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THE CHARACTERIZATION OF A FABRY-PEROT
INTERFEROMETER AND A dc ARC
PLASMA JET FOR SPECTROCHEMICAL ANALYSIS

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Based on a M.S. thesis submitted to Iowa State University

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The characterization of a Fabry-Perot
interferometer and a dc arc
plasma jet for spectrochemical analysis

by

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The characterization of a Fabry-Perot
interferometer and a dc arc
plasma jet for spectrochemical analysis¹

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A system involving the use of a Fabry-Perot interferometer in combination with a dc arc plasma jet has been constructed and characterized for spectrochemical analysis. Parameters such as flow rate ratio, observation region, electrode composition and orifice size have been considered. Improvements such as noise reduction and dry aerosol introduction of samples were suggested.

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I. INTRODUCTION

The recent revival of interest in atomic emission spectroscopy as a tool for chemical analysis stems from advances in two separate categories of spectroscopic instrumentation. These categories are (a) the emission source and (b) the dispersing element.

Of the many developments in excitation sources over the past decade, the advances in the area of electrical discharge sources are the most prominent. Likewise, much of the progress in the area of dispersion in recent years has emphasized high speed detection systems such as echelle grating, programmable monochromators and interferometers.

The present trend in emission spectrochemical analysis is toward the use of new light source in conjunction with new dispersion or signal processing systems to provide a high speed and nearly universal method of analysis.

A. Literature Review

The inability of flame sources to provide high temperature, because of the limitations due to thermodynamic properties of chemical compounds, has directed the interest of spectrochemists toward the electrical discharge as a means of atomic excitation. The application of the electrical discharge is not new to spectrochemical analysis,

since the arc and spark are basic and common methods in analytical spectroscopy.

Although many advances and improvements have been made in arc and spark discharges, errors due to the instability of the discharge and changes in the sample upon excitation decreases the precision of a given analysis. Also, the convenience obtained by the use of liquid samples rather than solid samples has forced analysts to seek other sources for excitation. Among the many types of sources studied are gas-stabilized electrode systems, spark-in flames, and plasma sources. The latter has become the most favored because of its ability to produce excitation at very high temperatures.

Research that involves the use of electrical discharge plasma sources can be separated into two distinct areas: the inductively coupled radiofrequency plasma and the dc arc plasma jet. This thesis involves the characterization of the latter as a source for emission spectroscopy.

A plasma, as defined by Fassel (1), is any luminous gas in which a significant fraction of its atoms or molecules are ionized. According to Greenfield, McGeachin and Smith (2), a plasma jet is formed when the current density to be dissipated on the surface of an arc electrode is larger than can be removed by radiation and conduction alone. Although a theoretical treatment of the plasma jet will be

discussed in a later section, Rippetoe and Vickers (3) characterized the plasma jet by a flow of partially ionized gas that is forced through a small orifice at a high velocity. This characterization is suitable to the version of the plasma jet studied in this investigation.

Although devices such as gas stabilized dc arcs and transfer electrode devices (4,5) have been referred to as plasma jets, Rippetoe and Vickers (3) point out that there is an important distinction between plasma sources.

This distinction is based on whether the region of observation is a current-carrying plasma or a noncurrent-carrying plasma and is crucial for understanding the properties of the source. The flame-like protrusion that occurs in the plasma source studied in this and other work (6) is a noncurrent-carrying region and is called the plume.

Literature reviews by Fassel (1), Greenfield, McGeachin and Smith (2), and Keirs and Vickers (7), have described the various types of plasma jets used during the past two decades. The characterization of the various types of plasma jets is dependent upon the particular geometry of the device. The geometrical design provides the optimum conditions so that spectroscopic observations can be made. For example, the source studied by Margoshes and Scribner (4) was designed such that observations were

made in the current carrying portion of the plasma, whereas those designed by McGinn (8), Kranz (9), Elliott (6), and Valente and Schrenk (10) allowed observations to be made in the plume portion of the plasma. The design utilized in the Spectrametrics, Inc. Spectra Jet II (11) allows observations to be made in neither the current-carrying region nor the plume. Observations are made in a region below the inverted "V"-shaped arc column. This particular region is acclaimed to have a background emission which is much lower than that of the plume (11).

The dream that the dc arc plasma jet will replace the flame in spectrochemical analysis is far from reality at the present time. According to Merchant and Veillon (12), most plasma jets suffer from two limitations: (a) the high background emission, and (b) the failure of the aerosol to enter the discharge due to the large thermal gradient. These devices are also plagued with interference effects, such as the depressing effect of phosphate on the intensity of calcium emission, as pointed out by Rippetoe et al. (13). These basic limitations cause the detection limits to be poorer than those obtained by the use of a flame source.

Despite the limitations mentioned, the plasma jet has been applied successfully as a spectrochemical source (14, 6,15-18). Although multielemental atomic spectroscopic

methods have been reviewed extensively (19,20), the combination of these methods with a dc arc plasma jet is lacking.

The exception is in the case of Spectrametric, Inc., which

involves the use of the dc arc plasma jet with an echelle grating spectrometer. The problem with the use of conventional spectrographs is the difficulty in the processing or retrieval of data. The data may be analyzed in one of two ways: (a) the use of photographic emulsion to obtain quantitative information, and (b) the use of the photoelectric method of gathering data. The photographic emulsion method is too slow and tedious for routine analysis. The photoelectric method is a more direct process but when used with prism or grating spectrographs, a photoelectric detector is required for each spectral line studied.

The present trend is toward automatic evaluation of emission spectra. Alternatives to conventional spectra evaluation, such as echelle spectrometers, microphotometers and programmable monochromators, is eloquently presented in a review by P.W.J.M. Boumans (21). According to Boumans, these systems offer a flexible and universal approach to spectrochemical data acquisition and processing, but the hardware and software development is very expensive.

Another approach is the combined use of a plasma source with a Fabry-Perot interferometer (FP) as a spectrochemical tool. This arrangement would be less expensive

than those mentioned previously. However, the arrangement of such a system may prove to be a technique whose applications are less than universal because of the limited spectral range of the FP. The real advantage of this method may be realized when comparing the FP/plasma jet to atomic absorption because no line source is needed and only one photomultiplier is required. Such an arrangement can provide multielement or single element analysis in a relatively inexpensive manner.

The application of the FP to flame emission spectrochemical methods has proven successful on several occasions (22-24). These investigations have prompted the following question: What, if any, is the possibility of using the FP with a source, such as a plasma jet, for the purpose of emission spectrochemical analysis of solutions?

B. Purpose

The purpose of this investigation was the construction and characterization of a dc arc plasma jet which can be suitably combined with a FP as a system for chemical analysis. This investigation will serve as a model for a similar system that can be operated in the ultraviolet region of the spectrum.

The emphasis in this study is on the source more than the FP, because the optics and operating parameters have

been established previously (24). The parameters of the source considered in this study are: (1) the electrode position, (2) the type of electrode material, (3) the flowrate of argon, (4) the region in which spectral information can be taken from, and (5) the orifice diameter of the vertical electrode. The relative detection limit of Na is attempted. This study serves as only the beginning for analysis with a FP/plasma jet system.

II. THEORETICAL ASPECTS

A. The Plasma Jet

The theoretical aspects of arcs in spectroscopy have been thoroughly investigated in the literature (25-27). According to Boumans (28), a great deal of the important advances in arc and dc arc plasma jet theory have occurred in the area of physics, rather than spectrochemistry. Thus, the task of spectrochemists is to select from the tremendous amount of physical literature, the theoretical information that can be solely applied to spectrochemical analysis.

Since the theoretical behavior of the plasma jet is very similar to that of the convention arc, an elaborate discussion will be omitted. Instead, a brief outline of the processes in the plasma jet will be mentioned.

The interest in the dc arc plasma jet as an emission source lies in its ability to produce a high temperature at a low cost. The high temperature is caused by the mechanisms of a thermal and magnetic pinch. The thermal pinch occurs when the flow of gas is restricted by forcing it through a narrow orifice. This causes the outer region of the arc column to cool and the current will tend to concentrate in the hotter central area, thus increasing the conductivity and temperature. The magnetic pinch occurs when the current density is high enough to cause charged particles flowing

through the plasma jet to move closer together. A constriction in the discharge occurs and causes the current density to further increase, thus increasing the temperature.

When a liquid sample is introduced to the plasma jet, the following processes occur: (a) sample evaporation, (b) sample atomization, and (c) sample excitation.

If the excitation is to be high enough to produce spectral emission of lines with adequate intensity, the source should be in a state of thermodynamic equilibrium. Thermodynamic equilibrium (2) is a state where every process of energy transfer is perfectly balanced by the reverse process. This state is not realized in plasmas because of uncompensated losses due to radiation and also because (28) there is always a net transport of energy and mass through the system. However, a state of partial equilibrium is obtained, if the rate at which energy is partitioned over different degrees of freedom (2,7,28). This partial state of equilibrium is called the "Local Thermal Equilibrium" (LTE), and implies that each volume element of the plasma is treated separately and is assigned a local temperature. The LTE also implies that (a) the population of energy levels for each kind of particle in the plasma follows a Boltzman distribution, (b) the ionization of each kind of particle is described by the Saha equation (29), and (c) the dissociation of molecules and radicals follows the equation

for chemical equilibrium (28). Greenfield (2) indicates that the presence of the LTE eliminates the effect of interferences, because the high kinetic energy from plasma temperatures causes molecular species to dissociate, thus eliminating the formation of molecules or radicals, as in the case of flames.

The process of spectral line emission follows excitation because electrons descend from excited states in atoms to the ground state. The frequency of the emission is given by,

$$\nu = (E_i - E_j)/h.$$

The intensity of the line of frequency ν is given by,

$$I = A_{ij} h \nu N_i,$$

where N_i is the number of atoms in the i^{th} level, A_{ij} is the transition probability, E_i is the energy of the i^{th} level, and h is Planck's constant.

The analyst at this point, constructs a calibration curve of intensity versus concentration. This curve allows one to deduce the concentration of an unknown sample from its intensity. Ideally, the analyst would be satisfied with the performance of the plasma jet if the processes of emission occurred in the manner described above. However, since there is a probability that LTE will occur, along with the presence of a very high temperature, then there is also

a probability that other processes will occur in plasma jets. According to Boumans (28), a chemical element in the plasma is not only present in the form of neutrally charged atoms, but also in the form of singly, doubly and triply charged ions. The relative concentration of the various species depends on the dissociation and ionization equilibria and the temperature. The question as to how the interdependence of ionization, dissociation and temperature occurs is critically reviewed by Boumans (28). Because the LTE implies that each species in the plasma is governed by a different temperature or temperature gradient, it is obvious that plasma emission is not a single process.

B. The Fabry-Perot Interferometer

An interferometer is an optical device based on the principle of optical interference. The interference of light occurs generally when two or more light beams from the same source travel different path lengths and then arrive at a point in space. The interference is constructive if the beams arrive at the point in the same phase, and destructive if the phases are different. According to Jacquinot (30) interference may be divided into two classes according to the number of interfering rays, two or several. FP's are classified as multiple-beam interferometers and the Michelson interferometer is classified as a two-beam interferometer.

The FP consist of two parallel plates in which the faces are covered with reflecting coating. The coefficient of the reflecting is designated as R. The transmission coefficient is denoted as T and the absorption coefficient is $A = 1-R-T$. The plates are arranged such that the faces with reflective coatings face each other. The outer faces are coated with an antireflective coating in order to eliminate double cavity formations. A light ray incident upon the FP undergoes multiple reflections and transmissions. The transmitted rays recombine at infinity and interfere, thus forming a fringe pattern.

Light transmission occurs in accordance to the following formula:

$$n\lambda = 2\mu d \cos \theta$$

where n is the order of interference, λ is the wavelength, μ is the refractive index, d is the length of the cavity, and θ is the angle of the incident ray with the normal of the mirror or plates. When $d = n\lambda/2\mu \cos \theta$, light transmission is a maximum and constructive interference occurs. When two wavelengths are transmitted simultaneously, the separation between them is called the Free Spectral Range (FSR), given by

$$\text{FSR} = \lambda^2/2\mu d.$$

The finesse of a FP interferometer enables the device to resolve closely spaced spectral lines. The finesse of the interferometer depends mainly on the reflectivity of the coatings and the flatness (31), and is given by

$$F_R = \frac{\pi \sqrt{R}}{1 - R}$$

The throughput or maximum transmission of the interferometer determines the FP interferometer's sensitivity to weak light sources, thus relating to detection capabilities. This is given by

$$t_{\max} = \left(\frac{1 - A}{1 - R} \right)^2.$$

The FP interferometer's usefulness as a spectrometric device is realized when it functions in a scanning mode. By varying the mirror distances the FP is made to scan over a certain spectral range. It should be noted at this point that the region of the spectrum in which the FP is used is determined by the properties of the reflective coatings. By use of the proper coating substrate, the FP can be operated in ultraviolet as well as the visible region of the spectra. However, difficulties arise in the former spectral region; because of the present coating technology.

III. INSTRUMENTATION

A. The Plasma Jet

Although a multitude of plasma jets have appeared on the scene since its invention in 1959 (4,32), the characterization of a given plasma jet depends on its design. Of the various types reviewed in the literature, the device considered for this study was patterned after the instrument used by Elliott (6). This consideration was based upon the idea that the geometrical configuration permitted the separation of the plume and the arc column. The isolation of the plume and the arc column is important for the elimination spectral noise due to continuum emission. The construction of the source is illustrated in Figure I. The lower electrode consists of a modified Varian Techtron 02-100036-00, nebulizing chamber and an aluminum disk which supports a hollow graphite electrode. The graphite electrode is a 8.5 mm in diameter rod whose outer surface is threaded. Threads allow the rod to be connected to the cap and an electrical lead is fastened to the electrode via a nut. The upper electrode consists of a tungsten rod which is threaded on one end such that it can be attached to a steel rod for the purpose of lengthening the rod. The electrode is held by a brass water-cooled electrode holder. The tungsten electrode is encased in a quartz "T"-shaped tube

Figure I. The construction of the plasma source
illustrating the lower and upper electrodes

which is connected to a sheet of asbestos. The function of the quartz "T" is to direct the flow of argon gas around the tungsten electrode. The intersection of the flow of gas from the upper and lower electrodes defines the shape of the arc column, which is a curve. Figure II outlines the flow of gas throughout the plasma jet. Figure III illustrates the construction of the plasma source. The plasma source is powered by an Applied Research Laboratories Model No. 26300 power supply at 15 amps and 115 volts. A schematic diagram of the circuit is shown in Figure IV.

B. The Optical and Detection System

The optical system employed in the study was used previously by Korba (24) in the application of the FP interferometer to flame emission spectroscopy. A diagram of the optics and detection system is shown in Figure V. The light emitted by the plasma jet is collected by a condenser lens, whose dimensions are 60 mm in diameter and 68 mm in focal length. The fraction of light collected by the condenser is focused onto a 4.0 mm pinhole. Then the cone of light diverging from the pinhole is collected and focused into the FP cavity by a lens whose dimensions are 130 mm in diameter and 200 mm in focal length. Since light from the FP is a diverging beam, a lens whose diameter is 105 mm and focal length is 150 mm is positioned

Figure II. The gas flow system of argon to the plasma jet

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Figure III. A photograph of the dc arc plasma jet and the stand which allows vertical positioning of the plasma jet. Beyond the circular aperture is the optical system and the Fabry-Perot

Figure IV. The schematic diagram of the power supply is shown. The circuit is part of an Applied Research Laboratories (ARL) arc source

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Figure V. A diagram of the optical and detection system.
The line with arrows on them illustrates the
input and output of voltage to and from the
electrical components

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between the FP and the photomultiplier tube (PMT), in order to focus the beam onto the aperture of the PMT. The PMT in this work is an RCA model IP21 and has a spectral sensitivity that ranges from about 320 nm to 600 nm. The maximum sensitivity occurs at about 400 nm. The distances between optical components shown in Figure V are listed in Table I.

Table I. Spacing between optical components in Figure V.

Distance, mm	Alphabet
90	A
240	B
220	C
995	D
120	E
160	F

The chief component of the optical system is the FP interferometer which is a Tropel model CL-100. The FP mirrors are 0.375 inches in thickness, 0.591 inches in diameter and has a wedge angle of approximately 30'. The mirror spacing is variable from 0.002 to 0.400 inches.

The variation in mirror spacing is produced by a piezoelectric crystal which moves the mirrors 0.75 microns (μ) per 300 volts of applied potential. The maximum potential allowed to the crystals is 350 volts.

Another set of piezoelectric crystals are used to finely align the FP mirrors. Fine alignment is accomplished by adjusting the three knobs on a Tropel model pzm power supply which moves the mirrors 4 μ per 1000 volts of applied potential. The maximum amount of voltage required to operate the crystals is 1000 volts. Coarse alignment is obtained by adjusting the three micrometers on the back face of the FP. A sawtooth voltage is generated by a Tektronix model 7904 oscilloscope which produces a ramp that rises from 0 to 8 volts. This ramp is amplified by the high voltage amplifier (24) from 0 to approximately 300 volts. The rise of the ramp causes the scanning of the FP and the scan rate can be varied by changing the time scale of the oscilloscope. The output of the PMT is displayed on the vertical scale of the oscilloscope and is photographed by a Tektronix model C27 camera.

IV. EXPERIMENTATION

A. The Order of Experimental Procedure

Before the task of characterizing the dc arc plasma jet was undertaken, considerable emphasis was placed upon the design of the experiments. The experimental design was selected such that the outcome of a particular experiment would not be influenced by another experimental parameter. Those parameters that gave rise to the best plume-column separation were considered and studied. The study of the experimental parameters were based on one of two observations: 1) the appearance of the plasma, and 2) the intensity of emission. Thus, the order in which the experiments were conducted was as follows; (a) the shape of the plasma, (b) the amount or volume of plume, (c) the region of observation in the plume, (d) the type of material in which the electrodes were composed of, (e) the detection capacity of the instrument, and (f) the effect of orifice size on emission.

B. The Determination of the Plasma Shape

The experimental parameter that was of greatest importance for adequate construction of the plasma jet was the shape of the arc column. The shape of the arc column affected the separation of the plume and the arc column.

It was found that the geometry of the electrodes gave rise to the shape of the column. Normally, the arc column had the appearance of a ninety degree elbow in which the plume protruded from the center of the elbow bend.

By increasing the distance vertically between the electrodes, separation of the plume and the arc column is achieved. If the distance of the horizontal electrode from the vertical axis was increased, the plume and arc column separation was increased further. The optimum separation distances of the electrodes were found to be 9.5 mm vertically and 7.0 mm horizontally. Distances greater than the above caused the arc column to extinguish and those less than the above gave rise to the dominance of the arc column so that there was little separation of the plume and arc column.

C. The Optimization of the Plume Volume

The plume volume is the amount of noncurrent carrying portion of the plasma. The greater the amount or volume of plume, the greater the ease at which spectral observations can be achieved in the plume region. It was found that the flowrate of argon gas through both the vertical and horizontal electrodes influenced the size of the plume. The optimum volume of the plume could be obtained if the proper gas flowrates were used. The flowrates were

measured on Brook (type 1355-00A1FAA) flowmeters in units of liters per minute.

The above experiment was carried out and a value for the flowrates was obtained. However, it was found that this value changed when the experiment was repeated. Further investigation led to the belief that the relationship between the plume volume and flowrate was dependent upon the ratio of the flowrate of argon gas in the lower electrode to that of the upper electrode. The flowrate ratio behavior was determined for plumes of similar volumes. Thus, the flowrate behavior is shown in Figure VI as a measure of flowrate ratio with respect to the intensity of sodium emission. In Figure VI, each curve shows that the intensity of emission increases as the ratio of flowrate 2 to flowrate 1 increases. The numbers beside each curve denote the maximum value of the flowrate of argon in the lower electrode. Flowrate 1 denotes the flowrate of argon gas through the upper electrode and flowrate 2 denotes the flowrate of argon gas through the lower electrode. The values for emission intensity were taken from the average five scans. The voltage applied to the PMT had to be changed in order to keep the signal output on the scale of the oscilloscope. The relationship between the voltage applied to the tube and the sensitivity of the tube of emission was needed. This information was obtained from

Figure VI. Graph of the relationship between the
flowrate ratio of argon in the upper and
lower and the intensity of sodium emission

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the manufacturer of the PMT and is shown in Figure VII. Since the points on the curves for 500 volts and above appear linear, the curves were extrapolated to zero volts.

The appearance of the curves in Figure VI at low ratios remain unaccounted for. However, it is observed that at low ratios a large plume results from a small arc column. Since the arc column is small, there may be less resistance to the penetration of aerosol into the plasma, thus increasing the emission of Na. Whatever the case may be, data at these ratios cannot be used because the plasma suffers from a high degree of instability.

D. The Determination of the Optimum Region for Spectroscopic Observation

The region of observation was studied by positioning the plasma jet such that the image of the plasma could be projected onto the pinhole of the optical system. By moving the electrodes vertically and horizontally, various regions of the plasma could be studied as shown in Figure VIII.

The evaluation of each region in Figure VIII was based on the measurement and comparison of the signal to noise ratio (S/N) of a 10000 ppm sodium solution. The results of these measurements are shown in Table II. Region 3 was chosen because it gave the highest S/N value.

Figure VII. The relationship between the PMT sensitivity and the voltage applied (in values of 100). All points below 500 volts are extrapolated values, whereas the ones above 500 volts were obtained from the manufacturer (RCA) for this particular PMT, IP21

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Figure VIII. Photograph of the plasma jet in operation.
The cloudy region is the plume and the white
lines are the arc columns. The numbers
denote the basic regions of spectrographic
investigation

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Table II. The region of observation in the plasma

Region	Signal-to-Noise Ratio
1	6
2	6
3	8
4	2

E. The Composition of Electrode

Material

Although the plasma jet used in this study is similar to that used by Elliott (6) and the use of a graphite and tungsten electrode was taken from Elliott's system, it was interesting to see the effect in which a graphite-graphite or tungsten-tungsten or a graphite-tungsten arrangement would have on the background emission.

In this experiment, the background noise was observed with respect to each of the following electrode arrangements; (a) graphite-graphite, (b) graphite(L)-tungsten(U), (c) tungsten-tungsten, and (d) graphite(U)-tungsten(L), where "L" denotes the lower electrode and "U" denotes the upper electrode. The results of the experiment were as

follows:

- (a) The graphite-graphite arrangement offered low background emission, but the electrodes easily eroded.
- (b) The tungsten-tungsten arrangement gave rise to high background emission and thus proved inadequate for use.
- (c) The electrode arrangement incorporating a lower tungsten electrode and an upper graphite electrode also proved inadequate because the tungsten electrode, whose orifice diameter was 1/4 mm and outer diameter was 1 mm, was too small and allowed a small amount of solution to enter the plasma.
- (d) The graphite(L)-tungsten(U) arrangement provided the best compromise because the background emission was low and a greater amount of sample could be aspirated into the plasma.

F. The Detection Capability of the Instrument

The dynamic range or detection capability of the Fabry-Perot/Plasma Jet system was investigated. Solutions of sodium were aspirated into the plasma whose concentration

ranged from 10,000 ppm to 10 ppm. To avoid errors in dilution and problems that might have been due to contamination, the solutions were made by taking dilution from a 10,000 ppm stock solution which was made up in triply deionized water. The results are shown in Figure IX. The points on the graph of intensity versus concentration were obtained from the average of five scans.

G. The Optimum Orifice Size

The final experiment was concerned with the effect of size of the orifice in the vertical electrode on the intensity of emission. The investigation was carried out with the use of a 10,000 ppm solution of Na. The size of the orifice was varied by using three electrodes with three different size orifices drilled through the center. The orifice diameters were 1.0, 3.5 and 5.0 millimeters. The flowrates and electrode separation distances were kept constant for each orifice diameter. The results are shown in Table III. Therefore, the orifice diameter of 1.0 mm was considered as optimum, because it gave the greatest S/N value.

Figure IX. A calibration curve for sodium in units of parts per million (ppm) versus the relative intensity

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Table III... The optimum orifice size

Orifice Diameter (mm)	Relative Intensity (volts)
1.0	25.0
3.5	17.0
5.0	17.0

V. SUGGESTIONS FOR IMPROVEMENT

As stated earlier, this study serves only as a starting point for the FP-Plasma jet system. Thus, at this point there stands a large amount of room for improvement of the system. These improvements can be classified into three categories; (a) electrical, (b) optical, and (c) mechanical. Some of the major drawbacks of the present system are background noise and instability in the arc column. The high degree of background that results from continuum emission in the arc column and plume limits the detection capability of the instrument. The instability in the arc column that results from changes in the position of the column and turbulent gas flow is the source of inconsistent data and fluctuations in PMT output.

Most of the background noise in the plume region may be eliminated if this problem is approached from an electrical point of view. The use of a low pass active filter that passes signals above a certain frequency would aid in the reduction of high frequency noise. These filters are common in the literature and can be easily constructed from op amp circuits (33).

Further complications due to instability and fluctuations in the plume can be eliminated if the problem is approached from a mechanical point of view. One of the

major sources of fluctuations in emission intensity is the formation of large droplets of liquid which causes inconsistent flashes to occur during excitation. These droplet formations can be eliminated with the use of a desolvation system. Although there are many kinds (34,35) of desolvation systems, all are based on the principle of removal of the solvent and allowing a dry aerosol to enter the plasma. The problems caused by the wandering of the arc column can also be approached from a mechanical point of view. The major weakness of the design of the apparatus used in this study is that of the lower electrode. The size of the lower electrode allows the arc column to wander from any point around the orifice. A design is needed such that the arc will remain in the center of the orifice as illustrated by Elliott (6). So instead of a hollow lower electrode, the system in this study requires a smaller solid graphite electrode within a larger hollow graphite cylinder or ring. In this configuration, the arc will remain in the center where greater excitation can occur.

The final major suggestion for improvement of the system lies in its use in the ultraviolet spectral region instead of the visible region. The ultraviolet region offers less background noise due to continuum emission and a larger selection of elements for spectrochemical analysis.

According to Bradley, Bates, Juulman and Majumdar (36), there are two factors affecting the extension of the spectral range to the ultraviolet region, the transmission and optical quality of the interferometer flats and the availability of suitable reflecting coatings. Although little success has been reported in the processing of multilayer dielectric coatings for the ultraviolet region, Bradley et al., (36) suggest the use of Al-MgF₂ reflecting coatings and the use of fused quartz for ultraviolet studies. If such an improvement is created, then the FP-Plasma jet combination is not only useful in spectrochemical analysis but also in fields such as plasma diagnostic studies, laser source studies and space research.

In conclusion, it cannot be overemphasized that improvements such as those discussed must be met before an assessment of the performance of the Fabry-Perot/Plasma Jet can be obtained. These performance characteristics include such concepts as accuracy, reproducibility, concentration range, sensitivity of detection and reliability.

A system involving the introduction of a Fabry-Perot and a dc arc plasma jet to spectrochemical analysis has been characterized. Although the system suffers greatly from limitations due to noise, it is believed that if the fundamental improvements, as discussed above, are made, then such a system will be able to compete with many of the techniques used in spectrochemical analysis.

VI. BIBLIOGRAPHY

1. V. A. Fassel, Electrical 'flame' spectroscopy, 16th Coll. Spectrosc. Intern., Heidelberg, 1971, Plenary lectures and reports, p. 63, Hilger, London, 1972.
2. S. Greenfield, H. McD. McGeachin and P. B. Smith, Talanta, 22, 1 (1975).
3. W. E. Rippeto and T. J. Vickers, Anal. Chem., 47, 2082 (1975).
4. M. Margoshes and B. F. Scribner, Spectrochim. Acta, 15, 138 (1959).
5. L. E. Owen, Appl. Spectrosc., 15, 150 (1961).
6. W. G. Elliott, Am. Lab. 3, No. 8, 45 (1971).
7. C. D. Keirs and T. J. Vickers, Appl. Spectrosc., 31, 273 (1977).
8. J. H. McGinn, Proc. 5th Int. Conf. Ionization Phenomena, Munich, 1961 1, 967 (1962).
9. E. Kranz, in Proc. 12th Coll. Spectrosc. Intern., p. 524, Hilger, London, 1965.
10. S. E. Valente and W. G. Schrenk, Appl. Spectrosc., 24, 197 (1970).
11. Spectrametries, Inc., Model 5300 Spectra Jet II Argon Plasma Jet Instruction Manual.
12. P. Merchant and C. Veillon, Anal. Chim. Acta, 70, 17 (1974).
13. W. E. Rippeto, E. R. Johnson and T. J. Vickers, Anal. Chem., 47, 436 (1975).
14. D. W. Golightly and J. L. Harris, Appl. Spectrosc., 29, 234 (1975).
15. S. S. Karacki and F. L. Corcoran, Jr., Appl. Spectrosc., 27, 41 (1973).
16. M. Marinkovic and B. Kimitrijevic, Spectrochim. Acta, 23B, 257 (1968).

17. M. S. W. Webb and P. C. Wildy, *Nature*, 198, 1218 (1968).
18. A. W. Fagan and H. M. Klein, *Anal. Chem.*, 40, 2041 (1968).
19. K. W. Busch and G. H. Morrison, *Anal. Chem.*, 46, 712A (1973).
20. J. D. Winefordner, J. J. Fitzgerald and N. Omenetto, *Appl. Spectrosc.*, 29, 5 (1975).
21. P. W. J. M. Boumans, *Proc. Analyt. Div. Chem. Soc.*, 143 (1977).
22. C. Veillon and P. Merchant, Jr., *Appl. Spectrosc.*, 27, 361 (1973).
23. R. Prusikma, J. Zimmer and E. S. Yeung, *Anal. Chem.*, 48, 667 (1976).
24. G. Korba, Master's Thesis, Iowa State University, 1977 (unpublished).
25. S. C. Haydon, An Introduction to Discharge and Plasma Physics, The University of New England, Armidale, N. S. W., Australia (1964).
26. N. W. H. Addink, D.C. Arc Analysis, Philips Research Laboratories, Eindhoven, The Netherlands (1971).
27. P. W. J. M. Boumans, Theory of Spectrochemical Excitation, Hilger and Watts LTD., London (1966).
28. P. W. J. M. Boumans, XIV Coll. Spectrosc. Intern., p. 23, Hilger, London (1967).
29. P. W. J. M. Boumans, in Analytical Emission Spectroscopy, edited by E. L. Grove, Marcel Dekker, Inc., New York (1968).
30. P. Jacquinet, *Rep. Prog. Phys.*, 23, 269 (1960).
31. M. Born and E. Wolf, Principles of Optics, p. 323, Pergamon Press, Oxford (1964).
32. V. V. Korolev and E. E. Vainshtein, *Zh. Anal. Khim.*, 14, 658 (1959).

33. L. P. Hvelsman, Active Filters: Lumped, Distributed, Integrated, Digital and Parametric, McGraw-Hill Book Company, New York (1970).
34. H. Raab; J. Phys. E: Scientific Instruments, 5, 779 (1972).
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- 35. D. J. Bradley, B. Bates, C. Juulman and S. Majumdar, Jap: J. Appl. Phys., 4, (Suppl.: I), 467 (1967).
36. F. W. J. Garton, W. Ramsden, R. Taylor and R. J. Webb, Spectrochim. Acta, 8, 94 (1956). 167 (1957).
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