the Ca (II) at 393.37 nm was used as a response function in this study.)

48. Movement of the observation height as a function of the simplex vertex number. The observation height is expressed by the distance above the quartz tube.

49. Movement of the length of plasma as a function of the simplex vertex number.

50. Movement of the current as a function of the simplex vertex number.

51. Movement of the sample carrier gas flow rate as a function of the simplex vertex number.

52. Movement of the plasma gas flow rate as a function of the simplex vertex number.

53. Movement of the sample uptake rate as a function of the simplex vertex number.
Figure

54. Variation of the background emission intensity as a function of the simplex vertex number.

55. Horizontal distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/PO₄ molar ratio (2.5 μmol/mL Ca). The plasma length is 30 mm and the observation height is 6 mm above the top of the quartz tube. Molar ratio of Ca to PO₄; (O) 1:0; (+) 1:100.

56. Vertical distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/PO₄ molar ratio (2.5 μmol/mL Ca). The plasma length is 30 mm. Molar ratio of Ca to PO₄; (O) 1:0; (+) 1:100.

57. Vertical distribution of the Ca neutral atom line emission intensity at 422.67 nm as a function of Ca/PO₄ molar ratio (2.5 μmol/mL Ca). The plasma length is 30 mm. Molar ratio of Ca to PO₄; (O) 1:0; (+) 1:100.

58. Normalized horizontal distribution of the Ca ion line emission intensity at 393.37 nm with the Ca/PO₄ molar ratio of 500 (2.5 μmol/mL Ca). The plasma length is 30 mm and the observation height is 6 mm above the top of the quartz tube. Molar ratio of Ca to PO₄; (−) 1:0; (Δ) 1:500; (O) normalized 1:500.

59. Horizontal distribution of the Ca atom line emission intensity at 422.67 nm as a function of Ca/PO₄ molar ratio (2.5 μmol/mL Ca). The plasma length is 25 mm and the observation height is 6 mm above the top of quartz tube. Molar ratio of Ca to PO₄; (O) 1:0; (+) 1:4; (O) 1:10.

60. Vertical distribution of the Ca neutral atom line emission intensity at 422.67 nm as a function of Ca/PO₄ molar ratio (2.5 μmol/mL Ca). The plasma length is 25 mm. Molar ratio of Ca to PO₄; (O) 1:0; (+) 1:4; (O) 1:10.

61. Vertical distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/PO₄ molar ratio (2.5 μmol/mL Ca). The plasma length is 25 mm. Molar ratio of Ca to PO₄; (O) 1:0; (+) 1:4; (O) 1:10.

62. Horizontal distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/Al molar ratio (2.5 μmol/mL Ca). The plasma length is 30 mm. Molar ratio of Ca to Al; (O) 1:0; (+) 1:10; (O) 1:100.

63. Vertical distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/Na molar ratio (0.5 μmol/mL Ca). The plasma length is 25 mm. Molar ratio of Ca to Na; (O) 1:0; (+) 1:25; (O) 1:250.
64. Horizontal distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/Na molar ratio (0.5 μmol/mL Ca). The plasma length is 25 mm and the observation height is 6 mm above the top of the quartz tube. Molar ratio of Ca to Na; (⊙) 1:0; (+) 1:25; (○) 1:250.

65. Vertical distribution of the Ca neutral atom line emission intensity at 422.67 nm as a function of Ca/Na molar ratio (0.5 μmol/mL Ca). The plasma length is 25 mm. Molar ratio of Ca to Na; (⊙) 1:0; (○) 1:25; (×) 1:250.

66. Vertical distribution of the Cd neutral atom line emission intensity at 228.80 nm as a function of Cd/Na molar ratio (0.5 μmol/mL Cd). The plasma length is 25 mm. Molar ratio of Cd to Na; (⊙) 1:0; (+) 1:25; (○) 1:250.

67. Vertical distribution of the Cd ion line emission intensity at 214.44 nm as a function of Cd/Na molar ratio (0.5 μmol/mL Cd). The plasma length is 25 mm. Molar ratio of Cd to Na; (⊙) 1:0; (+) 1:25; (○) 1:250.

68. Boltzmann plot for nine Fe(I) lines. The plasma length is 30 mm and the observation height is 6 mm above the top of the quartz tube. \( \ln(X) \) represents \( \ln(\text{gf}/I\lambda^3) \).

69. Fe excitation temperature profile along the sample aerosol channel for a 25-mm plasma length.

70. Fe excitation temperature profile along the sample aerosol channel for a 30-mm plasma length.

71. Horizontal distribution of Fe excitation temperature at an observation height of 8 mm above the top of the quartz tube for plasma lengths of (+) 25 mm; (⊙) 30 mm. The sample carrier gas flow rate is 0.71 L/min.

72. Horizontal distribution of electron number density at an observation height of 8 mm above the top of the quartz tube for plasma lengths of (+) 25 mm; (⊙) 30 mm. The sample carrier gas flow rate is 0.71 L/min.
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Dimensions of the three concentric quartz tubes of the horizontal 4-electrode plasma torch. (O.D.: outer diameter; I.D.: Inner diameter)</td>
<td>15</td>
</tr>
<tr>
<td>2.</td>
<td>Specifications of DC power supply, single phase regulated TCR 40S45 with constant voltage / constant current automatic crossover.</td>
<td>24</td>
</tr>
<tr>
<td>3.</td>
<td>The pin description of the terminal strip in TCR 40S45 DC power supply.</td>
<td>26</td>
</tr>
<tr>
<td>4.</td>
<td>Experimental facilities for the multi-electrode plasma sources.</td>
<td>61</td>
</tr>
<tr>
<td>5.</td>
<td>Typical experimental conditions for the determination of detection limits.</td>
<td>131</td>
</tr>
<tr>
<td>6.</td>
<td>Detection limits for vertical 4-electrode plasma source, mg/L.</td>
<td>132</td>
</tr>
<tr>
<td>7.</td>
<td>Log-log slopes and background RSD for the vertical 4-electrode plasma source.</td>
<td>133</td>
</tr>
<tr>
<td>8.</td>
<td>Comparison of detection limits of the multi-electrode plasma sources, mg/L.</td>
<td>134</td>
</tr>
<tr>
<td>9.</td>
<td>Possible experimental variables and response functions in the vertical 4-electrode plasma source.</td>
<td>144</td>
</tr>
<tr>
<td>10.</td>
<td>Boundaries for the experimental variables.</td>
<td>145</td>
</tr>
<tr>
<td>11.</td>
<td>Energy levels and gf-values for Fe(I) lines.</td>
<td>188</td>
</tr>
<tr>
<td>12.</td>
<td>Comparison of various results of excitation temperature measurements with different data for Fe(I).</td>
<td>189</td>
</tr>
<tr>
<td>13.</td>
<td>gf values for Fe(I) lines used in temperature measurements.</td>
<td>190</td>
</tr>
</tbody>
</table>
Atomic emission spectroscopy has long been a standard analytical tool, which can be used with all the metals and with certain nonmetals such as boron and phosphorus [1-5]. Atomic emission spectroscopy is a process whereby the light emitted by excited atoms or ions is measured. After excitation of a free atom or ion to an unstable energy state by sufficient collisional energy, emission occurs when the excited atom or ion returns to a lower state or the ground state. The wavelengths of radiation emitted are specific to the elements present in the sample to be analyzed.

Due to the nature of atomic emission spectroscopy, the excitation source is a very critical component in atomic emission instruments. Both the pattern and the intensity of lines produced by a species are greatly influenced by the excitation source in an atomic emission spectrometer. As a result, the excitation source in emission spectroscopy must serve the following basic functions. First, the source must provide sufficient energy to convert the constituents of a liquid or solid sample into the vapor state and/or to convert the individual components to gaseous atoms or ions. The next basic function is to provide sufficient energy to excite a fraction of the resulting elementary particles to an upper electronic energy level. It is essential that each of those processes be carried out in a
reproducible manner.

The earliest energy sources for excitation were simple combustion flames. However combustion flames sometimes do not provide sufficient energy to excite certain elements such as refractory elements, and also suffered from background emissions and interference effects. Later, electrical discharge sources such as DC and AC arcs and high-voltage spark systems were used for analyzing solid samples because arc and spark excitations are more sensitive than combustion flames. Since processes of the arc and spark excitations have the virtue of providing information rapidly due to relatively simple sample preparation, they are used in situations where speed is important. In the early days these sources were mostly used for qualitative analysis rather than for quantitative analysis because of difficulties encountered in reproducing radiation intensities. As a result, especially for the analysis of liquid samples, atomic emission spectroscopy did not share universal popularity with the atomic absorption technique in the 1960's and 1970's. Recently the developments of the dc argon plasma (DCP) and the inductively coupled plasma (ICP) have caused a dramatic increase in atomic emission spectroscopy utilization and a virtual renaissance of atomic emission spectroscopy in handling solutions, because they do not exhibit many of the problems associated with past excitation sources.

The ICP and DCP, plasma emission techniques, were initially developed as alternatives to atomic absorption and other techniques such as arc and spark atomic emission spectroscopy. In a relatively short time, it was recognized that both the ICP and DCP are often superior to other emission techniques as well as atomic absorption
spectroscopy in terms of the precision, accuracy, dynamic range, interference effects, and detection limits.

However the initial and operating costs for these plasma emission techniques, especially in the case of the ICP, are relatively expensive. The operating costs for an ICP are mainly gaseous and/or liquid argon for the nebulizer and gas flows (usually 12-20 L/min) to the torch. As a result, for the past several years, many scientists including the commercial ICP manufacturers have done extensive research to modify the standard ICP torch design to reduce the radio-frequency power and the argon gas-flow requirements without sacrificing the analytical performance of the standard ICP torch [6-12]. Commercial plasma torches of reduced size are now available such as the ARL Minitorch™ (Applied Research Laboratories Inc., Dearborn, Michigan) and the MAK™ torch (Sherritt Gordon Mines Limited/Sherritt Research Centre, Alberta, Canada).

Most electrical plasma sources, especially in the case of the DCP, have also suffered from their inability to obtain enough contact between hot plasma and the sample aerosol stream to provide enough time to atomize and excite sample aerosol [13,14]. Due to the presence of this apparent disadvantage in the DCP sample introduction system, the DCP is less popular than the ICP even though the initial and operating costs of the DCP are less expensive than those of the ICP.

In our laboratory, research to develop plasma sources with multiple electrodes that entrain a sample stream in the center of hot plasma was initiated in 1976. After several modifications, 4- and 6-electrode plasma sources with a moderate consumption rate of argon
were developed, in which the sample stream is surrounded by the hot plasma the same as in an ICP. In this way, the problems described above can be overcome by means of using electrodes to help control the shape of the plasma in order to entrain an aerosol sample stream efficiently in the center of hot plasma for a longer period of time. In the research study reported here, the new 4- and 6-electrode plasma sources have been characterized and evaluated as new excitation sources for atomic emission spectroscopy.
II. HISTORICAL DEVELOPMENT

1. INDUCTIVELY COUPLED PLASMA (ICP)

The ICP operating at atmosphere pressure was first described by Babat. The results of Babat's research into the properties of high frequency (HF) ICP were published in 1942 in Russian [15] and after World War II in English [16]. When Babat employed a HF (2 to 77 MHz) vacuum tube oscillator with an output reaching 100 kW, powerful electrodeless discharges with air were obtained inside quartz tube cylinders 15 cm in diameter and 150 cm long at pressures ranging from 0.1 to 760 torr. Babat suggested that the radio-frequency discharges could be utilized for industrial applications such as heating and fusion of fireproof materials and creating high-intensity economic light sources.

Stabilization of an inductively heated plasma discharge operated at atmosphere pressure and in gases flowing through an open-ended tube was achieved in the early 1960s. ICP discharges in a flowing gas at atmosphere pressure were first generated in 1961 by Reed [17,18] as a technique for growing crystals under high temperature conditions. An ICP torch was operated at atmosphere pressure with argon alone or mixed with other gases and powered by a 10-kW radio frequency (rf) heating unit operating at a frequency of 4 MHz. In the followed paper [19], Reed described many of the physical properties of these plasmas and suggested their possible application as spectral sources for solids.

The analytical potential of ICP discharges followed from the work
of Greenfield [20] and Wendt and Fassel [21]. These two groups were stimulated by Reed's publication to begin work independently toward establishing the spectrochemical practicality of ICP discharges.

In 1964 Greenfield used a 2.5-kW, 36-MHz generator to produce an argon gas plasma. A demountable torch with three concentric tubes was described, and the tail flame above the plasma was used as the spectroscopic source. Argon was fed tangentially into the inner quartz tube, the rf field applied by the work coil and a pilot plasma produced by a Tesla coil or graphite rod. The reported analytical results obtained using the ICP source indicated that the source was capable of high sensitivity [20]. It was also established that the source exhibited freedom from matrix effects. In 1965 Greenfield reported the determination of aluminum and phosphorus in a phosphatic rock sample [22], indicating that the well-known interference of phosphorus and aluminum on the emission from calcium was completely eliminated.

In 1965 Wendt and Fassel [21] described an ICP torch with laminar flow for which was claimed the advantage of less turbulence and perhaps greater stability than was obtained with vortex flow. This torch was used with a 3.4-MHz, 5-kW generator and ultrasonic nebulizer for aerosol generation. Detection limits (D.L.) were reported and were relatively low.

Dunken and Pforr [23] used a three-tube torch similar to that of Greenfield [20] with a 1- to 2-kW, 40-MHz generator and an ultrasonic nebulizer. The atomic and ionic lines of the elements introduced showed very good signal-to-background ratios. In 1967 Pforr reported the practical use of the ICP for the determination of wear metals in
oils [24].

The torch described by Hoare and Mostyn [25] consisted of three quartz tubes and an ultrasonic nebulizer with a facility for sample changing, powered by a 2.5-kW, 36-MHz generator. The top of the outer tube was cut at an angle of 45° and it was claimed that this improved the stability of the gas-flows and led to more effective viewing of the emission. A powder-injection system was also described.

A two-tube torch was constructed by Mermet and Robin [26] who demonstrated that greater stability was obtained when an aerosol was injected into the plasma by means of a water-cooled injector, than when fed into the plasma gas stream. Veillon and Margoshes [27] were the first to report the presence of matrix effects.

In 1969 Dickinson and Fassel [28] published an account of their continuing investigations into the analytical applications of plasma torches, demonstrating the improvements that could be made from careful attention to operating conditions. They reported detection limits of 0.1-10 ng/mL range for many elements, which meant an improvement by two or more orders of magnitude compared to the results achieved previously and shown to compare favorable with other atomic spectroscopic techniques. In addition, these authors commented on the matrix effects reported by Veillon and Margoshes and suggested that these were due to the experimental conditions used in the experiment.

In the 1960s and early 1970s the efforts of many researchers exploring the potentialities of ICPs were the precursor of the most important event for routine ICP analysis, the development of commercially available ICP systems. Since the first modern commercial ICP instrument was introduced in 1974 by the Applied Research
Laboratories, explosive engineering developments have been still underway at a number of other companies.

The design of a plasma tube assembly for practical use in spectrochemical analysis is based partly on theoretical considerations including computer simulation of torches with different dimensions [29-32] and partly on empiricism [33]. The computational methods used to describe the plasma system are based on the cylinder model and thus a number of assumptions, such as no interelement effects, isothermal free turbulent gas stream, constant density gas, and no desolvation energy, are made in order to simplify the system for computational purposes. Therefore, it was almost impossible to completely take into account all aspects with the theoretical considerations alone. However, by using the mathematical method developed by Miller and Ayen [29], and modified by Barnes and Schleicher [30] in conjunction with a flow model which simulates the steady-state flow in a plasma source, a relatively complete computer simulation was developed and thus provided sufficiently accurate information to be used in designing new ICP torch arrangements. Based upon both theoretical and experimental considerations, the most promising and practical designs of new inductively coupled plasma torches have been constructed by several scientists [34-36].

Since the early 1970s, developments of the ICP discharge as a spectrochemical source have intensified until today it is recognized as a unique spectrochemical source with high sensitivity, remarkable stability, and versatility. However, the ICP has a number of limitations, many of which are currently being investigated and, hopefully, overcome. Among these limitations, the most important from
a practical standpoint include the expensive initial and operating costs of an ICP. As a result, a number of workers have sought to modified the ICP torch design to reduce the power and gas-flow requirements of the resulting plasma without sacrificing the analytical performance of the standard ICP torch [37-39]. Further improvements in the present sample introduction system of the ICP have also been undertaken.

Recently many researchers have extensively spent their efforts to characterize the physical properties of the ICP discharge and investigate the fundamental processes that control the excitation mechanism of analyte species in the discharge [40-42]. Ultimately, these fundamental studies promise to both improve and expand the applications of plasma spectroscopy. In addition to improvements due to increasing familiarity with ICP characteristics, an important advance in the 1980s has been the increasingly sophisticated use of computers. This has aided instrument management and improvements in data handling considerably.

2. DIRECT CURRENT PLASMA (DCP)

The first applications of DCPs to spectrochemical analysis were reported in 1959 independently by Korolev and Vainshtein [43] and Margoshes and Scribner [44]. The Korolev and Vainshtein "plasma jet" [43], which is the simplest form of a plasma jet, used a graphite rod as the anode and a graphite ring as the cathode. An arc burns in a chamber between a graphite anode and a perforated graphite cathode. A
stream of N\textsubscript{2} gas as the plasma gas introduced into the chamber ejects the plasma through the cathode orifice to form a jet. Solution samples were sprayed in a chamber-type nebulizer.

The Margoshes and Scribner "plasma jet" [44] employed a ring-shaped anode (lower electrode) through which aerosol from a direct nebulizer was fed. The arc was operated with currents in the range of 15 to 20 A from a standard dc arc power supply. However, this device was not successful for spectrochemical analysis because of the tendency of the cathode spot to wander, and ineffective mixing of the sample aerosol with the plasma. Modifications to improve the stability of the plasma jet and the efficiency of sample injection was followed by Owen's work published in 1961 [45]. The modified configuration [46] no longer is a plasma jet but a gas-stabilized arc with additional wall stabilization by an electrically floating graphite ring, and with this device observations are normally made in the current-carrying portion of the plasma.

Different types of gas-stabilized arcs have been investigated by Kliska [47], Marinkovic [48], and Piepmeier [49]. Marinkovic [48,50] investigated the effects of adding Na matrix as buffers. He reported that the temperature of arc was greatly dependent on the buffer concentration, and concluded that this matrix effect might be considered its weakness. Marinkovic's plasma jet [48,50] is also referred to as a "cascade arc".

Kranz [51] exploited turbulent mixing of the sample aerosol and the plasma in a DCP, developed from a wall-stabilized arc. This device was modified on the basis of McGinn's design [52], and mainly used for physical investigations. The effect of ionization
interference by adding Na matrix was investigated in a modified Kranz plasma jet by Schirrmeister [53,54]. On the whole, the analytical results of these devices were reported, but they were not impressive.

Elliott's plasma jet [55] similar to Owen's gas-stabilized arc [45] was adopted in a commercial DCP as the Spectrametrics, Inc. SpectraJet. The tungsten rod cathode was positioned off the central arc column axis, producing a nearly right-angle bend in the column. Sample aerosol generated by a pneumatic nebulizer was introduced tangentially into the plasma chamber and turbulently mixed with the plasma column at the base of the graphite thermal pinch ring. Usually an observation zone was located in a flame-like plasma formed above the bent primary arc. The SpectraJet required 5 L/min of argon gas and 500 W of input power. The plasma jet which appeared to be quite similar in design to the SpectraJet was further characterized by Merchant and Veillon [56] in 1974.

An inverted "V" configuration of the plasma jet was described by Valente and Schrenk [57]. The Valente-Schrenk plasma jet consisted of the two chambers for cathode and anode. The two chambers were first aligned vertically to strike an arc by extending the cathode until it touched the anode. After ignition of the arc, the cathode was withdrawn to its proper position inside the chamber. Then, one of the chambers was rotated about the center of the discharge to a position so that there was an angle of approximately 30° between the jets emerging from the two chambers. The plasma then appeared approximately as an inverted "V". Measurements were made in the plume above the bent arc column and thus above the strongly emitting plasma core thereby improving line-to-background ratios.
Valente and Schrenk [57] investigated the emission intensities of a Ca (I) and a Ca (II) line and the background as a function of the various experimental parameters. They concluded that the careful selection of an observation zone with low background and high analyte emission intensities led to unusually good detection limits. Eventually the inverted "V" configuration of the Valente-Schrenk plasma jet was adopted in a commercial two-electrode DCP [58] known as SpectraJet II.

In the SpectraJet II [58], the plasma was formed between two thoriated tungsten electrodes partially withdrawn into ceramic sleeves through which argon flowed as the coolant gas. Sample aerosol was introduced from below the inverted "V" independently of the gases forming the plasma jet. The observation zone was positioned at just below the apex of the inverted "V" where a portion of the sample aerosol appeared to be trapped. Thus the emission spectrum of the elements was intense and virtually free from the high background of the plasma core. Detection limits of this device were in many instances at least one order of magnitude lower than the best obtained with conventional plasma jet configurations. This device required about 5 L/min of argon gas and operated from specially designed dc power supply with a power dissipation of 500 W.

Unfortunately the results using SpectraJet II were subject to drift [59] which was apparently attributed to positional instability of the apex of the plasma. This resulted in the development of a third commercial DCP (SpectraJet III) with three electrodes, two graphite anodes, and a tungsten cathode, each flushed with an argon jet. Therefore, two independent plasma jets with a single common
cathode were generated such that the resulting plasma adopted an inverted "Y" configuration. The introduction of the third electrode led to improved stability. The total consumption of argon was about 8 L/min made up of 4 L/min for the nebulizer, 1 L/min for each of the anodes and 2 L/min for the cathode. A dc power supply provided a regulated current of 7 A to each of the two arcs.

Decker [60] concluded that the three-electrode DCP had analytical characteristics which were superior to those of conventional plasma jets and which approached those of the ICP. He reported that the principal advantages of the three-electrode DCP were low detection limits, relatively high precision, good stability, high versatility for various types of sample, and three orders of magnitude dynamic range. He also pointed out that the disadvantages were identified as the extremely small excitation region favorable for measurement, the difficulties of achieving compromise conditions for multielement analysis, and interference effects from alkali metals.

As we have seen in this section, the major shortcoming for most electrical plasma sources, especially in the case of 3-electrode DCP, is their inability to obtain sufficient contact between the hot plasma and the sample aerosol stream. In addition, since sample must pass the discharge region of the 3-electrode DCP, power dissipation will be varied from sample to sample. As a result, the excitation and ionization mechanisms of 3-electrode DCP are more complicate than those of ICP.

It is obvious that further developments in DC plasma jet can lead to more complete understanding of the principles of operation and consequently to improved and greater use than we see today.
III. INSTRUMENTATION

1. INTRODUCTION

Three different types of multi-electrode plasma sources for atomic emission spectroscopy were developed and investigated. The most critical component of the entire new plasma source is the plasma tube arrangement and its design. Basically, the plasma tube assemblies for the three types of multi-electrode plasma sources are almost the same except for the number of electrodes and quartz tubes. Horizontal 4-electrode plasma source consists of three concentric quartz tubes (outer, inner, and sample introduction tubes) and two pairs of 2% thoriated tungsten electrodes. The vertical 4- and 6-electrode plasma source consist of only two concentric quartz tubes (inner and sample introduction tubes) and three pairs of 2% thoriated tungsten electrodes.

The outer and inner diameters of the three concentric quartz tubes were examined and the dimensions of the three concentric precision quartz tubes (clear fused silica, Wilmad Glass Company Inc., Buena, NJ) listed in Table 1 were found to be critical. The following factors have been considered to obtain the optimum diameters of the three concentric quartz tubes.

Due to a combination of high temperature and pressure of the plasma discharge, sample aerosols introduced into the plasma discharge tend to flow around the high temperature regions of the discharge. Also with low velocity of sample carrier gas, the sample aerosol stream tends to spread out from a tip of a sample introduction tube
Table 1. Dimensions of the three concentric quartz tubes of the horizontal 4-electrode plasma torch. (O.D.: outer diameter; I.D.: inner diameter)

<table>
<thead>
<tr>
<th>Tubes</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer tube</td>
<td></td>
</tr>
<tr>
<td>O.D.</td>
<td>17.32 mm</td>
</tr>
<tr>
<td>I.D.</td>
<td>15.00 mm</td>
</tr>
<tr>
<td>Inner tube</td>
<td></td>
</tr>
<tr>
<td>O.D.</td>
<td>14.60 mm</td>
</tr>
<tr>
<td>I.D.</td>
<td>12.60 mm</td>
</tr>
<tr>
<td>Sample introduction tube</td>
<td></td>
</tr>
<tr>
<td>O.D.</td>
<td>4.16 mm</td>
</tr>
<tr>
<td>I.D.</td>
<td>2.00 mm</td>
</tr>
<tr>
<td>Inner diameter of stabilization inlet</td>
<td>1.00 mm</td>
</tr>
<tr>
<td>Inner diameter of plasma inlet</td>
<td>2.00 mm</td>
</tr>
<tr>
<td>Inner diameter of sample tip</td>
<td>1.00 mm</td>
</tr>
<tr>
<td>Annulus space</td>
<td>0.20 mm</td>
</tr>
</tbody>
</table>
instead of remaining constant in width. Consequently, the inner
diameter of the tip of the sample introduction tube has to be small
enough to generate a relatively high velocity of sample aerosol stream
in order to pass through the plasma. It has been reported that it is
necessary to use high velocity sample carrier gas streams in order to
force sample aerosols into the ICP discharge [61,62]. In addition, a
small inner diameter of the tip of the sample introduction tube is
also needed to produce a small sample aerosol stream that can be
effectively surrounded by the plasma columns for better desolvation,
atomization and excitation of analyte species. An inner diameter of
1.0 mm to 1.5 mm was found to be the best for the multi-electrode
plasma sources with a Meinhard concentric nebulizer. Since about
0.7-1.0 L/min of sample aerosol carrier gas flow rate is required to
generate fine aerosols with the Meinhard concentric nebulizer, the
above sizes of sample tips are suitable to provide the small sample
aerosol stream required for effective contact with the plasma columns
and a relatively long residence time.

In addition, the inner diameter of the sample introduction tube
has to be large enough to avoid back pressure and condensation of
sample aerosol on the wall of the inside of sample introduction tube.
Usually a 2-mm inner diameter sample introduction tube was used in
these studies.

Due to the nature of the horizontal 4-electrode plasma source,
this plasma source was not stable enough to run for a long period of
time with the sample introduction tube described above. As a result,
modification of the sample introduction system was required for better
stability. This will be discussed in detail below.
The inner diameter of the inner quartz is chosen initially, taking into account both the amount of argon gas consumed per unit time and the length of the plasma column. The larger the inner diameter of the inner quartz tube, the more argon gas required to sustain a stable discharge. If a larger inner diameter is chosen, then this is the factor that will mainly limit the minimum consumption of the argon gas. On the other hand, the inner diameter has to be large enough so that the gap between the plasma columns (generated by each pair of electrodes) is wide enough to pass the sample aerosol through the plasma columns without extinguishing them. As in a conventional ICP torch, an inner quartz tube with a 12.6-mm inner diameter and 1-mm wall thickness was selected for our application.

In the case of the horizontal 4-electrode plasma source, the choice of the inner diameter of the outer quartz tube is mainly influenced by the flow pattern of the stabilization argon gas. The role of stabilization argon gas in the horizontal 4-electrode plasma source is very different from that in the ICP. That is, in our application the stabilization argon gas is used to push the parallel arcs toward the center of sample stream to get good contact between the arcs and the sample. In the ICP, the stabilizing gas is used to prevent the quartz tubes walls from melting and to position the plasma discharge radially at the center of the tube. More importantly, the stabilizing gas is used to help form the discharge into an annular shape through which a sample aerosol can be transported by the sample aerosol carrier gas. In the ICP, a vortex stabilization is accomplished by introducing a gas into a plasma tube tangentially, which causes it to flow spirally down the walls. Therefore, the
tangential flow of the argon gas, which is typically in the 10 L/min range, for a conventional ICP torch is very critical for the analytical performance of the ICP, as is also the annular spacing between the outer and inner quartz tubes. However stabilization argon gas in the horizontal 4-electrode plasma source is simply used to position the parallel arcs. The vortex stabilization flow with high velocity was obtained with 0.20-mm annular spacing between the inner and outer quartz tubes. With the commercial precision bore quartz tubing manufactured by Wilmad Glass Company, a 15.00-mm inner diameter outer quartz tube was selected for the our application in order to get on annular spacing of 0.20 mm between the inner and outer quartz tubes.

2. SYSTEM COMPONENTS

2.1 Plasma tube arrangements

2.1.1 Horizontal 4-electrode plasma source

The horizontal 4-electrode plasma source consists of three concentric quartz tubes (outer, inner, and sample introduction tubes) and two pairs of 2% thoriated tungsten electrodes with the ends of the electrodes at the corners of a horizontal square. The schematic diagram of the horizontal 4-electrode plasma torch assembly is shown in Figure 1. In general, the horizontal 4-electrode plasma torch has the same features as conventional ICP torches [63-67], that is, an assembly of three concentric quartz tubes with three gas flows such as the stabilization gas flow through the annular spacing between the
Figure 1. Schematic diagram of the horizontal 4-electrode plasma source: a) top view  b) side view.
outer and inner tubes, the plasma gas flow through the annular spacing between the inner and sample introduction tubes, and the sample carrier gas flow through the sample introduction tube. As in the conventional ICP torch, both the stabilization and plasma gases are introduced tangentially. The dimensions of the three quartz tubes and the inner diameter of the gas inlet are listed in Table 1.

In order for maintenance to be simple and easy, the plasma torches are constructed in a demountable manner. Because of versatility, demountable plasma torches have been constructed by several researchers [68-73] especially for the investigation of the new plasma torch systems. In our applications, the plasma tube assembly is mounted in two aluminum blocks with a double 0-ring seal around each tube. The inner aluminum block holds the outer quartz tube with three 4-40 set screws and the outer aluminum block holds the inner aluminum block with three 6-32 set screws. In this way, the distance between the top of the inner and outer quartz tubes is readily controlled by moving the inner aluminum block holding the outer quartz tube. The length of outer quartz tube is 100 mm and that of inner quartz tube is 118 mm. The distance between the top of the outer quartz tube and that of the inner quartz tube is adjustable from 7 mm to 13 mm. In addition, damaged parts such as melted or broken quartz tubes are readily replaced and also various dimensions of quartz tubes can be investigated with simple modifications of the plasma torch assembly.

2.1.2 Vertical 4-electrode plasma source

The vertical 4-electrode plasma source has two pairs of
electrodes positioned so that two vertical columns of arc are formed on either side of the vertically rising sample stream. This configuration was used to overcome several problems associated with the sample introduction system and stability of the horizontal 4-electrode plasma torch. Essentially the configuration of the plasma torch is the same as that of the horizontal 4-electrode plasma torch except for the positions of the electrodes and the number of the quartz tubes used. The vertical 4-electrode plasma torch assembly consists of only two concentric quartz tubes (inner and sample introduction tubes) and an aluminum block. The dimensions of the two concentric quartz tubes are exactly the same as those of the horizontal 4-electrode plasma source. A schematic diagram of the vertical 4-electrode plasma torch assembly is shown in Figure 2. Compared to the horizontal 4-electrode plasma torch, a pair of electrodes were taken out of the inner quartz tube and positioned at a 45 degree angle right at the top of the inner quartz tube. One of the main advantages of the vertical 4-electrode plasma source is that the plasma length can be easily controlled by moving the lower electrodes up and down. Consequently, the residence time experienced by the analyte species can be adjusted without interruption even during the operation of the plasma.

2.1.3 Vertical 6-electrode plasma source

The vertical 6-electrode plasma source is obtained by simply adding a pair of electrodes to the vertical 4-electrode plasma source, and stationing the vertical pairs 120 degrees from each other. Therefore, the vertical 6-electrode plasma source consists of two
Figure 2. Schematic diagram of the vertical 4-electrode plasma source: a) side view, b) top view

Figure 3. Schematic diagram of the vertical 6-electrode plasma source (top view).
concentric quartz tubes (inner and sample introduction tubes) and three pairs of 2\% thoriated tungsten electrodes.

A top view is shown schematically in Figure 3. With the proper choices of some of the experimental parameters such as the argon flow rate, the current, and the plasma length, the sample aerosol stream can be completely surrounded by hot plasma the same as in an ICP. For other experimental conditions, the sample stream may be so large that the plasma forms three separate parallel plasma columns with the sample stream in the center.

2.2 Electrical power system

2.2.1 Power supply

In the multi-electrode plasma sources, each adjacent pair of electrodes is powered by a separate DC power supply (TCR 40S45, Electronic Measurement Inc., Neptune, NJ). Due to the nature of the multi-electrode plasma source, well regulated DC power supplies are required in order to get a stable plasma. The specifications of this power supply are listed in Table 2. The TCR 40S45 power supply is a constant voltage/constant current automatic crossover source of regulated dc power. The voltage and current controls set the boundary limits for the output voltage and current, respectively. The relationship of load resistance to the control settings determines whether the power supply is operating in a constant voltage or constant current mode. Automatic crossover between constant voltage and constant current modes occurs at the following load resistance value:
Table 2. Specifications of DC power supply, single phase regulated TCR 40S45 with constant voltage / constant current automatic crossover

<table>
<thead>
<tr>
<th>Specifications</th>
<th>AC Input</th>
<th>DC Output</th>
<th>Output Ripple Voltage</th>
<th>Stability</th>
<th>Transient</th>
<th>Temperature Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>115 V plus or minus 10%</td>
<td>Voltage : 0 - 40 V</td>
<td>100 mV a full load</td>
<td>The output voltage or current will remain with 0.05% for 8 hours after warm-up, with constant external effects</td>
<td>Upon instant application of loads up to 50% or the maximum rating of the supply, the output voltage will typically recover to within 1.0% of its final value within 50 ms.</td>
<td>Voltage : 0.02% per degree of °C</td>
</tr>
<tr>
<td></td>
<td>47 - 63 Hz</td>
<td>Current : 0 - 45 A at 40°C</td>
<td></td>
<td></td>
<td></td>
<td>Current : 0.03% per degree of °C</td>
</tr>
</tbody>
</table>
Load resistance (ohms) = \frac{\text{Voltage Control Setting (V)}}{\text{Current Control Setting (A)}}

At a higher load resistance, the power supply operates in the constant voltage mode and at a lower resistance in the constant current mode. In addition to the constant voltage and constant current modes, several different modes of operations are included in this power supply for different kinds of applications. Its mode of operation can be selected by making strap connections between terminals on the terminal strip which is bolted to the rear panel of the power supply. The pin description of the terminal strip is shown in Table 3.

The normal mode of operation is usually used in the our application. The pin connections of the terminal strip for the normal mode of operation are shown in Figure 4.

Other modes of operations may be selected based upon applications. The remote sensing mode of operation may be selected in applications where the effect of the voltage drop (IR) of the dc load wires would adversely affect the performance of the load, and it would be possible to sense the voltage at the load instead of the output terminals of the power supply. This power supply may also be operated in a remote programmed mode (externally controlled) by the use of an external resistance, voltage, or current. With parallel or series modes of operations, currents or voltages from more than one power supply can be combined. In the parallel mode of operation, the power supply designated the master is used to control the voltage and current operation of the other supplies.
Table 3. The pin description of the terminal strip in TCR 40S45 DC power supply.

<table>
<thead>
<tr>
<th>Pin Number</th>
<th>Pin Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+ Voltage (+V)</td>
</tr>
<tr>
<td>2</td>
<td>+ voltage Remote (+V REM)</td>
</tr>
<tr>
<td>3</td>
<td>Voltage Programming Current (V PROG I)</td>
</tr>
<tr>
<td>4</td>
<td>Voltage Amplifier (V AMP IN)</td>
</tr>
<tr>
<td>5</td>
<td>Voltage Programming Resistive (V PROG R)</td>
</tr>
<tr>
<td>6</td>
<td>Voltage Programming Resistive Common (V PROG R COM)</td>
</tr>
<tr>
<td>7</td>
<td>- Voltage Remote (-V REM)</td>
</tr>
<tr>
<td>8</td>
<td>- Voltage (-V)</td>
</tr>
<tr>
<td>9</td>
<td>Current Programming Current (I PROG I)</td>
</tr>
<tr>
<td>10</td>
<td>Current Amplifier (I AMP IN)</td>
</tr>
<tr>
<td>11</td>
<td>Current Programming Resistive (I PROG R)</td>
</tr>
<tr>
<td>12</td>
<td>- Shunt (-I)</td>
</tr>
<tr>
<td>13</td>
<td>Inverted Amplifier (IN AMP IN)</td>
</tr>
<tr>
<td>14</td>
<td>+ Shunt (+I)</td>
</tr>
</tbody>
</table>
Figure 4. Pin connection for normal mode operation in the TCR 40S45 power supply.
2.2.2 Electrical circuit

The electrical circuits for the multi-electrode plasma sources are relatively simple. As shown in Figure 5, adjacent pairs of electrodes in the horizontal 4-electrode plasma source are powered by separate DC power supplies. For easy ignition of the plasma in the current regulation mode, variable resistors, rheostats (Ohmite, Radar Electric, Portland, OR), were employed. Each rheostat installed in series in the circuit is rated at 500-watt, 22.3-A, 1-ohm, and is 8-inches in diameter. Two rheostats are connected in parallel with each other to handle high current flows up to about 45 A for each pair of electrodes. Two rheostats connected in parallel is equivalent to a 0.5-ohm and 1000-watt resistor for each pair of electrodes. The multi-electrode plasma ignites most easily when the rheostat for each pair of electrodes is set between 0.35 ohms to 0.5 ohms. After ignition of the plasma, each rheostat is reset to a lower value (i.e., less than 0.3 ohms) of resistance in order to reduce the power dissipation across each rheostat. Voltage and current meters (Simpson Electric Co., Chicago, Illinois) installed in the circuit are used to monitor changes in the rheostats and to help determine power dissipation in the plasma.

Basically the electrical circuits for the vertical 4- and 6-electrode plasma sources are exactly the same as those for the horizontal 4-electrode plasma source except for the number of electrodes and power supplies.

2.2.3 Electrode and electrode holder

In the horizontal 4-electrode plasma source, the plasma arcs are
Power Supplies: TCR 40S45
(Electronic Measurements, Inc.)

Figure 5. Electrical circuit for the horizontal 4-electrode plasma source.
formed between two pairs of 2% thoriated tungsten electrodes (Tungsten Electrodes, Teledyne Wah Chang, Huntsville, Alabama) with the ends of the electrodes at the corners of a horizontal square. Power dissipation is typically 500 W for each pair of electrodes. Each pair of electrodes consists of one 1/16-inch and one 3/32-inch diameter electrode. Each electrode is ground finished and 7-inches in length. Due to the faster erosion rate of the cathode, the larger diameter is used for the cathode. In general, the erosion rates of the 1/16- and 3/32-inch diameter electrodes with typical experimental conditions are 0.36 mm/h and 0.009 mm/h, respectively. The ends of the electrodes are initially flat and 6.0 mm apart from each other. Since polarities of each electrode pair on each side are opposite, a "half-donut" shape plasma column is expected on each side of plasma due to the existence of the magnetic repulsion force between the two horizontal plasma columns. However, it was observed that the shape of the plasma was affected more by the argon gas flow pattern than by the magnetic repulsion force.

Since there is less than a 0.5-mm gap between the inner quartz tube and the electrode, it is very important to position the electrodes very precisely. Otherwise not only will the inner quartz tube be melted by direct contact with hot plasma but also the shapes of the plasma will be distorted, which results in bad analytical performance. The two baseplates of MACOR\textsuperscript{TM} (Leed Plastics Corporation, Los Angeles, CA) were used to adjust the height and the position of the electrodes in the plasma torch precisely. The electrodes can be moved freely through holes in the upper MACOR baseplate, which is attached at the bottom of the outer aluminum block.
with an O-ring and a pair of set screws in order to get enough space between the electrode and the inner quartz tube. Each of the electrodes is secured in place by an aluminum block electrode holder through which electrical contact is also established. Electrical contacts to both the cathode and anode are established to the aluminum blocks by 4.76-mm diameter stainless steel screws. The electrodes in the torch are cooled by tangentially injected argon gas. The lower baseplate is employed to hold aluminum block electrode holders firmly in position. Each of the aluminum block electrode holders can be freely moved to adjust the distance between the two electrodes and the shape of the plasma. The lower baseplate is attached to a translation stage with a micrometer adjustment so that the height of the electrodes can be controlled easily and precisely. Due to the nature of the MACOR, the plasma torch assembly is also electrically isolated from the electrodes.

In the vertical 4-electrode plasma source, a pair of electrodes is positioned at the top of the plasma quartz tube with an angle of 45 degrees to the vertical as shown in Figure 2. For effective cooling of the upper electrodes, these electrodes are located in water cooled blocks. The upper electrodes can be moved relative to each other for ignition. The upper electrodes holders are made of bronze and continually water cooled at a water flow rate of 900 mL/min, Figure 6. The cooling water supply assembly consists of a submersible coolant pump with a 117 VAC drive motor in a 15-gallon glass vat. Argon gas is introduced around electrodes not only to cool the electrodes but also to reduce oxidation of the electrodes and lower the voltage drop by excluding air. As in the commercial DCP
Figure 6. Schematic diagram of upper electrode holder for the vertical multi-electrode plasma sources.
A pair of 1/16-inch diameter upper electrodes and a pair of 3/32-inch diameter lower electrodes are used in this torch configuration. Power dissipation with typical experimental conditions is about 600 W for each pair of electrodes. The erosion rates of the upper and lower electrodes are about the same as those in the horizontal 4-electrode plasma source. As in the horizontal 4-electrode plasma source, two MACOR baseplates attached to a micrometer translation stage are employed to adjust the height of the plasma and position the electrodes in the plasma torch precisely. The MACOR baseplates have the proper sizes of holes for the sample introduction tube and the lower electrodes so that they can freely slide through them without loss of argon gas.

In the vertical 6-electrode plasma source, as described above, the only difference from the vertical 4-electrode plasma source is the number of electrodes. This plasma configuration consists of three 1/16-inch and three 3/32-inch diameter electrodes for the upper and lower electrodes, respectively. Power dissipation across the electrodes on each side is typically 500 W. All of the upper electrode holders are placed on a stainless steel base so that the angles of the electrode holders can be independently controlled. In this way, the noise associated with the well defined sample aerosol excitation zone, which can be disturbed by the upper argon gas stream,
can be minimized and thus a more stabilized plasma is obtained. By moving the stainless steel base up and down, the angles of electrodes can be selected. Usually angles between 30-45 degrees were used.

2.3 Gas flows and operating arcs

2.3.1 Horizontal 4-electrode plasma source

There are three different argon gas flows. Four L/min of plasma argon gas is introduced into the annular space between the inner quartz and sample introduction tubes. Plasma argon gas is ionized by electrical energy and forms two parallel plasma columns. A tangential flow of argon is introduced at a rate of 1 L/min into the annular spacing between the inner and outer quartz tubes so that vortex stabilization of the plasma can be established. This vortex stabilization technique is suggested by Reed [77]. In addition to the vortex stabilization, this stabilization argon gas in the horizontal 4-electrode plasma source is also used to push the parallel arcs toward the center of the sample aerosol stream to get good contact between the arcs and sample. This stabilization argon gas is mainly used to change the shapes and positions of the parallel arcs.

Positional instability of the apex of the plasma was observed in the horizontal 4-electrode plasma source because of the turbulence of the stabilization argon gas flow. This kind of positional instability of the apex of plasma is very similar to that observed in the first commercial 2-electrode DCP spectrometer [78,79], which resulted in the development of a new source in which two independent plasma jets with a single common cathode are burnt to form an inverted Y configuration with great positional stability.
Sample aerosol carrier argon gas is introduced at the rate of 1.0 L/min to transport sample aerosol through the sample introduction tube positioned at the center of the torch. Since a Meinhard concentric nebulizer is used to produce the aerosol, at least 0.7-1.0 L/min of sample carrier gas flow is required in this plasma torch system. However, since the two parallel arcs are oriented exactly perpendicular to the direction of the upward sample aerosol stream, the fast flow rate of sample carrier gas causes fluctuation of the arcs, resulting in noise and drift in the analytical signals or even extinction of arcs eventually. As a result, the sample aerosol stream must be split and thus only a small portion of the sample aerosol stream is introduced into the plasma for excitation. This will be discussed in detail in the Sample Introduction section. The total argon flow required is therefore about 6.0 L/min.

To ignite the plasma, at first each rheostat is adjusted to about 0.5 ohms for easy ignition. The lower electrodes are raised up just above the top of the inner quartz tube, and argon gases and power are turned on in that order. Then a 6.0-mm diameter graphite rod is inserted between two electrodes momentarily to establish electrical contact [80,81]. When the arc has been struck, the graphite rod is removed and each rheostat is reset to about 0.3 ohms to reduce the power dissipation across the rheostat. Once the two parallel arcs are established, the electrodes are lowered down and the gas flow rates, current, and height of the sample introduction tube are adjusted to get the best analytical performance. At least 10-15 min of warm-up time is necessary to stabilize the plasma. Then sample aerosol produced by the Meinhard concentric nebulizer is introduced between
the two parallel plasma arcs to be excited and emit its characteristic analytical signals.

In our experiments, a 8.0-mm distance between the top of the outer and inner quartz tubes is chosen. The ends of the electrodes and the tip of the sample introduction tubes are usually 4 and 6 mm below the top of the outer quartz tube, respectively. By means of the one-factor-at-a-time optimization method, the above positions of the three quartz tubes and the electrodes were found to be the optimum experimental conditions.

2.3.2 Vertical 4- and 6-electrode plasma sources

Basically the gas flows, and the way to operate the plasma for both the 4- and 6-electrode plasma sources are exactly the same except for the number of electrodes. In both the 4- and 6-electrode plasma sources, there are three different gas flows. As in the horizontal 4-electrode plasma source, 4-5 L/min of plasma gas is tangentially introduced into the annular space between the plasma quartz tube and the sample introduction tube and is ionized by electrical energy supplied by two or three separate DC power supplies. In order to sustain the vertical plasma discharge, at least 2 L/min of plasma argon gas is necessary for the vertical multi-electrode plasma sources.

In contrast with the horizontal 4-electrode plasma source, the fast flow rate of sample carrier argon gas does not effect the stability of the plasma at all due to the nature of the vertical 4- and 6-electrode plasma sources. Therefore, with the Meinhard concentric nebulizer 0.7-1.0 L/min of sample carrier argon gas has
been used in most of our applications without any problem.

In each upper electrode holder, about 0.5 L/min of argon gas is introduced around the upper electrode. Then the electrodes are cooled and the ceramic sleeves are protected from melting by contact with hot plasma as well as from oxidation by air. The total flow rates of argon gases for the upper electrodes in the vertical 4- and 6-electrode plasma sources are therefore 1.0 and 1.5 L/min, respectively.

The vertical plasma arcs can be established by either direct contact with each other or insertion of the graphite rods between the cathode and anode momentarily. However, even though the vertical plasma can be established by direct contact between electrodes as is done in the commercial 3-electrode DCP spectrometer, in the most of the our applications the plasma discharge has been established by inserting the graphite rod between two electrodes because this is easier. As a matter of fact, in our experiment the ignition by direct contact with each electrode was not successful because it was difficult to position both the upper and the lower electrodes precisely. As a result, sometimes only one or two plasma discharges are established and then the graphite rod is employed to ignite the other plasma discharges. After the ignition of the plasma, the upper electrodes are completely withdrawn into the ceramic sleeves and the height of the lower electrode is adjusted to get the proper plasma length columns.

In the vertical 4-electrode plasma source, the two vertical columns of arc are formed on either side of the vertically rising sample stream. However, as shown in Figure 7, the two vertical
Figure 7. Formation of two vertical columns of plasma with the sample stream in the vertical 4-electrode plasma source (Without sample stream, the plasma appears as a vertical sheath.)
columns of arc are combined together when no sample is introduced. For the given experimental conditions, the degree of separation of each vertical column of arc mainly depends upon the velocity of the sample carrier gas in the plasma torch. The faster the velocity of the sample carrier argon gas, the greater the separation from each other. Of course, the flow rate of the sample carrier argon gas is not the only factor to affect the degree of separation of the vertical columns of arc. As the power dissipation across the electrodes is increased, the vertical columns of arc get thicker. As a result, the sample aerosol stream hardly penetrates through the plasma discharge. Eventually the vertical columns of arc combine with each other. And as the length of the plasma is increased by moving the lower electrodes down, the upper portion of the plasma also tends to combine because the sample carrier gas stream becomes weaker as it travels upwards. Therefore, the sample aerosol stream does not reach the upper portion of the plasma discharge and spreads out to the open air. These three experimental parameters are very significant in shaping the structures of the vertical columns of arc.

The sample uptake rate, the plasma gas flow rate, the observation height, and the variables described above were all optimized by means of a modified simplex optimization procedure [82-92]. The optimization criterion was the line-to-background ratio of the emission intensity at the Ca(II) 393.37 nm.

2.4 Sample introduction

2.4.1 Aerosol generation

Sample introduction with the multi-electrode plasma sources is in
many ways similar to that with the ICP. Among the several types of nebulizers, a Meinhard concentric glass nebulizer model TR-50-C1 (J. E. Meinhard Inc., Santa Ana, CA) is used in our applications. An input pressure of the carrier argon gas of 40 psig is required to obtain a flow rate of 1.0 L/min. The sample carrier gas flow is fed from its own gas cylinder thus enabling independent flow regulation. The gas flow is controlled by means of pressure regulators and flow meters. A mass flow meter (Tylan Corp., CA, Model FM 360) is employed to monitor the gas flow rate. The flow meter facilitates control of the sample carrier gas flow rate to within 1%, over a range between about 0.5-1.0 L/min. Such a precise control of this flow rate was found convenient, primarily to ensure high reproducibility of the conditions for the multi-electrode plasma sources during simplex optimization and interference measurements.

The sample solution is pumped to the Meinhard concentric nebulizer using a 4-channel Gilson Miniplus 2 peristaltic pump (Gilson International, France) in order to ensure a constant uptake rate irrespective of the liquid level in the sample beaker or of the viscosity of the liquid sample. This pump has 10 rollers to minimize pulsation of nebulization. Two pieces of 0.76-mm I.D. Tygon PVC tubings are employed to deliver a liquid sample to the Meinhard concentric nebulizer as well as to drain a waste sample. The pumping speed is regulated by a three-digit potentiometer and continuously adjustable from 1 to 25 RPM, which corresponds to 0.1- to 1.3-mL/min sample uptake rate.

A Scott type [93] spray chamber (Spray Chamber PN 5037, Plasma-Therm, Kresson, NJ) is employed with the Meinhard concentric
nebulizer so that fluctuations in the aerosol are reduced by separate forward and reverse aerosol flows. With a spray chamber a small portion of the atomized sample is delivered to the plasma while the larger droplets deposit on the walls and are drained away. Particularly in multi-electrode plasma sources the design of the spray chamber is important to the stability of the plasma. This is due, in part, to its ability to control the amount and size of sample aerosols delivered to the plasma.

2.4.2 Performance of multi-electrode plasma sources

In vertical 4- and 6-electrode plasma sources, by means of a modified simplex optimization procedure [82-92], the optimal experimental conditions are found to be at a sample uptake rate of 1.3 mL/min (about half of the free uptake rate) and a sample carrier gas flow rate of 0.702 L/min. The Meinhard concentric nebulizer and Scott type spray chamber described above are suitable with the optimized sample carrier gas flow rate for the vertical 4- and 6-electrode plasma sources. However, in the horizontal 4-electrode plasma source, the sample introduction system described above does not work very well. As discussed previously, due to the nature of the horizontal 4-electrode plasma source, the 0.8-1.0 L/min gas flow rate required for the best performance of the Meinhard concentric nebulizer causes fluctuation of the two horizontal plasma arc columns and also provides a relatively short residence time for the analyte species. Figure 8 shows the different shapes of two horizontal plasma columns with slow and fast sample carrier gas flow rates. With the fast flow rate, the region of the sample aerosol stream is expanded, which results in
Figure 8. Influence of sample carrier gas flow rate on the shape of the plasma columns in the horizontal 4-electrode plasma source. (a) slow flow rate (b) fast flow rate
lowering its contact with the plasma. In addition to that, the relatively fast velocity of the sample carrier gas does not provide enough time to atomize and excite the sample aerosol. As a result, the analytical performance of the horizontal 4-electrode plasma source with the relatively fast flow rate is not good, even if really small fine droplets are produced with the Meinhard concentric nebulizer. Positional instability of the apex of the plasma, which is very similar to that observed in the first commercial 2-electrode DCP spectrometer, is also observed. As a result, 1.0 L/min of sample carrier gas flow rate which is necessary to generate fine sample aerosols causes instability, relatively short residence time, and eventually extinguishes the plasma. In addition, although a slow flow rate, 0.2-0.5 L/min, stabilizes the plasma and helps to get better contact with the plasma columns, it is almost impossible to make fine sample aerosols with the present Meinhard concentric nebulizer using such a low flow rate. Therefore, significant volatilization interferences are observed with the large fraction of aerosol droplets produced by the low flow rates. As a matter of fact, emission line intensity of Cu(I) at 327.4 nm is undetectable with such a low flow rate.

In the multi-electrode plasma sources, the sizes and shapes of the plasma columns and the sample aerosol stream are dependent upon a number of parameters, including plasma and sample carrier gas flow rate, current dissipated across the electrodes, tip size of the sample introduction tube, and electrode diameter. Especially the shapes of the plasma columns and the sample aerosol stream are significantly affected by the sample carrier gas flow as discussed above. Due to
the nature of the horizontal 4-electrode plasma source, low flow nebulizers such as the Babington [94-96] nebulizer and the fritted-disk [97] nebulizer would be required for the best analytical performances with the present design. These nebulizers work typically with 0.2-0.5 L/min argon gas flow rates.

In our experiment to overcome the problems associated with the high flow of the Meinhard concentric nebulizer, a bypass tube was used to direct some of the flow away from the plasma sample introduction tube. By splitting the sample stream into two parts with the by-pass system, the plasma can be operated without any problem since only a small portion of sample aerosol stream is introduced into plasma torch. As a result, the sample throughput into the plasma torch can be readily controlled so that optimum conditions for operation are obtained. The sample introduction system with the by-pass seems to work very well with the horizontal 4-electrode plasma source except for pulsation due to the condensation of sample droplets inside the small by-pass tubing. Drops formed inside of the by-pass tubing cause pulsations of drain liquid and eventually the resulting pressure variations affect the magnitudes of the emission line intensities. The problems associated with the sample introduction system in the horizontal 4-electrode plasma source are the primary causes for poor analytical performance of this kind of plasma source.

2.5 Spectroscopic measurement systems

2.5.1 Introduction

The demands on spectrometers for plasma spectroscopy can be quite different from those encountered in other applications of quantitative
spectroscopy. The relatively broad lines encountered in plasma spectroscopy somewhat alleviate the need for high resolving power. Lines emitted from local thermal equilibrium (LTE) plasmas in the visible range are usually not much narrower than 0.02 nm because of collisional and Stark broadening, almost always much more important than Doppler broadening, and because of hyperfine structure. Only toward shorter wavelengths and in non-LTE plasmas does Doppler broadening tend to be the dominant collisional and stark broadening, but lines are usually still not much narrower than 0.01 nm, except for lines in the vacuum-ultraviolet range and below. However, at high temperatures, all chemical bond energies are exceeded and only atoms and ions exist. Usually the temperature of an atmospheric argon plasma is in the range 4000-10000 K and this high temperature plasma produces much excitation of energy levels. Therefore, spectral interferences will be present because of the richness of spectral lines at the plasma temperature. Furthermore, some stray light is more of a problem in plasma spectroscopy than in other atomic spectroscopy techniques because of the richness of the spectra. As a result, plasma spectroscopy would not be a powerful and useful analytical technique without a high resolution spectrometer to separate the many hundreds of spectral lines resulted from many elements emitting light simultaneously.

In our application a high resolution echelle spectrometer manufactured by Leeman Labs Inc. was used to isolate the analytical lines. The utilization of an echelle spectrometer incorporating a combination of an echelle grating and an order-sorting prism to obtain a two-dimensional spectral array has emerged rapidly during the past
decade. The advantages of an echelle spectrometer are the high resolution available while maintaining a larger aperture (low f-number) and the ability to select a wavelength-order combination within the range of maximum grating efficiency for the most sensitive atomic lines of nearly all elements. Especially the advantages of an echelle spectrometer have been recognized when high background atomization or excitation sources such as the nitrous oxide/acetylene flame or various plasma sources are used, and actually significant improvement in detection limits has been achieved in the direct current plasma spectroscopy. With the Plasma Spec high resolution echelle spectrometer (Leeman Labs Inc., Lowell, MA), the mercury doublet at 313 nm with a separation of 0.029 nm is essentially completely resolved in the 72nd order. Also spectral interferences, such as Ti 235.46 and 235.51 nm on Sn 235.48-nm atomic emission, or Al 309.35 nm on V 309.31-nm atomic emission, are eliminated as shown in Figure 9. A molecular band emission such as CaOH is completely resolved from Ba 553-nm atomic emission. And also with its excellent dispersion, the echelle spectrometer can use relatively large slits, resulting in high energy throughput and better performance. Since multi-electrode plasma sources are high temperature and high background excitation sources, the important practical properties, such as excellent resolution and high energy throughput, of an echelle spectrometer are of great importance in our application.

2.5.2 Dispersive device

The echelle grating was first described by G. R. Harrison [98] in 1949 and led to the development of a commercial system in 1953 [99].
Figure 9. Spectrum indicating excellent resolution for the Plasma-Spec Echelle Spectrometer: a) 1 ppm Sn, using a line at 235.48 nm, is resolved from strong lines from 1000 ppm Ti at 235.46 and 235.51 nm. b) Strong Al interference 0.04 nm from V at 309.31 nm.
Other commercial echelle spectrometers were introduced in 1970's [100,101]. Each of these was originally intended primarily for use in atomic emission spectrometry. A DC plasma as the excitation source [100-102] was combined with later versions of the echelle spectrometer to take advantage of plasma spectroscopy. The echelle optical design represents a break-through in spectrometers with very high dispersion being achieved without loss of efficiency. This high energy throughput is the result of all wavelengths being read at or very near the blaze angle, regardless of their wavelength. With the spectrometer operating in multiple orders, the angular change in the dispersed rays in any one order is relatively so small that all wavelengths are measured at or near their optimum blaze angle. As a result, physical dimensional constraints are eliminated with the two-dimensional spectral pattern resulting from the use of echelle optics and thus optical stability is increased because of its short focal length.

In the Plasma-Spec high resolution echelle spectrometer, radiation emitted from a source is focused on a MgF$_2$ coated spherical source mirror controlled by a computer and passed through a relatively large entrance slit in order to ensure high energy throughput. In order to improve resolution in other spectrometers, sometimes a very narrow entrance slit is used, thereby reducing the amount of light energy reaching the detector. As a result, good resolution and high energy throughput have to be compromised for the best analytical performance in conventional spectrometers using fine ruled or holographic gratings. Because of excellent dispersion, an echelle spectrometer can use a relatively large entrance slit,
resulting in high energy throughput. The Plasma-Spec dispersion system typically uses 80-µm entrance and 40-µm exit apertures achieving an average spectral resolution of 0.01 nm. The typical resolution of Plasma-Spec echelle spectrometer is 0.0075 nm (at 200 nm) to 0.024 nm (at 800 nm). A MgF₂ coated spherical concave mirror is used as a collimating mirror in order to focus radiation into echelle grating.

The echelle is a coarse but precisely ruled diffraction grating, coated with MgF₂, having broad flat grooves, 79 grooves/mm, which is used at high angles of incidence and is blazed at an angle of 63°26'. In an echelle the spacing from one step to the next is much greater than the wavelength of the light being dispersed. Consequently, many overlapping orders of radiation leaving the grating are inevitable. Thus the many higher orders must be separated from each other in some way, which is not generally necessary in conventional spectrometers. This is accomplished by placing a second dispersing element, usually a single pass, focusing, and cross-dispersion prism, in the spectrometer so that the prism disperses wavelengths perpendicular to the direction of the grating wavelength dispersal and thus effectively separate the orders. The use of a single-pass prism/lens with echelle grating also minimizes stray light by reducing first surface reflection.

The wavelength-dispersed and order-separated radiation with the echelle grating is then reflected from a plane mirror to the exit slits on an aperture plate. The aperture plate is tilted to match the focal plane so that proper focusing at different wavelengths is ensured. High dispersion of all wavelengths from 190 to 800 nm in a compact array is obtained on the aperture plate by the two-dimensional
display. Usually the high orders, approximately 30 to 120, are used to provide the high dispersion of the system for quantitative as well as qualitative analysis.

The Plasma-Spec echelle spectrometer has fixed-optics to improve stability. The detector is moved to the focal point for the desired wavelength in the desired order on the aperture plate. In other echelle spectrometers and conventional spectrometers, usually wavelength scanning is done by rotating components in the optical path so that an image of the desired wavelength and/or order is selected and passed across a fixed detector. However the mechanical changes in the optical path in the echelle spectrometer are very difficult to do reproducibly. In addition the difficulties associated with moving a grating over very small angles and trying to peak on a spectrum line at trace concentration levels or when elements being investigated have strong adjacent lines will be minimized with the fixed-optics spectrometer.

2.5.3 Signal measurement and detection system

Since the Plasma-Spec echelle spectrometer has fixed-optics, the detector has to move to the proper focal point of the desired spectral line. There are hundreds of pre-set exit slits photoetched on the aperture plate and the locational information of the exit slits is stored in permanent computer memory. Each spectral line has its own spectral exit slit in the selected order. Recently a new aperture plate was developed in order to be able to access any emission line between 190 and 800 nm. With either aperture plate when an element wavelength is selected, the computer retrieves the corresponding X-Y
coordinates and drives the detector to that position. Therefore, the
detector and aperture plate containing pre-set apertures must be
positioned precisely so that optimized analytical data can be
obtained. However due to mechanical vibrations and temperature
fluctuations, sometimes unsatisfactory results may be obtained.

As a result, a quality control procedure is necessary in order to
maintain alignment of the instrument. For this purpose, a mercury
light source is built into the Plasma-Spec spectrometer. An aperture
plate alignment on an operator selectable (0 to 99 minutes) time basis
is initiated either automatically by computer or manually. During the
quality control procedure, a computer based on a Zilog Z-80
microprocessor initiates an automatic aperture plate alignment with
respect to the mercury reference line at 296.7 nm. Any adjustments
required in the position of the aperture plate are made as necessary
by the computer to assure the exact position of this peak in the X-Y
plane of the aperture plate. And then these adjustments made in the
alignment routine are stored in the computer for further use in
aperture plate alignment routines for the other spectral lines. Two
computer directed micro positioners that move the aperture plate
horizontally and vertically are employed for the purpose of aperture
plate alignment. The alignment routine described above can be done at
any time manually by depressing the PEAK key on the keyboard of the
spectrometer.

To optimize the position of the source mirror in the Plasma-Spec
spectrometer, a different type of the alignment routine, Peak Source X
and Peak Source Y, can be selected by the operator. The source mirror
controlled in the X and Y directions by computer directed micro
Positioners will be peaked to position the source image on the entrance slit. After the peaking for the both directions, the intensity profiles along with the X and Y directions will be displayed on the CRT screen and then the peak routine automatically shifts the peak to the centers for both directions. Spatial distribution profiles, such as the horizontal and vertical spatial profile of emission intensity, line-to-background ratio, or excitation temperature were readily obtained with the use of this computer controlled source mirror. Scanning across the plasma for both X and Y directions was accomplished by interfacing the spectrometer computer to a PDP 11-73 computer. Thus more stable experimental data were collected.

A wide range photomultiplier tube that covers 190 to 800 nm with a consistently high signal-to-background response (Hamamatsu Inc., Model 1463) is used. The size of the detector is so small (0.5 inches diameter and 3 inches length) that up to 45 photomultiplier tubes could be readily positioned at the appropriate exit slits on the aperture plate for simultaneous multiple determinations.

2.5.4 Operation modes and computer control system

Three modes, sequential multielement analysis, simultaneous multielement analysis, and combined system modes, are available in a Plasma-Spec echelle spectrometer. The basic procedures for both the sequential and simultaneous multielement modes are based on a sequential single element procedure. Up to 20 or 45 elements in a single sample can be analyzed in less than one minute by a sequential or simultaneous mode, respectively. In the sequential multielement
analysis, after each element the detector moves to the next selected wavelength automatically by computer and the single element procedure is repeated. In the simultaneous multielement mode, a bank of up to 45 fixed-position photomultipliers, above a masking aperture plate, monitors wavelengths simultaneously. Therefore time consuming, peak seeking routines are eliminated due to the nature of the fixed-optics in Plasma-Spec echelle spectrometer. Thus less than 1 sec is needed to move the detector from one wavelength to the next and time required for typical analyses is relatively very fast. Typical analysis time is about 85 sec for 10 elements with three 2-sec integrations each. Therefore in the case of 10 elements per sample, typical analytical speed including rinse time between samples is 25 or 60 samples per hour by the sequential or simultaneous modes, respectively. In order to take advantage of combining high sample throughput and versatile wavelength selection, both simultaneous detectors and a scanning detector may be present in a single echelle spectrometer. In either mode, precision and detection limits are the same for both because the same fixed optics and detection system are used for both modes.

In the Plasma-Spec echelle spectrometer, a computer based upon a Zilog Z-80 microprocessor is used for aligning the spectrometer, data acquisition, display, manipulation, and optional operation by operator interface. The control software are written in machine code with 8085 language and designed for ease of those operations. The following functions are controlled by the computer.

As described before, aligning the spectrometer is initiated by the computer. The optical alignment routine using the mercury lamp can be initiated by the operator or on a pre-set time schedule.
selected by the operator in order to maintain optical alignment of the spectrometer. A "peak wavelength" routine critically aligns the selected analytical wavelength. A "peak source X and Y" routine automatically positions the source image on the entrance slit for signal optimization horizontally and vertically. For data acquisition, display, and manipulation including generating and using a calibration curve, a series of analytical programs are stored in programmable read-only memory chips. More importantly, the ability to execute each routine separately provides great versatility to our application.

A choice of menus allows entry to various levels of the operational program. The higher level menu, EXPERIMENTAL, provides both a high degree of automation and versatility by interfacing with the PDP 11/73 computer via a serial port. The pseudo code, PCODE (program operation code), is used while converting program operation into machine code. All experimental data throughout our research were obtained and manipulated by the EXPERIMENTAL operation with several software programs written for the PDP 11/73 computer.
IV. ANALYTICAL CHARACTERIZATION OF THE SAMPLE ENTRAINING
MULTI-ELECTRODE PLASMA SOURCES FOR ATOMIC EMISSION SPECTROSCOPY

PART I: PRELIMINARY STUDIES

by

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The analytical capabilities of several multi-electrode plasma sources are evaluated. Multi-electrode plasma sources use electrodes to shape the plasma in order to entrain a sample stream in the center of hot plasma over long periods of time, in a process similar to an inductively coupled plasma (ICP) source. In this way, the residence time can be readily adjusted to allow sufficient time to atomize and excite various types of aerosol samples without interruption, even if this becomes necessary during the operation of the plasma. Generally, a total of less than 6 L/min of argon gas is required to operate the plasma. In this study, the influence on the spatial profile of the Mg line emission intensity, and the line-to-background (L/B) ratios on the length of plasma, on the current, on the sample carrier gas flow rate, on the plasma gas flow rate, on the position of the tip of the sample introduction tube, and on the observation height are reported. The spatial emission characteristics of the multi-electrode plasma sources are very similar to those observed in the ICP. With the vertical 4-electrode plasma source, 4 to 5 orders of magnitude of linear dynamic range are obtained and detection limits for some elements are comparable to those obtained with an ICP. The residence time of an analyte species in the observation zone is about 23 msec with a plasma length of 25 mm. The short term stability of the plasma is less than 2%, when expressed as the relative standard deviation of a blank solution. These results suggest that the vertical multi-electrode plasma sources show great promise as new sources of excitation for atomic emission spectroscopy.
2. INTRODUCTION

Atomic emission spectroscopy is a generally accepted standard analytical technique, which may be used for all the metals and for certain nonmetals, such as boron and phosphorus [103-107]. Due to the nature of atomic emission spectroscopy, the source of excitation is a critical component in atomic emission measurement instruments. Both the pattern and the intensity of lines produced by a species are greatly influenced by the excitation source in an atomic emission spectrometer. As a result, the sources of excitation in emission spectroscopy must serve two basic functions. First, the sources must provide sufficient energy to desolvate and vaporize constituents of a liquid or a solid sample and to convert individual analyte species into gaseous atoms or ions. The second function is to provide sufficient energy to excite a fraction of the resulting gaseous atoms or ions to their higher electronic energy levels. It is essential that each of those processes are carried out in a reproducible manner.

The earliest energy sources used as sources of excitation were simple combustion flames. However, combustion flames often fail to provide sufficient energy to excite certain elements (e.g., refractory elements) and they are affected by background emissions and interference effects. Subsequently, electrical discharge sources such as DC and AC arcs and high-voltage spark systems were used to analyze solid samples because they are more sensitive than combustion flames. Since the arc and spark excitation processes have the virtue of providing information rapidly due to relatively simple sample preparation requirements, they have been primarily used for the direct
analysis of metals in production control. Arc excitation sources are used more for qualitative analysis than for quantitative analysis because of difficulties encountered in reproducing radiation intensities. The detection limits of the spark were relatively poor. Solutions were difficult to analyze by arcs and sparks. As a result, atomic emission spectroscopy did not share universal popularity with the atomic absorption technique during the 1960’s and 1970’s, particularly for liquid sample analysis. Recently the development of the dc argon plasma (DCP) and the inductively coupled plasma (ICP) techniques have caused a dramatic increase in the utilization of atomic emission spectroscopy. These techniques were initially developed as alternatives to atomic absorption and such techniques as arc and spark atomic emission spectroscopy. In a relatively short period of time, it was recognized that both the ICP and DCP techniques are often superior to other atomic emission spectroscopic methods as well as atomic absorption spectroscopy (AAS), in terms of the precision, accuracy, dynamic range, interference effects, and detection limits. In fact, the plasma spectroscopy technique is one of the best analytical methods to handle liquid samples because it does not exhibit many of the problems associated with the past sources of excitation.

However, both the initial and the operating costs for plasma emission techniques, especially the ICP source, are relatively expensive. The operating costs for an ICP are mainly gaseous or liquid argon for the nebulizer and gas flows (usually 12 to 20 L/min) to the torch. As a result, many scientists, including the commercial ICP manufacturers, have conducted extensive research for several years
in order to modify standard ICP torch design to reduce the radio-frequency power and the argon gas-flow requirements without sacrificing the analytical performance of the standard ICP torch [108-114]. Commercial plasma torches of reduced size, such as the ARL Minitorch™ (Applied Research Laboratories Inc., Dearborn, Michigan) and the MAK™ torch (Sherritt Gordon Mines Limited/Sherritt Research Centre, Alberta, Canada), are now available.

Most electrical plasma sources, especially in the case of the DCP, have also suffered from their inability to obtain sufficient contact between the hot plasma and the sample aerosol stream to provide adequate time to atomize and excite the sample aerosol [115,116]. Due to this apparent disadvantage in the DCP sample introduction system, the DCP source is less popular than the ICP source despite the less expensive initial and operating costs of the DCP technique. Furthermore, most electrical plasma sources suffer from high plasma background emission, limiting the powers of detection that may be achieved [117,118].

In our laboratory, research to develop plasma sources with multiple electrodes that entrain a sample stream in the center of hot plasma was initiated in 1976. After several modifications, 4- and 6-electrode plasma sources with a moderate argon consumption rate were developed in which the sample stream is surrounded by the hot plasma, as with the ICP source. In fact, the multi-electrode plasma sources could be classified as "DCP like ICP" because the torch design and sample introduction system are similar to the methods used with an ICP source, with the exception of the use of a DC power supply as the energy source. In this way, the problems described above can be
overcome by the use of electrodes to help control the shape of the plasma, which allows the efficient entrainment of an aerosol sample stream in the center of hot plasma over longer periods of time. Although spectral interferences from the electrode material atoms occasionally occur, the observation regions of the vertical multi-electrode plasma sources are not located in current-carrying columns, and high plasma background continuum emission is eliminated in the measurement of analytical signals.

In this study, 4- and 6-electrode plasma sources were characterized by investigating the emission profiles under different experimental conditions. Analytical results and the evaluation of these new excitation sources for atomic emission spectroscopy are reported. In the subsequent paper [119], several kinds of the interference effects and the spatial distribution of the excitation temperature of Fe (I) under different experimental conditions will be presented.

3. EXPERIMENTAL

The experimental facilities for the multi-electrode plasma sources are listed in Table 4.

3.1 Plasma tube arrangements

3.1.1 Horizontal 4-electrode plasma source

The horizontal 4-electrode plasma source consists of three concentric quartz tubes (outer, inner, and sample introduction tubes) and two pairs of 2% thoriated tungsten electrodes, with the ends of
Table 4. Experimental facilities for the multi-electrode plasma sources

<table>
<thead>
<tr>
<th>Experimental Facilities</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma tube assembly</td>
<td>Two or three concentric quartz tubes (cf. Fig 1, 2, and 3, and Table 1)</td>
</tr>
<tr>
<td>DC power supply</td>
<td>TCR 40S45 regulated DC power supply (Electronic Measurement Inc., NJ) with series 1-ohm and 22.3-A rheostat for easy ignition.</td>
</tr>
<tr>
<td>Electrodes</td>
<td>1/16- and 3/32-inch diameter 2% thoriated tungsten electrodes</td>
</tr>
<tr>
<td>Aerosol generator</td>
<td>Meinhard concentric nebulizer, model TR-50-C1 (J. E. Meinhard Inc., CA), with Scott type spray chamber.</td>
</tr>
<tr>
<td>Peristaltic pump</td>
<td>Gilson Miniplus 2 peristaltic pump (Gilson International, France), with 4 channels and 10 rollers to minimize pulsation.</td>
</tr>
<tr>
<td>Mass flow meter</td>
<td>Model FM 360 and FM 361 (TYLAN Co. CA) to control gas flow rates very precisely.</td>
</tr>
<tr>
<td>Spectrometer</td>
<td>Plasma-Spec high resolution echelle spectrometer (Leeman Labs Inc., Lowell, MA).</td>
</tr>
<tr>
<td>Computer</td>
<td>PDP 11/23, PDP 11/73 computers, and Corona computers for data acquisition and manipulation.</td>
</tr>
</tbody>
</table>
electrodes at the corners of a horizontal square (Figure 1). In general, the horizontal 4-electrode plasma torch has the same features as conventional ICP torches [120-124], that is, an assembly of three concentric quartz tubes with three gas flows. The dimensions of the three quartz tubes and the inner diameter of the gas inlet are listed in Table 1. In order to simplify maintenance, the plasma torches are constructed in a demountable manner, which is a technique that has been developed and tested by several researchers [125-130]. The plasma tube assembly is mounted in two aluminum blocks with a double o-ring seal around each tube. The inner aluminum block holds the outer quartz tube with three 4-40 set screws and the outer aluminum block holds the inner aluminum block with three 6-32 set screws. By moving the inner aluminum block (the outer quartz tube), the distance between the top of the inner and outer quartz tubes is adjustable from 7 mm to 13 mm. In addition, damaged parts, such as melted or broken quartz tubes may be readily replaced, and quartz tubes of various dimensions may be investigated with simple modifications of the plasma torch assembly.

3.1.2 Vertical 4-electrode plasma source

The vertical 4-electrode plasma source has two pairs of electrodes positioned so that two vertical columns of arc are formed on either side of a vertically rising sample stream, as shown in Figure 2. The upper electrodes are positioned at a 45° angle at the top of the inner quartz tube. The inner and sample introduction tubes are only employed in this design. The configuration of the plasma torch is the same as for the horizontal 4-electrode plasma torch, with
the exception of the positions of the electrodes and the number of quartz tubes used. This configuration was used to overcome several problems associated with the sample introduction system and the stability of the horizontal 4-electrode plasma torch. One of the advantages of the vertical 4-electrode plasma source is that the length of the plasma can be easily controlled by moving the lower electrodes up and down. Consequently, the residence time experienced by the analyte species can be adjusted to allow sufficient time to atomize and excite an aerosol sample, without interruption during operation of the plasma.

3.1.3 Vertical 6-electrode plasma source

The vertical 6-electrode plasma source is obtained by simply adding a pair of electrodes to the 4-electrode plasma source, and stationing the vertical pairs 120° from each other. A top view is shown schematically in Figure 3. In this way, the sample stream can be completely surrounded by hot plasma, just as in an ICP, or for some experimental conditions the sample stream may be so large that the plasma forms three separate parallel plasma columns with the sample stream in the center.

3.2 Electrical power system.

As shown in Figure 5, the electrical circuits for the multi-electrode plasma sources are relatively simple. In the horizontal 4-electrode plasma source, adjacent pairs of electrodes are powered by separate current-regulated DC power supplies. For easy ignition of the plasma with the current regulation system, rheostats
were employed. Two 1-ohm, 22.3-A rheostats are connected in parallel to handle high current flows, up to an approximate maximum of 45 A for each pair of electrodes. The multi-electrode plasma ignites most easily when the rheostat resistance for each pair of electrodes is set between 0.35 and 0.5 ohms. Following ignition of the plasma, each resistance is reset to a lower value, less than 0.3 ohms, in order to reduce power dissipation across each rheostat and make more power available for the plasma. Basically, the electrical circuits for the vertical 4- and 6-electrode plasma sources are exactly the same as those for the horizontal 4-electrode plasma source, except for the number of electrodes and power supplies.

3.3 Electrodes and electrode holders

3.3.1 Horizontal 4-electrode plasma source

In the horizontal 4-electrode plasma source, the plasma arcs are formed between two pairs of 2% thoriated tungsten electrodes, with the ends of the electrodes at the corners of a horizontal square. Typical power dissipation is 500 W for each pair of electrodes. Each pair of electrodes consists of one 1/16-inch and one 3/32-inch diameter electrode as anode and cathode, respectively. Their respective erosion rates are 0.36 mm/h and 0.09 mm/h.

Since there is less than a 0.5-mm gap between the inner quartz tube and the electrode, it is very critical that the electrodes be positioned with precision. Otherwise, not only will the inner quartz tube be melted by direct contact with hot plasma, but the shapes of the plasma will be distorted, resulting in poor analytical performance. Two MACORTM (Leed Plastics Co., Los Angeles, CA)
baseplates were used to precisely adjust the height and the position of the electrodes in the plasma torch. The electrodes can be moved freely through holes in the upper MACOR baseplate, which is attached at the bottom of the outer aluminum block with an o-ring and a pair of set screws. Each of the electrodes is secured in place by an aluminum block electrode holder, through which electrical contact is also maintained. The lower baseplate holds the aluminum block electrode holders firmly in position. Each of the aluminum blocks can be moved freely to adjust the distance between the two electrodes, thus controlling the shape and size of the plasma. The lower baseplate is attached to a translation stage with a micrometer adjustment so that the height of the electrodes can be easily and precisely controlled. Because MACOR is an insulator, the plasma torch assembly is electrically isolated from the electrodes.

3.3.2 Vertical multi-electrode plasma sources

In the vertical 4-electrode plasma source, a pair of electrodes is positioned at the top of the inner quartz tube at an angle of 45 degree from the vertical, as shown in Figure 2. For effective cooling purposes, the upper electrodes are located in water cooled bronze blocks, continually cooled at a water flow rate of 900 mL/min. The water cooling supply assembly consists of a submersible coolant pump with a 117 VAC drive motor. As in the commercial DCP spectrometer [131-134], ceramic sleeves are placed at the ends of the upper electrode holders in order to contain, direct, and shape the structure of the plasma and also prevent contact with sample aerosol. The ceramic sleeves have a 0.125-inch I.D., a 0.190-inch O.D., and
0.635-inch length. A pair of 1/16-inch diameter upper electrodes and a pair of 3/32-inch diameter lower electrodes are used in this torch configuration. Typical power dissipation between the electrodes is 600 W for each pair of electrodes.

In the vertical 6-electrode plasma source, the only difference from the vertical 4-electrode plasma source is the number of electrodes. This plasma configuration consists of three 1/16-inch and three 3/32-inch diameter electrodes for the upper and lower electrodes, respectively. Typical power dissipation between the electrodes on each side is 500 W. All of the upper electrode holders are placed on a stainless steel base so that the angles of the electrode holders can be independently controlled. By moving the stainless steel base up and down, the vertical angles of the electrodes can be selected. In general, angles between 30° to 45° from the horizontal plane were used in our application.

3.4 Gas flows

In the horizontal 4-electrode plasma source, there are three different argon gas flows. Plasma argon gas, at the rate of 3 L/min, is introduced into the annular space between the inner quartz and sample introduction tubes, where it is ionized by electrical energy and formed into two parallel plasma columns. A tangential flow of argon is introduced at a rate of 2 L/min into the annular spacing between the inner and outer quartz tubes so that vortex stabilization of the plasma can be obtained, as suggested by Reed [135]. This stabilization argon gas is also used to push the two parallel plasma columns toward the center of sample aerosol stream, resulting in good
contact between the plasma columns and the sample. However, the use of stabilization argon gas for positioning the two parallel plasma columns results in severe problems, which will be discussed below. For nebulization with a Meinhard concentric nebulizer, a flow rate of 0.7 to 1.0 L/min of sample carrier gas is used. Therefore, the total argon flow required in the horizontal 4-electrode plasma source is approximately 6.0 L/min.

In the vertical 4- and 6-electrode plasma sources, as in the horizontal 4-electrode plasma source, a flow rate of 2 to 3 L/min of plasma gas is tangentially introduced into the annular space between the plasma quartz and sample introduction tubes where it is ionized by electrical energy supplied by two or three separate DC power supplies. In contrast to the horizontal 4-electrode plasma source, the relatively fast flow rate (1 L/min) of sample carrier argon gas does not affect the stability of the plasma, due to the nature of the vertical multi-electrode plasma sources. In addition, a flow rate of 2 to 3 L/min of argon gas is used to shield the upper electrodes from contact with air. As a result, a total flow rate of 5 to 7 L/min of argon gas is required for the vertical multi-electrode plasma sources.

3.5 Sample introduction system

The introduction of the sample in multi-electrode plasma sources is in many ways similar to methods used for an ICP. For the application used in this study, a Meinhard concentric glass nebulizer, model TR-50-C1 (J. E. Meinhard Inc., Santa Ana, CA), was used. An input pressure of 40 psig is required to obtain a carrier argon gas flow rate of 1.0 L/min. The sample carrier gas flow is fed from its
own gas cylinder, enabling independent flow regulation. Gas flow is controlled by means of pressure regulators and flow meters. A mass flow meter (Tylan Corp., CA, Model FM 360) is employed to monitor the gas flow rate. The flow meter facilitates control of the sample carrier gas flow rate to within 1%, over an approximate range of 0.5 to 1.0 L/min. Precise control of this flow rate was convenient in ensuring high reproducibility of conditions during simplex optimization and interference measurements.

The sample solution is pumped to the Meinhard concentric nebulizer, using a 4-channel Gilson Miniplus 2 peristaltic pump (Gilson International, France), in order to assure a constant uptake rate irrespective of the liquid level in the sample beaker or of the viscosity of the liquid sample. The Miniplus 2 pump has 10 rollers which minimize the pulsation of nebulization. Two pieces of 0.76-mm I.D. Tygon PVC tubing are employed to deliver a liquid sample to the Meinhard concentric nebulizer, as well as to drain a waste sample. Pumping speed is regulated by a three-digit potentiometer and continuously adjustable from 1 to 25 RPM, corresponding to a 0.1- to 1.3-mL/min sample uptake rate. When a new sample is introduced, pumping speed can be temporarily increased with a switch to shorten the intensity equilibration time.

A Scott-type [136] spray chamber (Spray Chamber PN 5037, Plasma-Therm, Kresson, NJ) is employed with the Meinhard concentric nebulizer so that fluctuations in the aerosol are reduced by separate forward and reverse aerosol flows. With a spray chamber a small portion of the atomized sample is delivered to the plasma, while the larger droplets are deposited on the walls and are drained away. In
multi-electrode plasma sources the design of the spray chamber is of particular importance to the stability of the plasma, just as in an ICP and DCP. This is partially due to its ability to control the amount and size of sample aerosols delivered to the plasma.

3.6 Operating the multi-electrode plasma sources

To ignite the horizontal 4-electrode plasma, each series resistance is first adjusted to about 0.5 ohms for easy ignition. The lower electrodes are raised just above the top of the inner quartz tube, and the power and argon gases are turned on in that order. A 6.0-mm diameter graphite rod is then momentarily inserted between two electrodes to establish electrical contact. When the arc has been struck, the graphite rod is removed and each series resistance is reset to about 0.3 ohms to reduce the power dissipation across the rheostat. The vertical multi-electrode plasma arcs can be established by either direct contact with each other or by momentary insertion of the graphite rods between the cathode and the anode. After ignition of the plasma, the upper electrodes are completely withdrawn into the ceramic sleeves and the height of the lower electrode is adjusted to produce plasma columns of the desired length. After adjusting plasma length and gas flow rate to stabilize the plasma, the sample aerosol is introduced into the discharge.

3.7 Echelle spectrometer

The demands on spectrometers in plasma spectroscopy can be quite different from those encountered in other quantitative spectroscopy applications. At high temperatures, most chemical bond energies are
exceeded and only atoms and ions exist. The usual temperature of the plasma is in the range 4000 to 10000 K. Therefore, some severe spectral interferences will be present because of the richness of spectral lines at the high plasma temperatures. Furthermore, stray light is a problem in plasma spectroscopy more than in other atomic spectroscopy techniques because of the many spectral lines that can contribute to stray light. As a result, plasma spectroscopy requires a powerful spectrometer to isolate the analyte lines from the matrix and background emissions.

In our application a Plasma Spec high resolution echelle spectrometer (Leeman Labs Inc., Lowell, MA, 01854) was used to isolate the analytical lines. The advantages of an echelle spectrometer are the high resolution available while maintaining a larger aperture (low f-number) and the ability to select a wavelength-order combination within the range of maximum grating efficiency for the most sensitive atomic lines of nearly all elements. In particular, the advantages of an echelle spectrometer have been recognized when high background atomization or excitation sources, such as the nitrous oxide/acetylene flame or various plasma sources, are used [137]. Significant improvements in detection limits have been achieved in direct current plasma spectroscopy using the echelle spectrometer [138]. With a Plasma Spec high resolution echelle spectrometer, the mercury doublet at 313 nm with a separation of 0.029 nm, is essentially completely resolved in the 72nd order. In addition, spectral interferences, such as Ti 235.46 and 235.51 nm on Sn 235.48-nm atomic emission, or Fe 249.782 and W 249.748 nm on B 249.773-nm atomic emission, are eliminated. Molecular band emission of CaOH is completely resolved.
from the Ba 553-nm atomic emission line. Furthermore, with its excellent dispersion the echelle spectrometer can use relatively large slits, resulting in high energy throughput. Since multi-electrode plasma sources are high temperature and high background excitation sources, the important practical properties of an echelle spectrometer are of great importance in this study.

The high resolution echelle spectrometer was interfaced with the PDP 11/73 minicomputer via an RS-232 serial port interface. The PDP 11/73 minicomputer was used to control the stepper motor driven X-Y source mirror via the spectrometer's computer in order to obtain spatial distribution and also for purposes of data manipulation.

3.8 Standards preparation

The 1000 mg/L stock solutions listed in Appendix 1 are prepared with high purity metals or metal oxides as suggested by Dean and Rains [139]. An aliquot of each stock solution was diluted in order to obtain an appropriate series of the analytical standard solution for the calibration curve. All standard solutions were acidified to 0.16 M with nitric or 0.12 M with hydrochloric acid so that any acid effect would not bias the measurement. Solutions were stored in high density polyethylene (HDPE) plastic containers.

4. RESULTS AND DISCUSSIONS

4.1 Performance of the multi-electrode plasma sources

In the vertical 4-electrode plasma source, two vertical columns
of arc are formed on either side of the vertically rising sample stream.

As shown in Figure 7, the two vertical columns of arc are merged into a vertical sheet of plasma when no sample is introduced. The separation of the vertical columns of arc is dependent upon the velocity of the sample carrier gas in the plasma torch: the higher the velocity of the sample carrier argon gas, the greater the separation of the two columns (Figure 7). The flow rate of the sample carrier argon gas is not the only factor to affect the degree of separation of the vertical columns of arc. As the power dissipation between the electrodes is increased, the vertical columns of arc become larger in diameter. As a result, it is difficult for the sample aerosol stream to penetrate through the plasma discharge and eventually the vertical columns of arc combine with each other. In addition, as the length of the plasma is increased by adjusting the lower electrodes downward, the upper portions of the plasma tend to merge because of the weakening of the sample carrier gas stream as it travels upward. Therefore, the sample aerosol stream does not reach the upper portion of the plasma discharge. The flow rate of sample carrier gas, the power dissipation between the electrodes, and the length of plasma are significant in shaping the structures of the vertical columns of arc.

In the vertical 6-electrode plasma source, the plasma appears on top as a dome between the three upper electrodes when no sample is introduced. When the sample is introduced into the discharge, the inner diameter of the tip of the sample introduction tube is critical to the shape of the plasma as shown in Figure 10. With the 1.2-mm I.D. sample introduction tube tip, three separate parallel plasma
Figure 10. Influence of I.D. of the tip of sample introduction tube on the shape of the plasma columns in the vertical 6-electrode plasma source. a) small I.D. b) large I.D.
columns form because the sample stream in the center of the plasma is too large in diameter. The smaller diameter tip (0.7-mm I.D.) is employed to ensure that the sample stream is completely surrounded by the hot plasma. Nevertheless, worse analytical results than those with the 1.2-mm I.D. sample nozzle were obtained with the present vertical multi-electrode plasma sources. This is due to the fast velocity of the sample aerosol and the relatively low particle density in the observation zone. However, for some experimental conditions, the sample stream could be completely surrounded by hot plasma without sacrificing analytical performance. Modifications to improve the source are now being made in our laboratory.

In the horizontal 4-electrode plasma source, positional instability of the apex of the plasma was observed. Instability of the apex of the plasma caused a long-term drift in the analytical signal similar to that observed in the first commercial 2-electrode DCP spectrometer [140,141]. The instability of the apex of the plasma in the horizontal 4-electrode plasma source, in fact, resulted in the development of the vertical multi-electrode plasma sources with improved positional stability.

4.2 Sample introduction systems

In the multi-electrode plasma sources, the sizes and shapes of the plasma columns and the sample aerosol stream are dependent upon a number of parameters, including the plasma and sample carrier gas flow rate, the power dissipated across the electrodes, the tip size of the sample introduction tube, and the electrode size. In particular, the shapes of the plasma columns and the sample aerosol stream are
significantly affected by the sample carrier gas flow.

By means of a modified simplex optimization procedure, the best Ca(II) line-to-background ratio was obtained for a sample uptake rate and sample carrier gas flow rate of 1.3 mL/min (about one-half of the free uptake rate for the 0.76-mm I.D. pump tubing) and 0.70 L/min, respectively, for the vertical 4-electrode plasma source. The Meinhard concentric nebulizer and the Scott-type spray chamber described above are suitable for the vertical 4- and 6-electrode plasma sources with the optimized sample uptake rate and sample carrier gas flow rate.

However, for the horizontal 4-electrode plasma source, the sample introduction system described above does not perform in a satisfactory manner. A Meinhard concentric nebulizer was used to produce the sample aerosol, requiring a flow rate of at least 0.7-1.0 L/min for the sample carrier gas. Since the two parallel plasma columns are oriented perpendicular to the direction of the upward sample aerosol stream, the fast flow rate of the sample carrier gas caused plasma fluctuations, resulting in noise and drift in the analytical signals and even the eventual extinction of the plasmas. Although a slower flow rate, from 0.2 to 0.5 L/min, stabilizes the plasma and assures longer residence time of the analyte species and better contact with the plasma columns, it is not feasible to make fine sample aerosols using the Meinhard concentric nebulizer with such a low flow rate. Therefore, significant volatilization interferences are observed because of the large aerosol droplets produced by the lower flow rates. In fact, an emission line intensity of Cu (I) at 327.4 nm is undetectable at such low flow rates. As a result, the nebulizer was
operated at the higher flow rates and a bypass tube was used to direct some of the flow away from the plasma sample introduction tube. Consequently, the sample throughput was apparently decreased, resulting in degradation of the sensitivity of the plasma source relative to an ICP [142]. However, the sample introduction system with the by-pass performs satisfactorily with the horizontal 4-electrode plasma source, except for pulsation due to the condensation of sample droplets inside the small by-pass tubing. The drops formed inside the by-pass tubing cause pulsations of the drain liquid and eventually the resulting pressure variations affect the emission line intensities. All of the problems associated with the sample introduction system in the horizontal 4-electrode plasma source are primary causes for the poor analytical performance of this kind of plasma source.

Alternatively, low flow nebulizers, such as the ultrasonic nebulizer [143], the Babington nebulizer [144-145] and the fritted-disk nebulizer [146], would be required to improve analytical performance with the present design. The typical argon gas flow rates for these nebulizers are from 0.2 to 0.5 L/min, which is a proper flow rate for the horizontal 4-electrode plasma source.

4.3 Dependence of emission profiles on experimental parameters

To investigate the dependence of the emission intensity profiles on several experimental parameters, Mg aqueous solution was introduced into the vertical 6-electrode plasma torch. Vertical and horizontal profiles of emission intensities for both the Mg neutral atom line at 285.21 nm and Mg ion line at 280.27 nm were determined. Eight
vertical scans at 2-mm increments from the top of the quartz tube were done in order to determine the spatial distributions of Mg neutral atom and ion lines. For each vertical scan, 32 data points were collected to determine the horizontal profile.

4.3.1 The influence of observation height

Smoothed horizontal-vertical spatial emission profiles for the Mg neutral atom line (285.21 nm) and ion line (280.27 nm) are shown, respectively, in Figures 11 and 12. In these figures the vertical scale for the Mg ion emission is 10 times that for the Mg neutral atom emission. Thus, the intensity of the ion line is much stronger than that of atom line, as is commonly observed in plasma sources. Generally, the points of the maximum intensity for the Mg neutral atom and ion lines are observed at 6 to 10 mm above the quartz tube. However, the points of maximum intensity could be shifted in the sample aerosol channel by varying the experimental parameters. For example, Figure 13 shows the emission intensity profile for the Mg ion line as a function of current at different observation heights. As the current is increased from 15 to 19 A, the point of maximum intensity is observed at 10 mm above the quartz tube. In contrast to this finding, by increasing the length of plasma the point of maximum intensity is shifted lower in the sample aerosol channel as shown in Figure 14. As a result, to obtain the best analytical results for the vertical multi-electrode plasma sources, the observation height has to be optimized for any given set of experimental conditions. Dependence of the shift of the point of maximum intensity on experimental parameters will be discussed in detail in a following section.
Figure 11. Horizontal-vertical spatial emission profile for the Mg neutral atom line at 285.21 nm. (Maximum intensity is at 6 mm above the quartz tube.)
Figure 12. Horizontal-vertical spatial emission profile for the Mg ion line at 280.27 nm. (Maximum intensity is at 8 mm above the quartz tube.)
Figure 13. Emission profile for the Mg ion line at 280.27 nm as a function of current at different observation heights. 
(○) 2 mm; (+) 4 mm; (◊) 6 mm; (△) 8 mm; (×) 10 mm above the quartz tube.
Figure 14. Emission profile for the Mg ion line at 280.27 nm as a function of length of plasma at different observation heights. (□) 2 mm; (+) 4 mm; (○) 6 mm; (△) 8 mm; (×) 10 mm above the quartz tube.
4.3.2 Influence of plasma length

For the horizontal 4-electrode plasma source, since the two plasma columns are perpendicular to the direction of the upward sample aerosol stream, the length of the plasma in contact with the sample stream is roughly equal to the diameter of plasma column, about 5.0 mm. As a result, a relatively short residence time was experienced by the analyte species, causing poor analytical performance.

For the vertical multi-electrode plasma sources, the length of plasma is one of the most important experimental parameters. One of the main advantages of the vertical multi-electrode plasma sources is that the length of the plasma can be readily controlled by moving the lower electrodes up and down even during plasma operation. Consequently, the residence time experienced by the analyte species can be adjusted to provide sufficient time to atomize and excite an aerosol sample. Thus, analytical performance is significantly affected by varying the length of the plasma.

Figures 15 and 16 illustrate some of the more important and typical features of the vertical 6-electrode plasma system. The horizontal intensity profiles for both the neutral atom and ion were observed at 8 mm above the quartz tube for a current of 19 A for each pair of electrodes. As the plasma length increases from 15 to 25 mm, the emission intensities at the center of the plasma for both the ion line and the neutral atom line increase by factors of 140 and 15, respectively. The ion/atom ratio increases by a factor of 10 as the plasma length increases from 15 to 25 mm. Therefore, the degree of ionization for a 25-mm plasma length is much greater than that for shorter lengths. It is evident that the longer the length of plasma,
Figure 15. Horizontal distribution of Mg neutral atom line emission intensity at 285.21 nm with three different lengths of plasma. (○) 15 mm; (+) 20 mm; (◇) 25 mm. (The center of the plasma is located at 3.7 mm on the horizontal axis; the emission intensities were observed at 8 mm above the quartz tube; a current of 19 A for each pair of electrodes was used.)
Figure 16. Horizontal distribution of Mg ion line emission intensity at 280.27 nm with three different lengths of plasma. (○) 15 mm; (+) 20 mm; (□) 25 mm. (The center of the plasma is located at 3.7 mm on the horizontal axis; the emission intensities were observed at 8 mm above the quartz tube; a current of 19 A for each pair of electrodes was used.)
the greater the degree of desolvation, vaporization, atomization, and ionization.

Moreover, narrower horizontal net emission intensity profiles for the shorter lengths of the plasmas are observed in Figures 15 and 16. As the length of plasma is shortened, the sample aerosol stream becomes physically wider because of the reduced confining effect of the shorter plasma columns. Even though the widths of the sample aerosol stream for the short plasma lengths are wider than those for the long plasmas, analyte species have less time to diffuse horizontally away from the sample stream, causing narrower horizontal net emission intensity profiles for the Mg neutral atom line, as well as the ion line. This is probably due to the reduced heat transfer between the sample and the plasma, resulting in less atomization and ionization.

Figures 17 and 18 demonstrate that the vertical intensity profiles for both the neutral atom and ion lines are significantly changed by varying the length of the plasma. In the case of the Mg neutral atom line, maximum intensity was observed at 8 mm above the quartz tube for a 25-mm plasma length. However, at shorter lengths of plasma, the points of maximum intensity shift to a higher position in the plasma tail flame. Thus, the points of maximum intensity for 20- and 15-mm plasma lengths were found, respectively, to be at 10 and 12 mm above the quartz tube. A similar trend was observed for the Mg ion line, but the spatial shifts in the emission profiles were greater than that for Mg neutral atom line. In the case of the Mg ion line, maximum intensities for 25-, 20- and 15-mm plasma lengths were observed, respectively, at 6, 10, and 14 mm above the quartz tube.
Figure 17. Vertical distribution of Mg neutral atom line emission intensity at 285.21 nm with three different lengths of plasma. A current of 19 A for each pair of electrodes was used. (○) 15 mm; (+) 20 mm; (□) 25 mm.
Figure 18. Vertical distribution of Mg ion line emission intensity at 280.27 nm with three different lengths of plasma. A current of 19 A for each pair of electrodes was used. (o) 15 mm; (+) 20 mm; (o) 25 mm.
For the longer lengths of plasma, it may be that the sample aerosol stream loses most of its vertical velocity component at the top of the discharge due to the longer path lengths of the sample aerosol travelling through the discharge. In the high region from 12 to 16 mm above the quartz tube, the intensity and loss of intensity per mm appeared to be the same. The loss rate may be caused by interaction with the atmosphere, which would be relatively independent of what happens lower in the plasma. The maximum is higher and shifted downward for a longer plasma. The higher intensity indicates more excited atoms or ions in the optical path, probably due to more energy being transferred to the sample stream. The shift is probably caused by a shift in the balance point between the excitation mechanisms and the loss mechanisms. The longer plasma also transfers its energy to the sample stream while the stream is lower in the torch than for a short plasma. Therefore, as the length of plasma is increased, the point of maximum intensity shifts from higher to lower positions in the sample aerosol channel in the center of the plasma. As the RF power in an ICP source increases, the same trend in the shift of the maximum intensity point was observed by several researchers [147-150].

As the length of plasma is increased, the plasma background emission intensities at the same observation height become more intense due to the shift of the apex of the sample stream downward. Thus lower line-to-background (L/B) ratios result. A decreasing L/B ratio of the Mg neutral atom line was observed when the length of plasma was increased even though the net emission intensity increased by a factor of 15. However, in the case of the Mg ion line the degree of ionization was much greater than the degree of increasing plasma
Figure 19. Horizontal distribution of line-to-background ratios for the Mg ion line at 280.27 nm with three different lengths of plasma. (\(\circ\)) 15 mm; (+) 20 mm; (\(\square\)) 25 mm. (The observation height is 8 mm above the quartz tube; A current of 19 A for each pair of electrodes was used.)
Figure 20. Vertical distribution of line-to-background ratios for the Mg ion line at 280.27 nm with three different lengths of plasma. A current of 19 A for each pair of electrodes was used. ($\circ$) 15 mm; (+) 20 mm; ($\odot$) 25 mm.
background emission intensity, resulting in an increasing L/B ratio. In Figure 19, as the length of the plasma with the 19-A current per plasma column was increased from 15 to 25 mm, the L/B ratio for the ion line increased from 15 to 520, while the L/B ratio for the neutral atom line decreased from 20 to 10.

The L/B ratio for the Mg ion line for a 15-mm plasma length is much smaller than those at 20 and 25 mm, because the shorter lengths of plasma do not provide sufficient time to atomize and ionize the sample aerosols. However, in contrast to the L/B ratio for the Mg neutral atom line, the L/B ratio of the Mg ion line was increased by increasing the length of plasma as mentioned above. This trend is demonstrated in Figure 20, which also shows the vertical profiles of the L/B ratios for the Mg ion line for three different lengths of plasma. The maximum L/B ratio for a 25-mm plasma length occurred at 4 mm above the quartz tube, indicating that the apex of the sample aerosol stream is located close to 4 mm above the quartz tube, and the maximum L/B ratio for the 20-mm length of plasma is observed at 10 mm above the quartz tube. At 10 mm above the quartz tube, the L/B ratio for the 25-mm plasma length is smaller than that for the 20-mm length. This indicates that the plasma background emissions at 10 mm above the quartz tube for a 25-mm plasma length, are so dominant that a smaller L/B ratio is obtained.

In summary, the shape and size of the sample aerosol stream in the discharge are significantly affected by the length of the plasma. Consequently, an optimal observation point will also vary with different lengths of plasma. An optimal observation point may be shifted lower in the plasma tail flame by increasing the length of the
plasma. With the vertical 6-electrode plasma source sample carrier gas flow rate and sample injection tube used in this study, a plasma length of more than 30 mm shifted the optimal observation point to a position below the top of the quartz tube.

4.3.3 Influence of current

The influence of current on the net emission intensity spatial distribution for different plasmas lengths (i.e., 20 and 25 mm) is now considered.

For a plasma length of 25 mm and currents from 16 to 19 A, the horizontal emission profiles for the Mg neutral atom and ion lines are shown in Figures 21 and 22, respectively. As the current increases from 16 to 19 A, the emission intensities for the neutral atom and ion lines increase only 1.5 and 2.5 times, respectively. And the ion/atom ratio increases only by a factor of 2 as the current increases from 16 to 19 A. Compared to the influence of the length of plasma on net emission intensities, the effects of current on net emission intensities are not significant for a 25-mm plasma length. As indicated above, the 25-mm length of plasma apparently provides sufficient time to vaporize, atomize, and ionize the sample aerosol, while increasing the current does not greatly affect the analytical emission characteristics.

Moreover, the horizontal emission profiles for the lower current are observed to be narrower just as they are for the shorter length of plasma as we saw earlier. Since the plasma column radius is increased by increasing the current, improved contact with the sample aerosol for the higher current plasma results in more effective heat transfer
Figure 21. Horizontal distribution of the Mg neutral atom line emission intensity at 285.21 nm as a function of current for a 25-mm plasma length at an observation height of 8 mm above the quartz tube. (○) 19 A; (+) 18 A; (○) 17 A; (Δ) 16 A.
Figure 22. Horizontal distribution of the Mg ion line emission intensity at 280.27 nm as a function of current for a 25-mm plasma length at an observation height of 8 mm above the quartz tube. (□) 19 A; (+) 18 A; (○) 17 A; (△) 16 A.
from the plasma to the sample stream.

According to the model developed by Boumans [151] for a free-burning arc in air, the power dissipated per centimeter in the arc column is proportional to the square of the current and is inversely proportional to the electrical conductivity of the gas. And the electrical conductivity of the gas is proportional to the square of the column radius. Therefore, if the plasma column radius, hence its electrical conductivity, is increased by increasing the current, the power dissipation per unit length in the arc column would not be substantially changed. M. Margoshes and B. F. Scribner [152] have reported that the temperature in the arc column is rather insensitive to the arc current. As a result, rather than the temperature of the arc column, the efficiency of the heat transfer to the sample aerosol in the vertical 6-electrode plasma source (25-mm plasma length) caused by a change in plasma shape may be the main factor causing different horizontal emission profiles at different current levels.

Figure 23 shows the horizontal profiles of the L/B ratio for the Mg ion line at different currents. As the current is increased from 16 to 19 A, plasma background emission also increases due to the expansion of the plasma column. As a result, the L/B ratio at 19 A is somewhat less than at 16 A because of the high plasma background emission and the relatively small increase in the net Mg ion emission intensity at the higher current.

Figures 24 and 25 show the respective vertical net emission intensity profiles for the Mg neutral atom and ion lines, and further indicate that the optimal observation points were not changed by varying the current for the 25-mm plasma length. The optimal
Figure 23. Horizontal distribution of the line to background ratios for the Mg ion line at 280.27 nm as a function of current. The length of the plasma is 25 mm and the observation height is 8 mm above the quartz tube.

(☐) 19 A; (Δ) 16 A.
Figure 24. Vertical distribution of the 285.21-nm Mg neutral atom line emission intensity at the center of the plasma as a function of current. The length of the plasma is 25 mm. (©) 19 A; (+) 18 A; (©) 17 A; (Δ) 16 A.
Figure 25. Vertical distribution of the 280.27-nm Mg ion line emission intensity at the center of the plasma as a function of current. The length of the plasma is 25 mm. (Ο) 19 A; (+) 18 A; (Ο) 17 A; (Δ) 16 A.
observation points for both the neutral atom and ion lines occurred at 8 mm above the quartz tube. This suggests that the vertical analyte emission behavior resulted from the fact that sample residence time and the transport properties of sample aerosols are not greatly affected by varying the current from 16 to 19 A for the 25-mm plasma length. However, the spatial behavior of the Mg neutral atom line is quite different from that of the Mg ion line. At 4 mm above the quartz tube the net emission intensity for the Mg neutral atom line remained constant despite the current increase from 16 to 18 A. In contrast to the Mg neutral atom line, the net emission intensity for the Mg ion line at the same observation height increased by a factor of 2 when the current was increased from 16 to 18 A, indicating the degree of ionization increased.

For a plasma length of 20 mm, the horizontal emission profiles at currents from 16 to 19 A for the Mg neutral atom and ion lines are shown in Figures 26 and 27. Since the wavelengths are only 5 nm apart, it is clear that the net emission intensity of the Mg neutral atom line is smaller than the emission intensity of the Mg ion line. The spatial behaviors for the 20-mm plasma length are very similar to those with the 25-mm length of plasma. However, since the 20-mm length of plasma may not provide sufficient time to vaporize, atomize, and ionize the sample aerosol, the changes in emission intensities for both the Mg neutral atom and ion lines are sensitive to changing current. As the current is increased from 16 to 19 A, the respective emission intensities for the Mg neutral atom and ion lines at the center of the plasma increase 6 and 35 times. Furthermore, the L/B ratio for the Mg ion line increases from 20 to 420 as shown in Figure
Figure 26. Horizontal distribution of the 285.21-nm Mg neutral atom line emission intensity at the center of plasma as a function of current. The length of the plasma is 20 mm and the observation height is 8 mm above the quartz tube. (○) 19 A; (+) 18 A; (⊙) 17 A; (△) 16 A; (×) 15 A.
Figure 27. Horizontal distribution of the Mg ion line emission intensity at 280.27 nm as a function of current for a 20-mm plasma length at an observation height of 8 mm above the quartz tube. (□) 19 A; (+) 18 A; (○) 17 A; (△) 16 A; (×) 15 A.
Figure 28. Horizontal distribution of the line to background ratios for the Mg ion line at 280.27 nm as a function of current. The length of the plasma is 20 mm and the observation height is 8 mm above the quartz tube. (○) 19 A; (+) 18 A; (○) 17 A; (△) 16 A; (×) 15 A.
Figure 29. Vertical distribution of the 285.21-nm Mg neutral atom line emission intensity at the center of the plasma as a function of current. The length of the plasma is 20 mm. (O) 19 A; (+) 18 A; (O) 17 A; (Δ) 16 A; (x) 15 A.
Figure 30. Vertical distribution of the 280.27-nm Mg ion line emission intensity at the center of the plasma as a function of current. The length of the plasma is 20 mm. (O) 19 A; (+) 18 A; (O) 17 A; (A) 16 A; (x) 15 A.
28 and the ion/atom ratio increases by a factor of 9, illustrating that the degree of ionization is greater at the higher current.

Figures 29 and 30 demonstrate that the points of maximum intensity for the Mg ion line shifts upward in the plasma tail flame as current is decreased, while the maximum for the Mg neutral atom line first decreases and then increases slightly in height. For a 20-mm plasma length, the optimal observation height is observed at 10 mm above the quartz tube. When compared to the optimal observation height for a 25-mm plasma length in Figures 24 and 25, the optimal observation height is 2 mm higher because of the shorter length of plasma.

Figure 31 shows the vertical intensity profile of the L/B ratio for the Mg ion line when the current is varied from 15 to 19 A with the 20-mm plasma length. As the current is increased from 15 to 19 A, the point of the maximum L/B ratio for the Mg ion line shifts from 12 to 10 mm above the quartz tube.

As the current increases from 16 to 19 A, the change in the emission intensity for a 20-mm plasma length is more sensitive than that for a 25-mm length because a 20-mm plasma length does not provide sufficient time to atomize, and ionize the analyte species. Thus, for a 20-mm plasma length the emission profiles for both the Mg neutral atom and ion lines are greatly affected by varying the current.

Figures 32 and 33 show the horizontal net emission intensity profiles for both the Mg neutral atom and ion lines for a 15-mm plasma length, indicating an increase in net emission intensities for both lines as the current is increased from 18 to 21 A. However, severe depressions of the emission intensities for both the Mg neutral atom
Figure 31. Vertical distribution of the line-to-background ratios for the Mg ion line at 280.27 nm as a function of current for a 20-mm plasma length. (○) 19 A; (+) 18 A; (○) 17 A; (Δ) 16 A; (×) 15 A.
Figure 32. Horizontal distribution of Mg neutral atom line emission intensity at 285.21 nm as a function of current for a 15-mm length of plasma. (○) 21 A; (+) 20 A; (◊) 19 A; (Δ) 18 A.
Figure 33. Horizontal distribution of Mg ion line emission intensity at 280.27 nm as a function of current for a 15-mm length of plasma. (○) 21 A; (+) 20 A; (○) 19 A; (△) 18 A.
and ion lines are observed at the center of the sample stream. The increase of the relative depression of the Mg ion emission intensity with a decrease in current is greater than that of the Mg neutral atom line. This indicates that the residence time of the analyte species for the 15-mm plasma length is not sufficient to desolvate, vaporize, atomize, and ionize the sample aerosol. In addition, the depressions for both the Mg neutral atom and ion lines diminish with increasing current, indicating that the plasma at the lower current is not as hot.

In Figure 34, the influences of the current and the length of plasma on the L/B ratio for the Mg ion line are shown. The 15-mm plasma length was not stable enough to use less than 17 A of current. The L/B ratios for a 25-mm plasma length were not changed significantly by increasing the current from 15 to 19 A. However, the L/B ratios for 20- and 15-mm plasma lengths were gradually increased by increasing the current, suggesting that these plasma lengths do not provide sufficient temperature and sample residence time when compared with the 25-mm plasma length. Figure 35 shows a L/B ratio profile for the Mg neutral atom line similar to that in Figure 34. An interesting feature is that as the current increases from 15 to 19 A, the L/B ratios for 25- and 20-mm plasma lengths decreases because increasing the current results in an increase in plasma background emission intensity. However, the L/B ratios for the 15-mm plasma length increased. Since the plasma background emission intensity is increased by increasing the current, a compromise must be sought in both the choice of the length of plasma and the magnitude of current in order to obtain optimal analytical performance. The same
Figure 34. Influences of length of plasma and current on the line-to-background ratios of the Mg ion line at 280.27 nm. (□) 25 mm; (+) 20 mm; (○) 15 mm.
Figure 35. Influences of length of plasma and current on the line-to-background ratios of the Mg neutral atom line at 285.21 nm. (○) 25 mm; (+) 20 mm; (◇) 15 mm.
dependence of the plasma background emission on the power level has been noted in ICP systems [147,153,154].

4.3.4 Influence of position of the tip of the sample introduction tube

The position of the tip of the sample introduction tube relative to the discharge is a critical experimental parameter in the multi-electrode plasma source, as it is in ICP sources [155,156]. If the tip of the sample introduction tube is very close to the plasma discharge, then decomposed sample material is deposited at the tip of the nozzle, either clogging the nozzle or deflecting the sample aerosol flow. In this case the sample introduction tube would be overheated and melt. On the other hand, if the tip of the sample introduction tube is positioned too far from the discharge, a major portion of the sample aerosol would be reflected and swept around the plasma periphery. Thus, only a small portion of the sample aerosol would enter into the discharge, resulting in a significant decrease of the analyte density and inefficient transfer of energy to the sample stream. In addition, if the tip of the sample introduction tube were too cool, the sample aerosol could condense on its walls, causing the formation of liquid obstructions.

Figure 36 shows the horizontal profiles of the net emission intensity for the Mg ion line at 285.27 nm for five positions of the sample introduction tube. As the distance between the tip of the sample introduction tube and the bottom of the discharge is increased from 2 to 10 mm, the net emission intensity decreases about 50 times. As described above, this behavior results from the decreasing
Figure 36. Horizontal distribution of Mg ion line emission intensity at 280.27 nm for several positions of the tip of the sample introduction tube. The position of the tip of the sample introduction tube is expressed with respect to the end of inner electrode. A current of 17 A for each pair of electrodes was used. (□) 2 mm; (+) 4 mm; (○) 6 mm; (△) 8 mm; (×) 10 mm.
Figure 37. Horizontal distribution of Mg neutral atom line emission intensity at 285.21 nm for several positions of the tip of the sample introduction tube. The position of the tip of the sample introduction tube is expressed with respect to the end of inner electrode. A current of 17 A for each pair of electrodes was used. (○) 2 mm; (+) 4 mm; (△) 6 mm; (△) 8 mm; (×) 10 mm.
transport of the sample aerosol into the discharge caused by lowering the position of the sample introduction tube. Due to the reflection of the sample aerosol by the plasma, most of sample aerosol passes around the plasma columns, causing lower atomic concentration in the observation zone and deposits on the wall of the quartz tube. Similar results are obtained for the Mg neutral atom line, Figure 37.

Figures 38 and 39, respectively, show the vertical emission intensity profiles for the Mg neutral atom and ion lines. The points of maximum intensity for both the Mg neutral atom and ion lines are located between 10 to 12 mm above the quartz tube. An interesting characteristic is that the points of maximum intensity for both the neutral atom and ion lines do not shift greatly when the height of the sample introduction tube is varied. This indicates, together with the change in intensity of the maximum, that the sample residence time in the discharge is not greatly affected by the height of the sample introduction tube, but that the amount of sample aerosol penetrating into the discharge is affected.

Figure 40 shows that when the tip of the sample introduction tube is located at more than 4 mm below the bottom of the discharge, the horizontal profiles of the L/B ratios for the Mg ion line are noisy due to the turbulence in the sample aerosol flow. The noise associated with the turbulence of the discharge is significant when the tip of the sample introduction tube is positioned too far from the bottom of the discharge. In fact, the best L/B ratios for both the Mg neutral atom and ion lines are obtained when the tip of the sample introduction tube is located at 2 to 4 mm below the bottom of the discharge.
Figure 38. Vertical distribution of Mg neutral atom line emission intensity at 285.21 nm for several positions of the tip of the sample introduction tube. The position of the tip of the sample introduction tube is expressed with respect to the end of inner electrode. A current of 17 A for each pair of electrodes was used. (○) 2 mm; (+) 4 mm; (△) 6 mm; (Δ) 8 mm; (×) 10 mm.
Figure 39. Vertical distribution of Mg ion line emission intensity at 280.27 nm for several positions of the tip of the sample introduction tube. The position of the tip of the sample introduction tube is expressed with respect to the end of inner electrode. A current of 17 A for each pair of electrodes was used. (O) 2 mm; (+) 4 mm; (O) 6 mm; (A) 8 mm; (x) 10 mm.
Figure 40. Horizontal distribution of line-to-background ratios for the Mg ion line at 280.27 nm for several positions of the tip of the sample introduction tube. A current of 17 A for each pair of electrodes was used. (O) 2 mm; (+) 4 mm; (O) 6 mm; (A) 8 mm; (x) 10 mm.
Figure 41. Influences of the plasma gas flow rate on the Mg ion and neutral atom line intensities. (O) Mg neutral atom line at 285.21 nm; (+) Mg ion line at 280.27 nm.
4.3.5 Influence of plasma gas flow rate

The effects of the plasma gas flow rate on the emission of Mg neutral atom and ion lines are shown in Figure 41. Increasing the plasma gas flow rate increases the emissions of both the neutral atom and ion. In the vertical 6-electrode plasma source, plasma gas is used not only to maintain the vertical plasma discharge but also to prevent the quartz tube from overheating when it is tangentially introduced into the annular space between the plasma quartz and sample introduction tubes. In this way, vortex stabilization [135] is established, resulting in a spiral flow up the tube with a low pressure region toward the center and a high velocity flow of plasma gas along the walls. Since the low pressure at the center of the quartz tube produced by the tangential introduction of plasma gas is a function of mass flow rates, the sample aerosol enters more easily into the discharge at a higher flow rate of plasma gas.

In addition, the enhancement of emission intensity results from a thermal pinch effect that occurs when there is a higher flow velocity of plasma gas around the plasma columns [157]. The peripheral regions of the plasma columns are cooled by the plasma gas stream and thus tend to become less conductive. The plasma columns tend to move away from this cooling effect toward a more conductive region, in this case the center of the torch. This produces more efficient contact with the sample stream. Thus, the emission intensities for both the Mg neutral atom and the ion lines increase approximately 10 times as the plasma gas flow rate is increased from 1.8 to 4.0 L/min. The fact that there is so little change in the ion/atom ratios indicates that there is relatively little change in temperature of the sample stream.
Figure 42. Vertical distribution of the Mg ion line emission intensity as a function of plasma gas flow rate. 
(●) 2.92 L/min; (+) 2.74 L/min; (○) 2.56 L/min; 
(△) 2.38 L/min; (×) 2.19 L/min; (▽) 2.01 L/min.
The increase in intensities is therefore caused by increased atom and ion densities, perhaps due to more complete atomization of the sample stream.

Figure 42 shows the vertical profiles of emission intensity for the Mg ion line at different flow rates of plasma gas. As the plasma gas flow rate increases from 2.01 to 2.92 L/min, the points of maximum intensity are found at 8 to 10 mm above the quartz tube. However, the emission intensities of the Mg ion line gradually increase as the flow rate is increased. As described above, this spatial behavior results from the transport properties of the sample aerosol into the discharge as well as the thermal pinch effect.

4.3.6 Influence of sample carrier gas flow rate

Figures 43 and 44 illustrate the influence of the sample aerosol carrier gas flow rate on the horizontal emission profiles of the Mg neutral atom and ion lines, respectively, in the region 8 mm above the quartz tube. The effects of sample carrier gas flow rate on the spatial profiles of Mg neutral atom and ion line emissions were similar to those observed for an ICP [147, 149].

A dramatic change in analyte emission characteristics was observed when the sample carrier gas flow rate was changed slightly. When the sample carrier gas flow rate was increased from 0.7 to 0.9 L/min, the emission intensity of the Mg ion decreased sharply, while that of the Mg neutral atom decreased slightly. Although a high flow rate of sample carrier gas enables production of fine aerosol particles and a high sample throughput into the discharge, the short residence time, as well as the cooling effects of the fast flow rate,
Figure 43. Horizontal distribution of the Mg neutral atom line emission intensity for several sample carrier gas flow rates. Observation height is 8 mm above the quartz tube. (□) 0.7 L/min; (+) 0.8 L/min; (○) 0.9 L/min.
Figure 44. Horizontal distribution of the Mg ion line emission intensity for several sample carrier gas flow rates. Observation height is 8 mm above the quartz tube. (□) 0.7 L/min; (+) 0.8 L/min; (○) 0.9 L/min.
Figure 45. Vertical distribution of the Mg ion line emission intensity for several sample carrier gas flow rates. (o) 0.7 L/min; (+) 0.8 L/min; (o) 0.9 L/min.
results in decreasing the emission intensity of the Mg ion line in the vertical 6-electrode plasma source. As shown in Figure 45, it is clear that the spatial shift in the point of maximum intensity is a function of the sample carrier gas flow rate. As the sample carrier gas flow rate is increased, the points of the maximum intensity shift upward in the plasma due to the high velocity of the sample aerosol. As we saw earlier, similar trends in spatial shifts are observed when the current is changed or the length of plasma is modified. However, a flow rate of less than 0.7 L/min for the sample carrier gas could not be used with the present design due to inefficient nebulization.

4.4 Stability of plasma

In order to investigate the quantitative stability of the vertical 6-electrode plasma source, 10 mg/L of aqueous iron solution was introduced and the iron emission signal at 371.9 nm was monitored continuously. For 45 min a series of analyte intensities were collected from 32 consecutive 1-sec integrations. No adjustments of operating conditions were made during this period. No apparent long-term drift in the signal was observed during 45 min. Figure 46 shows the short-term stability of the vertical 6-electrode plasma source which was determined from the relative standard deviation of the individual measurements. Each point on the graph represents the relative standard deviation of the 32 measurements. In all cases the precision was less than 1.6% and there was no evidence to indicate that leaving the plasma operational for 20 to 30 min prior to analysis is advantageous. In addition, the relative standard deviation of the background emission for 12 elements are listed in Table 7, all of
Figure 46. Stability of the plasma as expressed by the relative standard deviation of analyte emission intensity for plasma operation of one hour. Each point in the plot represents the RSD of 32 measurements each with 1-s integration time.
which are less than 1.4% with the exception of 2.7% for Na(I) at 589.59 nm.

After approximately 9 hours of operation, the plasma tended to flicker, due to the deposit of elements on the wall of the inner quartz tube, resulting in the formation of an undesired arc between the electrodes and the quartz tube. The deposit of elements on the wall of the inner quartz tube could result from either the laterally diffused analyte species or the electrode materials. Therefore, experimental conditions have to be chosen to minimize any lateral diffusion of the analyte species as discussed previously, and graphite electrodes would help to avoid any contamination from the electrode materials. In addition, because of a relatively small long-term drift in analyte signals near the end of the useful lifetime of the electrodes, regular electrode replacement or recalibration for optimal analytical results would be required for long-term use, as is done for the DCP.

To evaluate long-term plasma stability for the horizontal 4-electrode plasma source, 100 mg/L of Cu standard solution was introduced into the plasma for three hours without recalibration. Emission intensity gradually drifted and close to a 15% decrease in emission intensity was observed, at which point the experiment was terminated. This decrease is evidently due to the positional instability of the apex of the plasma, resulting from fluctuations of the gas flow and sample aerosol stream, and most importantly, from the erosion of the electrodes. However, 2 to 3% short-term precision was found throughout a series of 10 consecutive blank emission measurements.
4.5 Residence time of analyte species in plasma

It has been shown that the injection velocity of the sample aerosol into the plasma is critical to the analytical performance of the multi-electrode plasma sources, as well as an ICP source [109]. If the injection velocity is too low, the sample aerosol cannot penetrate the plasma, causing most of the sample to sweep around the plasma. On the other hand, if the injection velocity is too high, then the sample aerosol does not have enough time to desolvate, vaporize, atomize, and become excited as discussed earlier. Assuming that the linear velocity of analyte species and carrier gas atoms is the same and remains constant, then the residence time of the analyte species would be the same as that for the carrier gas atoms. Since the injection velocity of the sample aerosol into the plasma is inversely proportional to the square of the orifice diameter, at a constant argon flow rate, the approximate injection velocity for the vertical multi-electrode plasma sources can be calculated [158,159].

With an injection tip orifice diameter of 1.2 mm and a sample carrier gas flow rate of 0.75 L/min, the injection velocity obtained is 1100 cm/s. Compared to previously reported results [109], 3500 cm/s for the mini ICP (orifice size = 0.75-mm i.d.; flow rate = 0.92 L/min) and 2800 cm/s for the conventional ICP (orifice size = 1.0-mm i.d.; flow rate = 1.32 L/min), a lower injection velocity was obtained with the present system. As a result, the residence time for an analyte species in the observation zone with a 25-mm length of plasma is expected to be approximately 2.3 ms, which is longer than those of the mini and conventional ICP sources. Approximately 1.5 ms for the conventional ICP and 0.8 ms for the mini ICP were calculated at
observation heights of 30 and 20 mm [109], respectively. It is apparent that the vertical multi-electrode plasma sources provide sufficient residence time to desolvate, vaporize, atomize, and excite the analyte species. Furthermore, the residence time may be adjusted without interruption during the course of the operation, if necessary.

4.6 Analytical curves and detection limits

The detection limits of the multi-electrode plasma sources were determined and compared to those of a conventional ICP source. The typical experimental conditions for determination of the detection limits of the multi-electrode plasma sources are listed in Table 5.

The detection limits of the 12 elements for the vertical 4-electrode plasma source are listed in Table 6. The detection limits for the vertical multi-electrode plasma sources are much better in comparison to those of the horizontal 4-electrode plasma source and are comparable to the those of an ICP source for some elements. The linear log-log analytical working curves, which show a dynamic range of 4 to 5 orders of magnitude, have slopes of unity for 12 elements, as shown in Table 7, demonstrating that the vertical 4-electrode plasma source is comparable to an ICP source in this respect.

The detection limits for the vertical multi-electrode plasma source are comparable to those of the DCP, but the linear dynamic range is one to two orders of magnitude greater than that for the DCP. This is apparently due to the relatively long residence time experienced by the analyte species in the vertical multi-electrode plasma sources. However, since tungsten electrodes were used because of the limitation of the present DC power supply, spectral
Table 5. Typical experimental conditions for the determination of detection limits.

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Table 6. Detection limits for vertical 4-electrode plasma source, mg/L

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength(nm)</th>
<th>4-Electrode</th>
<th>ICP [161]</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(I)</td>
<td>309.27</td>
<td>0.1</td>
<td>0.02</td>
<td>5</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>393.37</td>
<td>0.0004</td>
<td>0.0002</td>
<td>2</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>214.44</td>
<td>0.021</td>
<td>0.003</td>
<td>7</td>
</tr>
<tr>
<td>Cr(I)</td>
<td>357.87</td>
<td>0.07</td>
<td>0.02</td>
<td>4</td>
</tr>
<tr>
<td>Cu(I)</td>
<td>324.75</td>
<td>0.02</td>
<td>0.005</td>
<td>4</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>259.94</td>
<td>0.05</td>
<td>0.006</td>
<td>8</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>280.27</td>
<td>0.0008</td>
<td>0.0003</td>
<td>3</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>259.37</td>
<td>0.02</td>
<td>0.002</td>
<td>10</td>
</tr>
<tr>
<td>Na(I)</td>
<td>589.59</td>
<td>0.3</td>
<td>0.07</td>
<td>4</td>
</tr>
<tr>
<td>Si(I)</td>
<td>288.16</td>
<td>0.2</td>
<td>0.03</td>
<td>7</td>
</tr>
<tr>
<td>V(II)</td>
<td>309.31</td>
<td>0.02</td>
<td>0.005</td>
<td>4</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>202.55</td>
<td>0.03</td>
<td>0.004</td>
<td>8</td>
</tr>
</tbody>
</table>
Table 7. Log-log slopes and background RSD for the vertical 4-electrode plasma source.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>Slope</th>
<th>Background RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(I)</td>
<td>309.27</td>
<td>0.99 ± 0.01</td>
<td>0.8</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>393.37</td>
<td>1.00 ± 0.03</td>
<td>1.4</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>214.44</td>
<td>0.99 ± 0.01</td>
<td>1.2</td>
</tr>
<tr>
<td>Cr(I)</td>
<td>357.87</td>
<td>1.03 ± 0.02</td>
<td>1.3</td>
</tr>
<tr>
<td>Cu(I)</td>
<td>324.75</td>
<td>1.001 ± 0.002</td>
<td>1.1</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>259.94</td>
<td>0.97 ± 0.02</td>
<td>1.4</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>280.27</td>
<td>0.99 ± 0.02</td>
<td>0.8</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>259.37</td>
<td>0.96 ± 0.03</td>
<td>1.3</td>
</tr>
<tr>
<td>Na(I)</td>
<td>589.59</td>
<td>1.002 ± 0.003</td>
<td>2.7</td>
</tr>
<tr>
<td>Si(I)</td>
<td>288.16</td>
<td>0.970 ± 0.007</td>
<td>0.5</td>
</tr>
<tr>
<td>V(II)</td>
<td>309.31</td>
<td>1.012 ± 0.009</td>
<td>1.3</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>202.55</td>
<td>0.998 ± 0.006</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Table 8. Comparison of detection limits of the multi-electrode plasma sources, mg/L.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>4-Electrode</th>
<th>6-Electrode</th>
<th>ICP [161]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Horizontal</td>
<td>Vertical</td>
<td></td>
</tr>
<tr>
<td>Al(I)</td>
<td>396.15</td>
<td>0.5</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>393.37</td>
<td>0.3</td>
<td>0.0004</td>
<td>0.0007</td>
</tr>
<tr>
<td>Cu(I)</td>
<td>324.75</td>
<td>0.07</td>
<td>0.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Interference was observed in our measurements. For example, in the cases of Mn(II) at 259.37 nm and Si(I) at 288.16 nm, the spectral interference with W(I) at 259.34 nm and W(I) at 288.11 nm caused a detection limit 10 and 7 times worse than those of the ICP, respectively. The analytical curves and detection limits obtained with the present vertical 6-electrode were not significantly different from those of the vertical 4-electrode plasma source.

As shown in Table 8, for the horizontal 4-electrode plasma source the detection limits of some elements are not as good as those for the ICP or for the DCP. The linear dynamic range is typically 3 orders of magnitude. However, the linear log-log analytical working curves do not always have slopes of unity, indicating that self-absorption may be present in some cases. In the horizontal 4-electrode plasma source, since the outer argon gas is used to push the parallel arcs toward the center of the sample stream to assure good contact between the arcs and the sample, the positional instability of the apex of the plasma and the relatively short residence time experienced by the analyte species are the primary causes for the poor analytical performance of this source.

5. CONCLUSION

This study has shown that the vertical multi-electrode plasma sources show promise for a new excitation source for atomic emission spectroscopy. In this preliminary investigation when several of the experimental parameters were varied, the spatial emission profiles
reflected many of the characteristics associated with an ICP. In addition, the effects of the vaporization and ionization interferences in the vertical multi-electrode plasma sources are similar to those of an ICP. The analytical results, such as detection limits, linear dynamic range, and long- and short-term stability were found to be comparable to those of an ICP. For a 25-mm plasma length, a relatively long residence time of the analyte species (23 msec) in the plasma was calculated, indicating sufficient time for desolvation, vaporization, atomization of the sample when compared to the ICP. In fact, the vertical multi-electrode plasma sources, for which the length of plasma can be readily increased without interrupting plasma operation could prove to be useful for the direct analysis of solutions with high salt or suspended solids content. The energy transfer required for the complete atomization of such sample aerosols could be readily accomplished by elongating the vertical multi-electrode plasmas rather than increasing the electrical power, as has been done for ICP sources.

Due to the relatively short residence time and positional instability of the apex of the plasma, it has been determined from this preliminary study that the horizontal 4-electrode plasma source is not as suitable an excitation source for atomic emission spectroscopy. Nevertheless, since the temperature of the plasma is much hotter than that of a flame, the suitability of a newly designed horizontal 4-electrode plasma as an atomizing source for atomic absorption spectroscopy is currently under investigation in our laboratory. The higher temperatures of the plasma would reduce sample matrix interference effects caused by incomplete or slower atomization
in the lower temperature flames. This has recently been tested using graphite electrodes, and preliminary analytical working curves have been obtained with an atomic absorption spectrophotometer.

Possible spectral interferences due to the use of the tungsten electrodes could be avoided by employing graphite electrodes. In the vertical 6-electrode plasma source, the sample stream could be completely surrounded by hot plasma for some experimental conditions. It is feasible that better analytical results could be obtained with this modification of the vertical multi-electrode plasma sources used in this study. Clearly, further studies are warranted, not only to characterize the physical nature of these kinds of plasmas, but to improve the analytical performance of the vertical multi-electrode plasma sources.

ACKNOWLEDGMENT

This work was supported by the NSF (Grant CHE-8206692) and performed by G. H. Lee in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.
V. SIMPLEX OPTIMIZATION OF THE VERTICAL 4-ELECTRODE PLASMA SOURCE FOR ATOMIC EMISSION SPECTROSCOPY

by

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for submission to Spectrochim. Acta B.
1. ABSTRACT

In the development of the vertical 4-electrode plasma source for atomic emission spectroscopy, optimization is necessary to achieve the best analytical result. By means of a sequential simplex optimization method, six experimental variables were optimized. The line-to-background (L/B) ratio for the Ca(II) at 393.37 nm was used as measure of the response function. The optimal experimental conditions were found to be at a current of 27.8 A, a plasma length of 28.8 mm, a sample uptake rate of 1.3 mL/min, a sample carrier gas flow rate of 0.7 L/min, a plasma gas flow rate of 4.9 L/min, and an observation height of 6.4 mm above the top of the quartz tube.

2. INTRODUCTION

The optimization of the experimental variables is important for the multi-electrode plasma sources to ensure the best analytical performance. Several systematic experimental methods are available for optimization. The factorial experimental method [162,163] is most powerful when used to detect differences caused by two or more discrete possibilities and is often used to evaluate the relative significance of several experimental variables. The factorial design can explore either a small region comprehensively or a large region superficially. However, since a very large number of experiments would often be required to determine an optimum precisely, regions that might ultimately be of no interest would be explored. In
general, the one-factor-at-a-time method [163,164] is slow, but yields a considerable amount of information about the influence and critical nature of each experimental variable. The one-factor-at-a-time method is probably one of the most common techniques of optimization in analytical chemistry when the experimental variables can be changed quickly and continuously over a wide range. If the experimental variables do not interact with each other, each experimental variable could be optimized independently of the other experimental variables. However, since the experimental variables in the vertical multi-electrode plasma sources are closely interrelated with each other (this is also true for an ICP), a traditional one-factor-at-a-time investigation may be potentially misleading and also time consuming. Simplex optimization has proved to be a simple, fast, and effective means of optimizing systems which have interrelated experimental variables. As a result, the modified sequential simplex optimization method [165-168], which allows numerous interrelated experimental variables to be optimized, was employed in order to search for the optimum experimental conditions in this study. A one-factor-at-a-time experiment, in which five of the experimental variables were held constant and the sixth varied as the L/B ratio was measured, was used to confirm the success of the simplex optimization.
3. EXPERIMENTAL

3.1 Instrumentation

The experimental facilities for the vertical 4-electrode plasma source used in this study are identical to those described previously [119].

3.2 Experimental variables and response functions

In the vertical 4-electrode plasma source, the possible experimental variables and response functions are listed in Table 9. Preliminary experiments showed that several experimental variables which affect the analytical performance of the vertical 4-electrode plasma source are closely interrelated with each other. For example, as the sample carrier gas flow rate is increased, the point for the maximum emission intensity shifts to a higher position in the discharge. Consequently, the optimal sample carrier gas flow rate will be different from region to region in the plasma. In addition, the position of the point for the maximum emission intensity is also significantly affected by varying the current and the length of plasma. Thus a true optimum experimental condition cannot be readily achieved by varying one factor while keeping the others constant.

In order to perform the modified sequential simplex optimization [165-168] for the vertical 4-electrode plasma source successfully, the experimental variables had to be chosen very carefully. Among the possible experimental variables in the vertical 4-electrode plasma source, the six chosen, current, length of plasma, observation height, sample carrier gas flow rate, plasma gas flow rate, and sample uptake
rate, were selected to be optimized based upon the following considerations. First, because of the nature of the operation of the modified sequential simplex optimization, each experimental variable should be readily adjustable by the operator during the operation of the plasma without interruption. Since the sizes of the quartz tube and electrodes were impossible to change without extinguishing the plasma during operation, those variables were eliminated from the modified sequential simplex optimization. Second, in the selection of experimental variables for simplex optimization, all experimental variables which are thought to have a possible effect on the response should be included. However, position of tip of the sample introduction tube which is considered to be insignificant was omitted in this study. For the vertical multi-electrode plasma sources, the significance of each experimental variable has already been determined in a previous one-factor-at-a-time experiment [119].

The possible response functions optimized in this study are also listed in Table 9. Noises in the vertical multi-electrode plasma sources-echelle spectrometer have not been fully characterized yet. However, it is known that source flicker noise is usually the limiting noise in plasma spectroscopy as well as many spectrochemical measurements. Then the L/B ratio alone will govern the detection power, the RSD of the background being dominated by source flicker noise. A prerequisite for this is that shot noise in the background signal is negligible over the entire range of background signals covered in the optimization experiment. In this single-element optimization study, the line-to-background (L/B) ratio for the Ca(II) at 393.37 nm was selected as a response function.
3.3 Boundaries for the experimental variables

The lower and upper bounds for the six experimental variables to be optimized are listed in Table 10. The boundary for each experimental variable is defined by various practical considerations, especially by the physical limits of the instruments since the simplex may well require experimental conditions beyond the capabilities of the instruments.

Although the DC power supply was rated at 45 A, the upper limit was selected at 30 A because the erosion rate of the electrodes was very fast and the ceramic sleeves tended to melt. Below about 20 A, the plasma would be weak and unstable under certain experimental conditions. That is, a short plasma operated below 20 A was not stable and the noise associated with source flicker was dominant, frequently resulting in moving the simplex in the wrong direction. Since a short plasma length would not provide sufficient time to desolvate, vaporize, atomize and excite the analyte species, the lower bound for the length of plasma was chosen at 10 mm. The upper limit was set at 40 mm which was the maximum length that could be obtained with the mechanical design used in this study. The observation height was measured from the top of the quartz tube to the observation zone focused onto the entrance slit of the echelle spectrometer. The lower limit was set at the top of the quartz tube and the upper limit was set by the length of the sample aerosol channel above the quartz tube. The upper and lower bounds for the sample carrier gas flow rate were set by the limitations of the Meinhard concentric nebulizer. The lower limit was set at 0.5 L/min to avoid poor nebulization efficiency as well as severe vaporization interference due to the relatively
Table 9. Possible experimental variables and response functions in the vertical 4-electrode plasma source.

Experimental Variables

Current
Length of Plasma
Observation Height
Sample Carrier Gas Flow Rate
Plasma Gas Flow Rate
Sample Uptake Rate
Position of Tip of the Sample Introduction Tube
Sizes of Quartz Tubes (including Sample Tip Size)
Sizes of Electrodes

Response Functions

Line/Background Ratio
Signal/Noise Ratio
Atom/Ion Line Ratio
Emission Intensity
Excitation Temperature
Electron Density
Table 10. Boundaries for the experimental variables.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Lower Bound</th>
<th>Upper Bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current, A</td>
<td>20.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Length of Plasma, mm</td>
<td>10.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Observation Height, mm (a)</td>
<td>0.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Sample Carrier Gas, L/min</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Plasma Gas, L/min</td>
<td>2.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Sample Uptake Rate, mL/min</td>
<td>0.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

(a) Observation height is expressed by the distance above the top of the quartz tube.
large sample droplets. Also the lower limit was set to be able to penetrate the plasma. The upper limit for the plasma gas flow rate was set at the maximum gas flow rate which would not extinguish the plasma. The lower limit for the plasma gas flow rate must be sufficiently high to sustain the plasma. The boundary limits for the sample uptake rate were set by the limitation of the present peristaltic pump, which is from 0.3 to 1.3 mL/min with 0.76-mm I.D. tubing.

3.4 Operation of the modified sequential simplex optimization

Basically the variable step-size simplex optimization algorithm suggested by Nelder and Mead [165-168] was used in this study. A computer program, called SIMPLEX.BAS, was written in BASIC and consists of the two subroutines: (1) a subroutine for implementing the simplex method, (2) a subroutine for obtaining the L/B ratio from Plasma Spec echelle spectrometer. A PDP 11/73 mini computer was used to carry out the simplex optimization experiment. The experimental variables were adjusted manually.

After the initial simplex had been constructed, the rules of the simplex algorithm [165-168] were used to move the simplex to search for the optimal experimental conditions for the vertical 4-electrode plasma source. With the continuous introduction of 10 mg/L of Ca standard solution into the plasma, the L/B ratio of the Ca (II) at 393.37 nm was optimized. The L/B ratio at each vertex was determined from the mean value of 32 measurements each with 1-s integration time in order to reduce the effect of noise on the simplex optimization.

At the beginning of the simplex, a relatively large initial step
size was chosen to ensure that most of the factor space was explored before the simplex collapses onto the optimum. When the simplex indicates the instrumental settings beyond the physical limits of the instruments, the simplex is forced back into bounds. However, fortunately, boundary violations did not occur during our experiment, except for the sample uptake rate at the end of simplex operation. Finally, the simplex was stopped when the step size became less than 2% of the domain of each experimental variable or when the differences in response approached the value of the experimental error (1.4% RSD).

4. RESULTS AND DISCUSSIONS

The result of the simplex optimization for the vertical 4-electrode plasma source is shown in Figure 47, illustrating the variations in L/B ratios as a function of simplex vertex number. The vertices for the failed movements are also included in this figure. The trend in Figure 47 demonstrates the rapid improvement in L/B ratio during the course of the simplex optimization. Compared with the L/B ratios at the beginning of the simplex optimization, progress towards the optimum by the simplex procedure was fairly rapid in this study. The simplex optimization was halted at the 56th vertex and the L/B ratio was found to be 207. However, it should be pointed out that the best L/B ratio was obtained at the 36th vertex. Since this was due to a brief moment of excessive signal associated with burning of an impurity in the electrode, the L/B ratio at the 36th vertex was not considered to be an optimum.
Figure 47. Movement of the L/B ratio as a function of the simplex vertex number. (The L/B ratio for the Ca (II) at 393.37 nm was used as a response function in this study.)
Figure 48 illustrates that there is a marked trend, during the optimization, for the optimal observation height to shift higher in the plasma. The optimal observation height was determined to be 6.4 mm above the quartz tube. This is in good agreement with the results of a previous one-factor-at-a-time experiment [119], which showed that the optimal observation height in the vertical 4-electrode plasma source was 6 to 8 mm above the quartz tube.

Figure 49 shows a plot of the length of the plasma as a function of the simplex vertex number. The optimal length of the plasma was found to be 28.8 mm. There was not much change in the length of the plasma during the optimization, indicating the initial plasma length (27 mm) was long enough to desolvate, vaporize, atomize, and excite the analyte species. Theoretically, the longer the length of the plasma, the longer the residence time experienced by the analyte species. However, with the present vertical multi-electrode plasma sources, a plasma longer than 30 mm did not provide good analytical results because of the shift of the optimal observation height to a position below the top of the quartz tube. Signals below the top of the quartz tube were attenuated by residue on the inside of the quartz tube.

A plot of the current as a function of the simplex vertex number is shown in Figure 50. The optimal current for the vertical 4-electrode plasma source was found to be 27.8 A. As the current was increased, the L/B ratio decreased due to the higher plasma background emission. In addition, the shift of the point of the maximum intensity to the lower position in the plasma was observed, resulting in a decrease in L/B ratio.
Figure 48. Movement of the observation height as a function of the simplex vertex number. The observation height is expressed by the distance above the quartz tube.
Figure 49. Movement of the length of plasma as a function of the simplex vertex number.
Figure 50. Movement of the current as a function of the simplex vertex number.
Figure 51 illustrates the movement of the sample carrier gas flow rate as a function of the simplex vertex number. The result demonstrates that a flow rate of 0.7 L/min for the sample carrier gas is optimum for the plasma. This was confirmed by the previous one-factor-at-a-time experiment, which showed that a flow rate of 0.7 L/min for the sample carrier gas provided not only sufficient residence time for the analyte species in the plasma, but also effective nebulization of sample with the Meinhard concentric nebulizer.

Figures 52 and 53 show the variations of the plasma gas flow rate and the sample uptake rate as a function of the simplex vertex number, respectively. There were gradual increases in both the sample uptake rate and the plasma gas flow rate during the simplex optimization. Optimal experimental conditions were found to be at a sample uptake rate of 1.3 mL/min, a value which is about one-half of the free uptake rate, and a plasma gas flow rate of 4.9 L/min.

Figure 54 demonstrates that as the simplex moves toward the optimum, there is a trend for the background emission intensity to decrease gradually.

In summary, the performance of modified sequential simplex optimization was rapid and successful in this study. The optimum experimental conditions were achieved in approximately 45 steps and agreed with one-factor-at-a-time searches in a previous study [119]. Although the simplex method did not provide complete information on the influence of each experimental variable on the performance of the plasma, the optimum experimental conditions for the vertical 4-electrode plasma source were obtained relatively fast and easily.
Figure 51. Movement of the sample carrier gas flow rate as a function of the simplex vertex number.
Figure 52. Movement of the plasma gas flow rate as a function of the simplex vertex number.
Figure 53. Movement of the sample uptake rate as a function of the simplex vertex number.
Figure 54. Variation of the background emission intensity as a function of the simplex vertex number.
VI. ANALYTICAL CHARACTERIZATION OF THE SAMPLE ENTRAINING
MULTI-ELECTRODE PLASMA SOURCES FOR ATOMIC EMISSION SPECTROSCOPY
PART II: INTERELEMENT EFFECTS AND EXCITATION TEMPERATURE MEASUREMENTS

by

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for submission to Spectrochim. Acta B.
1. ABSTRACT

Interelement effects are reported for the vertical 4-electrode plasma source. The magnitude and direction of the interelement effects are greatly influenced by the experimental conditions. For a 30-mm plasma length, the interference effect of either phosphate or aluminum on calcium emission is insignificant over the entire vertical region of the plasma. Ionization interference effects on Ca(II) emission produced by an easily ionized element (EIE) are in general agreement with observations in an inductively coupled plasma (ICP). The effect of Na is to generally enhance Ca(II) emission in the lower regions, and to depress the emission in the higher regions in the plasma. However, the position at which a crossover from enhancement to depression occurs is dependent on the ionization potential and degree of ionization of the analyte species.

Nine Fe(I) lines were used to determine the excitation temperature from the slope of a Boltzmann plot. The excitation temperature in the center of the plasma at 8 mm above the quartz tube is 5000±300 K. As the plasma length increases from 25 to 30 mm, the excitation temperature in the sample aerosols channel increases by 2000 K and electron number density increases by a factor of 10. Under an assumption of local thermal equilibrium (LTE), the electron number density obtained from Saha-Eggert equation is about $1.0 \times 10^{15}$ cm$^{-3}$ for a 30-mm plasma. As the sample carrier gas flow rate decreases from 0.85 to 0.71 L/min, the excitation temperature for a 30-mm plasma decreases by 1000 K.
2. INTRODUCTION

A preliminary study [169] has shown that the vertical multi-electrode plasma sources, in which the sample stream is surrounded by the hot plasma, show promise as new excitation sources for atomic emission spectroscopy. The vertical 4-electrode plasma source requires less than 6 L/min of argon gas. Because of the relatively long residence time of the analyte species and the efficient entrainment of an aerosol sample stream in the center of the discharge, the linear log-log analytical working curves have slopes of unity over a dynamic range of 4 to 5 orders of magnitude for 12 elements. The vertical 4-electrode plasma source is comparable to an ICP source and better than a commercial 3-electrode direct current plasma (DCP) source in this respect. One of the main advantages of the vertical 4-electrode plasma source is that the plasma length can be readily increased without interrupting plasma operation, which could prove to be useful for optimizing analytical results, especially when directly analyzing solutions with high salt or suspended solids content. The energy required for the complete atomization of such sample aerosols could be accomplished by elongating the vertical multi-electrode plasma. In addition, detection limits and long- and short-term stability were also found to be comparable to those of an ICP.

In this paper solute vaporization interference effects often observed in flames, and interference effects by adding easily ionized elements (EIE) (i.e. the alkali elements) are reported for the vertical 4-electrode plasma source, because the susceptibility to
interelement interferences is an important characteristic of an excitation source. In addition, the excitation temperature of Fe was determined by the slope method. The influences of several experimental parameters on the excitation temperature and the electron number density were also investigated.

2.1 Interelement effects

Solute vaporization interferences, such as the influences of phosphate on calcium and of aluminum on calcium, have been extensively studied with the ICP [170-175], DCP [176,177] and flame [178-180]. These solute vaporization interferences are attributed to the formation of involatile compound particles under participation of oxygen [178,181] and to the occlusion of Ca in a refractory aluminum oxide matrix [171,182], whose greater thermal stabilities lead to a reduced efficiency of free-atom formation. The influences of phosphate on calcium and of aluminum on calcium in the flame are explained by processes in the condensed phase and not in the gaseous phase [179,180]. The studies in the flame have shown that the interference effects can be minimized after addition of a releasing agent or with the use of the C$_2$H$_2$-N$_2$O flame [183,184]. However, in the ICP and DCP, seemingly contradictory experimental results for the vaporization interference effects have been reported over the past two decades, although the reduced levels of interference in the ICP and DCP have often been used to demonstrate the superiority of the ICP and DCP over the flame for analytical applications [185,186]. It has been cited [171,187] that the contradictory results with an ICP can be ascribed to different experimental conditions, and incomplete
vaporization is not solely responsible for these interference effects. Nevertheless, the fundamental processes that control the interferences have not been fully characterized yet.

The ionization interference effect created by the introduction of EIE into the plasmas is an analytically important feature that helps to understand the physical nature of the plasmas. Numerous researchers have devoted their efforts to understand the mechanism of this ionization interference effect and have postulated a variety of possible mechanisms, such as shifts in ionization equilibrium [188, 189], enhanced collisional excitation [190-192], ambipolar diffusion [193-195], volatilization effects [171, 193, 196], penning ionization by metastable argon [197-199], radiation trapping [197, 200, 201], and non-thermal mechanisms [202]. It is apparent that none of these mechanisms provide a completely satisfactory explanation for the contradictory analytical results related to the ionization interference effects reported in the literature. However, it has been suggested that this could be due to the result of a complex interaction of several of them, although the effects of one mechanism may tend to oppose the effects of another [200].

The EIE interference effects in a flame and dc arc plasma are well known [179, 180, 203-205]. The enhancement effect for the neutral atom line in a flame has been rationalized on the basis of a shift in the ionization equilibrium of the analyte atom, ion, and electrons. The degree of enhancement has been shown to be a function of the ionization potential of the added EIE [206]. In a dc arc, the addition of an EIE changes the excitation conditions in the arc plasma. The addition of an EIE into an arc causes an increase in
electron density and essentially results in a decrease in arc temperature and no change in thermal conductivity [207]. This leads to a shift in the ionization equilibrium and an increase in residence time of the analyte species in the arc. Thus, the combined effects produce either suppression and enhancement of the emission intensities depending upon the types of species and on the excitation energies needed to excite the analyte species.

Since the vertical multi-electrode plasma sources have a shape similar to the ICP, along with an electrical plasma similar to the DCP, the fundamental processes that control the interference effect may provide useful information to understand the differences between the mechanisms in the ICP and DCP [208,209]. In the previous report [169], when plasma length, current, observation height, sample aerosol carrier gas flow rate, plasma gas flow rate, position of sample introduction tube, and sample uptake rate were varied, the spatial emission profiles reflected many of the characteristics associated with an ICP. However, the excitation mechanism in the ICP and the vertical multi-electrode plasma sources might be entirely different due to different excitation conditions. In this paper, the influences of phosphate on calcium and of aluminum on calcium and the ionization interference effects of easily ionized elements are investigated.

2.2 Excitation temperature

The investigation of the dependence of the temperature and the electron number density on the experimental parameters is one of the prerequisites leading to the definitive understanding of the emission characteristics of the analyte species in the plasma. Measurements of
these parameters have been extensively carried out in an ICP [210-214] and DCP [215-217], and used to not only further characterize the excitation mechanisms which take place in the plasma but also improve the performance and analytical utility of the plasma sources.

In this study, we investigate the influences of the spatial profile of the excitation temperature on the experimental parameters, such as plasma length, sample carrier gas flow rate, current, and observation height. The excitation temperature was obtained from the slope of a Boltzmann plot for nine iron lines [210-217] without Abel inversion, and also the electron number density was determined from the Saha-Eggert equation [207,218]. Temperatures determined in this way are lower limits to the radially resolved temperatures. However, although the absolute values of temperature and electron number density may be in error due to the lack of Abel inversion, and the assumption of local thermal equilibrium (LTE) in the vertical 4-electrode plasma source, the dependences of these calculated values on the experimental conditions provides useful information to understand the emission characteristics.

3. EXPERIMENTAL

3.1 Instrumentation

The experimental facilities for the vertical 4-electrode plasma source used in this study are identical to those described previously [169]. The typical experimental conditions chosen for the interelement study were plasma lengths of 25 and 30 mm, a total power
dissipation of 1 kW, a sample carrier gas flow rate of 0.74 L/min, and a plasma gas flow rate of 3.96 L/min. These are conditions close to the optimum determined by the sequential simplex optimization method [169].

3.2 Reagents

Reagent grade salts or pure metals were used to prepare analyte (Ca, Cd, and Fe) stock solutions as suggested by Dean and Rains [219]. The Al and PO₄ concomitant solutions were, respectively, prepared from the pure metal and reagent grade (NH₄)₂HPO₄. For the study of ionization interference, sodium stock solution was prepared from reagent grade NaCl. All solutions were acidified to 0.16 M with nitric or 0.12 M with hydrochloric acid so that any acid effect would not bias the measurements.

3.3 Procedure

3.3.1 Investigation of interference effects

A BASIC computer program, called SCAN.BAS, was written to command the spectrometer and collect the data for the spatial profiles of the emission intensities. To obtain a typical lateral scan, the source mirror of the echelle spectrometer was moved horizontally, obtaining 32 data across the plasma. This process provided the emission intensity as a function of horizontal displacement at a specific height. The lateral scans at eight different heights with 2-mm increments measured from the top of the quartz tube allowed complete spatial profiles of emission intensities to be obtained. All these processes were controlled by a PDP-11/73 computer interfaced with a
Plasma Spec high resolution echelle spectrometer (Leeman Labs Inc., Lowell, MA) via a RS-232 serial port.

3.3.2 Measurements of excitation temperature

Excitation temperature was determined from the slope of a Boltzmann plot of nine Fe(I) lines. The emission intensity of an atomic line can be expressed by the following Einstein-Boltzmann equation [207].

\[ I = \frac{N}{u} \frac{8\pi^2 e^2 h g f}{m \lambda^3} \exp\left(\frac{-E}{kT}\right) \]

where \( N \) is the particle density of the atoms, \( u \) is the partition function of the atom, \( g \) is the statistical weight of the upper level, \( f \) is Ladenburg's oscillator strength for the emitted line, \( e/m \) is the specific charge of the electron, \( I \) is the intensity, \( \lambda \) is the wavelength of the atomic line, \( h \) is Plank's constant, \( k \) is Boltzmann's constant, \( E \) is the energy, and \( T \) is the temperature of a source which follows a Boltzmannian distribution of energy. Then the excitation temperature can be calculated from a plot of \( \ln(gf/I\lambda^3) \) versus \( E \). From the slope of the straight line, which will be \(-1/kT\), we can determine \( T \).

Since a Plasma Spec high resolution echelle spectrometer was used for temperature determinations, a BASIC computer program, called FELINE, was written to access nine Fe(I) lines, most of which are not in the spectrometer's library. The nine Fe(I) lines were found to be accessible through some of the over 700 exit slits in the aperture plate of the spectrometer. Use of these extra lines was made
relatively easy by external computer control using ASCII characters sent and received via the RS-232 serial interface of the spectrometer. A FESCAN.BAS program was then used to control the spectrometer and obtain data.

Since the absolute values of electron number density are not of primary concern in this study, the Saha-Eggert equation is used to calculate the electron number density for the emission lines of Mg(I) at 285.2 nm and Mg(II) at 280.3 nm under assumption of complete LTE.

In order to eliminate the non-uniform response of the spectrometer and photomultiplier as a whole, the emission intensities used in those calculations were corrected by calibration with a standard lamp. A 40-W deuterium arc lamp (Optronic Laboratories Inc., Model UV-40R Ultraviolet Radiance Standards), which was calibrated for spectral radiance in units of W/sr·cm$^2$ over the wavelength region of 180-400 nm, was employed for this purpose.

4. RESULTS AND DISCUSSION

4.1 A study of interelement effects

4.1.1 Ca/PO$_4$ and Ca/Al interference effects

As we have seen in a previous paper [169], the emission behavior of the vertical multi-electrode plasma source is significantly affected by the plasma length. In general, a point of maximum intensity may be shifted lower in the plasma by increasing the plasma length. Thus, the sample injection velocity and the residence time of the analyte species in the plasma are affected, resulting in changes
in analyte emission characteristics. In this study, the interference effects in the Ca/PO₄ system were investigated for 25- and 30-mm plasma lengths.

Figure 55 shows the horizontal intensity profile for the Ca ion at 393.37 nm in the presence and absence of a phosphate matrix for a 30-mm plasma length. The effect of PO₄ concomitant on Ca emission intensity at 6 mm above the quartz tube is insignificant up to PO₄/Ca molar ratios of 100. The horizontal emission profile for the Ca neutral atom line at 422.67 nm is much the same as that of Ca(II) when the PO₄ concomitant is present. The knee depression in the plot of emission intensity versus mole ratio observed in some combustion flames is not observed.

Figure 56 shows the vertical emission intensity profile for the Ca ion line, and further indicates that no major interference effect is observed up to PO₄/Ca molar ratios of 100 along the vertical axis. In contrast to Figure 56, the vertical emission intensity profile for the Ca neutral atom line in Figure 57 shows a different trend in the interference effect. Either an enhancement or a depression on Ca neutral atom emission is observed, depending on the height of the plasma which is observed, whereas a slight depression on Ca ion emission is measured regardless of what portion of the plasma is observed. Interestingly, Savage and Hieftje reported the same trends in the ICP source [173] as those observed in this study.

Figure 58 shows the horizontal emission intensity profiles for the Ca ion line in the absence and presence of phosphate concomitant, Ca:PO₄ molar ratio of 1:500. Depression of the Ca ion line emission intensity is present across the plasma. To check the shapes of the
Figure 55. Horizontal distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/PO₄ molar ratio (2.5 μmol/mL Ca). The plasma length is 30 mm and the observation height is 6 mm above the top of the quartz tube. Molar ratio of Ca to PO₄: (○) 1:0; (+) 1:100.
Figure 56. Vertical distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/PO₄ molar ratio (2.5 µmol/mL Ca). The plasma length is 30 mm. Molar ratio of Ca to PO₄: (○) 1:0; (+) 1:100.
Figure 57. Vertical distribution of the Ca neutral atom line emission intensity at 422.67 nm as a function of Ca/P\textsubscript{O\textsubscript{4}} molar ratio (2.5 μmol/mL Ca). The plasma length is 30 mm. Molar ratio of Ca to P\textsubscript{O\textsubscript{4}}; (O) 1:0; (+) 1:100.
Figure 58. Normalized horizontal distribution of the Ca ion line emission intensity at 393.37 nm with the Ca/PO₄ molar ratio of 500 (2.5 μmol/mL Ca). The plasma length is 30 mm and the observation height is 6 mm above the top of the quartz tube. Molar ratio of Ca to PO₄: (—) 1:0; (Δ) 1:500; (○) normalized 1:500.
curve, the intensity of the horizontal emission profile for the PO₄/Ca molar ratio of 500 was normalized to the curve for zero mole ratio and plotted as squares on top of the zero mole ratio curve. Since the shapes of the curves are essentially the same, lateral diffusion effects based on delayed volatilization apparently are not a major cause of the interference effect. Lateral diffusion effects have been discussed by Boumans and de Boer [193] and observed in an ICP [170] and flame [220,221]. In the ICP, a lateral diffusion effect results in a depression of emission at the center of plasma, and an enhancement of emission at the edges of a radial analyte distribution. Therefore, the suppression that is observed here may be mainly attributable to nebulizer aerosol formation and transport interferences resulting from solution viscosity effects. The solution with a PO₄/Ca molar ratio of 500 here is equivalent to 1250 \( \mu \)mol/mL of \((\text{NH}_4)_2\text{HPO}_4\). This solution was visibly more viscous than water.

For a 25-mm plasma length, the horizontal emission profiles at 6 mm above the quartz tube plotted in Figure 59 show the depression on Ca(I) emission for Ca:PO₄ molar ratios of 1:4 and 1:10. The similar depression effect at the same observation height is observed for Ca(II). This increase in interference relative to the 30-mm plasma is probably due to the relatively short residence time of the analyte species in this shorter plasma.

The vertical emission profiles for Ca(I) and Ca(II) in the presence of PO₄ matrix are also shown in Figures 60 and 61, respectively, for the 25-mm plasma. In Figure 60 either a depression or an enhancement on Ca(I) emission depending on the observation height is observed. The same trend in Ca(I) emission is observed for
Figure 59. Horizontal distribution of the Ca atom line emission intensity at 422.67 nm as a function of Ca/PO₄ molar ratio (2.5 μmol/mL Ca). The plasma length is 25 mm and the observation height is 6 mm above the top of quartz tube. Molar ratio of Ca to PO₄: (○) 1:0; (+) 1:4; (○) 1:10.
Figure 60. Vertical distribution of the Ca neutral atom line emission intensity at 422.67 nm as a function of Ca/PO$_4$ molar ratio (2.5 µmol/mL Ca). The plasma length is 25 mm. Molar ratio of Ca to PO$_4$; (0) 1:0; (+) 1:4; (0) 1:10.
Figure 61. Vertical distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/PO₄ molar ratio (2.5 μmol/mL Ca). The plasma length is 25 mm. Molar ratio of Ca to PO₄; (○) 1:0; (+) 1:4; (◇) 1:10.
the 30-mm plasma as discussed in the previous section. However, as 
the plasma length changes from 30 to 25 mm, the vertical emission 
profiles for Ca(II) in the presence of PO₄ are quite different from 
each other. Both a depression and an enhancement on Ca(II) emission 
are observed for a 25-mm plasma depending on the observation height, 
whereas only a slight depression is observed for a 30-mm over entire 
vertical region in the plasma. This apparent difference is most 
likely caused by the point of maximum intensity being shifted lower in 
the plasma for the longer plasma.

In addition, as the plasma length increases from 25 to 30 mm, the 
Ca(I) emission intensity decreases while the Ca(II) emission intensity 
increases. This type of differing emission behavior can be described 
in terms of "soft" and "hard" lines as suggested by Boumans and de 
Boer [193,222,223].

Spatial emission profiles for Ca(I) and Ca(II) in the presence of 
Al matrix were also investigated. Figure 62 shows the horizontal 
emission profiles for Ca(II) at 6 mm above the quartz tube as a 
function of Ca/Al molar ratio. Similar depression in Ca(II) emission 
intensity is observed for Al as PO₄, but the degree of the 
interference is more with the Al concomitant. The vertical emission 
profiles for Ca(I) and Ca(II) in the presence of Al matrix are also 
similar to those in the presence of PO₄ matrix as described above, 
except for the degree of interference.

4.1.2 Ionization interference effects by adding an EIE

For the study of the ionization interference effects on Ca and Cd 
emission intensities in the presence of a Na matrix, a plasma length
Figure 62. Horizontal distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/Al molar ratio (2.5 μmol/mL Ca). The plasma length is 30 mm. Molar ratio of Ca to Al: (○) 1:0; (+) 1:10; (○) 1:100.
of 25 mm was used. The other experimental conditions for this study were the same as in the previous section.

Figure 63 shows the vertical emission profiles for Ca (II) at 393.37 nm in the presence and absence of Na matrix (Ca:Na molar ratios of 1:0, 1:25, and 1:250). At the Na/Ca molar ratio of 250, a slight enhancement on Ca(II) emission is observed in the lower regions of the sample aerosol channel, whereas a large depression is observed in the regions higher than 6 mm above the quartz tube. The degree of depression in the higher regions in the plasma is found to be dependent on the molar ratio of Na to Ca. The same observations were reported in an ICP source [175,196]. However, at the Na/Ca molar ratio of 25, the effect of Na is generally to depress the Ca(II) emission over the entire vertical region in the center of the plasma. The degree of the interference effect on Ca(II) emission gradually increases up to the observation height at which the maximum Ca(II) emission intensity is observed. Then the degree of interference is reduced and eventually no interference effect is observed at 16 mm above the quartz tube.

Figure 64 shows the horizontal emission profile for Ca(II) emission at 10 mm above the quartz tube. The depression in emission is especially noticeable in the center of the plasma.

In Figure 65, the influence of the Na matrix on the vertical emission profiles of the Ca neutral atom line is illustrated, which is quite different from that of the Ca ion line. A depression in Ca(I) emission for the Na/Ca molar ratio of 25 is observed in the observation zone up to 14 mm above the quartz tube, and a slight enhancement is observed above that height. In general, this Ca(I)
Figure 63. Vertical distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/Na molar ratio (0.5 μmol/mL Ca). The plasma length is 25 mm. Molar ratio of Ca to Na; (○) 1:0; (+) 1:25; (□) 1:250.
Figure 64. Horizontal distribution of the Ca ion line emission intensity at 393.37 nm as a function of Ca/Na molar ratio (0.5 μmol/mL Ca). The plasma length is 25 mm and the observation height is 6 mm above the top of the quartz tube. Molar ratio of Ca to Na; (○) 1:0; (+) 1:25; (●) 1:250.
Figure 65. Vertical distribution of the Ca neutral atom line emission intensity at 422.67 nm as a function of Ca/Na molar ratio (0.5 μmol/mL Ca). The plasma length is 25 mm. Molar ratio of Ca to Na; (○) 1:0; (△) 1:25; (×) 1:250.
emission behavior is quite opposite to that observed in an ICP [175,196]. In an ICP, it has been reported that the effect of Na matrix is to generally enhance the emission of both the Ca(I) and Ca(II) lines in the lower regions, and to depress the emission in regions higher above the load coil [173,175,196,224]. No explicit interpretation for this differing behavior is available. However, this is probably due to the different excitation conditions in the plasmas.

At a Na/Ca molar ratio of 25, the position of the observation height at which crossover from Ca(I) line radiance depression to enhancement occurs is found at 14 mm above the quartz tube. In contrast to this, at a higher Na/Ca molar ratio of 250, the crossover point shifts lower in the plasma to 11 mm above the quartz tube. The degree of enhancement or depression for the Na/Ca molar ratio of 250 is much greater than that for 25. Nevertheless, as demonstrated in Figures 63 and 65, the interference in the presence of a fixed concentration of Na can be minimized by selecting the proper observation height.

The interference of Na on Cd(I) at 228.80 nm and Cd(II) at 214.44 nm were also investigated. Figures 66 and 67, respectively, show the vertical emission profiles for Cd(I) and Cd(II) emissions in the presence of Na matrix for Cd/Na molar ratios of 1:0, 1:25, and 1:250. In general, the effects of Na on Cd(II) and Ca(II) are generally the same except for the position of the crossover from enhancement to depression. The emission profiles for Cd are shifted to a higher position in the plasma. Because Cd has a higher ionization potential, this could be explained if a longer residence time were need for Cd to
Figure 66. Vertical distribution of the Cd neutral atom line emission intensity at 228.80 nm as a function of Cd/Na molar ratio (0.5 μmol/mL Cd). The plasma length is 25 mm. Molar ratio of Cd to Na; (O) 1:0; (+) 1:25; (C) 1:250.
Figure 67. Vertical distribution of the Cd ion line emission intensity at 214.44 nm as a function of Cd/Na molar ratio (0.5 μmol/mL Cd). The plasma length is 25 mm. Molar ratio of Cd to Na; (□) 1:0; (+) 1:25; (○) 1:250.
reach the higher temperature necessary for the crossover to occur. In contrast to Cd(II), the depression on Cd(I) emission is observed over the entire vertical region in the center of the plasma. The degree of depression is found to be dependent on the molar ratio of Cd/Na.

4.2 Fe(I) excitation temperature measurement by Boltzmann plot

The wavelengths, the lower and upper energy levels, and gf-values of the nine Fe(I) lines used in this study are summarized in Table 11. A 30-mm plasma length was used, and the emission intensities for these lines were observed at 6 mm above the quartz tube. Then the intensities corrected for the D2 lamp calibration are used for a plot of -ln(gf/\lambda^3) versus E. A linear least square fit is employed to determine the best line. With the transition probability values from Ref. [229], an excitation temperature of 5000 K is calculated from the slope of the Boltzmann plot shown in Figure 68. Because lateral intensities (integrated over the optical path) rather than radial intensities are used in this Boltzmann plot, the temperature is a lower limit to the maximum temperature along the optical path.

In general, the accuracy of the temperature determination by the slope method is directly dependent on the accuracy of transition probability data for nine Fe(I) lines. Despite a large amount of effort to determine more accurate transition probability values, there are still large disagreements among published absolute transition probabilities. For example, the excitation temperatures calculated from using sets of transition probability values given in several compilations [225-231] are summarized in Table 12. The numerical values of gf are also listed in Table 13. According to the transition
Figure 68. Boltzmann plot for nine Fe(I) lines. The plasma length is 30 mm and the observation height is 6 mm above the top of the quartz tube.
Table 11. Energy levels and gf-values for Fe(I) lines.

<table>
<thead>
<tr>
<th>Wavelength, nm</th>
<th>gf [229]</th>
<th>Energy level, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>302.11</td>
<td>0.646</td>
<td>416 - 33507</td>
</tr>
<tr>
<td>303.74</td>
<td>0.372</td>
<td>888 - 33802</td>
</tr>
<tr>
<td>344.39</td>
<td>0.0813</td>
<td>704 - 29733</td>
</tr>
<tr>
<td>346.59</td>
<td>0.115</td>
<td>888 - 29733</td>
</tr>
<tr>
<td>347.55</td>
<td>0.145</td>
<td>704 - 29469</td>
</tr>
<tr>
<td>361.88</td>
<td>1.91</td>
<td>7986 - 35612</td>
</tr>
<tr>
<td>373.71</td>
<td>0.316</td>
<td>416 - 27167</td>
</tr>
<tr>
<td>384.04</td>
<td>0.646</td>
<td>7986 - 34017</td>
</tr>
</tbody>
</table>
Table 12. Comparison of various results of excitation temperature measurements with different data for Fe(I).

<table>
<thead>
<tr>
<th></th>
<th>Number of lines</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>King and King, 1938 [225]</td>
<td>6</td>
<td>4500 ± 300</td>
</tr>
<tr>
<td>Crosswhite, 1958 [226]</td>
<td>6</td>
<td>4500 ± 400</td>
</tr>
<tr>
<td>Corliss and Bozman, 1962 [227]</td>
<td>9</td>
<td>4500 ± 400</td>
</tr>
<tr>
<td>Margoshes and Scribner, 1963 [228]</td>
<td>6</td>
<td>5000 ± 300</td>
</tr>
<tr>
<td>Kirkbright and Sargent, 1970 [229]</td>
<td>8</td>
<td>5000 ± 300</td>
</tr>
<tr>
<td>Bridges and Kornblith, 1974 [230]</td>
<td>6</td>
<td>5500 ± 300</td>
</tr>
<tr>
<td>Fuhr and Martin, 1981 [231]</td>
<td>7</td>
<td>5800 ± 400</td>
</tr>
</tbody>
</table>
Table 13. gf values for Fe(I) lines used in temperature measurements.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>302.11</td>
<td>0.34</td>
<td>0.773</td>
<td>0.48</td>
<td>0.512</td>
<td>0.646</td>
<td>NA</td>
<td>0.4365</td>
</tr>
<tr>
<td>303.74</td>
<td>0.24</td>
<td>0.437</td>
<td>0.31</td>
<td>0.292</td>
<td>0.372</td>
<td>0.24</td>
<td>0.2239</td>
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<tr>
<td>344.39</td>
<td>NA</td>
<td>NA</td>
<td>0.061</td>
<td>NA</td>
<td>0.0813</td>
<td>0.042</td>
<td>0.0389</td>
</tr>
<tr>
<td>346.59</td>
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<td>0.094</td>
<td>NA</td>
<td>0.115</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>347.55</td>
<td>NA</td>
<td>NA</td>
<td>0.12</td>
<td>NA</td>
<td>0.145</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>361.88</td>
<td>1.6</td>
<td>1.1</td>
<td>1.9</td>
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<td>1.91</td>
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<tr>
<td>371.99</td>
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<td>0.288</td>
<td>NA</td>
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<td>0.3715</td>
</tr>
<tr>
<td>373.71</td>
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<td>0.215</td>
<td>0.32</td>
<td>0.22</td>
<td>0.316</td>
<td>0.269</td>
<td>0.2667</td>
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<tr>
<td>384.04</td>
<td>0.47</td>
<td>0.371</td>
<td>0.57</td>
<td>0.335</td>
<td>0.646</td>
<td>0.347</td>
<td>0.3119</td>
</tr>
</tbody>
</table>

NA : not available
probability values used it is possible to obtain 4500 K just as easily as 5800 K due to the uncertainty of the gf values used in the calculations. The average of the excitation temperatures listed in Table 12 is 5000 K.

4.3 Effect of the experimental parameters on excitation temperature profile.

For a complete set of spatial profiles of excitation temperature along the sample aerosol channel, the two-line method was employed due to the simplicity and the desire for fast data acquisition time. The Fe(I) 371.99-nm and 373.71-nm lines were chosen for the temperature determination because for the slope method, the slope of these spectral lines fell close to the slope of the line of best fit. In addition, other factors considered in the selection process were: (1) availability of sufficiently intense emission; (2) minimal spread in emission intensities to reduce the error in photoelectric intensity measurements; (3) freedom of spectral interferences from plasma background emissions. Although the absolute value of the excitation temperature by using the two-line method may be in error as discussed above, the observed trends in the temperatures are meaningful.

Figures 69 and 70 show the excitation temperature profiles along with sample aerosol channel for 25 and 30-mm plasma lengths, respectively. As the plasma length increases from 25 to 30 mm, the points of maximum excitation temperature shift to a lower position in the sample aerosol channel. The points of the maximum excitation temperature for the 25- and 30-mm plasma lengths are 8 and 2 mm above the quartz tube, respectively, and the maximum excitation temperature
Figure 69. Fe excitation temperature profile along the sample aerosol channel for a 25-mm plasma length.
Figure 70. Fe excitation temperature profile along the sample aerosol channel for a 30-mm plasma length.
for a 30-mm plasma length is 2000 K greater than that for a 25-mm length. The spatial profiles for the excitation temperature as a function of plasma length are similar to those for the emission intensity of the analyte species.

Figure 71 illustrates the horizontal profiles for the excitation temperature as a function of plasma length. A maximum excitation temperature of 7000-8000 K is observed in the sample aerosol channel for a 30-mm plasma length. The excitation temperature increases significantly as the plasma length increases. Irregular variations in the temperature profile for a 25-mm plasma length were caused by errors of the intensity measurements because of relatively weak emission intensities.

The spatial profile of the electron number density shown in Figure 72 reflects excitation temperature distribution. For a 30-mm plasma length, the electron number density obtained from the Saha-Eggert equation is about $1.0 \times 10^{15}$ cm$^{-3}$. As we have seen in the previous section, the emission behavior for the 25- and 30-mm plasma lengths are significantly different from each other. Evidently, the differing emission behavior can be attributed to the changes in the excitation temperature and the electron number density experienced by the analyte species.

The influences of the sample carrier gas flow rate and current on the excitation temperature were also investigated. As the sample carrier gas flow rate increases from 0.71 to 0.85 L/min, the excitation temperature in the center of the plasma decreases by 1000 K. This is apparently due to the relatively short residence time of
Figure 71. Horizontal distribution of Fe excitation temperature at an observation height of 8 mm above the top of the quartz tube for plasma lengths of (+) 25 mm; (□) 30 mm. The sample carrier gas flow rate is 0.71 L/min.
Figure 72. Horizontal distribution of electron number density at an observation height of 8 mm above the top of the quartz tube for plasma lengths of (+) 25 mm; (○) 30 mm. The sample carrier gas flow rate is 0.71 L/min.
the analyte species and cooling effects caused by the fast flow rate, which has been also reported in an ICP [214,232].

5. CONCLUSION

This spatial study of interelement effects on analyte emission intensity has provided useful information to understand the physical nature of the vertical 4-electrode plasma source. It shows that the degree and direction of the interelement effects are strongly influenced by the plasma length and observation height. Nevertheless, it has been demonstrated that the interelement effects can be minimized by selecting the proper experimental conditions in the vertical 4-electrode plasma source.

Unlike the results for a 25-mm plasma length, for a 30-mm plasma length, the interference effects of PO₄ matrix on Ca(II) emission at 393.37 nm are found to be insignificant over the entire vertical region studied in the plasma. The volatilization interference effects due to the formation of the involatile compounds were found to be minimal for the longer plasma lengths. This indicates that longer plasma lengths produce longer analyte residence times. The interference effects of Al on Ca emission intensities are found to be similar to those of PO₄.

For a 25-mm plasma, the ionization interference effect of Na on Ca(II) emission is in general agreement with the observations in an ICP [173,175,196,224]. The effect of Na is to generally enhance the emission of Ca(II) in the lower regions, and to depress the emission
in the higher regions in the sample aerosol channel. Increased electron collisional excitation resulting from an increase in electron density from Na ionization may cause the enhancement of Ca(II) emission in the lower regions. On the contrary, the opposite interference effect of Na matrix on Ca(I) emission observed in this study suggests the involvement of a shift in ionization equilibrium which could take place with an increase in electron density. To further clarify this observation, measurements of the population of particles in the ground state must be carried out.

We have studied the spatial distributions of the excitation temperature and electron number density under a variety of conditions of plasma length, sample carrier gas flow rate, current, and observation height. Most importantly, as the plasma length increases from 25 to 30 mm, the excitation temperature in the center of plasma increases by 2000 K and the electron number density increases by a factor of 10. As we have seen in a previous study [169], this is apparently due to a longer residence time of analyte species for a 30-mm plasma.

The analytical characteristics of this new plasma source reflect many of those associated with an ICP source. It is entirely possible that the vertical multi-electrode plasma sources can offer some of the same advantages as other high temperature plasmas and some unique advantages as well.
VII. CONCLUSION

This research has shown that the vertical multi-electrode plasma sources show promise for a new excitation source for atomic emission spectroscopy. When several of the experimental parameters were varied, the spatial emission profiles reflected many of the characteristics associated with an ICP. The analytical results, such as detection limits, linear dynamic range, and long- and short-term stability were found to be comparable to those of an ICP. Because of the relatively long residence time of the analyte species and the efficient entrainment of an aerosol sample stream in the center of the discharge, the linear log-log analytical working curves have slopes of unity over a dynamic range of 4 to 5 orders of magnitude for 12 elements. One of the main advantages of the vertical multi-electrode plasma sources is that the plasma length can be readily increased without interrupting plasma operation, which could prove to be useful for optimizing analytical results, especially when the directly analyzing solutions with high salt or suspended solids content. The energy required for the complete atomization of such sample could be accomplished by elongating the vertical multi-electrode plasma rather than increasing the electrical power, as has been done for ICP sources from 1.2 KW up to 5 KW [160].

The effects of the vaporization and ionization interferences in the vertical multi-electrode plasma sources are found to be similar to those of an ICP. It has been shown that the degree and direction of the interelement effects are strongly influenced by the plasma length and observation height. Nevertheless, it has been demonstrated that
the interelement effects can be minimized by selecting the proper experimental conditions in the vertical multi-electrode plasma source.

As the plasma length increases from 25 to 30 mm, the Fe excitation temperature in the center of the plasma increases by 2000 K and electron number density increases by a factor of 10. This is apparently due to a longer residence time of analyte species for a 30-mm plasma. Evidently, the differing emission behaviors can be attributed to the change in the excitation temperature and the electron number density experienced by the analyte species.

Possible spectral interferences due to the use of the tungsten electrodes could be avoided by employing graphite electrodes. In the vertical 6-electrode plasma source, the sample stream could be completely surrounded by hot plasma for some experimental conditions. It is feasible that better analytical results could be obtained with this modification of the vertical multi-electrode plasma sources used in this study. Accordingly, it is entirely possible that the vertical multi-electrode plasma sources can offer some of the same advantages as other high temperature plasmas and some unique advantages as well.
VIII. REFERENCES


IX. APPENDICES
Appendix I. 1000 mg/L of Standard Stock Solutions.

<table>
<thead>
<tr>
<th>Element</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Dissolve 1.000g Al wire in minimum amount of 2M HCl and dilute to a final volume of 1 liter.</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Dissolve 2.282g $3\text{CdSO}_4\cdot8\text{H}_2\cdot0$ in water and dilute to a final volume of 1 liter.</td>
</tr>
<tr>
<td>Calcium</td>
<td>Place 2.4973g CaCO$_3$ in volumetric flask with 300 mL water, carefully add 10 mL HCl, after CO$_2$ is released by swirling, dilute to a final volume of 1 liter.</td>
</tr>
<tr>
<td>Chromium</td>
<td>Dissolve 2.829g $K_2\text{Cr}_20_7$ in water and dilute to a final volume of 1 liter.</td>
</tr>
<tr>
<td>Copper</td>
<td>Dissolve 3.929g fresh crystals of $Cu\text{SO}_4\cdot5\text{H}_2\cdot0$ and dilute to a final volume of 1 liter.</td>
</tr>
<tr>
<td>Iron</td>
<td>Dissolve 1.000g of Fe wire in 20 mL of 5M HCl and dilute to a final volume of 1 liter.</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Dissolve 1.000g Mg in 50 mL of 1M HCl and dilute to a final volume of 1 liter.</td>
</tr>
<tr>
<td>Manganese</td>
<td>Dissolve 3.0764g $\text{MnSO}_4\cdot\text{H}_2\cdot0$ (dried at 105°C for 4 hr) in water and dilute to a final volume of 1 liter.</td>
</tr>
<tr>
<td>Sodium</td>
<td>Dissolve 2.5421g NaCl in water and dilute to a final volume of 1 liter.</td>
</tr>
<tr>
<td>Vanadium</td>
<td>Dissolve 2.2963g $\text{NH}_4\text{VO}_3$ in 100 mL of water plus 10 mL of nitric acid and dilute to a final volume of 1 liter.</td>
</tr>
<tr>
<td>Zinc</td>
<td>Dissolve 1.000g Zn in 10 mL of HCl and dilute to a final volume of 1 liter.</td>
</tr>
</tbody>
</table>
Appendix 2. Computer programs.

**SIMPLEX.BAS**

This program consists of the two subroutines: (1) a subroutine for implementing the simplex method, (2) a subroutine for obtaining the L/B ratio from plasma spectrometer. This program was written by Gae Ho Lee on Oct. 31, 1985.

10 REM ****************************************************
20 REM SIMPLEX.BAS
30 REM ****************************************************
40 REM THIS PROGRAM CONSISTS OF THE TWO SUBROUTINES: (1) A SUBROUTINE FOR IMPLEMENTING THE SIMPLEX METHOD, (2) A SUBROUTINE FOR OBTAINING THE L/B RATIO FROM PLASMA SPEC ECHELLE SPECTROMETER.
50 REM THIS PROGRAM WAS WRITTEN BY GAE HO LEE ON OCT. 31, 1985.
60 REM ****************************************************
70 REM THIS PROGRAM CONSISTS OF THE TWO SUBROUTINES: (1) A SUBROUTINE FOR IMPLEMENTING THE SIMPLEX METHOD, (2) A SUBROUTINE FOR OBTAINING THE L/B RATIO FROM PLASMA SPEC ECHELLE SPECTROMETER.
80 REM THIS PROGRAM WAS WRITTEN BY GAE HO LEE ON OCT. 31, 1985.

90 REM A SUBROUTINE FOR OBTAINING THE L/B RATIO FROM SPECTROMETER

100 PRINT:PRINT"TYP-100000.

110 PRINT:PRINT"SCAN(1) OR RELATIVE INTENSITY(0)".

120 PRINT:PRINT"INTEGRATION DURATION(1 TO 20)".

130 PRINT:PRINT"DO YOU WANT TO USE THE ORIGINAL DATA? YES(1), NO(0)".

140 PRINT:PRINT"DO YOU WANT TO USE THE ORIGINAL DATA? YES(1), NO(0)"

150 PRINT:PRINT"ENTER 1 TO DO SIMPLEX ", INPUT Z5

160 IF Z5 = 1 THEN GOTO 1620

170 IF Z5 = 1 THEN GOTO 1620

180 HOW MANY LINES DO YOU WANT TO USE? (1-11)". INPUT N9

190 IF Z5 = 1 THEN GOTO 1620

200 FOR I = 1 TO N9: REM READ PMT X,Y AND SLIT X,Y

210 READ W(I,1), W(I,2), W(I,3), W(I,4), W(I,5)

220 NEXT I

230 GOSUB 1170: REM ENTER PROGRAM INTO SPECTROMETER

240 FOR Q = 1 TO 3000: NEXT Q

250 PRINT#P9, "X": PRINT#P9, "11": PRINT#P9, "202"

260 PRINT#P9, "11": PRINT#P9, "148"

270 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

280 PRINT#P9, "10": PRINT#P9, "10": PRINT#P9, "10": PRINT#P9, "10": PRINT#P9, "2"

290 PRINT#P9, "10": PRINT#P9, "10": PRINT#P9, "10": PRINT#P9, "10": PRINT#P9, "2"

300 PRINT#P9, "10": PRINT#P9, "10": PRINT#P9, "10": PRINT#P9, "10": PRINT#P9, "2"

310 NEXT I

320 GOSUB 1170: REM ENTER PROGRAM INTO SPECTROMETER

330 FOR Q = 1 TO 3000: NEXT Q

340 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

350 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

360 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

370 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

380 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

390 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

400 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

410 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

420 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

430 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

440 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

450 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

460 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

470 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

480 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

490 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

500 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

510 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

520 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

530 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

540 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

550 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"

560 PRINT#P9, "9": PRINT#P9, "9": PRINT#P9, "2" PRINT#P9, "2"
216
700 LET Q=EXP(9,1765061,20):PRINT#9 "M":PRINT#9 "17":FOR Q=1 TO 6000:NEXT Q
710 LET Q=EXP(9,1765061,20):PRINT#9 "M":PRINT#9 "16":FOR Q=1 TO 6000:NEXT Q
720 GOTO 820 LET Q=EXP(9,1765061,20) : REM COLLECTING DARK SIGNAL
730 PRINT#9 "X":PRINT#9 "11":PRINT#9 "400"
740 LET Y=0: LET I=1
750 INSPEC A1(0),1472
760 IF Z=1 THEN LET I=1
770 PRINT "DATA RECEIVED ";
780 FOR I=0 TO 1472 STEP 46
790 LET Q=I/46:LET Y=Y+Q,A1(0)
800 NEXT I
810 PRINT "DATA STORED":I
820 REM NOW TRY SUBROUTINE AT LOC 170 TO MOVE ALL 4 MOTORS
830 LET Q=EXP(9,1765061,20)
840 FOR Q=1 TO 2000:NEXT Q
850 PRINT#9,"X":PRINT#9,"11":PRINT#9,"400"
860 FOR Q=1 TO 6000:NEXT Q:REM WAIT TILL DONE
870 LET Q=EXP(9,1765061,20):REM DO APERTURE X SCAN
880 FOR Q=1 TO 2000:NEXT Q
890 PRINT#9,"X":PRINT#9,"11":PRINT#9,"400"
900 LET Y=1
910 GOSUB 3600:REM GET 32 POINTS
920 IF Z=1 THEN GOTO 960
930 LET Q=EXP(9,1765061,26):REM PRINT ON PRINTER
940 FOR Q=1 TO 3600:NEXT Q:REM DELAY FOR PRINTER
950 REM
960 IF Z=1 THEN GOTO 2940
970 IF M=1 THEN GOTO 1060
980 LET Q=EXP(9,1765061,20):REM DO APERTURE Y SCAN
990 FOR Q=1 TO 3000:NEXT Q
1000 PRINT#9,"X":PRINT#9,"11":PRINT#9,"420"
1010 LET Y=N+1
1020 GOSUB 3600:REM GET 32 PTS
1030 IF Z=0 THEN GOTO 1060
1040 LET Q=EXP(9,1765061,26):REM PRINT ON PRINTER
1050 FOR Q=1 TO 3600:NEXT Q:REM DELAY FOR PRINTER
1060 NEXT I
1070 IF M=1 THEN GOTO 1110
1080 GOSUB 3100:REM TO FIND PEAK VALUES
1090 REM
1100 IF Z=1 THEN GOTO 2960
1110 PRINT "ENTER 1 TO PRINT RESULTS ON PRINTER":INPUT Q
1120 IF Q=1 THEN LET Q=25,PRINT#1,Y(1,0),32,2
1130 IF Z=1 THEN GOTO 2960
1140 PRINT "ENTER 1 TO DO ANOTHER RUN OR SIMPLEX":INPUT Q
1150 IF Q=1 THEN GOTO 130
1160 STOP
1170 PRINT "LOADING SPECTROMETER MEMORY WITH SPECIAL COMMANDS"
1180 PRINT#1
1190 PRINT=1
1200 PRINT=1
1210 LET Q=EXP(9,1765061,20):REM HG MIRROR MOTOR COMMAND CORRECTION
1220 FOR Q=1 TO 2000: NEXT Q
1230 PRINT#9,"X":PRINT#9,"9"
1240 PRINT#9,"53":PRINT#9,"3":PRINT#9,"0":PRINT#9,"6":PRINT#9,"6"
1250 REM DARK SIGNAL
1260 LET Q=EXP(9,1765061,20)
1270 PRINT#9,"X":PRINT#9,"3":PRINT#9,"395"
1280 FOR Q=1 TO 2000: NEXT Q
1290 PRINT#9,"21":PRINT#9,"148"
1300 PRINT#9,"6":PRINT#9,"53"
1310 PRINT#9,"21":PRINT#9,"400"
1320 PRINT#9,"21":PRINT#9,"186":REM HG MIRROR OUT, THEN IN
1330 PRINT#9,"21":PRINT#9,"198"
1340 PRINT#9,"21":PRINT#9,"124"
1350 PRINT#9,M6:PRINT#9,"23"
1360 PRINT#9,"21":PRINT#9,"132"
1370 PRINT#9,M6:PRINT#9,"24":REM FOUR COUNTS/STEP
1380 FOR Q=1 TO 2000:NEXT Q:PRINT#9,"14":PRINT#9,136
1390 PRINT#9,"2":PRINT#9,"403"
1400 PRINT#9,M6:PRINT#9,"23":PRINT#9,"28":PRINT#9,"12":REM RS232 XMIT
1410 PRINT#9,"23*:PRINT#9,"3":PRINT#9,"63.:PRINT#9,"0"
1420 FOR Q=1 TO 2400:NEXT Q
1430 REM SLIT VERTICAL SCAN
1440 LET Q=EXF(9,176506!,20)
1450 FOR Q-1 TO 2000 :NEXT Q
1460 PRINT#9,"X":PRINT#9,4":PRINT#9,"420":PRINT#9,"21":PRINT#9,124
1470 PRINT#9,M6:PRINT#9,37
1480 PRINT#9,14":PRINT#9,76
1490 PRINT#9,M6:PRINT#9,38:REM TWO COUNTS/STEP
1500 PRINT#9,14":PRINT#9,76
1510 PRINT#9,14":PRINT#9,76
1520 PRINT#9,14":PRINT#9,76
1530 PRINT#9,14":PRINT#9,76
1540 PRINT#9,14":PRINT#9,76
1550 PRINT#9,14":PRINT#9,76
1560 PRINT#9,14":PRINT#9,76
1570 PRINT#9,14":PRINT#9,76
1580 FOR Q=1 TO 2000:NEXT Q
1590 RETURN
1600 GOTO 3100
1610 GOTO 3100
1620 REM A SUBROUTINE FOR IMPLEMENTING THE SIMPLEX METHOD
1630 PRINT#1 " ******************************************************************
1640 PRINT#1 " SIMPLEX  "
1650 PRINT#1 " ******************************************************************
1660 PRINT
1670 PRINT " WELCOME TO SIMPLEX "
1680 PRINT " ******************************************************************
1690 PRINT
1700 PRINT " ENTER THE # OF THE VARIABLES ", INPUT NO
1710 PRINT " THIS PROGRAM IS WRITTEN FOR THE OPTIMIZATION OF PLASMA"
1720 PRINT " THE VARIABLES USED IN THIS SIMPLEX METHOD ARE :
1730 PRINT 1 ELECTRICITY ( A )
1740 PRINT 2 LENGTH OF PLASMA ( NM)
1750 PRINT 3 DISTANCE BTW ELECTRODE AND SAMPLE TUBE TIP ( MM)
1760 PRINT 4 OBSERVATION HEIGHT FROM QUARTZ TUBE ( MM)
1770 PRINT 5 SAMPLE GAS FLOW RATE ( L/MIN)
1780 PRINT 6 INNER GAS FLOW RATE ( L/MIN)
1790 PRINT 7 SAMPLE UPTAKEN RATE ( WITH 0.76 MM DIA.)
1800 PRINT"PRINT:PRINT "VARIABLES AND DELTA VALUES" (THE VALUE OF VARIABLE AND THE VALUE OF DELTA)"
1810 PRINT X(0,0)=-28:LETX(0,1)=19.6:LETX(0,2)=56:LETX(0,3)=.555:LETX(0,4)=4
1820 LET X(0,5)=819
1830 LET D(0)=2:LETD(1)=5:LETD(2)=5:LETD(3)=3:LETD(4)=7:LETD(5)=300 GOTO 2100
1840 FOR I=0 TO NO-1
1850 PRINT I+1,:INPUT X(O,I),D(I)
1860 NEXT I
1870 NEXT I
1880 REM GENERATION OF INITIAL ARRAY FOR SIMPLEX
1890 FOR A=1 TO NO : FOR B=0 TO NO-1
1900 LET X(A,B)=.2*D(B)+X(0,B)
1910 NEXT B
1920 NEXT A
1930 FOR C=1 TO NO
1940 LET F=C-1
1950 LET X(C,F)=.9*D(F)+X(0,F) : NEXT C
1960 REM PRINT OUT THE INITIAL SIMPLEX
1970 PRINT " INITIAL SIMPLEX FOR THIS EXPERIMENT "
1980 FOR A=0 TO NO-1
1990 PRINT D(A) ;:NEXT A:PRINT
2000 FOR A=0 TO NO : FOR B=0 TO NO-1
2010 PRINT X(A,B):
2020 NEXT B :PRINT :NEXT A
2030 REM INPUT REPONSE
2040 PRINT :PRINT
2050 PRINT " INPUT REPONSE FOR FOLLOWING VARIABLES"
2060 FOR A=0 TO NO : FOR B=0 TO NO
2070 LET A8=-A7-1 : IF A8 &gt;=0 THEN PRINT X(A8,B):NEXT B:PRINT
2080 FOR B=0 TO NO-1 : PRINT X(A7,B) ; : NEXT B : PRINT
2090 GOSUB 2890
2100 LET X(A7,NO)-H(N0+1)
2110 PRINT " EL LE DI OH SG IG SU RE "
2120 NEXT A
2130 PRINT " EL LE DI OH SG IG SU RE " : NEXT A : PRINT#1
2140 REM CENTROID CALCULATION
2150 PRINT *** CENTROID CALCULATION ***
2160 PRINT " FOR A=0 TO NO-1 : PRINT X(A,B) ; : NEXT B : PRINT
2170 PRINT *** CENTROID CALCULATION ***
2180 PRINT " FOR A=0 TO NO-1 : PRINT X(A,B) ; : NEXT B : PRINT
2190 FOR Q=1 TO 200 : NEXT Q
2200 FOR A=0 TO NO-1 : PRINT H(A) ; X(A,NO) ; : NEXT A
2210 REM CENTROID CALCULATION
2220 PRINT "*** CENTROID CALCULATION ***
2230 FOR A=0 TO NO : FOR B=0 TO NO : PRINT X(A,B) ; : NEXT B : PRINT : NEXT A
2240 PRINT *** CENTROID CALCULATION ***
2250 FOR A=0 TO NO-1 : FOR B=0 TO NO : PRINT X(A,B) ; : NEXT B : FOR Q=1 TO 200 : NEXT Q
2260 REM CENTROID CALCULATION
2270 FOR A=0 TO NO : LET X(A,NO)-H(N0+1)
2280 LET M5-EXF(25,MAX,H(0),N2)
2290 LET M5-EXF(25,MIN,H(0),N2)
2300 LET N5=-M5+1
2310 LET C(J)=0 : FOR I=0 TO NO
2320 LET C(J)=C(J)+X(I,J)
2330 NEXT I
2340 FOR Q=1 TO 200 : NEXT Q
2350 REM CENTROID CALCULATION
2360 PRINT C(J) ; : PRINT#1 C(J) ;
2370 NEXT J
2380 PRINT " REFLECT "
2390 PRINT *** REFLECT ***
2400 IF K9=0 THEN GOTO 3080
2410 GOSUB 2860
2420 GOSUB 2890
2430 REM CENTROID CALCULATION
2440 PRINT " EXPAND "
2450 PRINT *** EXPAND ***
2460 PRINT " FOR I=0 TO NO-1 : PRINT R(I) =2*R(I)-C(I)
2470 NEXT I
2480 LET X(N0+2,NO)-H(N0+1)
2490 GOSUB 2840
2500 GOSUB 2890
2510 REM CENTROID CALCULATION
2520 GOTO 3040
2530 REM CENTROID CALCULATION
2540 PRINT " CONTRACT "
2550 PRINT *** CONTRACT ***
2560 PRINT " FOR I=0 TO NO-1 : PRINT R(I) =2*R(I)-C(I)
2570 NEXT I
2580 PRINT " CONTRACT "
2590 IF H(N0+1)<X(N,NO) THEN GOTO 2610
2600 IF H(N0+1)>X(N,NO) THEN GOTO 2690
2610 REM RESPONSE FOR REACTION IS WORSE THAN WORST
2620 PRINT " CONTRACT "
2630 FOR I=0 TO NO-1 : LET R(I)=(C(I)+X(N,NO))/2 : NEXT I
2640 PRINT " CONTRACT "
2650 GOSUB 2840
2660 IF H(N0+1)<X(N,NO) THEN GOTO 2770
2670 GOTO 3040
2680 REM RESPONSE FOR REACTION IS WORSE THAN WORST
2690 REM RESPONSE FOR REACTION IS WORSE THAN WORST
2700 PRINT " CONTRACT "
2710 PRINT *** CONTRACT ***
2720 LET R(I)=(C(I)+X(N,NO))/2 : NEXT I
2730 GOSUB 2860
2740 GOSUB 2890
219

2750 IF H(N0+1) < X(N,NO) THEN GOTO 2770
2760 GOTO 3060
2770 REM SHRINKING THE SIMPLEX SIZE
2780 PRINT:PRINT "SHRINK";PRINT#1:PRINT#1 "***SHRINK SIMPLEX SIZE***"
2790 FOR A=0 TO NO : FOR B=0 TO NO-1
2800 LET X(A,B)=(X(A,B)+X(M,B))/2
2810 NEXT B
2820 NEXT A
2830 GOTO 1960
2840 REM PRINT OUT THE VARIABLES
2850 PRINT:PRINT "VARIABLES"
2860 FOR I=0 TO NO-1 : PRINT R(I);:NEXT I
2870 FOR I=0 TO NO-1 : PRINT#1 R(I);:NEXT I
2880 RETURN
2890 REM INPUT RESPONSE FOR THE VARIABLES
2900 PRINT "*** ENTER 0 TO DO DATA COLLECTION***
2910 PRINT "CHANGE THE VARIABLES"
2920 PRINT
2930 PRINT "ENTER 0 TO DO DATA COLLECTION":INPUT Q :IF Q=0 THEN GOTO 870
2940 REM CALCULATION OF L/B RATIO
2950 LET P3=EXF(25,MAX,Y(1,0),32,1)
2960 LET H(N0+1)=(Y(1,P3-1)-(Y(1,P5)+Y(1,P6))/2)/((Y(1,P5)+Y(1,P6))/2)
2970 PRINT P3,Y(1,P3-1)
2980 PRINT:PRINT "INPUT RESPONSE FOR ABOVE VARIABLES " ;H(N0+1);" ":PRINT
2990 PRINT#1:PRINT"INPUT RESPONSE FOR ABOVE VARIABLES " ;H(N0+1);":PRINT
3000 RETURN
3010 FOR I=1 TO NO-1 :LET X(N,I)=F(1).NEXT I:REM USE RES.FROM REFLECT AS NEW SIM
3020 FOR Q=.1 TO 200:NEXT Q:
3030 LET X(N,N0)=H(N0+1)
3040 GOTO 2150
3050 FOR I=1 TO NO-1
3060 LET X(N,I)=R(I)
3070 FOR Q=.1 TO 200 :NEXT Q
3080 LET X(N,N0)=H(N0+1)
3090 GOTO 2150
3100 PRINT:PRINT "BYE ":PRINT"YOUR JOB IS DONE ! ! ! ":
3110 GOTO 4010
3120 REM FIND PEAK VALUES
3130 PRINT "DO YOU WANT TO FINE PEAK VALUES ? YES(I) NO(O) "":INPUT H9
3140 IF H9=0 THEN GOTO 1090
3150 FOR I=1 TO 2*N9
3160 LET J=EXF(25,MAX,Y(I,0),K9,1)-1
3170 IF J<2 THEN LET Y(I,32)=5 : GOTO 3210
3180 LET Y(I,33)=J
3190 REM 5 POINT QUADRATIC FIT PEAK LOCATION
3200 LET T2=-2*Y(I,J-2)-Y(I,J-1)+Y(I,J+1)+2*Y(I,J+2)
3210 LET Y(I,32)=J+1-14*T2/(20*B2)
3220 NEXT I
3230 REM CALCULATES DIFFERENCES W.R.T. HG8
3240 FOR I=1 TO 2*N9
3250 LET Y2=Y(I,Y(I,33))/2 : REM HALF HT.
3260 FOR J=0 TO 31
3270 IF Y(J,J)<Y2 THEN NEXT J
3280 LET J1=J-1 : GOTO 3290
3290 FOR K=J TO 31
3300 IF Y(K,J)>Y2 THEN NEXT K
3310 LET J2=K+1+(Y2-Y(I,K))/((Y(I,K)-Y(I,K-1))
3320 LET Y(I,34)=(J1+J2)/2 : REM HALF WIDTH CENTER
3330 LET Y(I,35)=J2-J1 : REM HALF WIDTH IN STEPS
3340 REM CORRECT APER FOR NEW PEAKS
3350 IF I<N9 THEN LET W(I,3)=W(I,3)-(Y(I,34)-16)
3360 IF I>N9 THEN LET W(I-N9,4)=W(I-N9,4)-(Y(I,34)-16)
3370 IF I=N9 THEN PRINT1 "X-CHANGE = ";Y(I,34)-16
3380 IF I=N9 THEN PRINT1 "Y-CHANGE = ";Y(I,34)-16
3390 IF I=N9 THEN PRINT1 "X-CHANGE = ";Y(I,34)-16
3400 IF I=N9 THEN PRINT1 "Y-CHANGE = ";Y(I,34)-16
3410 NEXT I
220
3420 PUT W(0,0),FEXY
3430 PRINT "1"
3440 PRINT "DATA AFTER CORRECTION ARE"
3450 PRINT "WAVELENGTH","APER X","APER Y","PMT X","PMT Y"
3460 FOR 1 TO 9
3470 PRINT W(1,5),INT(W(1,3)+.5),INT(W(1,4)+.5),W(1,1),W(1,2)
3480 IF W(1,3)<64 THEN GOTO 3950
3490 IF W(1,3)>192 THEN GOTO 3950
3500 IF W(1,4)<48 THEN GOTO 3980
3510 IF W(1,4)>208 THEN GOTO 3980
3520 NEXT 1
3530 RETURN
3540 REM COORDINATES FOR NEW LINES
3550 REM PMTX PMTY APERX APERY WAVELENGTH
3560 REM
3570 REM
3580 DATA -282,799,151,198,393.31
3590 REM MERGE LINES FROM S3AN3 PROGRAM
3600 INSPEC 1,1472
3610 IF Z=1 THEN LET I=1
3620 PRINT "DATA RECEIVED"
3630 FOR 1 TO 1471 STEP 46
3640 LET O=12/46:LET Y(Y+1,Q)=VAL(13+12.24+12,A1(0))
3650 NEXT 1
3660 PRINT "DATA STORED";
3670 LET Q=EXF(25,PRINT,Y(Y+1-1,0),32,1):FORQ=1 TO 200:NEXTQ
3680 LET 0=0 :FOR 1 TO 31
3690 LET 0=Y(12,16)+05 :NEXT 16 ; LET 0=0/32
3700 PRINT "DARK SIGNAL IS = ";D5:"
3710 IF Y=2 THEN GOTO 3760
3720 IF Z=0 THEN GOTO 3760
3730 PRINT "ENTER NO OF STEPS ON THE LEFT AND RIGHT SIDES",;INPUT P5,P6
3740 IF Z=1 THEN RETURN
3750 IF M6=0 THEN GOSUB 3800
3760 IF M6=0 THEN GOSUB 3800
3770 RETURN
3780 FOR Q=1 TO 1500 : NEXT Q1
3790 RETURN
3800 REM PROGRAM FOR CALCULATION OF INT. AVERAGE AND STD. ERR.
3810 LET S2=O ; LET S3=O
3820 FOR 1 TO 31
3830 LET Q=Y(Y+1-1,12)
3840 LET S2=S2+Q
3850 LET S3=S3+Q*Q
3860 NEXT 12
3870 PRINT "INT. = ";S2/32,"STD. ERR. = ";SQR((32*S2-S2*S2)/(32*32))
3880 PRINT "FOR";W(1,5),INT(W(1,3)+.5),INT(W(1,4)+.5),W(1,1),W(1,2)
3890 PRINT "INT.";S2/32,"STD. ERR.";SQR((32*S2-S2*S2)/(32*32))
3900 PRINT "WAVELENGTH","APER X","APER Y","PMT X","PMT Y"
3910 PRINT W(1,5),W(1,3),W(1,4),W(1,1),W(1,2)
3920 PRINT
3930 RETURN
3940 PRINT
3950 PRINT "STEPPING MOTOR FOR X SCAN IS OUT OF RANGE ( 64 - 192 ) !!!!!!!"
3960 PRINT "STEPPING MOTOR FOR X SCAN IS OUT OF RANGE ( 64 - 192 ) !!!!!!!"
3970 GOTO 3510
3980 PRINT "STEPPING MOTOR FOR Y SCAN IS OUT OF RANGE ( 48 - 208 ) !!!!!!!"
3990 PRINT "STEPPING MOTOR FOR Y SCAN IS OUT OF RANGE ( 48 - 208 ) !!!!!!!"
4000 GOTO 3530
4010 PRINT "YOUR JOB IS DONE. GOOD BYE !!!"
4020 END
**FELINE.BAS**

**THIS PROGRAM WAS WRITTEN TO ACCESS THE FE LINES, WHICH IS NOT LISTED IN SPECTROMETER’S LIBRARY**

**WRITTEN BY D. H. PIEPMER**

**MODIFIED BY C. H. LEE**

**REMARKS**

**DIM Y(19,35), A1(245), F(100,4)**

**LET I7-1: LET 57-10000: REM DIGITS AFTER DECIMAL POINT TO PRINT**

**LET P9-3: LET K9-32: LET N9-19: REM NUMBER OF LINES TO SCAN**

**PRINT: PRINT "PRINT RESULTS ON SPECTROMETER PRINTER (YES-1)”; INPUT Z2**

**GOSUB 880**

**FOR Q-1 TO 400:NEXTQ**

**FOR I-1 TO N9**

**LET QEXF(9,176506!,20): REM SLIT HOME**

**PRINT "X"; PRINT "11": PRINT "202"**

**LET QEXF(9,1765061,20): REM PMT HOME**

**PRINT "X"; PRINT "11": PRINT "148"**

**IF M9=64 THEN LET M9=M9+128: GOTO 310**

**READ M1,M2,M9,M0**

**LET M0=M0+140: REM Y CENTER**

**LET QEXF(9,176506!,20): REM CHANGE MOTOR COMMANDS**

**FOR A-1 TO 200:NEXTQ**

**LET QEXF(9,1765061,20): REM DO APERTURE X SCAN**

**PRINT "X": PRINT "400"**

**LET Y0-1**

**GOSUB 2230**

**FOR Q-1 TO 5000:NEXT Q**

**NEXT I**

**STOP**

**PUT Y(0,0), Y64(F9)[9]**

**REM**
222

710 REM
720 GOSUB 1690:REM TO FIND PEAK VALUES
730 REM
740 REM
750 PUT Y(0,0),Y44(F9)9
760 GOTO 800:REM TO LOOP 20 TIMES
770 PRINT"ENTER 1 TO PRINT RESULTS ON PRINTER";:INPUTQ
780 IF Q=1 THEN LETQ=EXP(25,PRINT=1,Y(0,0),36,20)
790 GOTO 870
800 LET I=17+1
810 IF I>20 THEN STOP
820 FOR I=0 TO 4:LET F(F9,1,I)=F(F9,1):NEXT I
830 LET F9=F9+1:LET Y(0,0)=Y(0,0)+5:LET F(F9,3)=F(F9,3)+1
840 COSUB I610:REM STORE NEW VALUES
850 RESTORE
860 COTO 150:REM LOOP BACK
870 STOP
880 PRINT"LOADING SPECTROMETER MEMORY WITH SPECIAL COMMANDS"
890 LET Q=EXP(9,1765061,20):REM HG MIRROR MOTOR COMMAND CORRECTION
900 FOR Q=1 TO 200: NEXT Q
910 PRINT=9,'X':PRINT=9,"9"
920 PRINT=9,"3":PRINT=9,"3":PRINT=9,"6":PRINT=9,"6"
930 REM DARK SIGNAL
940 LET Q=EXP(9,1765061,20)
950 PRINT=9,'X':PRINT=9,"8":PRINT=9,"395"
960 FOR Q=1 TO 1200: NEXT Q
970 PRINT=9,"21":PRINT=9,"148"
980 PRINT=9,"6":PRINT=9,"53"
990 PRINT=9,"0":PRINT=9,"0"
1000 PRINT=9,"21":PRINT=9,"186":REM HG MIRROR OUT, THEN IN
1010 PRINT=9,"0":PRINT=9,"0"
1020 PRINT=9,"21":PRINT=9,"124"
1030 PRINT=9,"6":PRINT=9,"23"
1040 PRINT=9,"21":PRINT=9,"132"
1050 PRINT=9,"6":PRINT=9,"24":REM ONE COUNT/STEP
1060 FOR Q=1 TO 800: NEXT Q:PRINT=9,"420"
1070 PRINT=9,"2":PRINT=9,"403"
1080 PRINT=9,"6":PRINT=9,"23"
1090 PRINT=9,"28":PRINT=9,"12":REM RS232 XMIT
1100 PRINT=9,"23":PRINT=9,"0"
1110 FOR Q=1 TO 600: NEXT Q
1120 RETURN
1130 LET Q=EXP(9,1765061,20)
1140 FOR Q=1 TO 400: NEXT Q
1150 PRINT=9,"X":PRINT=9,"8":PRINT=9,"420"
1160 PRINT=9,"21":PRINT=9,"124"
1170 PRINT=9,"6":PRINT=9,"37"
1180 PRINT=9,"21":PRINT=9,"132"
1190 PRINT=9,"6":PRINT=9,"38":REM TWO COUNTS/STEP
1200 PRINT=9,"14":PRINT=9,"5"
1210 PRINT=9,"14":PRINT=9,"5"
1220 PRINT=9,"2":PRINT=9,"423"
1230 PRINT=9,"6":PRINT=9,"37"
1240 PRINT=9,"28":PRINT=9,"12":REM RS232 XMIT
1250 FOR Q=1 TO 400: NEXT Q
1260 RETURN
1270 REM
1280 REM
1290 REM
1300 GET F(0,0),FILES.HG
1310 PRINT"MONTH DAY YEAR","RUN# FILE NUMBER"
1320 FOR I=1 TO F(0,0):REM F(0,0) CONTAINS LAST FILE NUMBER USED
1330 FOR J=0 TO 3:PRINT F(I,J):;NEXT J
1340 PRINT I: NEXT I
1350 LET I=F(0,0)
1360 PRINT"IF NUMBERS ARE OK, PUSH RETURN"
1370 PRINT"TO CHANGE A NUMBER, ENTER NEW NUMBER AND PUSH RETURN"
223

PRINT"NEW FILE NUMBER WILL BE":1+1::INPUT Q
1400 IF Q=0 THEN LET F9=I+1:GOTO 1460
1410 IF Q>I+1 THEN LET F9=Q:GOTO 1460
1420 PRINT"THIS FILE NUMBER WILL WRITE OVER A PRESENT FILE."
1430 PRINT"IF YOU WANT TO TRY ANOTHER FILE NUMBER, ENTER IT NOW":INPUT Q1
1440 IF Q1<>0 THEN LET Q=Q1:GOTO 1410
1450 LET F9=Q
1460 PRINT"MONTH":F(I,0)::INPUT Q
1470 IF Q=0 THEN LET F(F9,0)-F(I,0):GOTO 1490
1480 LET F(F9,0)=Q
1490 PRINT"DAY":F(1,1)::INPUT Q
1500 IF Q=0 THEN LET F(F9,1)-F(1,1):GOTO 1520
1510 LET F(F9,1)=Q
1520 PRINT"YEAR":F(1,2)::INPUT Q
1530 IF Q=0 THEN LET F(F9,2)-F(1,2):GOTO 1550
1540 LET F(F9,2)=Q
1550 PRINT"TIME OF DAY":INPUT Y(0,5)
1560 PRINT"ROOM TEMPERATURE":INPUT Y(0,6)
1570 PRINT"BAROMETRIC PRESSURE":INPUT Y(0,7)
1580 PRINT"TODAY'S RUN NUMBER":F(I,3)+1::INPUT Q
1590 IF Q=0 THEN LET F(F9,3)-F(I,3)+1:GOTO 1610
1600 LET F(F9,3)=Q
1610 FOR I=0 TO 3:LET Y(I,0)-F(F9,1):NEXT I
1620 LET Y(0,4)=F9
1630 LET(F(0,0))=F9
1640 PUT F(0,0),FILES.HG
1650 RETURN
1660 REM
1670 REM
1680 REM FIND PEAK VALUES
1690 FOR I=1 TO 2*N9
1700 LET J-EXF(25,MAX(Y(1,0),K9,1)-1
1720 LET Y(I,33)-J
1730 REM 5-POINT QUADRATIC FIT PEAK LOCATION
1740 LET T2-2*Y(I,J-2)-Y(I,J-1)+Y(I,J+1)+2*Y(I,J+2)
1750 LET T3-2*Y(I,J-2)+Y(I,J-1)-2*Y(I,J)-Y(I,J+1)+2*Y(I,J+2)
1760 LET Y(I,32)-J+1.164*T2/(20*B2)
1770 NEXT I
1780 REM CALCULATE DIFFERENCES W.R.T. HG8
1790 FOR I=1 TO 2*N9
1800 LET Y2-Y(1,Y(I,33))/2:REM HALF HT
1810 IF J=0 TO 31
1820 IF Y(I,J)<Y2 THEN NEXT J
1830 LET J=J+1:(Y2-Y(I,J-1))/(Y(I,J)-Y(I,J-1))
1840 FOR K=J TO 31
1850 IF Y(I,K)>Y2 THEN NEXT K
1860 LET J2=K:(Y2-Y(I,K))/(Y(I,K)-Y(I,K-1))
1870 LET Y(I,34)=(J1+J2)/2:REM HALF WIDTH CENTER
1880 LET Y(I,35)=J2-J1:REM HALF WIDTH IN STEPS
1890 NEXT I
1900 PRINT"DIFFERENCES W.R.T. HG8 FOR FILE ":F9
1910 FOR I=1 TO N9
1920 PRINT"1,"INT((Y(8,32)-Y(I,32))*57+.5)/57,
1930 PRINT"11,"INT((Y(8+N9,32)-Y(I+N9,32))*57+.5)/57,
1940 PRINT"1,"INT((Y(8,34)-Y(I,34))*57+.5)/57,
1950 PRINT"11,"INT((Y(8+N9,35)-Y(I+N9,35))*57+.5)/57
1960 NEXT I
1970 RETURN
1980 REM
1990 REM
2000 REM THESE ARE MOTOR STEPS FROM HOME POSITIONS FOR THE 9 LINES
2020 REM PMTX PKTY APERX APERY
2030 DATA -242,670,64,-3
2040 DATA -242,670,64,144
2050 DATA -61,683,64,33
2060 DATA -60,684,64,19
2070 DATA -27,684,64,24
2080 DATA -233,686,64,-55
2090 DATA -318,751,64,-42
2100 DATA -189,753,64,36
2110 DATA -133,754,64,-53
2120 DATA -126,754,64,-54
2130 DATA -225,759,64,-47
2140 DATA -222,766,64,35
2150 DATA -271,772,64,30
2160 DATA -125,787,64,95
2170 DATA -125,787,64,20
2180 DATA -125,787,64,21
2190 DATA -407,798,64,-35
2200 DATA -77,798,64,-56
2210 DATA -79,800,64,22
2220 REM MERGE LINES FROM SCAN3 PROGRAM
2230 INSPEC A1(0),1472
2240 RETURN
2250 PRINT"DATA RECEIVED ";
2260 FOR I2=0 TO 1471 STEP 46
2270 LET Q-I2/46: LET Y(Y0+I, Q)=VAL(I2,12,24+I2,A1(0))
2280 NEXT I2
2290 PRINT"DATA STORED ";I
2300 RETURN
2310 FOR Q1=1 TO 900: NEXT Q1
2320 RETURN
2330 END
REM THIS PROGRAM WAS WRITTEN TO CONTROL THE SPECTROMETER AND OBTAIN DATA FOR SPATIAL PROFILE OF FE(1) EXCITATION TEMPERATURE AND EMISSION INTENSITY.

LET N9 = 0
DIM Y(19, 35), A1(245), F(100, 4), W(19, 4)
LET M6 = 0

REM PUT IS ON LINE 3615
GET W(0, 0), FEX
LET M6 = 0

PRINT: PRINT "SCAN(1) OR RELATIVE INTENSITY(0)"; INPUT Q
IF Q = 1 THEN LET M6 = 6
PRINT: PRINT "INTEGRATION DURATION(1 TO 20)"; INPUT T6
IF T6 < 1 THEN GOTO 190
PRINT: PRINT "PRINT RESULTS ON SPECTROMETER PRINTER(YES-1)"; INPUT Z2
PRINT
PRINT "DO YOU WANT TO USE THE ORIGINAL DATA? YES(1),NO(0)"; INPUT P1
IF P1 = 0 THEN GOTO 280
FOR I = 1 TO N9: REM READ NT X,Y AND SLIT X,Y
READ W(I, 1), W(I, 2), W(I, 3), W(I, 4)
NEXT I

GOSUB 1060: REM ENTER PROGRAM INTO SPECTROMETER
LET Q = EXF(9, 1765061, 20): REM SLIT HOME
FOR Q = 1 TO 1000: NEXT Q
PRINT P9, "X": PRINT P9, "11": PRINT P9, "202"
LET Q = EXF(9, 1765061, 20): REM PNT HOME
FOR Q = 1 TO 1000: NEXT Q
PRINT P9, "X": PRINT P9, "11": PRINT P9, "148"
FOR Q = 1 TO 1000: NEXT Q
FOR I = 1 TO N9: REM LINE SELECT AND DATA COLLECTION ROUTINE
IF I > 1 THEN GOTO 430
LET D1 = 0: LET D2 = 0: LET D9 = 0: LET DO = 0
IF M1 < 0 THEN LET D1 = 1
IF M9 < 0 THEN LET D9 = 1
IF M2 < 0 THEN LET D2 = 1
IF MO < 0 THEN LET DO = 1
LET Q = EXF(9, 1765061, 20)
FOR Q = 1 TO 1000: NEXT Q
PRINT P9, "X": PRINT P9, "11": PRINT P9, "202"
FOR Q = 1 TO (M1 * M2) * 2.5: NEXT Q: REM WAIT TILL DONE

10 REM
20 REM
30 LET Q-EXF(9.1765061,20):REM DO APERTURE X SCAN
35 PRINT#P9,"X":PRINT#P9,"11":PRINT#P9,"400"
40 LET Y0=1
50 GOSUB 2620:REM GET 32 POINTS
60 IF YZ=0 THEN 810
70 LET Q-EXF(9,1765061,26):REM PRINT ON PRINTER
80 FOR Q=1 TO 1800:NEXT Q:REM DELAY FOR PRINTER
90 REM
810 IF M6=0 THEN GOTO 910
800 LET Q-EXF(9.1765061,20):REM DO APERTURE Y SCAN
830 FOR Q=1 TO 1000:NEXT Q
840 PRINT#P9,"X":PRINT#P9,"420"
850 LET Y0=Y0+1
860 GOSUB 2620:REM GET 32 POINTS
870 IF Y2=0 THEN GOTO 910
890 LET Q-EXF(9.1765061,26):REM PRINT ON PRINTER
900 REM
910 NEXT I
920 REM
930 REM
940 REM
950 REM
960 IF M6=0 THEN GOTO 1000
970 GOSUB 1970:REM TO FIND PEAK VALUES
980 REM
990 REM
1000 PRINT"ENTER 1 TO PRINT RESULTS ON PRINTER";:INPUT Q
1010 IF Q=1 THEN LETQ-EXF(25,PRINTs1,Y(0,0),36,20)
1020 GOTO 1050
1030 LET Y9=Q
1040 GOTO 230:REM LOOP BACK
1050 STOP
1060 PRINT"LOADING SPECTROMETER MEMORY WITH SPECIAL COMMANDS"
1070 PRINT#1
1080 PRINT#1
1090 PRINT#1
1100 PRINT#1
1110 PRINT#1
1120 PRINT#1
1130 PRINT#1
1140 LET Q-EXF(9,1765061,20):REM HG MIRROR MOTOR COMMAND CORRECTION
1150 FOR Q=1 TO 1000:NEXT Q
1160 PRINT#P9,"X":PRINT#P9,"9"
1170 PRINT#P9,"53":PRINT#P9,"3":PRINT#P9,"0":PRINT#P9,"6":PRINT#P9,"6"
1180 REM DARK SIGNAL
1190 LET Q-EXF(9,1765061,20)
1200 PRINT#P9,"X":PRINT#P9,"8":PRINT#P9,"395"
1210 FOR Q=1 TO 1000:NEXT Q
1220 PRINT#P9,"21":PRINT#P9,"148"
1230 PRINT#P9,"6":PRINT#P9,"53"
1240 PRINT#P9,"O":PRINT#P9,0
1250 PRINT#P9,"21":PRINT#P9,"186":REM HG MIRROR OUT, THEN IN
1260 PRINT#P9,"21":PRINT#P9,"198"
1270 PRINT#P9,"21":PRINT#P9,"124"
1280 PRINT#P9,46:PRINT#P9,"28"
1290 PRINT#P9,"21":PRINT#P9,"132"
1300 PRINT#P9,46:PRINT#P9,"29":REM ONE COUNT/STEP
1310 FOR Q=1 TO 1000:NEXT Q:PRINT#P9,"14":PRINT#P9,403
1320 PRINT#P9,"2":PRINT#P9,"403"
1330 PRINT#P9,46:PRINT#P9,"28"
1340 PRINT#P9,"28":PRINT#P9,"12":REM RS232 XMIT
1350 PRINT#P9,"22":PRINT#P9,"3"
1360 PRINT#P9,"63":PRINT#P9,"0"
1370 FOR Q=1 TO 1200:NEXT Q
1380 REM SLIT VERTICAL SCAN
1390 LET Q-EXF(9.1765061,20)
1400 FOR Q=1 TO 800:NEXT Q
1410 PRINT#9, "X"; PRINT#9, "8"; PRINT#9, "1400 PRINT#9, "21": PRINT#9, "124"
1430 PRINT#9, M6: PRINT#9, "38": REM TWO COUNTS/STEP
1440 PRINT#9, "14": PRINT#9, T6
1460 PRINT#9, "21": PRINT#9, "15"
1470 PRINT#9, "36": PRINT#9, "423"
1480 PRINT#9, M6: PRINT#9, "38": REM TWO COUNTS/STEP
1490 PRINT#9, "28": PRINT#9, "12": REM RS232 XMIT
1500 PRINT#9, "23": PRINT#9, "3"
1510 PRINT#9, "63": PRINT#9, "0"
1520 FOR Q-1 TO 1000: NEXT Q
1530 RETURN
1540 GOTO 1940
1550 REM
1560 REM
1570 REM
1580 GET F(0,0), FILES.HG
1590 PRINT "MONTH DAY YEAR": "RUN": FILE NUMBER"
1600 FOR I-1 TO F(0,0): REM F(0,0) CONTAINS LAST FILE NUMBER USED
1610 FOR J-0 TO 3: PRINT F(I,J): NEXT J
1620 PRINT I: NEXT I
1630 LET I-F(0,0)
1640 PRINT "IF NUMBERS ARE OK, PUSH RETURN"
1650 PRINT "TO CHANGE A NUMBER, ENTER NEW NUMBER AND PUSH RETURN"
1660 PRINT
1670 PRINT "NEW FILE NUMBER WILL BE": I+1": INPUT Q
1680 IF Q-0 THEN LET F9-I+1: GOTO 1740
1690 IF Q-I+1 THEN LET F9-Q: GOTO 1740
1700 PRINT "THIS FILE NUMBER WILL WRITE OVER A PRESENT FILE."
1710 PRINT "IF YOU WANT TO TRY ANOTHER FILE NUMBER, ENTER IT NOW": INPUT Q1
1720 IF Q1<0 THEN LET Q-Q1: GOTO 1690
1730 LET F9-Q
1740 PRINT "MONTH-": F(I,0): INPUT Q
1750 IF Q-0 THEN LET F(F9,0)-F(1,0): GOTO 1770
1760 LET F(F9,0)-Q
1770 PRINT "DAY-": F(I,1): INPUT Q
1780 IF Q-0 THEN LET F(F9,1)-F(1,1): GOTO 1800
1790 LET F(F9,1)-Q
1800 PRINT "YEAR": F(I,2): INPUT Q
1810 IF Q-0 THEN LET F(F9,2)-F(1,2): GOTO 1830
1820 LET F(F9,2)-Q
1830 PRINT "TIME OF DAY": INPUT Y(0,5)
1840 PRINT "ROOM TEMPERATURE": INPUT Y(0,6)
1850 PRINT "BAROMETRIC PRESSURE": INPUT Y(0,7)
1860 PRINT "TODAY'S RUN NUMBER": F(I,3)+1": INPUT Q
1870 IF Q-0 THEN LET F(F9,3)-F(1,3)+1: GOTO 1890
1880 LET F(F9,3)-Q
1890 FOR I-0 TO 3: LET Y(0,1)-F(F9,1): NEXT I
1900 LET Y(0,4)-F9
1910 LET(F(0,0)-F9
1920 PUT F(0,0), FILES.HG
1930 RETURN
1940 REM
1950 REM
1960 REM
1970 REM FIND PEAK VALUES
1980 PRINT "DO YOU WANT TO FIND PEAK VALUES / YES(1), NO(0)": INPUT H9
1990 IF H9-0 THEN GOTO 980
2000 FOR I-1 TO 2*N9
2010 LET J-EXP(25, MAX, Y(I,0), F9.1)-1
2020 IF J<2 THEN LET Y(I,32)=5: GOTO 2080
2030 LET Y(I,33)=J
2040 REM 5-POINT QUADRATIC FIT PEAK LOCATION
2050 LET T2-2*Y(I,J-2)-Y(I,J-1)+Y(I,J+1)+2*Y(I,J+2)
2060 LET B2-2*Y(I,J-2)-Y(I,J-1)-2*Y(I,J)-Y(I,J+1)+2*Y(I,J+2)
2070 LET Y(I,32)=J+1.14*T2/(20*B2)
2080 NEXT I
REM CALCULATE DIFFERENCES W.R.T. HGS
FOR I=1 TO N9
LET Y2=-(Y(I,Y(I,33))/2: REM HALF HT.
FOR J=0 TO 31
IF Y(I,J)<Y2 THEN NEXT J
IF J<1 THEN LET J1=1:GOTO 2160
LET 11=34.(12-Y(1,J-1))/(Y(I,J)-T(1,J-1))
FOR K=4 TO 31
IF Y(I,K) >Y2 THEN NEXT K
LET J2=1(+14.(Y2-Y(1,K))/(Y(I,K)-Y(I,K-1))
LET Y(I,34)=(J1442)/2: REM HALF WIDTH CENTER
LET Y(I,35) -J2 -J1: REM HALF WIDTH IN STEPS
REM CORRECT APER FOR NEW PEAKS
IF I<-N9 THEN LET W(I,3)-w(I,3)+(Y(I,34)-16)
IF I>149 THEN LET W(1-N9,4)-W(1-N9,4)-3*(Y(1,34)-16)
IF I<-N9 THEN PRINT "X-CHANGE-";Y(1,34)-16
IF I>N9 THEN PRINT "Y-CHANGE-";Y(I,34)-16
IF DM THEN PRINT "Y-CHANGE-";Y(I,34)-16
NEXT I
PUT W(0,0),FEXY
PRINT*I
PRINT01
DATA AFTER CORRECTION ARE
FOR I-1 TO N9
IF W(I,3)<-I8 THEN COTO 2870
IF W(I,3)>-238 THEN GOTO 2870
IF W(I,4)<-50 THEN COTO 2900
IF W(1,4)>-206 THEN COTO 2900
PRINT W(I,1),W(I,2),INT(14/.3)+.5),INT(W(1,4)+.5)
NEXT I
FOR I=1 TO N9
PRINT01,INT((Y(8,32)-Y(I,32))*57+.5)/57,
PRINT01,INT((Y(84.149,32)-Y(1+N9,32))*S7+.5)/S7,
PRINT*I,INT((Y(8,34)-Y(I,34))*S7+.5)/S7,
PRINT01,INT((Y(8+N9,35)-Y(I4449,35))*S7+.5)/S7
NEXT I
RETURN
REM THESE ARE MOTOR STEPS FROM HOME POSITIONS FOR THE 9 LINES
REM PMTX PMTY APERX APERY
DATA -368,782,156,149
DATA -281,781,153,154
DATA -271,772,89,152
DATA -61,683,213,142
DATA -233,686,144,63
DATA -318,751,81,75
DATA -189,753,215,157
DATA -133,754,158,64
DATA -407,798,129,76
DATA -407,798,129,76
REM MERGE LINES FROM SCAN3 PROGRAM
INSPEC A1(0),1472
FOR Q1 =1 TO 1500:NEXTQ1
RETURN

REM PROGRAM FOR INT. MEASUREMENT AND STD. ERR. CALCULATION
LET S2 = 0: LET S3 = 0
FOR I2 = 0 TO 31
LET Q = Y(Y0 + I - 1, I2)
LET S2 = S2 + Q
LET S3 = S3 + Q * Q
NEXT I2
PRINT 'INT. -'; S2 / 32, "STD. ERR. -"; SQR((32 * S3 - S2 * S2) / (32 * 32 * 31))
PRINT "FOR"; W(I, 1), W(I, 2), INT(W(I, 3) + .5), INT(W(I, 4) + .5)
PRINT "INT -"; S2 / 32, "STD. ERR. -"; SQR((32 * S3 - S2 * S2) / (32 * 32 * 31))
PRINT "PMT X", "PMT Y", "APER X", "APER Y"
PRINT W(I, 1), W(I, 2), W(I, 3), W(I, 4)
RETURN
PRINT "STEPPING MOTOR FOR X SCAN IS OUT OF RANGE!!!!!!"
PRINT "STEPPING MOTOR FOR X SCAN IS OUT OF RANGE!!!!!!"
GOTO 2920
PRINT "STEPPING MOTOR FOR Y SCAN IS OUT OF RANGE!!!!!!"
PRINT "STEPPING MOTOR FOR Y SCAN IS OUT OF RANGE!!!!!!"
GOTO 2920
END