SPATIALLY RESOLVED LASER INDUCED FLUORESCENCE STUDIES
IN THE THREE ELECTRODE DIRECT CURRENT PLASMA

By

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ABSTRACT

Spectrochemical emission from analytes in the three electrode direct current plasma has been found to be sensitive to the presence of easily ionizable elements (EIEs) as concomitants in sample matrices. An understanding of the mechanisms by which these EIEs affect analyte emissions is complicated by the fact that both emission enhancements and suppressions of ion and atom lines have been observed. In order to gain further insight into this effect, a fluorescence spectrometer was built and used as a spatial and spectral probe to obtain analyte population distribution profiles in the plasma.

The spatial distribution of the analyte in the plasma was found to be quite complex. Most of the analyte skirted around the plasma core and did not enter the analytical emission zone. The area in the plasma where emission was observed was relatively small compared to the spatial population distribution of the analyte which suggests that the amount of analyte contributing to the emission was a small fraction of the total analyte population present.

Three dimensional fluorescence profiles of Ba$^+$ concentrations in the plasma were determined with and without sodium present as the EIE. The presence of the EIE in the sample did not alter the spatial distribution of the Ba$^+$ population significantly but did appear to cause an ionization suppression. Emission profiles of the Ba(I) 553.548 nm and Ba(II) 493.409 nm lines were also obtained with and without an EIE present in the sample matrix. In both cases, the presence of the EIE caused emission enhancements; however, the effect was greater for the Ba(I) line than for the Ba(II) line which supports with the proposed ionization suppression mechanism.
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INTRODUCTION

1.1 EVOLUTION OF THE DIRECT CURRENT PLASMA

The first reported observation of an emission spectrum was made by Sir Isaac Newton. This observation, the resolution of the Sun's spectrum, led him to the conclusion that colours are contained in light and not inherent in objects. Since then we have learned much about the nature of light and its use in characterizing materials. One of the most important analytical techniques developed so far is that of spectrochemical emission analysis for which many devices have been designed to serve as sources. For instance, a laboratory flame was used by Bunsen and Kirchhoff [1], considered to be the founders of spectrochemical analysis [2], in 1860 for their discovery of cesium, the first element to be discovered by spectroscopy.

Direct current arcs and sparks were developed specifically as emission sources for the analysis of conducting solids. These devices consist of two electrodes between which an arc is struck. The arc and spark differ in the duration and type of the applied current. While the spark usually results from a briefly applied AC current, the arc results from a DC current which may be sustained for several minutes. The sample, which may be the electrode itself or a solid placed upon it, is vaporized by the electrode's high temperature. These sources have somewhat limited utility for the analysis of liquids and gases which restricts their usefulness in routine chemical analysis. The spark is further restricted by its operational requirement that the samples be electrically conductive. The introduction of the direct current plasma arc devices [3-9] relaxed these restrictions. They provide the means for the spectrochemical emission analysis of liquids and gases thus providing a technique for the analysis of sample solutions.

Plasma arcs produce the high temperatures required for spectrochemical emission. In addition to being useful for the analysis of solutions, they supply a high degree of sample ionization which results in the emission of ionic lines as well as the atomic lines. Their
increased stability, over arcs and sparks, and resulting sensitivity also makes them effective sources for the use and investigation of spectrochemical emission.

Plasma arc devices were first introduced for solution spectrochemical analysis in 1959 by Margoshes and Scribner [3] and by Korolev and Vainshtein [4,5]. Margoshes and Scribner's device, a "plasma jet", used two graphite disk electrodes (Figure 1) as the anode and cathode. Argon was used as the nebulizer gas and helium served as a coolant gas which was introduced tangentially into the plasma chamber. This plasma jet was operated at currents of 10 to 15 amps from a standard direct current power supply. The plasma consisted of a conical "flame" and a current-carrying streamer in contact with the "flame" and cathode. The contact point of this streamer to the cathode wandered and caused the plasma "flame" to move around.

Korolev and Vainshtein's "plasmatron" was similar in design and used nitrogen as plasma gas. An improved design, shown in Figure 2, containing a rod-shaped cathode, soon followed [6].
Owen [7] showed that an external cathode improved the stability of the plasma jet. Scribner and Margoshes [8] modified their design accordingly. Their improved model, the gas stabilized arc, contained an external tungsten cathode. The original ring cathode became a control ring and had its own potential. Elliott [9] described a device, similar to Owen's gas stabilized arc [7], which was offered commercially as the Spectrametrics, Inc. SpectraJet, shown in Figure 3.
Several studies on this and similar designs soon followed [10-25]. These included characterization and optimization of the operating parameters [9-18], and application studies [19-25].

In 1970 Valente and Schrenk [26] designed and characterized a novel two electrode "dc-arc plasmajet". The anode and cathode were contained in similar cylindrical chambers. For ignition, the chambers were aligned and one electrode was manually pushed through both chambers until the electrodes came into contact (Figure 4).

![Figure 4: Electrode configuration of Valente and Schrenk's arc plasmajet in arc initiation mode [26].](image)

![Figure 5: Electrode configuration of Valente and Schrenk's arc plasmajet in operation mode [26].](image)
The electrode was then pulled back to its original position. Once ignited, one of the chambers was rotated until the two jets formed an angle of 30 degrees. This configuration, shown in Figure 5, reduced turbulence and heat dissipation problems thus improving the stability of the plasma.

Marinkovic and Vickers [27] designed a direct current plasma with a similar operating configuration. Their "stabilized dc arc" contained two parallel cylindrical electrodes (Figure 6). For ignition, two graphite rods were inserted through these electrodes and a third was used to complete the circuit. Once the arc was struck these three electrodes were removed. This design was characterized for emission spectrometric analysis by Rippetoe, Johnson and Vickers [28].

![Diagram of electrode configuration](image)

**Figure 6**: Electrode configuration of Marinkovic and Vickers' stabilized dc arc [27].

Murdick and Piepmeier [29] later improved this design slightly by making the two parallel electrodes adjustable, consequently only one external graphite rod was needed for ignition.

The Spectrametrics, Inc. SpectraJet II characterized by Skogerboe, Urasa and Coleman [30] was similar to Valente and Schrenk's plasmajet [27]. This design, described by Keirs and Vickers [31], also contained two electrodes with the cathode positioned off the
central axis. The angle formed by the two electrodes, shown in Figure 7, was approximately 90 degrees creating an inverted V-shaped plasma. The aerosol sample was introduced via a separate sample tube positioned under the inverted V. Coleman, Braun and Allen [32] found that the detection limits for chromium, copper and magnesium emission could be improved by a factor of approximately 2 by changing the angle to 45 degrees.

The SpectraJet II, also by Spectrametrics, Inc., contains a third electrode. Two graphite anodes form an angle of approximately 35 degrees and a tungsten cathode is positioned above these anodes. This design was used for the present study and is described in more detail in section 2.1.2.

1.2 THE THREE ELECTRODE DIRECT CURRENT PLASMA

The SpectraJet III three electrode direct current plasma (DCP) has attracted more interest than previous DCP designs [33-49]. This is mainly due to its success as an atomic emission source; detection limits have been reported [33,37] to be less than 1 ppm for many elements. These detection limits are usually approximately less than an order of magnitude larger than those obtained in the inductively coupled plasma (ICP). A linear dynamic range of
at least three orders of magnitude [33] has been reported for the DCP. The three electrode DCP is a versatile source and has been used to determine trace metals in organic as well as aqueous solutions and has sustained operation with total dissolved solids as high as 40 to 45 % [34] in sample solutions.

Its characteristics as an emission source are due, in part, to its geometry. The plasma has an inverted Y shape which is a result of the DCP's relative electrode positions (Figure 11). This creates an observation or analytical zone, characterized by a relatively high signal-to-background ratio, slightly below the centre of the inverted Y. This region has a cross-sectional area of approximately 0.25 mm$^2$ [33,35]. The exact position of this zone is determined by the argon gas flows around the anodes and also by the gas flow through the aerosol delivery channel [33].

A plasma is, loosely, an ionized gas and therefore an important parameter of the DCP is its electron number density. Since the DCP was designed to serve as a spectrochemical emission source, its temperature is also an important characteristic which must be considered. In order to better understand and possibly suggest methods to improve the DCP emission characteristics, temperatures and electron densities within the plasma have been measured [35-39,50]. Electron density measurements in the 3 electrode DCP typically yield values in the $10^{15}$ to $10^{16}$ cm$^{-3}$ range [35-39]. One method used for obtaining electron number densities is ion-to-atom emission line intensity ratios. This method assumes the plasma is in local thermodynamic equilibrium (LTE) where there is the requirement that the electron density be approximately $10^{16}$ cm$^{-3}$ or greater [50]. The electron density can also be determined using the Stark width of the H$\alpha$ (656.5 nm) line or of the H$\beta$ (485.6 nm) line [36]. The electron densities obtained by this method do not require the plasma to be in LTE. Since electron densities in the 3 electrode DCP are near the boundary of LTE and non-LTE conditions, it seems wiser to use the Stark width method. Results from such experiments show electron densities of $10^{15}$ to $10^{16}$ cm$^{-3}$ [35]. By virtue of not being in LTE, shown by these electron densities, the analytical zone does not have a unique temperature but rather, possesses
different temperatures depending on the state distribution being used for the measurement. These temperatures may be derived from electron densities or ion-to-atom ratios of spectroscopic indicator populations [50]. Results from these measurements fall in the range of 5100 to 7900 K [40] in the analytical zone.

1.3 EASILY IONIZABLE ELEMENTS (EIEs) IN DCP EMISSION STUDIES

Analyte emission line intensities in DCP spectrometric analysis have been shown to be sensitive to easily ionizable elements present in sample matrices [12,16,18,33,37,40,41-47,51-54]. In these studies both enhancement and suppression of analyte emission have been observed upon the addition of an EIE. Eastwood and Hendrick [47] and Nygaard [41] have shown that the magnitude of this effect depends on the total concentration of easily ionizable cations such as sodium, potassium, calcium and magnesium in the samples. Several authors [27,28,33,36,41,46] have reported changes in the plasma's spatial profile upon the addition of an EIE. This effect cannot be dismissed as it caused apparent changes in the size and shape of the observation zone and, consequently, the measured emission line intensity.

1.3.1 CHANGES IN TEMPERATURE

Several mechanisms have been proposed to describe the effect of adding an EIE to samples in DCP emission analysis. Some authors [27,37,46] have suggested that the effect is caused by a temperature change within the plasma. Marinkovic and Vickers [27] observed an emission suppression effect and attributed it to a temperature decrease. They proposed that the free atom concentration was increased due to decreased gas expansion, decreased ionization and decreased ambipolar diffusion. Johnson et al. [37] observed an increase in emission intensity and temperature. Their experiments qualitatively supported an increase in excitation and thus emission due to the temperature increase. Nygaard and Gilbert [46] obtained spatial profiles of analyte emission and suggested a flattening of the thermal gradient within the
plasma. They found that the addition of an EIE caused the temperature at the plasma's core to decrease and the temperature at its periphery to increase.

1.3.2 CHANGES IN ELECTRON PRESSURE

Golightly and Harris [18] and Felkel and Pardue [54] suggested changes in electron pressure by the addition of an EIE as the cause for changes in emission intensities. The latter proposed an equilibrium situation where increased electron pressure results in a shift toward lower analyte ionization states. Electron density spatial profiles obtained by Williams and Coleman [36] showed that the electron concentration in the body of the plasma remained unchanged while that of the current carrying core was increased by the presence of an EIE.

1.3.3 SPATIAL PROFILE EFFECTS

Some authors [28,33,41] have observed changes in the spatial profile of the plasma due to the addition of an EIE to their sample. Rippetoe et al. [28] observed a change from a "distinct zone" to a "diffuse zone" upon the addition of an EIE and a resulting increase in analyte emission. They suggested that this improved aerosol introduction into the plasma thus increasing the emission intensity. Decker [33] and Nygaard [41] also observed changes in spatial profiles. Decker noted that the position of maximum intensity moved upwards toward the centre of the plasma upon the addition of an EIE to the sample. Nygaard proposed that the changes in observed emission intensities were caused by spatial shifts in the plasma resulting in the photomultiplier tube viewing a different part of the plasma.

1.3.4 THE MILLER MODEL

Miller [40] proposed one of the most comprehensive models describing spectrochemical excitation in the DCP, including the effects of EIEs. This model assumes that argon serves as a channel for the transport of energy throughout the plasma via radiation transfer and collisional redistribution to analytes. An EIE acts primarily as an additional
channel for this energy transport. In the outer zones of the plasma the optically pumped EIE serves as an electron donor and increases the local electron density. This causes the Stark widths of argon and of the EIE to broaden thus raising their absorption cross-sections. The result is an increase in the net energy flow to the outer zone. These effects produce several phenomena. The increased rate of radiative transfer from the outer zone to the analytical zone \textit{via} argon in turn causes an increase in argon population inversion. As a result there is an increase in the Penning ionization of the analyte producing greater numbers of excited analyte species. The EIE may also interact with the analyte in a similar manner. Another mechanism is through relaxation of thermal gradients which increase energy redistribution by radiation and allows more penetration of the analyte into the analytical zone.

1.4 THESIS PROPOSAL

As seen earlier in 1.3.1, 1.3.2 and 1.3.3, the use of spatially resolved data gave significantly more information and insight concerning the DCP environment. In studies previously discussed [33,36,41,46], observations of spatial profiles were in two dimensions at most. Although it is not possible to obtain three dimensional emission data by virtue of the optical viewing geometry of analyte emissions in the DCP, it is obvious that obtaining data resolved in all three spatial dimensions will give a more complete picture of this system. The non-symmetrical nature of the source also prevents the use of numerical methods such as Abel inversion [55] to calculate spatially resolved analyte populations.

The third spatial dimension may be resolved using fluorescence to probe a specific volume element within an observation cell. This can be accomplished by using a spatially coherent light source, such as a laser, to excite analytes along one axis and then viewing the fluorescence along another. Overlap of the excitation and viewing cross-sections defines the spatial element. Fluorescence also permits selectivity of the transitions under observation. The use of lasers as sources for atomic fluorescence has been well documented [56].
narrow linewidths. The high peak power results in increased signal intensities and therefore increased signal-to-noise ratios. Temporal coherence permits time resolved studies to be performed and narrow linewidths result in increased selectivity of excitation transitions. Laser excited atomic fluorescence was used for this purpose in the present study. A brief review of fluorescence follows.

1.4.1 TYPES OF ATOMIC FLUORESCENCE

Atomic fluorescence is a radiative deactivation process by which an atom undergoes a transition from an upper excited electronic state to a lower electronic state. Winefordner and Omenetto [57] have proposed a system of nomenclature which encompasses five basic types of fluorescence transitions. These transitions, shown in Figure 8, are; resonance fluorescence, direct-line fluorescence, stepwise-line fluorescence, multiphoton fluorescence and sensitized fluorescence.

Figure 8: Examples of atomic fluorescence transition types.
The energy levels are for descriptive purposes only.
Resonance fluorescence occurs when the upper and lower energy levels for absorption and emission are the same. In direct-line fluorescence, only the upper level needs to be the same while stepwise-line fluorescence involves different upper levels. Sensitized fluorescence results when a donor species is excited and transfers excitation energy to an acceptor which then radiatively deexcites. Multiphoton fluorescence is defined as the radiational deexcitation of a species that has been excited by two or more photons. The nomenclature used above is based on the relationship between excitation and emission energy levels. Fluorescence may be characterized even further. Stokes fluorescence takes place when the excitation energy is greater than that of fluorescence. The reverse results in anti-Stokes fluorescence. When both excitation and emission involve excited states only, the process is called excited state fluorescence. Thermally assisted fluorescence occurs when collisional excitation follows radiational excitation.

1.4.2 FLUORESCENCE INTENSITY

Mathematical expressions describing fluorescence intensity have been tabulated by Omenetto and Winefordner [57]. These take into consideration such parameters as the number of energy levels in the atom, the type of fluorescence transition and the bandwidth of the exciting radiation. For this study it is sufficient to note that in all situations presented, fluorescence intensity is proportional to the analyte concentration.

1.4.3 FLUORESCENCE LIFETIMES AND QUANTUM YIELDS

In an atomic system with two energy levels $E_1$ and $E_2$, $E_2$ being of a higher energy, the rate of spontaneous decay from level $E_2$ to $E_1$ may be given by:

$$\frac{dN_2}{dt} = -A_{21}N_2$$ (1)
where $N_2$ represents the number density of atoms in level $E_2$ and $A_{21}$ represents the Einstein probability coefficient for spontaneous emissions. The natural radiative lifetime, $\tau^0$, for the transition is defined as the reciprocal of $A_{21}$. Integration of (1) and substitution of $\tau^0$ for $A_{21}$ yields:

$$N_2 = N_2^0 e^{-t / \tau^0}$$  \hspace{1cm} (2)

This indicates that, for resonance fluorescence with no quenchers present, the fluorescence intensity, which is proportional to $N_2$, will decay exponentially with respect to time. For practical applications we must also consider the effects of quenchers and other possible deexcitation pathways; thus the lifetime, $\tau'$, of the excited state must now be represented by:

$$\tau' = \frac{1}{\sum_j A_{2j}N_2 + \sum_k Q_kN_2}$$  \hspace{1cm} (3)

where $\sum_j A_{2j}$ is the sum of all the transition probabilities for deexcitation from level $E_2$ and $\sum_k Q_k$ is the sum of all the probabilities for the non-radiative deactivation processes. The relative quantum yield, $Y_F^0$, of an excitation and emission process is defined [58] as:

$$Y_F^0 = \frac{\text{number of quanta per unit time emitted from } A^* \text{ to } A}{\text{number of quanta per unit time absorbed by } A \text{ in going to } A^*}$$  \hspace{1cm} (4)

Where $A^*$ is the excited species and $A$ is the relaxed species. The radiative lifetime may be expressed in terms of the relative quantum yield for a particular transition process as follows.

$$\tau' = Y_F^0 \tau^0$$  \hspace{1cm} (5)
Note that $\tau'$ becomes an important parameter when the fluorescence excitation is caused by an incident radiation pulse whose width is on the same order.

1.5 SUMMARY

Direct current plasmas have evolved into useful sources for spectrochemical emission analysis of solutions. The three electrode DCP considered in this study has a small analytical zone with complex excitation processes which are not clearly understood. The use of emission to study these excitation processes is severely limited by the DCP's lack of cylindrical symmetry which prohibits spatial resolution of the emission. Spatial resolution may be obtained by using fluorescence as a high resolution spatial probe. In order to gain a better understanding of excitation processes in the DCP, fluorescence has been used to study an analyte's spatial distribution in the DCP and changes in this distribution induced by the addition of an EIE.
2 EXPERIMENTAL

2.1 INSTRUMENTATION

In order to satisfy the instrumental needs of this study, a computer controlled fluorescence spectrometer was designed. This spectrometer had the capability to resolve the fluorescence emission spatially and temporally as well as provide the inherent two fold, excitation and emission, spectral resolution of fluorometers. The spectrometer, shown schematically in Figure 9, consisted of a nitrogen pumped dye laser as the excitation source, a monochromator, a direct current plasma as the sample cell and the optics and electronics required for data acquisition and storage. The spatial resolution was obtained by the choice of excitation source and the geometry of the optical components. The laser source provided a spatially coherent light beam which excited analytes within the direct current plasma along one path. By observing the fluorescence from these analytes with a monochromator placed at 90 degrees to this path, a volume element was effectively selected providing spatial resolution.

For stability, the optical components were mounted on an optical rail system. The lasers were then mounted directly on these rails while the remaining optical components were fastened to a custom designed table top secured to the rails. This table top consisted of a one half inch thick aluminum plate with tapped holes every two inches and was designed to facilitate the alignment of the excitation and viewing optical components.

2.1.1 EXCITATION SOURCE

A Photochemical Research Associates Inc. (PRA International Inc., London, Ontario) model LN1000 nitrogen pulse laser was used to pump the dye laser and provided light pulses with a 337 nm wavelength and a pulse width of 800 ps. The manufacturer reported a maximum energy of 2.5 mJ per pulse under optimum conditions. This laser operated on power from a normal AC service outlet and used commercial grade nitrogen. To fire the laser, a mode setting differentiated between an internally timed variable pulse rate and a TTL compatible external trigger signal. There was also external control over the laser's internal
Figure 9: Experimental system (not drawn to scale); M1, M2 and M3 are mirrors.
high voltage power supply between 0 kilovolts and 20 kilovolts.

During data collection, the nitrogen laser was set at 16.5 kilovolts since this provided the best pulse-to-pulse reproducibility as measured by a Joulemeter. Although the manufacturer suggested a large spark gap electrode spacing of 2.4 mm, or 3.0 turns of the large spark gap electrode adjustment knob from the closed position, it was found that the laser operated better with a smaller electrode separation. A large spark gap electrode spacing of approximately 1.6 turns from the closed position, providing a spacing of 1.3 mm, was chosen as it represented the position where the laser's operation was optimum.

For these two adjustments a Gentec Inc. (Gentec Inc., Ste-Foy, Quebec) model ED-100A detector connected to a model PRJ-M peak reading Joulemeter, also from Gentec Inc., was positioned to measure the dye laser's output. Having selected the internal triggering mode, the nitrogen laser's repetition rate was then set at approximately 1 Hertz. Optimization of the parameters was seen as a minimum in the relative standard deviation and a maximum in the intensity of the laser's output as measured by the joulemeter. In five 100 shot trials the average relative standard deviation was found to be 3.7 %.

The dye laser used for the excitation of the sample was the Photochemical Research Associates Inc. model LN107 equipped with a digital drive model DD1790 (PRA International Inc.) to facilitate wavelength selection. The laser's operation was based on stimulated emission from an organic dye solution contained in two UV transparent cuvettes. The oscillator cavity containing the first cuvette was wavelength selective and provided the laser pulse whereas the second cuvette worked as an amplifier. A portion of the nitrogen laser pulse was used to create a region of population inversion in the dye contained within this second cuvette. The laser pulse from the oscillator subsequently passed through this region causing stimulated radiative emission thus amplifying the pulse's intensity.

The dye laser was wavelength selective and with the appropriate dye it could be tuned to wavelengths between 360 nm and 900 nm. In this case the Photochemical Research Associates Inc. dye number 7A665 was used which provided a tuning range of approximately
630 nm to 710 nm [59]. The laser pulses had a duration of approximately 500 ps and a spectral bandwidth of 0.04 nm [59]. These were aimed onto the direct current plasma via a 4.7 cm diameter and 75 cm focal length lens. Three mirrors (Figure 9) directed the beam in a horizontal line parallel to the plasma's two anodes and thus coplanar with the inverted Y-shaped plasma.

2.1.2 THE DIRECT CURRENT PLASMA

Fluorescence was observed in a SpectraMetrics Inc. (SpectraMetrics, Inc., Andover, Massachusetts) SpectraJet III direct current plasma with only slight modification to its jet translation assembly. Figure 10 shows a block diagram of the plasma's main components. Argon was delivered to the jet as nebulizer and plasma gas via a control module which permitted the regulation of pressure and gas flow rate to the nebulizer and each electrode. These pressures and flows were set as described in the SpectraJet III's operation manual. The nebulizer pressure was set at 14.5 psi and the sleeves' pressure was set at 50 psi. A transformer module together with the control module provided a direct current of 7 amps which resulted in a potential of approximately 60 volts between the anodes and the cathode while the plasma was in operation [33]. For sample introduction, a peristaltic pump fed the sample solution through a nebulizer and spray chamber which was connected to the aerosol delivery tube.

The jet assembly, shown in Figure 11, consisted of two graphite anodes and a tungsten cathode seated in water-cooled blocks. Ceramic sleeves channelled the electrode argon flows which defined the plasma's inverted Y profile. Sample aerosol flowed through the aerosol delivery tube which directed it up between the two anodes. In order to ignite the plasma jet, the gas flows were required to be on as well as the control module. An arc was struck between the cathode and the anodes by momentarily selecting the "ready" position of the "run / ready" toggle switch. This lowered the cathode block and extended all three electrodes thus bringing them into contact. At this point the toggle switch was placed to the
"run" position which raised the cathode block and withdrew the three electrodes into their operating position.

The SpectraJet III came equipped with a jet translation assembly which permitted translation of the jet along a vertical plane parallel to the anodes. Since easy translation along a horizontal plane was desired for this study, the translation assembly was rotated clockwise 90 degrees and clamped onto a 3/4 inch diameter rod screwed into the aluminum table top. This permitted the use of the two adjustment knobs on the translation assembly to move the plasma jet along a horizontal plane during the collection of data.

Figure 10 : Block diagram of SpectraJet III's main components.
2.1.3 THE MONOCHROMATOR

Fluorescence emission was spectrally resolved with a model 218 GCA/McPherson 0.3 metre monochromator (GCA Corporation, Precision Scientific Group, Acton, Massachusetts) installed with a 600 grooves/mm grating which provided a reciprocal linear dispersion of 5.31 nm/mm for the first order [60]. The monochromator was mounted to the proper observation height using three posts screwed into its casing and secured onto the aluminum plate. It was then aligned properly by removing its top cover and aligning its viewing mirror and entrance slit with the centre of the plasma jet. Its entrance slits were left unprotected to provide access to the horizontal slit for adjustments. Only the entrance was equipped with this horizontal slit which was set at 3 mm and positioned to allow the observation of fluorescence from the direct current plasma. This vertical mask also served as
a surface onto which the plasma's image was focused with a 50.8 mm diameter and 101.6 mm focal length lens providing visual information of the plasma's operation profile. This lens was also used to focus the image of the plasma and thus the fluorescence onto the monochromator's entrance for data collection. The monochromator's entrance and exit vertical slits were set at 0.100 mm for all data collection except where noted.

2.1.4. DATA ACQUISITION DEVICES

The spatially and spectrally resolved fluorescence was observed with a Hamamatsu (Hamamatsu Corporation, San Jose, California) photomultiplier tube (PMT) model R2083 which was effective between 300 nm and 650 nm. A 50 Ω terminator was placed on its output for impedance matching with the signal processing devices. The PMT was secured onto the monochromator's exit with a brass holder which prevented room lighting from falling onto the PMT's photocathode. The potential across the PMT was provided by a high voltage, low current power supply which was set at -2500 volts with respect to ground.

Intensity data from the PMT was collected using a model SR250 gated integrator and boxcar averager from Stanford Research Systems, Inc. (Stanford Research Systems, Inc., Sunnyvale, California). The cabling used to transfer fluorescence intensity data throughout the experimental system was RG58/U coaxial cable from Amphenol (Lisle, Illinois) with BNC connectors. Table 1 shows the settings chosen for the controls of the SR250.

The trigger input port was activated by setting the trigger rate to the external mode thus allowing an external voltage ramp from the photodiode to trigger the boxcar. The time delay between this trigger and the opening of the integration gate was determined by a voltage applied to the delay input on the back of the SR250 by a computer interface module. A setting of 100 ns of the delay scale knob generated a delay of 100 ns for every volt applied to this delay input. Since this experiment was designed with a further goal of obtaining fluorescence decay signals, an integration time of 1 ns was chosen since it represented the shortest gate available with this instrument. The signal sensitivity adjustment knob was set at 10 millivolts
<table>
<thead>
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<td>Last Sample</td>
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<tr>
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</tr>
</tbody>
</table>

Table 1: SR250 gated integrator and boxcar averager settings.

and caused a 10 millivolt input signal to produce a 1 volt signal at the output port. Setting the input filter to the >10 kHz position removed any noise below this frequency which may have been present in the PMT signal line. This noise included power line fluctuations and signals induced in the system by other laboratory equipment in the immediate vicinity. Since averaging by the boxcar was not wanted, the averaging knob was set at the "last sample" position thus causing the SR250 to act only as a gated integrator. Selecting the inverted mode of the polarity control provided a positive output instead of a negative potential as obtained from the PMT.

A 50 Ω terminator was placed on the signal output of the boxcar to prevent internal signal reflection. The boxcar was triggered by a high current 50 Ω photodiode (PD) model TF1850 from Instrument Technology Limited (The Technology Shop, Inc., Sudbury,
Massachusetts) and was positioned to observe partial reflection of the laser pulses off the focusing lens (the one used to focus the laser onto the plasma). This photodiode provided a voltage pulse sufficient to trigger the boxcar through its trigger input. Power requirements for the photodiode were met with a regulated direct current power supply set at -100 volts.

Data was acquired from the boxcar by a Stanford Systems, Inc. model SR245 computer interface module. This module also fired the laser by sending a TTL signal pulse through one of its digital ports to the trigger input of the LN1000 nitrogen pulse laser. The computer system, connected to the SR245 computer interface via RS232C ports, was a Commodore PC 10-II model 9100-00 (West Germany) equipped with two disk drives. Software written in BASIC and listed in appendix 1 was used to control data acquisition and storage.

2.1.5 TEMPORAL CONSIDERATIONS

The fluorescence signals from the atoms in the DCP were pulse-like in nature since the excitation source consisted of temporally short laser pulses on the order of 500 ps. The lifetimes of these fluorescence transitions, given by equation 5 in section 1.4.3, can be calculated to be on the order of nanoseconds, thus it was necessary to consider the temporal behaviour of the fluorescence spectrometer. It was important to realize that on such a short time scale the speed of light as well as the speed of electrical currents needed to be taken into account when the temporal parameters of the data acquisition devices were determined. Figure 12 shows the temporal characteristics of the fluorescence spectrometer designed for this study. Note that although the signal and integration gate do not seem to coincide, internal delays within the boxcar compensated for the apparent difference.

The time delays a, b and c were due to the transit time of the light pulses between the spectrometer's components. Delays c and f were internal delays within the PMT and PD respectively. Delays d and g were due to the transit time of the current pulses within the coaxial cables connecting the electronic devices. It should be noted that the 120 ns delay line
between the PMT and the boxcar was not simply due to their relative positions. This delay was found to be necessary in order to temporally move the sampling gate away from the trigger signal since this signal caused considerable interference in the sample signal within the boxcar for approximately 100 ns following the trigger pulse. The 120 ns delay was provided by 23.7 meters of RG58/U coaxial cable. Note that the velocity of propagation of current in this cable was 0.659 c [61] where c is the speed of light in a vacuum. The boxcar’s delay was set to 112 ns by the application of 1.12 volts on the rear delay input of the boxcar by the computer interface module. This delay, chosen to get overlap of the gate and the signal pulse, was determined by varying the delay in a time-resolved experiment described in section 2.2.2.
2.2 DATA ACQUISITION

Software written in BASIC was used to control all the acquisition of fluorescence intensity data from the spectrometer. Except where noted, all data was acquired using the program listed in appendix 1. This data was later reorganized by the programs listed in appendices 2 and 3 into a format readable by the Surfer (Golden Software, Inc., Golden, Colorado) computer program. "Surfer" was used for the creation of the fluorescence intensity planes and the isocontour plots presented in section 3.1 of this thesis using the options shown below in Table 2. Note that the data was first formatted into a form readable by Energraphics (Enertronics Research, Inc., St. Louis, Missouri), a plot program. This was done to provide quick visual access of the data as Surfer required over an hour to process the data and create the data grids (the fluorescence planes).

<table>
<thead>
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<tr>
<td><strong>Parameter</strong></td>
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<td>Limits</td>
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</tbody>
</table>

Table 2: Parameters used to create Surfer grids of fluorescence intensity.

Using these parameters the Surfer program produced the plots shown in Figures 20 to 24 and 26 to 35 from the fluorescence emission data. The grid size was chosen as 81 in order to produce grid lines which would intersect each data point. "Kriging" was the "Method"
option which produced surface grids most representative of the fluorescence intensity data. Kriging is a weighted averaging technique, described by Ripley [62], used to create interpolating surfaces from values obtained experimentally within the surface's area. For this Kriging, a search radius of 1 data unit was used to search for the 4 data points nearest the grid line intersections. The default values of the "Duplicate" and "Limits" options were used thus points at identical or "duplicate" positions on the surface were averaged and the grid's limit was chosen to fit all the data.

The sequence of events that occurred during data acquisition were the following. Once a series of prompts had been answered, the computer directed the computer interface to fire the laser. The nitrogen laser pumped the dye laser which excited the analyte species in the DCP and triggered the boxcar via the photodiode. The spatially and spectrally resolved fluorescence signal from the analyte was then observed by the PMT which sent the intensity data to the boxcar. The boxcar integrated the appropriate portion of this signal and sent it to the computer interface which subsequently sent its digital value to the computer. Having received the intensity data, the computer stored it on a disk and fired the laser once again. This process was repeated for 12 shots at which point the program paused until prompted again. Once the prompt, the depression of a key on the computer's keyboard, was given, the computer repeated this process. This continued throughout the collection of 40 sets of data each containing 12 data points.

2.2.1 THE ANALYTE

In order to study the population profiles of analyte species in the DCP and the effect of easily ionizable elements on these profiles, a non-resonance fluorescence transition in Ba\(^+\) was investigated. A partial energy level diagram of Ba\(^+\) (Figure 13) shows this anti-Stokes direct-line fluorescence transition.
The dye laser was used to excite an electron in the 5 d energy level to the 6 p energy level within the ion using the appropriate 649.690 nm wavelength. The 493.409 nm fluorescence emission observed resulted when the electron in the 6 p energy level radiatively deexcited down to the 6 s ground state. Transition probabilities for these transitions are $0.19 \times 10^8 \text{ s}^{-1}$ for the 493.409 nm line and $0.15 \times 10^8 \text{ s}^{-1}$ for the 649.690 nm line [63].

Sodium was chosen as the easily ionizable element since several authors (33,39,40,43,44 and 45) have reported it to alter analyte emission intensities in the DCP. Note that the first ionization potential of sodium is only 5.139 volts [64].

2.2.2 DETERMINATION OF THE SIGNAL'S TEMPORAL POSITION

In order to collect fluorescence profiles of the analyte populations within the DCP plasma jet, it was first necessary to obtain an overlap of the signal pulse with the integration gate of the SR250 boxcar. This was accomplished using a time-resolved experiment in which the temporal position of the gate was changed with respect to the signal pulse. The first step in this adjustment was to tune the dye laser and the monochromator to the same wavelength. Since the purpose here was to adjust temporal parameters only, the dye laser was tuned to approximately the wavelength of the dye's maximum emission intensity which was 665 nm.
A glass disk was then positioned at the centre of the three electrodes of the DCP's plasma jet such that the laser pulses were partially reflected onto the monochromator's entrance slit. To monitor the monochromator's output, it was necessary to remove the PMT from its exit and position a piece of white paper there to serve as a projection screen. The laser was then fired by setting the nitrogen laser to the internal mode and adjusting its repetition rate to approximately 2 Hertz. While scanning the monochromator manually, the approximate wavelength was determined by visual observation of the monochromator's output as projected onto the white paper screen. Once light pulses were observed on this screen, the PMT was replaced and the entrance and exit slits of the monochromator were closed down to 0.025 mm from 0.100 mm to prevent overloading the PMT.

Selecting the proper delay factor on the boxcar required running the data acquisition computer program with its temporal gate delay disabled. This was done by disconnecting the cable from the computer interface to the boxcar's rear delay input. While the laser was being fired by the computer interface as described in section 2.2, the boxcar's delay factor was manually scanned. The proper delay factor was found by selecting the one which provided the greatest intensity value as tabulated on the computer monitor by the data acquisition program. This delay factor was found to be 112 ns. In order to verify this value, the front delay factor was set to 0.0 while the rear delay input was reconnected. Delay factors of 110 ns to 114 ns were used in the computer program and the maximum intensity value was again found to be 112 ns. This value was subsequently written into the computer program and was used for all further experiments.

2.2.3 PREPARATION OF SAMPLE SOLUTIONS

The samples used in this study were aqueous solutions of water soluble salts. For the data presented in this thesis two solutions were prepared. One solution contained barium as the analyte species. The other, while still containing barium as the analyte, also contained sodium as an easily ionizable element. In both solutions 1.903 grams of barium nitrate,
Ba(NO₃)₂, were dissolved in 1.000 litre of deionized water resulting in barium concentrations of 1000 ppm or 7.282 × 10⁻³ molar. For the solutions containing sodium as an easily ionizable element, 6.594 grams of sodium chloride, NaCl, were also dissolved in this 1.000 litre of deionized water. This produced a solution containing 2594 ppm of sodium which represents a 0.1128 molar sodium concentration. The ratio of sodium to barium in this second solution was 15.49 which, as the data in section 3.1 shows, was sufficient to noticeably alter the fluorescence intensity from the barium ions thus providing the means to study the easily ionizable element's effect on the analyte populations.

2.2.4 TUNING THE MONOCHROMATOR

In order to tune the monochromator to the selected wavelength, the DCP was used as an emission source. A sample solution of 1000 ppm Ba, prepared as described in section 2.2.3 was aspirated through the operating DCP and provided the necessary Ba(II) spectral line emission. To locate the proper monochromator wavelength setting, the PMT was connected to a chart recorder through a Kikusui model COS5100 (Kikusui Electronics Corporation, Japan) 100 MHz oscilloscope and an emission spectrum was obtained. Since the wavelength dial on the monochromator was known to be accurate to within at least 1 nm it was only scanned over 3 nm around the chosen spectral line. Figure 14, which shows the results of this scan, was used to set the monochromator's wavelength dial to 493.7 nm which corresponded to 493.4 nm. Note that Figure 14 also shows the resolution of the monochromator with its entrance and exit slits set at 0.100 mm. To fine tune the monochromator, the oscilloscope was once again used to measure the PMT's output while the monochromator was slowly adjusted to the emission line's maximum intensity.
2.2.5 TUNING THE DYE LASER

Tuning the dye laser required the entire system to be in normal operation. The spectrometer was operated under the conditions described in section 2.1 using the computer program to control data acquisition. As described earlier, the computer program fired the laser 12 times and collected intensity data from the PMT after each shot and then required a keyboard prompt before collecting a further 12 points. In this case, the wavelength setting on the dye laser was varied prior to initiating this prompt. By monitoring the PMT's signal intensity it was possible to tune the dye laser to the 649.690 nm excitation line which was chosen in order to study Ba\(^+\) population profiles in the DCP. Due to the coarse nature of the wavelength selection mechanism on the dye laser it was necessary to find the excitation line by adjusting the wavelength dial back and forth using the digital drive's "jog" key until a maximum in the fluorescence signal was observed.
2.2.6 COLLECTION OF FLUORESCENCE PROFILES

In order to determine the population profile of Ba$^+$ within the DCP plasma jet, spatially resolved fluorescence profiles were obtained by collecting fluorescence intensity data points along several horizontal planes. The orientation of these planes is best described by Figure 15 which shows the position of the axes and plane with respect to the plasma jet's ceramic sleeves. The origin of the axes was arbitrarily chosen as the position where the three electrodes of the plasma jet met while in the "ready" mode. Note that, as mentioned earlier, observation of the fluorescence was made orthogonal to the incident excitation laser pulses.

![Cathode Ceramic Sleeve](Viewing Axis)

![Z-Axis](Laser)

![Y-Axis](Anode Ceramic Sleeves)

**Figure 15**: Spatial orientation of the data planes.

To determine the Z and Y axes origin, the jet assembly was positioned so that the laser pulses were incident upon the electrodes' point of contact while in the "ready" mode. Setting the X-axis origin required the plasma to be in operation. Once the plasma was lit the X-axis origin was found by adjusting the plasma's position such that its centre was projected onto the monochromator's entrance slit. Positioning the plasma jet vertically required clamping the translation assembly at the proper height on its support post as described in section 2.1.2. This was done first since it also varied the horizontal axes slightly. Adjustment of the horizontal axes simply required turning the positioning knobs of the jet translation assembly.
Using the data collection computer program and setting the spectrometer's parameters as described in section 2.1, fluorescence data along each horizontal plane were collected for both solutions, the barium solution and the barium and sodium solution. The plasma jet was first positioned to \(X = -6.40\) mm and \(Y = -3.04\) mm. While the solution was being aspirated, data acquisition was initiated; this meant manually scanning across the plane using the positioning knobs of the jet translation assembly. 12 fluorescence intensities were obtained at this position at which point the computer paused. At this time the jet translation assembly's \(Y\)-axis knob was turned clockwise \(1/4\) turn resulting in a \(0.16\) mm translation towards the centre. A prompt was then given to the computer which subsequently collected another 12 fluorescence intensities at this new position. The computer program paused once again during this procedure when the \(Y\)-axis \(3.20\) mm position fluorescence had been observed. The \(y\)-axis was then reset to \(-3.04\) mm and the \(X\)-axis knob turned \(1/2\) turn clockwise moving the jet assembly \(0.32\) mm towards the centre. Data collection along the \(Y\)-axis was then resumed. The fluorescence data for each plane was completed when the \(X = 6.40\) and \(Y = 3.20\) data points had been collected resulting in a data set containing fluorescence intensities for 41 \(X\) locations and 40 \(Y\) locations. In this manner, fluorescence intensities along each horizontal plane were gathered. Note that for every one of the 1640 positions, 12 measurements were made thus the data set for each horizontal plane contained 19 680 fluorescence intensity values.

The fluorescence emission's spatial resolution obtained with this spectrometer was a function of the vertical slit of the monochromator, the size of the laser beam in the plasma and the magnification factor of the projection optics. This magnification factor was measured as 1.52. In the \(Y\) dimension, the projection of the fluorescence onto the \(0.100\) mm vertical slit resulted in a spatial resolution of \(0.0658\) mm due to this magnification factor. In the \(X\) dimension, this magnification factor was obviously irrelevant and the resolution was only dependent on the diameter of the laser beam in the plasma, measured at \(0.5\) mm. The measurement of the laser beam's diameter at the plasma was made difficult by the laser dye's
fluorescence which enveloped this beam. The result was a measurement with relatively poor precision as indicated by the single significant figure in this value. In the Z dimension, a resolution equal to the diameter of the laser was also obtained since the projected image would have been 0.8 mm high which was smaller than the horizontal slit width. The volume element resolved was therefore a cylinder lying parallel to the Y-axis with a diameter of 0.8 mm and a length of 0.0658 mm.

2.2.7 COLLECTION OF EMISSION PROFILES

Since the three electrode DCP used in this study is a spectrochemical analysis emission source, lateral emission profiles of solutions containing Ba(NO$_3$)$_2$ with and without NaCl as an EIE were measured in order to compare the DCP’s emission behaviour with the fluorescence results. The emission lines measured were the Ba(II) 493.409 nm and the Ba(I) 553.548 nm lines. In order to prevent saturation problems and self absorption, the solutions used were the ones described earlier diluted by a factor of 10. This resulted in barium concentrations of 100.0 ppm and sodium concentrations of 259.4 ppm. For the data collection, the PMT was connected to a chart recorder through an oscilloscope as described in section 2.2.4. The plasma was manually scanned along the Y-axis in 0.32 mm increments and its emission monitored at each position for 10 seconds. The monochromator’s horizontal slit was set at 1.0 mm and its vertical slit set at 0.050 mm providing a spatial resolution of 0.658 mm in the Z dimension and 0.0329 mm in the Y dimension due to the 1.52 magnification factor of the viewing optics. Obviously there was no spatial resolution in the X dimension, along the viewing axis, since the monochromator viewed the entire signal along this axis.
3 RESULTS AND DISCUSSION

3.1 SPATIALLY RESOLVED FLUORESCENCE PROFILES

Spatially resolved intensity values for the fluorescence from Ba$^+$ in the three electrode DCP are shown for five vertical (Z) positions in Figures 16 to 20. These positions are -3.5 mm, -3.0 mm, -2.5 mm, -1.5 mm and -0.5 mm respectively. Figure 15 should be kept in mind when viewing these and subsequent data profiles since it shows the spatial orientation of these fluorescence intensity planes. These figures (16 to 20) clearly show the complexity of the Ba$^+$ population distribution within this plasma and should be considered in any attempt to understand excitation processes in the DCP.

An estimation of the precision of the fluorescence intensity values represented by these and subsequent fluorescence profiles is shown in Figure 21 and was calculated with the program listed in appendix 4. This figure is an isocontour plot of the relative standard deviation in the mean of the fluorescence intensity at the Z = -2.5 mm height. The isocontour shown encloses a region where there is a relative standard deviation in the mean of 10% or less. A comparison of this figure and Figure 18 shows that most of the fluorescence occurs within the area enclosed by the 10% isocontour. Since this plane was near the centre of the observation zone, the deviation in the data was assumed representative of all the fluorescence profiles.

It should be noted that the background emission was not subtracted from this data. In Figures 16 to 20 and Figures 23 to 27 the background emission can be seen as the ridge that runs parallel to the X-axis in the centre of the Y-axis. Since the emission was not experimentally resolved in the X dimension, changes in its profile along this axis, within a data plane, were due to the usual experimental noise and to the translation of the plasma. Although the emission was not resolved in the X dimension, the plasma was translated along this axis in order to obtain the fluorescence profiles. The image projected onto the entrance slits of the monochromator varied slightly as different parts of the plasma were brought into better, and worse, focus. This emission can be identified readily thus its subtraction from the
profiles is unnecessary. A description of the fluorescence profiles can be made by simply recognizing that the emission is seen as the ridge described above.

At the lowest observed height, the \( \text{Ba}^+ \) appears to be mostly confined to the aerosol delivery tube axis. At a vertical position of \( Z = -3.5 \text{ mm} \), shown in Figure 16, most of the analyte appears to be within a roughly circular zone with a radius of approximately 3 mm. Although the shape of the analyte's profile appears to be more oval than circular, this oval shape is most likely caused by the emission intensity present in the data. Even at this lower position, a saddle shape can be seen along the \( Y \)-axis of the profile with a higher analyte population toward the anodes. This saddle shape becomes more pronounced at higher positions in the plasma where the intensity difference between the peaks and the valley are greater as are the separation of the peaks. At the \( Z = -3.5 \text{ mm} \) position these peaks are only separated by approximately 0.7 mm while at the highest observed position of \( Z = -0.5 \text{ mm} \) the peak separation has become 1.9 mm.

There is also a saddle shape along the \( X \)-axis which becomes apparent at higher regions in the observed zone. In this case, the double peaks begin to appear around the \( Z = -3.0 \text{ mm} \) height but only become obvious at a height of \( Z = -2.5 \text{ mm} \). As can be seen in Figures 18 to 20, this peak separation is larger than the separation in the \( Y \) dimension with the fluorescence intensity between the peaks falling to near baseline values. The greatest separation, found at the highest measured horizontal plane, is 6.0 mm wide; over 3 times wider than the peak separation in the \( Y \) dimension.
Figure 16: Ba\(^+\) fluorescence intensity profile in the DCP at \(Z = -3.5 \text{ mm}\) for aqueous solution of \(\text{Ba(NO}_3\text{)}_2\). A) Intensity plot. B) Isocontour plot.
Figure 17: Ba$^+$ fluorescence intensity profile in the DCP at $Z = -3.0$ mm for aqueous solution of Ba(NO$_3$)$_2$. A) Intensity plot. B) Isocontour plot.
Figure 18: $\text{Ba}^+$ fluorescence intensity profile in the DCP at $Z = -2.5$ mm for aqueous solution of $\text{Ba(NO}_3\text{)}_2$. A) Intensity plot. B) Isocontour plot.
Figure 19: Ba$^+$ fluorescence intensity profile in the DCP at $Z = -1.5$ mm for aqueous solution of Ba(NO$_3$)$_2$. A) Intensity plot. B) Isocontour plot.
Figure 20: Ba\(^+\) fluorescence intensity profile in the DCP at Z = -0.5 mm for aqueous solution of Ba(NO\(_3\))\(_2\). A) Intensity plot. B) Isocontour plot.
Figure 21: Isocontour plot for a relative standard deviation in the mean of 10\% in the fluorescence intensity values at $Z = -2.5$ mm for the Ba(NO$_3$)$_2$ solution.
An overall look at Figures 16 to 20 shows that the $\text{Ba}^+$ is distributed over a wider area at higher positions in the plasma. There is also a certain degree of symmetry in the $X$ and $Y$ dimensions of the analyte's population profile which seems to decrease at higher vertical positions. As observations are made higher in the plasma, a decrease in the $\text{Ba}^+$ fluorescence intensity is seen in the ($+X$, $+Y$) and ($-X$, $-Y$) quadrants when compared to the ($-X$, $+Y$) and ($+X$, $-Y$) quadrants. The observations suggest that the $\text{Ba}^+$ analyte ions present in the plasma are distributed in a conical shape whose wide end points upward and is quadrifurcated as shown below in Figure 22.

![Figure 22: $\text{Ba}^+$ population zone shape in the DCP.](image)

Fluorescence intensity profiles of $\text{Ba}^+$ in the presence of sodium as an easily ionizable element are shown in Figures 23 to 27. Although the concentration of barium in the sample solution used here was the same as in the earlier set of profiles, there was a marked decrease in the fluorescence intensity upon the addition of an EIE to the sample. The distribution of $\text{Ba}^+$ in the plasma, as measured by its fluorescence intensity, remained relatively similar. These similarities in population profiles may be seen by comparing Figures 16 to 20 with Figures 23 to 27.
Figure 23: Ba\textsuperscript{+} fluorescence intensity profile in the DCP at $Z = -3.5$ mm for aqueous solution of Ba(NO$_3$)$_2$ and NaCl. A) Intensity plot. B) Isocontour plot.
Figure 24: Ba\(^{+}\) fluorescence intensity profile in the DCP at Z = -3.0 mm for aqueous solution of Ba(NO\(_3\))\(_2\) and NaCl. A) Intensity plot. B) Isocontour plot.
Figure 25: $\text{Ba}^+$ fluorescence intensity profile in the DCP at $Z = -2.5$ mm for aqueous solution of $\text{Ba(NO}_3\text{)}_2$ and $\text{NaCl}$. A) Intensity plot. B) Isocontour plot.
Figure 26: Ba\(^+\) fluorescence intensity profile in the DCP at Z = -1.5 mm for aqueous solution of Ba(NO\(_3\))\(_2\) and NaCl. A) Intensity plot. B) Isocontour plot.
Figure 27: Ba\(^+\) fluorescence intensity profile in the DCP at \(Z = -0.5\) mm for aqueous solution of Ba(NO\(_3\))\(_2\) and NaCl. A) Intensity plot. B) Isocontour plot.
Figure 28: Difference plots (Response with Ba(NO₃)₂ minus response with Ba(NO₃)₂ and NaCl in the solution) of Ba⁺ fluorescence intensity profile in the DCP at Z = -3.5 mm. A) Intensity plot. B) Isocontour plot.
Figure 29: Difference plots (Response with Ba(NO₃)₂ minus response with Ba(NO₃)₂ and NaCl in the solution) of Ba⁺ fluorescence intensity profile in the DCP at Z = -3.0 mm. A) Intensity plot. B) Isocontour plot.
Figure 30: Difference plots (Response with Ba(NO$_3$)$_2$ minus response with Ba(NO$_3$)$_2$ and NaCl in the solution) of Ba$^+$ fluorescence intensity profile in the DCP at $Z = -2.5$ mm. A) Intensity plot. B) Isocontour plot.
Figure 31: Difference plots (Response with Ba(NO₃)₂ minus response with Ba(NO₃)₂ and NaCl in the solution) of Ba⁺ fluorescence intensity profile in the DCP at Z = -1.5 mm. A) Intensity plot. B) Isocontour plot.
Figure 32: Difference plots (Response with Ba(NO₃)₂ minus response with Ba(NO₃)₂ and NaCl in the solution) of Ba⁺ fluorescence intensity profile in the DCP at Z = -0.5 mm. A) Intensity plot. B) Isocontour plot.
Before a mechanism for the suppression of the Ba\(^+\) analyte population by an EIE can be discussed, this suppression should be clearly characterized. For this purpose, the observed decrease in fluorescence intensity was calculated for each point on these planes. The results are plotted in Figures 28 to 32 which are, in effect, plots of the magnitude of the suppression caused by the addition of an EIE to the sample solution. By comparing these difference plots (Figures 28 to 32) to the original fluorescence intensity planes (Figures 16 to 20), it seems that the suppression of the Ba\(^+\) analyte population is approximately proportional to its concentration within the plasma. Further evidence of this relationship is shown in Figure 33 which is a plot of data calculated using the "Volume" option of the Surfer computer program and represents the integrated fluorescence intensities in the plasma with and without the presence of an EIE.

![Figure 33: Integrated fluorescence intensities from Ba\(^+\).](image)

Here, the suppression in the emission intensity, seen as the difference data, approximately follows the original barium solution's fluorescence intensity values. A closer look at the three planes at each height shows that the EIE introduced in the plasma also caused it to broaden slightly. This effect can be seen as a slightly greater peak separation, most obvious at the
Z = -0.5 mm position, resulting in the negative value areas in the difference plots (Figures 28 to 32).

3.2 THE CREATION OF THE EXCITED STATE ANALYTE ION

The processes that produce free analyte ions in the DCP from solutions of dissolved samples are not thoroughly understood but can be summarized in a series of steps describing the general phenomena of ion production in flames and plasmas [65]. The sample solution is first nebulized into aerosol droplets which have diameters on the order of 1 to 10 micrometers [65,66]. These are desolvated in the plasma to yield salt particles which, in turn, are vaporized by the plasma's high temperature into gas-phase molecular species. Free atoms are produced by the dissociation of these molecules. Free atoms are subsequently ionized by the loss of one or more electrons thus producing the atomic ion analytes. These ions are the result of thermal ionization and to a lesser degree Penning ionization involving argon metastable states. Thermal ionization proceeds through the collision of an atom and an electron as described in equation 6. Penning ionization, described by equation 7, occurs when an excited argon atom in state m collides with an analyte atom, transferring energy sufficient to ionize the analyte atom.

\[
X + e^- \rightleftharpoons X^+ + 2e^- \quad (6)
\]

\[
X + Ar^m \rightleftharpoons X^+ + Ar + e^- \quad (7)
\]

Further processes such as ion-electron recombinations and the formation of stable molecules such as refractory oxides may then reduce the ion populations in the plasmas. A complete understanding of the data presented in Figures 16 to 20 would require a detailed knowledge of all the processes occurring in the DCP. Such a thorough discussion is beyond the scope of this thesis; however, some of these processes are discussed below.
3.3 FACTORS DETERMINING THE Ba⁺ DISTRIBUTION PROFILE

The population distribution of the analyte ion in the plasma may be explained by considering the thermal gradients and the gas flow dynamics present in the plasma. Since the analyte is introduced into the plasma via the aerosol delivery tube, its distribution in the lower part of the plasma is determined mainly by the size of the jet's nozzle. This can be seen in Figure 16 where the analyte is present within an area whose radius is approximately 3 to 4 mm and coincides with that of the jet's nozzle orifice whose inside diameter is 7 mm. At higher positions in the plasma, the behaviour of the analyte becomes more complex as it approaches the steep thermal gradients at the centre of the plasma. These thermal gradients have been measured in spatially resolved experiments [33, 46] and may be as high as several thousand K per millimeter. These gradients act as thermal barriers whose effects in the plasma can be seen clearly in Figures 16 to 20 and Figures 23 to 27 where the analyte ions seem to have been deflected away from the centre, or core, of the plasma. This interpretation agrees with that of Nygaard and Gilbert [46] who measured a vertical profile of cobalt's effective temperature in the DCP. The maximum effective temperature for cobalt was found to be approximately 5800 K which is significantly lower than the plasma core's temperature of 11 000 to 14 000 K. They suggested that most analyte atoms are deflected away from the plasma core and thus never encounter the core's high temperature.

Elliott [66] quantified these deflections by measuring vertical and horizontal velocities of Al₂O₃ particles introduced into the plasma. The minimum in the vertical velocity of these particles was found at a height of Z = -2.8 mm where the vertical velocity was measured as nearly zero. At this same height the horizontal velocity of the particles was measured as about 1.6 m/s, a maximum in this measurement. This data agrees with the observations made at Z = -3.0 mm and at Z = -2.5 mm shown in Figures 17 and 18. In these figures it appears that the deflection resulted in a local minimum in the fluorescence intensity at the centre of each plane. These concurring results clearly show that particles were indeed deflected away from the centre of the plasma.
As the analyte reached the $Z = -2.5 \text{ mm}$ position, Figure 18, it appears as if it were deflected away from the plasma core protruding from the anodes. This may again be caused by the analyte being deflected by thermal gradients, measured by Decker [33], present towards the anodes or a result of the anodes' argon flows. Since analyte free argon flows were directed into the plasma by the anodes' and cathode's ceramic sleeves, it is likely that the analyte introduced into the plasma through the aerosol delivery tube were deflected by these flows away from the plasma core. Evidence of this deflection by the cathode argon flow is seen in Figure 20 at a vertical position of $Z = -0.5 \text{ mm}$. In this fluorescence profile the apparent decrease in fluorescence along a diagonal line approximately bisecting the $(+X, +Y)$ and $(-X, -Y)$ quadrants coincides with the directions of the argon flow from the cathode.

The deflection of analyte atoms by thermal gradients or barriers and by gas flows only partially explain the observations made in Figures 16 to 20. They do not explain the saddle shape profile apparent along the Y-axis. This saddle shape can be best explained by using the $Z = -0.5 \text{ mm}$ position as an example. A cross-section of the plasma at this position should look approximately as shown below in Figure 34.

![Figure 34: Schematic diagram of plasma cross-section at $Z = -0.5 \text{ mm}$](image-url)
This figure shows that the saddle shape, or twin peaks in the Y dimension, was probably caused by the creation of $\text{Ba}^+$ in the higher energy zones of the plasma. While the core zones contain thermal gradients too high for the analyte atoms to penetrate, the high energy on the periphery of these zones may be required to ionize barium atoms into $\text{Ba}^+$. The positions containing the maximum $\text{Ba}^+$ population can be considered to be those where thermal gradients and gas flows direct the barium atoms into contact with zones of sufficient energy to ionize these atoms.

3.4 EMISSION PROFILES

Lateral profiles of the emission of the Ba(II) and Ba(I) lines at 493.409 nm and 553.548 nm respectively were measured at four vertical positions in the DCP. These emission profiles, shown in Figures 35 to 38, represent horizontal scans along the Y-axis at vertical positions of -3.5 mm, -2.5 mm, -1.5 mm and -0.5 mm with the $X = 0$ plane in focus on the monochromator's entrance slit. The data plotted in these figures has been corrected for background emissions by using water as the reference. This emission data represents the sum of the emissions in the plasma along the viewing axis and its precision was estimated at 4 $\%$ from the scatter of the data at each position. In the emission profiles presented in Figures 35 to 38, the emission intensity units are arbitrary and not normalized to the fluorescence data. These arbitrary intensity units are different for both emission lines. Along the horizontal axis, the precision of the positions was on the order of 0.03 mm but the accuracy was only on the order of a millimeter. This relatively poor accuracy, when compared to the precision, was a result of the technique used to vary the Z-axis which required unclamping the plasma jet from its support post.

The emission from the barium atoms and from the barium ions in the DCP seems to have been confined to the central, or aerosol delivery tube, axis and was greater at higher positions in the plasma, nearer the plasma core. At each vertical position, the emission profiles have a single peak which is in the centre of the plasma along the Y dimension. The
zone of maximum emission can be deduced from the emission profiles in Figures 35 to 38 as being about 2.5 mm wide in the Y dimension and about the same height. Upon the addition of an EIE, both atom and ion emissions show an enhancement effect. This enhancement is plotted in Figure 39 which shows that the enhancement of the ion line is less than that of the atom line at each vertical position.

The magnitude of the enhancement effect, caused by the presence of an EIE in the sample, on the emission intensity of the atom and ion lines appears to be spatially dependent. At higher positions in the plasma the enhancement increases for the atom line while decreasing for the ion line. At the lowest two vertical positions in the plasma, the emission enhancement for the atom and ion lines are between 44 % and 54 %. As observations were made higher in the plasma, the emission enhancement for the atom increased while that of the ion decreased. This is seen clearly in Figure 39 which also shows a certain degree of symmetry in this effect where the enhancement increase in the atom line emission seems balanced by the enhancement decrease in the ion lines emission.
Figure 35: Emission profile in the DCP at Z = -3.5 mm.
- represents data for \( \text{Ba(NO}_3\text{)}_2 \) solution.
• represents data for \( \text{Ba(NO}_3\text{)}_2 \) and NaCl solution.
A) \( \text{Ba(I)} \) 553.548 nm line. B) \( \text{Ba(II)} \) 493.409 nm line.
Figure 36: Emission profile in the DCP at $Z = -2.5$ mm.

- represents data for Ba(N03)2 solution.
- represents data for Ba(NO3)2 and NaCl solution.

A) Ba(I) 553.548 nm line. B) Ba(II) 493.409 nm line.
Figure 37: Emission profile in the DCP at $Z = -1.5$ mm.

- represents data for $\text{Ba(NO}_3\text{)}_2$ solution.
- represents data for $\text{Ba(NO}_3\text{)}_2$ and $\text{NaCl}$ solution.

A) $\text{Ba(I)}$ 553.548 nm line. B) $\text{Ba(II)}$ 493.409 nm line.
Figure 38: Emission profile in the DCP at $Z = -0.5$ mm.

- □ represents data for Ba(NO$_3$)$_2$ solution.
- ● represents data for Ba(NO$_3$)$_2$ and NaCl solution.

A) Ba(I) 553.548 nm line. B) Ba(II) 493.409 nm line.
3.5 IONIZATION SUPPRESSION BY THE EIE

The observations made in this study indicate that the presence of an EIE in sample solutions introduced into the DCP causes two distinct effects. The first effect occurs throughout the plasma and is an ionization suppression of the analyte. The second effect is the enhancement of the emission from the analyte ions and atoms which was observed in the centre of the plasma where the maximum emission is located.

Figures 28 to 32 clearly show that the addition of the EIE caused a decrease in the fluorescence intensity from Ba\(^+\). Since the thermal emission was not experimentally resolved in the X dimension, a change in its intensity would be observed parallel to this axis in the difference plots (Figures 28 to 32). This change, however, was negligible when compared to that of the fluorescence intensity; thus, the change in the emission intensity can be attributed mainly to a change in the fluorescence emission. Further evidence of this can be seen by comparing Figures 16 to 20 with Figures 28 to 32. The similarity of the fluorescence
suppression plots to the original fluorescence profiles, without the EIE, suggests that this suppression was approximately proportional to the original fluorescence intensity.

The observed decrease in fluorescence from the Ba⁺ species, upon the addition of an EIE to the sample, may be explained by the suppression mechanism proposed and by a decrease in the amount of barium being admitted into the plasma. The later effect could be the result of a change in the nebulizer efficiency or solute vaporization interferences upon the addition of an EIE to the sample. Vaporization interferences are defined as [43] "the conversion of the analyte population(s) to compounds which exhibit some degree of stability in the excitation medium". Experiments done by Johnson et al. [43] showed that solute vaporization effects are of minimal significance for the three electrode DCP. Since the nebulizer introduces the analyte into the plasma, changes in its efficiency caused by an EIE's presence could also contribute to the analyte's suppression. To test this possibility, Johnson et al. [44] introduced the analyte and the EIE into the plasma using two separate nebulizers. Samples were first nebulized using one nebulizer to aspirate a solution containing the analyte and the EIE. Solutions containing the EIE and the analytes were then nebulized separately using two nebulizers. The results showed that each trial agreed within experimental error (3%) thus implying that nebulizer efficiencies were not being varied by the presence of the EIE. Since the amount of barium being admitted into the plasma was not decreased by the presence of an EIE in the sample, the barium ion's fluorescence intensity decrease was most likely caused by the proposed ionization suppression mechanism.

In this experiment, the proportionality between the fluorescence intensity and the analyte concentration cannot be taken for granted. While Omenetto and Winefordner [57] have shown that the fluorescence intensity in a system is proportional to the concentration of the analyte under observation, their conclusions assume that the rate of radiative and collisional energy transfer, as well as the quantum efficiencies of the analytes, remain constant. Miller et al. [40] suggested that these may be perturbed in the species within the DCP by the presence of an EIE. While the observed fluorescence intensity suppression
cannot be explained by these effects, they do explain the emission enhancement at the centre of the plasma. The reason is that according to Miller et al. [40], the presence of an EIE in the plasma increases the rate of radiative and collisional energy transfer, as well as the quantum efficiencies of the analytes resulting in emission enhancement.

An emission enhancement was, in fact, observed in the central region of the plasma. As noted earlier, the emission from both the Ba(I) and Ba(II) lines were restricted to a relatively small zone in the plasma where the concentration of the analyte, as measured by fluorescence from the ion, was quite small. It appears that most of the observed emission came from a small fraction of the total analyte population where the ion and atom came in contact with the plasma.

The emission enhancements, plotted in Figure 39, also support the proposed ionization suppression mechanism. Although both atom and ion emission intensities were enhanced, the atom line was enhanced to a greater degree than the ion line. There is also a certain degree of symmetry in Figure 39 which further suggests an ionization shift from the ion to the atom upon the addition of an EIE. This figure shows that where the atom line emission was enhanced the most, the ion line emission was enhanced the least.

The barium ion's fluorescence intensity suppression and the ion and atom emission enhancement behaviour suggest that the effect of adding an EIE to a sample introduced into the DCP is complex. While emission enhancements do occur, the main effect of the EIE in the plasma is to cause an ionization suppression in the analyte population.

4 CONCLUDING REMARKS

In this study, a fluorescence spectrometer was designed and built in order to study analyte populations in the three electrode direct current plasma. Laser induced fluorescence has been useful for determining the spatial distribution of the analyte in the DCP. This spatial distribution was found to be quite complex with most of the analyte in regions of the plasma other than the analytical emission zone. The results presented in this thesis support an
ionization suppression mechanism as the main effect caused by the presence of an easily ionizable element in samples introduced into the plasma. These observations also suggest that the emission originates from a region in the plasma where the analyte concentration is relatively small since most of the analyte is in regions where there is very little emission.

Future studies of the effect of the presence of an EIE in the three electrode DCP should include such spatial experiments as those done in this study with variations in the EIE used and its concentration. These would give a more comprehensive picture of the effect of the EIE in the plasma. Furthermore, using the temporal characteristics of the spectrometer would allow the measurement of fluorescence lifetimes in the DCP which should give considerable insight into the excitation enhancement and ionization suppression mechanisms occurring in the plasma environment.
References


60. GCA/McPHERSON INSTRUMENT Model 218 0.3 meter scanning monochromator operation manual, GCA/McPherson Instrument, Acton, Massachusetts (1968).


APPENDIX 1

DATA ACQUISITION PROGRAM IN BASIC

10' *****************************************************
20 ' PROGRAM NAME : GRIDER.ONE
30 ' BY : CHARLES W. LE BLANC 1989
40 ' *****************************************************
50 NUMHITS =12 : REM this is the number of laser hits per position
60 DIM A(50,NUMHITS): DIM TAVER(IOO)
70 SLOWER = 35 : REM SLOWER SLOWS DOWN LASERFIRE RATE 100 - 0.3 SECONDS
80 CLS
90 PRINT " "
100 PRINT " MAIN MENU "
110 PRINT " ***********
120 PRINT " "
130 PRINT " 1 ' SIMPLE.SAM ' ( collect data )
140 PRINT " 2 ' READ DATA SAVED BY SIMPLE.SAM (must be used before options 3 to7)"
150 PRINT " 3 ' CONVERT SAM DATA TO ENERGRAPHICS FILE"
160 PRINT " 4 ' AVERAGE SHOTS AT SAME DELAY WINDOW"
170 PRINT " 5 ' PRINT AND VIEW DATA"
180 PRINT " 6 ' CONVERT AVG DATA TO DADiSP DATA (ASCII)"
190 PRINT " 7 ' PLOT DATA ON SCREEN"
200 PRINT " 8 ' EXIT TO BASIC"
210 PRINT " "
220 PRINT " "
230 PRINT "
240 PRINT " 1 ' SIMPLE.SAM ' ( collect data )
250 PRINT " 2 ' READ DATA SAVED BY SIMPLE.SAM (must be used before options 3 to7)"
260 PRINT " 3 ' CONVERT SAM DATA TO ENERGRAPHICS FILE"
270 PRINT " 4 ' AVERAGE SHOTS AT SAME DELAY WINDOW"
280 PRINT " 5 ' PRINT AND VIEW DATA"
290 PRINT " 6 ' CONVERT AVG DATA TO DADiSP DATA (ASCII)"
300 PRINT " 7 ' PLOT DATA ON SCREEN"
310 PRINT " 8 ' EXIT TO BASIC"

This is the "Simple Sampler" subroutine
It's purpose is to transfer information to and from the SR245 computer interface for data collection.
ANALOG PORT 1 is the data port
ANALOG PORT 8 is used to control the SR250 rear delay
DIGITAL PORT 2 sends a signal to fire the laser
FIRELASER$="PB2" : REM this variable fires the laser
BELLS=CHR$(7) : REM this variable rings the bell
TINTERVAL = 1 : REM STEPS MUST BE SET IN NS TO GATEWIDTH OF SAMPLER
STINT =TINTERVAL/100 : REM DENOMINATOR IS DELAYFACTOR ( FOR INS )

Start data collection

600 CLS
INPUT "What filename do you want to use USE B: PREFI";FILENAME$
INPUT "Sample name ";SAMPNAME$
WHEN$=TIME$
DAYS=DATE$
REM
PRINT "Laser wavelength (default ";WAVEIN$;") ";
IF WAVEIN$="" THEN GOTO 710
WAVEIN$=WAVE1$
REM
PRINT "Fluorescence wavelength (default ";WAVEOUT$;") ";
IF WAVEOUT$="" THEN GOTO 750
WAVEOUT$=WAVE2$
DELAYFACTOR$="100 ns per volt"
INPUT "Are you ready to collect data ";EXPERIMENTS$
IF EXPERIMENTS="Y" OR EXPERIMENTS="y" GOTO 810
INPUT "Do you wish to exit sampler ";FIN$
IF FIN$="y" OR FIN$="Y" GOTO 1260
GOTO 760

' Save the leader information
OPEN "O",#2, FILENAME
PRINT #2, FILENAME$:PRINT #2, SAMPNAME$:PRINT #2, WHEN$
PRINT #2, DAYS$:PRINT #2, WAVEIN$:PRINT #2, WAVEOUT$
PRINT #2, NUMHITS$:PRINT #2, DELAYFACTOR$
PRINT #2, TINTERVAL

Obtain set of data at 12 ns delay
To change this delay change variable DELVAR$ in line 1050
For time resolved experiment use DELVAR$=DELMULT$
GOSUB 1200 : REM OPENS COM LINE 1 TO INTERFACE
PRINT #1,"14" : REM SET FIRST 4 PORTS AS INPUTS
FOR DELMULT = 1 TO 1.4 STEP STINT
PRINT "HIT ANY KEY TO CONTINUE"
PRO$=INKEY$:IF PRO$="" GOTO 980
DELMULT$=STR$(DELMULT)
FOR HIT = 1 TO NUMHITS
PRINT #1, DELVARS
PRINT #1, FIRELASERS
INPUT #1, INTENSITY$
FOR LAZY=1 TO SLOWER:ZZZ=ZZZ:NEXT LAZY: REM slow down loop
INTENSITY=VAL(INTENSITY$
PRINT USING " ##.### ";INTENSITY;
NEXT DELMULT
GOTO 1250

SERIAL COMMUNICATIONS SETUP USING RS232C PORT
SETS PORT#1 FOR 9600 BAUD, NO PARITY, 8DATA BITS, 2 STOP BITS
OPEN "COM1:9600,N,8,2,CS,DS,CD" AS #1
PRINT#1,""
PRINT#1, "MR;W25"
RETURN
CLOSE#1 : REM CLOSES LINE TO INTERFACE
CLOSE #2 : REM CLOSES LINE TO DISK FILE

RETURN

This is the file reader subroutine

CLS

PRINT:PRINT:PRINT:PRINT

PRINT "This subroutine reads files created by SAM"

INPUT "Is data disk in drive A or B "; WHEREDISK$

PRINT:PRINT

IF WHEREDISK$="A" OR WHEREDISK$="a" GOTO 1410

IF WHEREDISK$="B" OR WHEREDISK$="b" GOTO 1430

PRINT "Enter A or B please ": GOTO 1350

FILES:"A:"

GOTO 1440

FILES:"B:"

PRINT:PRINT

PRINT "This subroutine reads files created by the SIMPLE SAM subroutine.

PRINT "This opens, reads, then closes data files created

by the SIMPLE SAM subroutine.

OPEN "I", #3, REDERS

INPUT #3, FILENAMES

INPUT #3, SAMPNAME$

INPUT #3, WHEN$

INPUT #3, DAY$

INPUT #3, WAVEIN$

INPUT #3, WAVEOUTS

INPUT #3, NUMHITS

INPUT #3, DELAYFACTORS

INPUT #3, TINTERVAL

FOR TIME = 0 TO 39

FOR HIT = 1 TO NUMHITS

INPUT #3, A(TIME, HIT)

NEXT HIT

NEXT TIME

CLOSE #3

CLS

This subroutine converts data created with the SIMPLE SAM subroutine into files usable by ENERGRAPHICS (Enertronics Research, Inc. St. Louis, Missouri)

INPUT "What is the destination drive for the ENG file "; WHEREDISK$

INPUT "What filename do you want to use 'prefix only' "; EFILE$

IF WHEREDISK$="A" OR WHEREDISK$="a" THEN ENERFIL$="A:"+EFILE$+.ENG

IF WHEREDISK$="B" OR WHEREDISK$="b" THEN ENERFIL$="B:"+EFILE$+.ENG

IF WHEREDISK$ = "A" OR WHEREDISK$ = "a" THEN GOTO 1850

IF WHEREDISK$ = "B" OR WHEREDISK$ = "b" THEN GOTO 1850

PRINT "ENTER A OR B PLEASE !": GOTO 1770

PRINT"CONVERTING FILE BE PATIENT ...

OPEN "O", #4, ENERFIL$

PRINT #4, "FLUORESCENCE TIME PROFILE"

PRINT #4, "LINE"

PRINT #4, "RELATIVE INTENSITY"

PRINT #4, "TIME IN NANOSECONDS"

WRITE #4, 2, NUMHITS

PRINT #4, "A"
1930 WRITE #4, 0,1
1940 WRITE #4, 0,40,TINTERVAL
1950 LINCOUNT=0
1960 FOR LINUM = 1 TO NUMHITS
1970 IF LINCOUNT > 7 THEN LINCOUNT = 0
1980 LINSHAPE = 16*LINCOUNT + 1
1990 WRITE #4, 40,LINSHAPE,0,5,48
2000 IF LINUM = 1 THEN PRINT #4, FILENAME$: REM this is the subtitle
2010 IF LINUM <> 1 THEN PRINT #4, 
2020 WRITE #4, -20,5,1
2030 FOR TIME = 0 TO 49:WRITE #4,TIME,A(TIME,LINUM):NEXT TIME
2040 LINCOUNT = LINCOUNT + 1
2050 NEXT LINUM
2060 FOR BLANK -= 1 TO 40: PRINT #4, 
2070 FOR ZEROS = 1 TO 10: WRITE #4,0:NEXT ZEROS
2080 CLOSE #4
2090 RETURN

2100 ' This subroutine averages the data at each delay and saves it.
2120 '
2140 PRINT "Data is being averaged."
2150 FOR TIME = 0 TO 39
2160 TAV = 0
2170 FOR HIT = 1 TO NUMHITS
2180 TAV = TAV + A(TIME,HIT)
2190 NEXT HIT
2200 TAVER(TIME) = TAV/NUMHITS
2210 NEXT TIME
2220 PRINT "This averaged data will now be saved as a SAM file."
2240 INPUT "What is the destination drive you want to use 'prefix only' ";:WEREDISK$:
2250 IF WEREDISK$="A" OR WEREDISK$="a" THEN AVNAME$="A:"+AFILE$+.AVG
2260 IF WEREDISK$="B" OR WEREDISK$="b" THEN AVNAME$="B:"+AFILE$+.AVG
2270 IF WEREDISK$ = "A" OR WEREDISK$ = "a" THEN GOTO 2300
2280 IF WEREDISK$= "B" OR WEREDISK$ = "b" THEN GOTO 2300
2290 PRINT "ENTER A OR B PLEASE AS FILE DESTINATION ":GOTO 2230
2300 PRINT:PRINT:PRINT
2310 PRINT "SAVING ";AVNAME$
2320 OPEN "O", #5, AVNAME$
2330 PRINT #5, AVNAME$
2350 PRINT #5, SAMPNAME$
2350 PRINT #5, WEH$
2350 PRINT #5, DAYS$
2370 PRINT #5, WAVEIN$
2380 PRINT #5, WAVEOUT$
2390 PRINT #5, 1
2400 PRINT #5, DELAYFACTOR$
2410 PRINT #5, TINTERVAL
2420 FOR TIME= 0 TO 39
2430 PRINT #5, TAVER(TIME)
2440 NEXT TIME
2450 CLOSE #5
2460 RETURN

2480 ' Subroutine to view and print data
2490 
2500 CLS
2510 INPUT "Is data now in memory ";DATMEM$
2520 IF DATMEM$ = "Y" OR DATMEM$ = "y" THEN GOTO 2560
2530 PRINT " You must first load data with option 2 
"2540 FOR XXXX=1 TO 500: ZZZZ=XXXX: NEXT XXXX
2550 RETURN
2560 INPUT "Do you want to send data to (S)creen or to (P)rinter ";STSP$
2570 IF STSP$ = "S" THEN GOTO 2600
2580 IF STSP$ = "P" THEN GOTO 2750
2590 GOTO 2560
2600 PRINT "Filename is : ";FILENAMES$  
2610 PRINT "Sample name : ";SAMPNAMES$  
2620 PRINT "Sampling time : ";WHENS$; " Sampling date : ";DAYS$  
2630 PRINT "Excitation wavelength : ";WAVEIN$  
2640 PRINT "Fluroescence wavelength : ";WAVEOUT$  
2650 PRINT:PRINT  
2660 PRINT " ******************  DATA  *********************"  
2670 PRINT:PRINT  
2680 FOR TIME = 0 TO 39  
2690 FOR HIT = 1 TO NUMHITS  
2700 PRINT USING " ##.### ";A(TIME,HIT);  
2710 NEXT HIT  
2720 PRINT " ";  
2730 NEXT TIME  
2740 GOTO 2900  
2750 LPRINT "Filename is : ";FILENAMES$  
2760 LPRINT "Sample name : ";SAMPNAMES$  
2770 LPRINT "Sampling time : ";WHENS$; " Sampling date : ";DAYS$  
2780 LPRINT "Excitation wavelength : ";WAVEIN$  
2790 LPRINT "Fluroescence wavelength : ";WAVEOUT$  
2800 LPRINT:LPRI:
2810 LPRINT " ******************  DATA  *********************"  
2820 LPRINT:LPRI:
2830 FOR TIME = 0 TO 39  
2840 FOR HIT = 1 TO NUMHITS  
2850 LPRINT USING " ##.### ";A(TIME,HIT)/  
2860 NEXT HIT  
2870 LPRINT " ";  
2880 NEXT TIME  
2890 GOTO 2900  
2900 RETURN  
2910 ' This subroutine converts averaged into files readable  
2920 ' by DADiSP (DSP Development Corporation, Cambridge, Massachusetts)  
2930 '  
2940 '  
2950 CLS  
2960 PRINT " The averaged data will now be saved as a DAV file."  
2970 INPUT "What is the destination drive for the DAV file ";WHEREDISKS$  
2980 IF WHEREDISKS$="A" OR WHEREDISKS$="a" THEN DAVNAMES$="A:"+FILE$+".DAV"  
2990 IF WHEREDISKS$="B" OR WHEREDISKS$="b" THEN DAVNAMES$="B:"+FILE$+".DAV"  
3000 IF WHEREDISKS$="A" OR WHEREDISKS$="a" THEN GOTO 3040  
3010 IF WHEREDISKS$="B" OR WHEREDISKS$="b" THEN GOTO 3040  
3020 PRINT "ENTER A OR B PLEASE AS FILE DESTINATION ":GOTO 2970  
3030 PRINT:PRINT:PRINT  
3040 PRINT:PRINT  
3050 PRINT "SAVING ";DAVNAMES$  
3060 OPEN "O", #6, DAVNAMES$  
3070 FOR TIME= 0 TO 39  
3080 PRINT #6, TAVER(TIME)  
3090 NEXT TIME  
3100 RETURN  
3110 ' Scalling of data for plotting  
3120 '  
3130 ' END OF PROGRAM  
3140 '  
3150 '  
3160 '
3250 NEXT TIME
3260 LARGEST = TAVER(0): SMALLEST = TAVER(0)
3270 FOR TIME = 0 TO 39
3280 IF TAVER(TIME) > LARGEST THEN LARGEST = TAVER(TIME)
3290 IF TAVER(TIME) < SMALLEST THEN SMALLEST = TAVER(TIME)
3300 RANGE = LARGEST - SMALLEST
3310 NEXT TIME
3320 LOCATE 1, 1: PRINT USING "##.##"; LARGEST
3330 LOCATE 20, 1: PRINT USING "##.##"; SMALLEST
3340 FOR TIME = 0 TO 39
3350 SCRX = (TIME * 12) + 50
3360 SCRY = 155 - (((TAVER(TIME) - SMALLEST) * 150) / RANGE)
3370 LINE -(SCRX, SCRY)
3380 NEXT TIME
3390 LZERO = 5 + (LARGEST * 150 / RANGE)
3400 LINE (45, LZERO) - (50, LZERO)
3410 LOCATE 24, 1; PRINT " HIT RETURN TO CONTINUE ";
3420 INPUT HRTC$ : IF HRTC$ <> "" THEN GOTO 3410
3430 SCREEN 0, 0, 0
3440 RETURN
3450 RETURN
3460 ' Quit subroutine
3470 ' CLS
3490 PRINT: PRINT
3500 PRINT: PRINT " ARE YOU SURE YOU WANT TO EXIT PROGRAM " ; LEAVES
3510 INPUT " Y" OR LEAVES = " y" THEN GOTO 3540
3520 IF LEAVES = " y" OR LEAVES = " Y" THEN GOTO 3540
3530 RETURN
3540 END
DATA FORMATTING PROGRAM

10 '**********************************************************************************************
20 'PROGRAM NAME : THREEDER.ONE
30 'BY CHARLES W. LE BLANC
40 'This program converts data collected by GRIDER.ONE
50 'into data usable by Energraphics in the three dimensional mode.
60 'It averages the values at each position after removing the end values.
70 'Baseline subtraction is also done on the data.
80 '**********************************************************************************************
100 '110 '120 DIM A(40,12): DIM TAV(40): DIM PTAVER(40): DIM BAT$(41): DIM DFILNUM(10)
130 CLS
140 REM
150 PRINT "PLACE THE SAM DATA DISK IN DRIVE A:"
160 PRINT "PLACE THE ENG DATA DISK IN DRIVE B:"
170 PRINT: PRINT "HIT RETURN TO CONTINUE";
180 INPUT HRTC$: IF HRTC$ <> "" THEN GOTO 170
190 PRINT: PRINT: PRINT "THIS IS A DIRECTORY OF YOUR DATA DISK.";
200 PRINT: PRINT
210 FILES "A:";
220 PRINT: INPUT " How many files do you wish to convert ( <41 ) " ; NUMFIL
230 SUBFIL = NUMFIL - 1
240 PRINT: PRINT
250 INPUT "ON HOW MANY DISKS IS YOUR DATA" ; NUMDISK
260 NU = 0
270 FOR I = 1 TO NUMDISK
280 PRINT "NUMBER OF FILES ON DISK # " ; I;
290 INPUT DFILNUM(I)
300 NU = NU + DFILNUM(I)
310 NEXT I
320 IF NU = NUMFIL GOTO 340
330 PRINT "YOUR TOTAL SHOULD BE " ; NUMFIL: GOTO 220
340 PRINT: PRINT
350 COUNT = 0
360 FOR X = 1 TO NUMDISK
370 DFILNUM(X) = DFILNUM(X) + COUNT
380 COUNT = DFILNUM(X)
390 NEXT X
400 FOR GATHER = 1 TO NUMFIL
410 INPUT "FILENAME : " ; BAT$(GATHER)
420 NEXT GATHER
430 PRINT: PRINT
440 PRINT "THESE ARE YOUR FILENAMES "
450 PRINT: PRINT
460 FOR GATHER = 1 TO NUMFIL
470 PRINT " # " ; GATHER; " : " ; BAT$(GATHER)
480 NEXT GATHER
490 PRINT: INPUT "DO YOU WISH TO CHANGE ONE " ; WTCA$
500 IF WTCA$ = "N" OR WTCA$ = "NO" THEN GOTO 560
510 INPUT " WHAT IS THE FILE # " ; NTC
520 PRINT " CHANGE " ; BAT$(NTC) ; " TO : "
530 INPUT BAT$(NTC)
540 PRINT: PRINT
550 GOTO 440
560 INPUT "WHAT WILL BE THE SURFACE FILE NAME " ; ENGNAME$
570 PRINT: PRINT: NUFI = 1
580 FOR GATHER = 1 TO NUMFIL
590 IF GATHER <= DFILNUM(NUFI) THEN GOTO 640
600 NUFI = NUFI + 1
610 PRINT "CHANGE TO DATA DISK ";NUFI
620 INPUT "HIT RETURN WHEN READY ";SBWR$
630 IF SBWR$ <> "" THEN GOTO 620
640 REM CONTINUE PROGRAM
650 SFILE$=BAT$(GATHER)
660 GOSUB 750 :REM READ DATA FROM SAM
670 GOSUB 1030 :REM AVERAGE DATA AND DROP HIGH AND LOW VALUE
680 GOSUB 1470 :REM BASELINE CREATION
690 GOSUB 1190 :REM SAVE DATA AS SURFACE FILE READABLE BY ENERGRAPHICS
700 NEXT GATHER
710 OPEN "A",#6,EGNAM$
720 FOR I%=1 TO 10 : WRITE #6,0: NEXT
730 CLOSE #6
740 END
750 •
760 •
770 ' This opens, reads, then closes data files created
780 ' by the Grider.one data acquisition programs.
790 ' 790 PRINT:PRINT:PRINT "READING A:";SFILE$
800 PRINT
810 REDER$="A:" + SFILE$
820 OPEN "I",#3, REDER$
830 INPUT #3, FILENAMES
840 INPUT #3, SAMPNAMES
850 INPUT #3, WHEN$
860 INPUT #3, DAYS
870 INPUT #3, WAVEINS
880 INPUT #3, WAVEOUT$
890 INPUT #3, NUMHITS
900 INPUT #3, DELAYFACTORS
910 INPUT #3, TINTERVAL
920 FOR TIME =0 TO 39
930 FOR HIT=1 TO NUMHITS
940 INPUT #3,A(TIME,HIT)
950 NEXT HIT
960 NEXT TIME
970 CLOSE #3
980 RETURN
990 '
1000 ' This subroutine averages the data at each position
1010 ' and removes the end values
1020 '
1030 PRINT " AVERAGING DATA 
1040 PRINT:PRINT
1050 FOR TIME = 0 TO 39
1060 TAV = 0
1070 LARGEST = A(TIME,1) : SMALLEST = A(TIME,1)
1080 FOR HIT = 1 TO NUMHITS
1090 TAV = TAV + A(TIME,HIT)
1100 IF A(TIME,HIT) > LARGEST THEN LARGEST = A(TIME,HIT)
1110 IF A(TIME,HIT) < SMALLEST THEN SMALLEST = A(TIME,HIT)
1120 NEXT HIT
1130 TAVER(TIME)=(TAV-(LARGEST+SMALLEST))/(NUMHITS-2)
1140 NEXT TIME
1150 RETURN
1160 '
1170 ' Subroutine to save data as a SUR file readable by Energraphics
1180 '
1190 PRINT:PRINT:PRINT " DATA IS NOW BEING STORED ON DRIVE B AS SUR FILE"
1200 PRINT:PRINT
1210 EGNAM$="B:"+ENGNAME$+.SUR"
1220 IF GATHER <> 1 THEN GOTO 1390
1230 OPEN "O",#6,EGNAM$
1250 WRITE #6, "ENGNAME$
1260 PRINT #6, "DAYS$
1270 WRITE #6, "Z-AXIS$
1280 WRITE #6, "Y-AXIS$
1290 WRITE #6, "INTENSITY$
1300 PRINT #6, NUMFIL, 40, 0, SUBFIL, 0, 39
1310 PRINT #6, .16, .16, 1.4, 109, 80
1320 PRINT #6, .30, 30, 3, 0
1330 FOR TIME = 0 TO 39
1340 PTAVER(TIME) = TAVER(TIME) - BASELINE
1350 PRINT #6, PTAVER(TIME)
1360 NEXT TIME
1370 CLOSE #6
1380 RETURN
1390 REM: GATHER<>1
1400 OPEN "A", #6, "ENGNAME$
1410 FOR TIME = 0 TO 39
1420 PTAVER(TIME) = TAVER(TIME) - BASELINE
1430 PRINT #6, PTAVER(TIME)
1440 NEXT TIME
1450 CLOSE #6
1460 RETURN
1470 REM BASELINE CALCULATION
1480 SUM = 0
1490 FOR I = 0 TO 4
1500 SUM = SUM + TAVER(I) + TAVER(I + 35)
1510 NEXT I
1520 BASELINE = SUM/10
1530 RETURN
DATA FORMATTING PROGRAM

10 CLS
20 '*************************************************************
30 ' PROGRAM NAME : SURFMKR.ONE
40 ' BY : CHARLES W. LE BLANC
50 ' THIS PROGRAM CONVERTS ENERGRAPHICS SUR FILES INTO
60 ' FILES USABLE BY SURFER (GOLDEN SOFTWARE, INC.,
70 ' GOLDEN, COLORADO)
80 '*************************************************************
90 '***************
100 DIM POINTS(41,40)
110 PRINT "PLACE THE ENERGRAPHICS DATA DISK IN DRIVE A:"
120 PRINT "PLACE THE SURFER DATA DISK IN DRIVE B:"
130 PRINT "HIT RETURN TO CONTINUE";
140 INPUT HRCS$ : IF HRCS$ <> "" THEN GOTO 60
150 PRINT:PRINT:PRINT "THIS IS A DIRECTORY OF YOUR DATA DISK."
160 PRINT:PRINT:PRINT "WHICH FILE DO YOU WANT TO CONVERT TO SURFER";
170 PRINT:PRINT
180 PRINT:PRINT:PRINT " WHICH FILE DO YOU WANT TO CONVERT TO SURFER ";
190 SURNAMES=ENGFLS + ".SUR"
200 OPEN "I",#1,SURNAMES$
210 INPUT #1,ENGNAMES$
220 INPUT #1,DAYS$
230 INPUT #1,XAXIS$
240 INPUT #1,YAXIS$
250 INPUT #1,ZAXIS$
260 FOR GATHER=1 TO NUMFIL
270 INPUT #1,NUMFIL,NX%,NY%,A,B,C
280 INPUT #1,D,E,F,G,H
290 FOR GATHER=1 TO NUMFIL
300 PRINT GATHER
310 PRINT GATHER
320 FOR TIME=0 TO 39
330 PRINT #2,GATHER,TIME,POINTS(GATHER,TIME)
340 NEXT TIME
350 NEXT GATHER
360 CLOSE #1
370 PRINT:PRINT:PRINT " WHAT WILL THE SURFER FILE BE NAMED";
380 SUNAM$=CHRS$(1+ATAN((NUMFIL/2)/(39/2)))*2-1,sunams$
390 OPEN "O",#2,SURFNAM$
400 FOR GATHER=1 TO NUMFIL
410 PRINT GATHER
420 PRINT GATHER
430 FOR TIME=0 TO 39
440 PRINT #2,GATHER,TIME,POINTS(GATHER,TIME)
450 NEXT TIME
460 NEXT GATHER
470 CLOSE #2
APPENDIX 4

STANDARD DEVIATION CALCULATION PROGRAM FOR SPATIAL PROFILES

10 '***************************************************************
20 'PROGRAM NAME : DEVIATOR.ONE
30 'BY CHARLES W. LE BLANC
40 'This program calculates the standard deviation of the data saved by
50 'GRIDER.ONE and places it into files usable by Energraphics in it's
60 'three dimensional mode.
70 '***************************************************************
90 '110 DIM A(40, 12): DIM TAVER(40): DIM BATS(41): DIM DFILNUM(10)
120 DIM SSTD(40): DIM STD(40)
130 CLS
140 REM
150 PRINT "PLACE THE SAM DATA DISK IN DRIVE A:";
160 PRINT "PLACE THE ENG DATA DISK IN DRIVE B:";
170 PRINT: PRINT "HIT RETURN TO CONTINUE";
180 INPUT HRCTS: IF HRCTS <> "" THEN GOTO 170
190 PRINT: PRINT: PRINT "THIS IS A DIRECTORY OF YOUR DATA DISK.";
200 PRINT: PRINT
210 FILES "A:";
220 SS(TIME) = SS(TIME) + (A(TIME,HIT)*A(TIME,HIT))
230 PRINT: INPUT " How many files are in the plane (<42) "; NUMFIL
240 SUBFIL=NUMFIL-1
250 PRINT: PRINT
260 INPUT "ON HOW MANY DISKS IS YOUR DATA "; NUMDISK
270 NU=0
280 FOR I=1 TO NUMDISK
290 PRINT "NUMBER OF FILES ON DISK "; I;
300 INPUT DFILNUM(I)
310 NU=NU+DFILNUM(I)
320 NEXT I
330 IF NU = NUMFIL GOTO 350
340 PRINT "YOUR TOTAL SHOULD BE "; NUMFIL: GOTO 230
350 PRINT: PRINT
360 PRINT "THESE ARE YOUR FILENAMES "; NUMDISK
370 NU=0
380 FOR I=1 TO NUMDISK
390 PRINT " NUMBER OF FILES ON DISK "; I;
400 INPUT DFILNUM(I)
410 NEXT I
420 IF NU = NUMFIL GOTO 350
430 PRINT "YOUR TOTAL SHOULD BE "; NUMFIL: GOTO 230
440 PRINT: PRINT
450 PRINT " THESE ARE YOUR FILENAMES "
460 PRINT: PRINT
470 FOR GATHER = 1 TO NUMFIL
480 PRINT "# "; GATHER; ": "; BATS(GATHER)
490 PRINT: PRINT
500 INPUT "DO YOU WISH TO CHANGE ONE "; WTCA$
510 IF WTCA$="N" OR WTCA$="NO" THEN GOTO 570
520 INPUT " WHAT IS THE FILE "; NT
530 PRINT " CHANGE "; BATS(NT); " TO : ";
540 INPUT BATS(NT)
550 PRINT: PRINT
560 IF GATHER <= DFILNUM(NUFI) THEN GOTO 650
610 NUFI = NUFI + 1
620 PRINT "CHANGE TO DATA DISK "; NUFI
630 INPUT "HIT RETURN WHEN READY "; SBWR$
640 IF SBWR$ <> "" THEN GOTO 630
650 REM CONTINUE PROGRAM
660 SFILES = BATS$(GATHER)
670 GOSUB 750 : REM READ DATA FROM SAM
680 GOSUB 1000 : REM CALCULATE THE STANDARD DEVIATION AT EACH POSITION
690 GOSUB 1320 : REM SAVE DATA AS SURFACE FILE READABLE BY ENERGRAPHICS
700 NEXT GATHER
710 OPEN "A", #6, EGNAM$
720 FOR I%=1 TO 10 : WRITE #6, 0: NEXT
730 CLOSE #6
740 END
750 ' This opens, reads, then closes data files created by the Gridr.one data acquisition programs.
760 PRINT: PRINT: PRINT "READING A: "; SFILES$ 
780 OPEN "I", #3, REDER$
790 INPUT #3, FILENAMES$ 
800 INPUT #3, SAMPNAMES$ 
810 INPUT #3, WHEN$ 
820 INPUT #3, DAYS 
830 INPUT #3, WAVEINS$ 
840 INPUT #3, WAVEOUTS$ 
850 INPUT #3, NUMHITS 
860 INPUT #3, DELAYFACTORS$ 
870 INPUT #3, TINTERVAL$ 
880 FOR TIME = 0 TO 39 
890 FOR HIT = 1 TO NUMHITS 
900 INPUT #3, A(TIME,HIT) 
910 NEXT HIT 
920 NEXT TIME 
930 CLOSE #3 
940 RETURN 
950 ' This subroutine calculates the standard deviation at each position without the end points.
960 PRINT "CALCULATING STANDARD DEVIATIONS" 
970 PRINT: PRINT
980 FOR TIME = 0 TO 39 
990 TAV = 0 
1000 LARGE = A(TIME,1) : SMALLEST = A(TIME,1) 
1010 FOR HIT = 1 TO NUMHITS 
1020 TAV = TAV + A(TIME,HIT) 
1030 IF A(TIME,HIT) > LARGE THEN LARGE = A(TIME,HIT) 
1040 IF A(TIME,HIT) < SMALLEST THEN SMALLEST = A(TIME,HIT) 
1050 NEXT HIT 
1060 TAVER(TIME) = (TAV-(LARGEST+SMALLEST))/(NUMHITS-2) 
1070 SS = 0: SSTD(TIME) = 0: STD(TIME) = 0 : DSS = 0 
1080 FOR HIT = 1 TO NUMHITS 
1090 IF LARGE = A(TIME,HIT) OR SMALLEST = A(TIME,HIT) THEN GOTO 1210 
1100 IF A(TIME,HIT) > LARGE THEN LARGE = A(TIME,HIT) 
1110 IF A(TIME,HIT) < SMALLEST THEN SMALLEST = A(TIME,HIT) 
1120 NEXT HIT 
1130 TAVER(TIME) = (TAV-(LARGEST+SMALLEST))/(NUMHITS-2) 
1140 SS = 0: SSTD(TIME) = 0: STD(TIME) = 0 : DSS = 0 
1150 FOR HIT = 1 TO NUMHITS 
1160 IF LARGE = A(TIME,HIT) OR SMALLEST = A(TIME,HIT) THEN GOTO 1210 
1170 SS = SS + (A(TIME,HIT)-A(TIME,HIT))**2 
1180 NTS = 10*(TAVER(TIME)**2) 
1190 NEXT HIT 
1200 DSS = SS - NTS 
1210 SSTD(TIME) = DSS/(NUMHITS-3) 
1220 SQ = ABS(SSTD(TIME)) 
1230 STD(TIME) = SQR(SQ) 
1240 NEXT TIME 
1250 RETURN
This subroutine saves the standard deviations to disk.

```
1300 ' This subroutine saves the standard deviations to disk.
1310 '  PRINT:PRINT:PRINT "STANDARD DEVIATIONS ARE BEING SAVED ON AS SUR FILE"
1330 PRINT:PRINT
1340 EGNAM$ = "B:" + ENGNAME$ + ".SUR"
1350 IF GATHER <> 1 THEN GOTO 1500
1360 OPEN "O", #6, EGNAMS
1370 REM
1380 WRITE #6, ENGNAME$
1390 PRINT #6, DAYS$
1400 WRITE #6, "Z-AXIS"
1410 WRITE #6, "Y-AXIS"
1420 WRITE #6, "INTENSITY"
1430 PRINT #6, NUMFIL, 40, 0, SUBFIL, 0, 39
1440 PRINT #6, .16, .16, 1.4, 109, 80
1450 PRINT #6, 30, 30, 3, 0
1460 FOR TIME = 0 TO 39
1470 PRINT #6, STD(TIME)
1499 RETURN
1500 OPEN "A", #6, EGNAMS
1510 GOTO 1460
1520 RETURN
```