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# The use of direct current argon plasma spectroscopy for quantitative analysis of geological samples

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THE USE OF DIRECT CURRENT ARGON PLASMA SPECTROSCOPY  
FOR QUANTITATIVE ANALYSIS OF GEOLOGICAL SAMPLES

by

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\* \* \* \* \*

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ABSTRACT

LIPSKY, STEPHEN The use of direct current argon plasma spectroscopy for quantitative analysis of geological samples. Department of Chemistry, June 1987.

The focus of this project was the development of a process of analyzing geological samples which contain moderate amounts of silica. The main emphasis was put upon the reduction of the amount of "wet" chemistry and laboratory time involved in such analysis.

Previous elemental analysis of such samples relied upon time consuming techniques such as combustion and precipitation reactions. Moreover, these analyses required the use of highly corrosive hydrofluoric acid (HF).

This project utilized a DC Argon Plasma Spectrometer (DCP) for all elemental analyses. Furthermore, the only chemical required for the project was concentrated nitric acid. This project proposed that treatment of the samples with hot concentrated nitric acid would serve to digest the samples sufficiently to extract all the ions for analysis by the DCP.

In summary, analyzed samples from the Thorne Smith Company were digested in hot concentrated nitric acid. The silica residue was filtered out and the samples made up to volume. They were then introduced to the DCP for analysis for Calcium, Magnesium, Iron and Aluminum. These values were converted to the oxide concentrations and compared to the literature data.

After two procedures failed to correlate with the classical results a third technique was developed which proved to be fairly accurate and very precise. This final technique involved three nitric acid treatments. It is felt that upon follow up work on this project the results of this method will correlate well with the literature data.

## ACKNOWLEDGEMENTS

I would like to take this opportunity to express my extreme thanks to Professor Robert W. Schaefer. For without his guidance and understanding, over the past year, this project could not have been possible. Furthermore, Professor Schaefer's guidance for the past four years has helped me to receive more from my undergraduate education and I will take his insights with me into my future endeavors.

I would also like to thank my parents, Charles and Carol Lipsky, for always being there when I needed them. Moreover, this project could not be possible without the funding they provided over the past four years.

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FOR  
HONORS THESIS BY  
STEPHEN NEIL LIPSKY

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## INTRODUCTION:

The world we live in is becoming more automated as we search for easier more direct methods of attaining our desired goals. This same principle is the underlying thrust of this research project. Likewise, the major aim of this project was to develop a method for analyzing mineral samples that contain high amounts of silica while reducing the amount of "wet" chemistry involved.

The major force behind these endeavors was the use of a DC Argon Plasma Spectrometer or DCP. The DCP is an emission based spectrometer. Under normal conditions, the atoms of a sample are all in the ground state. However, when a sample is heated, a finite population of excited atoms is created: argon plasma is an excellent source of the heat required. These excited atoms will eventually return to the ground state. When this return occurs a photon of radiation is emitted.<sup>1</sup> This is shown in Figure 1. Moreover, each element has its own characteristic emission lines. Furthermore, if one monitors the amount of radiation which is emitted at a characteristic wavelength of an element it is possible to perform quantitative determinations of the element since the amount of light emitted is proportional to the concentration of the element present.

The abilities of the DCP are focused around the argon based plasma flame source. Conventional gas/air flames have a maximum temperature of about 1900 degrees C and more advan-

ced flame sources are able to achieve a maximum of 3000 degrees C. The plasma, on the other hand, can reach up to 10,000 degrees K in the center of the arc and usually between 6000 and 7000 degrees K in the excitation region (see figure 3). The main advantage to such temperature capabilities can be explained by the Boltzman distribution equation. This equation provides a ratio between the population of the excited state ( $N_i$ ) and the ground state population of the element ( $N_j$ ). The Boltzman distribution equation is:

$$N_i/N_j = e^{-(E_i-E_j)/kT}$$

where  $E_i$  and  $E_j$  are the energies of the respective states and  $k$  is the Boltzman Constant. Most important, however, is the  $T$  which represents temperature. If one follows the mathematics, as  $T$  increases the ratio of excited species to ground state increases. Thus, the DCP is able to reach much lower detection limits than the cooler more simplistic flames since a significantly larger number of the atoms are excited. Detection limits for the DCP are as low as 1 ppb.

At this point a discussion of how the plasma is generated and maintained is appropriate. Figure 2 shows the configuration of the three electrodes before firing. The two electrodes labeled "back" and "front" are the anodes which are made of pyrolytic graphite and the third electrode is the cathode, made of 2% Th-tungsten.<sup>2</sup> Prior to ignition the three electrodes are in very close proximity with the cathode lightly touching the back anode. Additionally, a stream of



argon is being passed over the three electrodes from the base of the electrode blocks. When the power to the electrode configuration is turned on, a direct current of 15 amperes is passed across the electrodes. Next, the "run/ready" switch is changed to the run position and the electrodes move rapidly apart. This movement causes the argon in the small space between the electrodes to become ionized. Once this is accomplished the argon ions created will cause other argon atoms to ionize, perpetuating the plasma. Thus, once the plasma is created all one has to do is continue to supply the 15 amp current and argon and the plasma will be indefinitely sustained. This condition is shown in figure 3. As one can see from some of the measurements on fig 3, the location of the electrodes in relation to each other is quite important.

All samples introduced to the DCP are in solution form. The liquid samples are converted to fine aerosols and introduced as such into the excitation region of the inverted "y" as seen in figure 3. This conversion is accomplished by pumping the sample with a peristaltic pump to a ceramic nebulizer. At that point the solution is introduced to a forth argon stream which serves to nebulize the sample. The "mist" of the sample is carried through the spray chamber and introduced directly into the plasma. Figure 4 provides a pictorial view of this process.

Another forte of the DCP used in this project was the monochromator employed for processing of the electromagnetic

radiation emitted from the excited samples. The most valuable capacity of the optic components is the ability to process signals from 1900 A to 8000 A, thus, giving the instrument the ability to analyze a myriad of elements. The heart of the optic unit is the spectrometer. The DCP contains a Czerny-Turner type spectrometer with an echelle grating. This set-up is shown in figure 5. The echelle grating provides high dispersion and high resolution which are vital to the use of plasma spectroscopy since some emission lines differ by only 0.09 A as shown in figure 6. Some characteristics which make the echelle grating so good are that the blaze angle is much greater than conventional grating and the short side of the blaze is used as opposed to the long side. Also, the number of grooves is reduced to better facilitate processing of UV/visible signals.<sup>3</sup> Table I in the appendix shows some comparisons between the echelle grating and the conventional grating. Note that some data such as resolution and linear dispersion are superior by a factor of ten.

The need for quality linear dispersion and resolution for plasma spectroscopy has already been stated and is taken care of by the echelle grating. This same asset, however, brings along a problem in that the strait line dispersion from 1900 A to 8000 A would require a spectrum more than fifteen feet long.<sup>4</sup> Moreover, since the linear dispersion increases with order, one must employ many different orders

to cover a spectral range. The designers of the monochromator of the instrument took these facts into consideration in their design. As seen in figure 5 a 30 degree prism was placed in front of the grating. As a result, the normally long spectrum is presented in one four inch by five inch raster presentation as shown in figure 7.<sup>5</sup> Thus, the spectrum is no longer a linear spectrum but a two dimensional spectrum with increasing order in the y-direction and increasing wavelength in the x-direction. The SpectraSpan IV utilized in this project is the first instrument of its kind to successfully apply the echelle grating.<sup>6</sup>

The next step is to "peak" the instrument. This is basically adjusting the monochromator and the input slits in order to send the maximum signal to the detector. The detector is a photomultiplier tube or PMT. The focused photons of light strike the PMT and are proportional to the concentration of the element being analyzed. The amplified signal from the PMT is converted to a digital number and reported as "counts". This process of peaking will be discussed later in this report.

A third built-in strength of the DCP used in this project was the on-board computer section. This unit made the analysis of data simple and helped to make the data accurate and precise. The ability to analyze samples using integrated sampling where the sampling time and repetitions could be varied helped to increase precision. Moreover, the instru-

ment automatically sets the electronic gain necessary to amplify the signal of a high standard to 50% of full scale. (Standards will be covered in the PROCEDURE section of this report) This allows the experimenter the freedom of a wide range of sample responses varying from much lower to much higher than the high standard. Furthermore, values for a high and low standard can be entered into the microprocessor along with their respective "digital counts" and the computer prepares the standard curve used to determine a value for the sample being analyzed. The computer also helps the experimenter to tune the instrument by providing "Status" messages when something is not set properly (see appendix A for "Status" Messages). Other controls exist for the DCP; however, coverage of all of these is not necessary at this point.

There are other innate qualities of a plasma source for quantitative work. As mentioned previously, the achievement of elevated temperatures is a strong asset. A DC plasma source when tuned correctly is a very stable source for six to eight hours; at this time the graphite anodes begin to erode and stability is lost, a minor defect. Furthermore, the configuration of the DCP components is such that the signal is relatively noise free since the emitted radiation is monitored at a right angle to the plane of the plasma. This is better understood if figure 3 is viewed as the plane of the plasma and one's eye is imagined to be the input slit.

As a result, with proper positioning of the excitation region along with the stability of the plasma the only radiation entering the input slit is that of emission from the sample. There is a slight possibility of matrix interference based on the type of solution the sample is dissolved in. According to Skoog at low analyte concentration there is a possibility for background noise due to recombination of argon ions with electrons.<sup>7</sup> In general, however, the plasma source is relatively simplistic while being extremely quantitatively valuable.

This project was directed towards the development of a simple yet accurate and precise method of determining the percent composition of silica based mineral samples. The samples used were previously analyzed limestone samples. These samples are referred to as Thorne Smith samples in this report since the Thorne Smith Co. prepared and analyzed the samples using older "wet" techniques. The four main elements of interest were calcium, magnesium, iron and aluminum.

Most learning and development processes require a number of steps to be comprehended before the actual process is mastered. This is applicable to the use of the DCP and development of the procedure desired. Thus, one must learn to tune before analyzing and to analyze before concluding.

Keeping in line with this theory, the first part of the project was devoted to becoming familiar with the instrument. The DCP has a great deal of subtle intricacies associated

with tuning it to provide the accurate and precise data desired. This was accomplished through the preparation of standard samples of known concentration and moving on to other controlled circumstances.

Once tuning had been reasonably understood analysis was undertaken. This turned out to be both invigorating and frustrating. Through all the frustration, however, more and more insight into the DCP was gained.

Lastly, once the DCP had been mastered it was time to utilize these skills towards the testing of the many proposed preparations of the samples.

Simultaneously intertwined with the understanding and use of the DCP was the method of preparation of the silica based samples. The older methods used to perform the analyses on these samples employed many classical quantitative procedures including; combustion reactions, precipitation reactions, and other procedures, all of which required lengthy periods in the lab. Moreover, these classical methods called for the use of highly corrosive agents such as hydrofluoric acid (HF).

The preparation portion of this project was devoted to the reduction in laboratory time and use of strong caustic agents. The solution pursued was a "hot nitric acid system". This system applied nitric acid as the only chemical agent (besides deionized water) used in the digestion of the sample in preparation to be sent to the DCP.

The main concern with the success of this method was whether or not the iron and aluminum bound to the silica could be freed with hot nitric system. Following a number of preparation trials, this concern has been reasonably eliminated based on correlation with the Thorne Smith data. As a result, it is believed that a satisfactory preparation method has been developed for metasilicate samples which can be applied to other samples of the same nature. The details of this procedure can be found in the PROCEDURE section of this report.

The contents of this introduction would lead one to believe that the operation of the DCP and the development of the digestion process were reasonably simple. Leaving this section with this impression would be misleading. It is true that the final application of the DCP along with the experimental results obtained were extremely satisfying; however, attaining proficiency with the DCP and, moreover, quality results, had a number of difficulties associated with them. The alleviation of these problems in order to arrive at the final procedures was the objective of this project and will be covered within this report.

fig.1

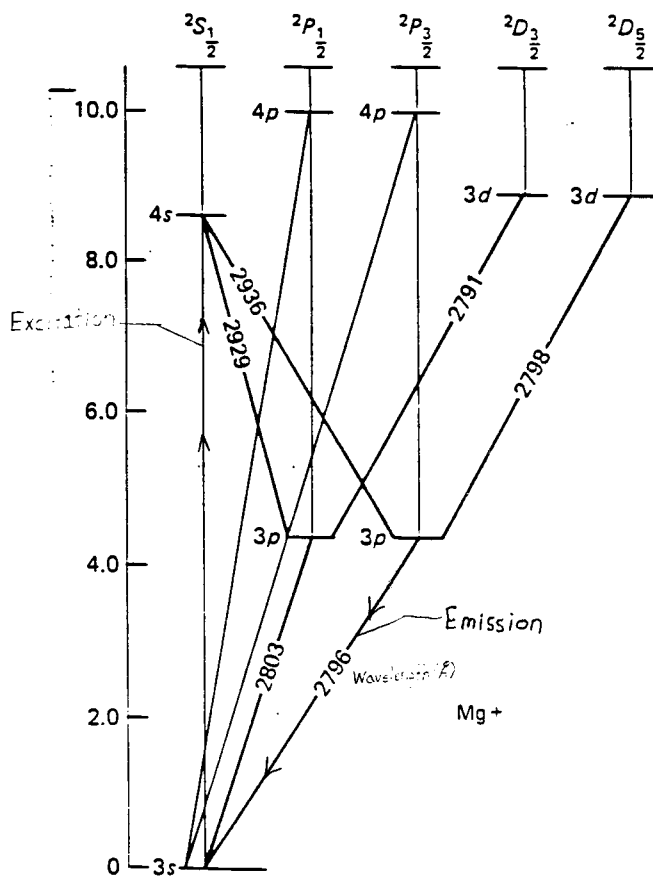
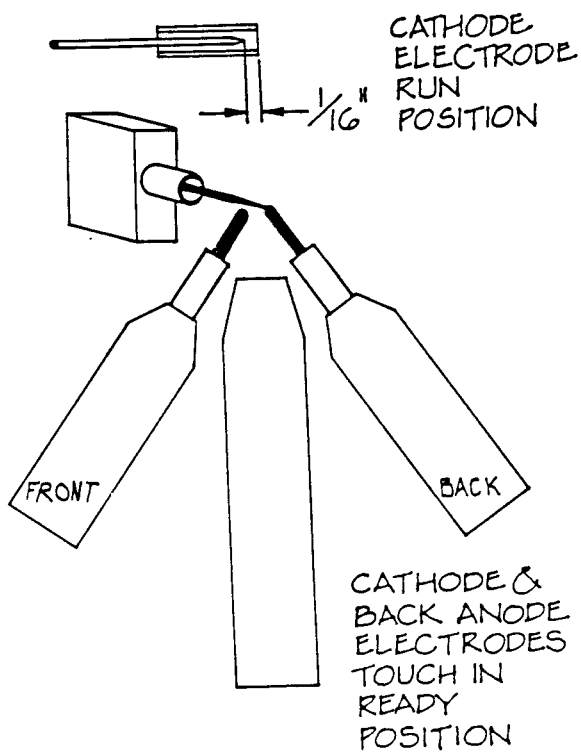
Mg<sup>+</sup> Emission Spectrum



fig. 2



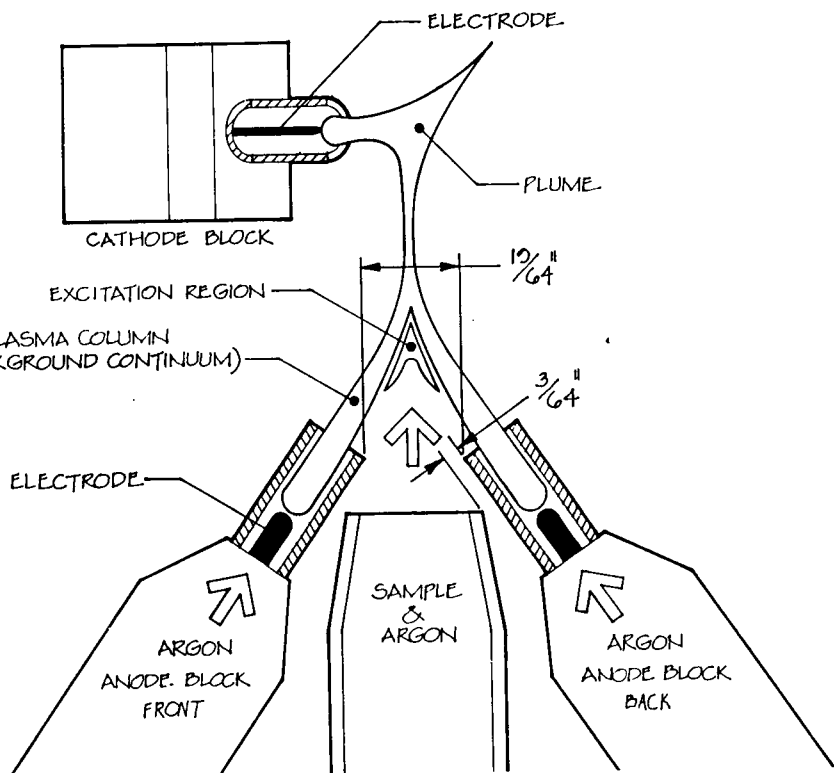
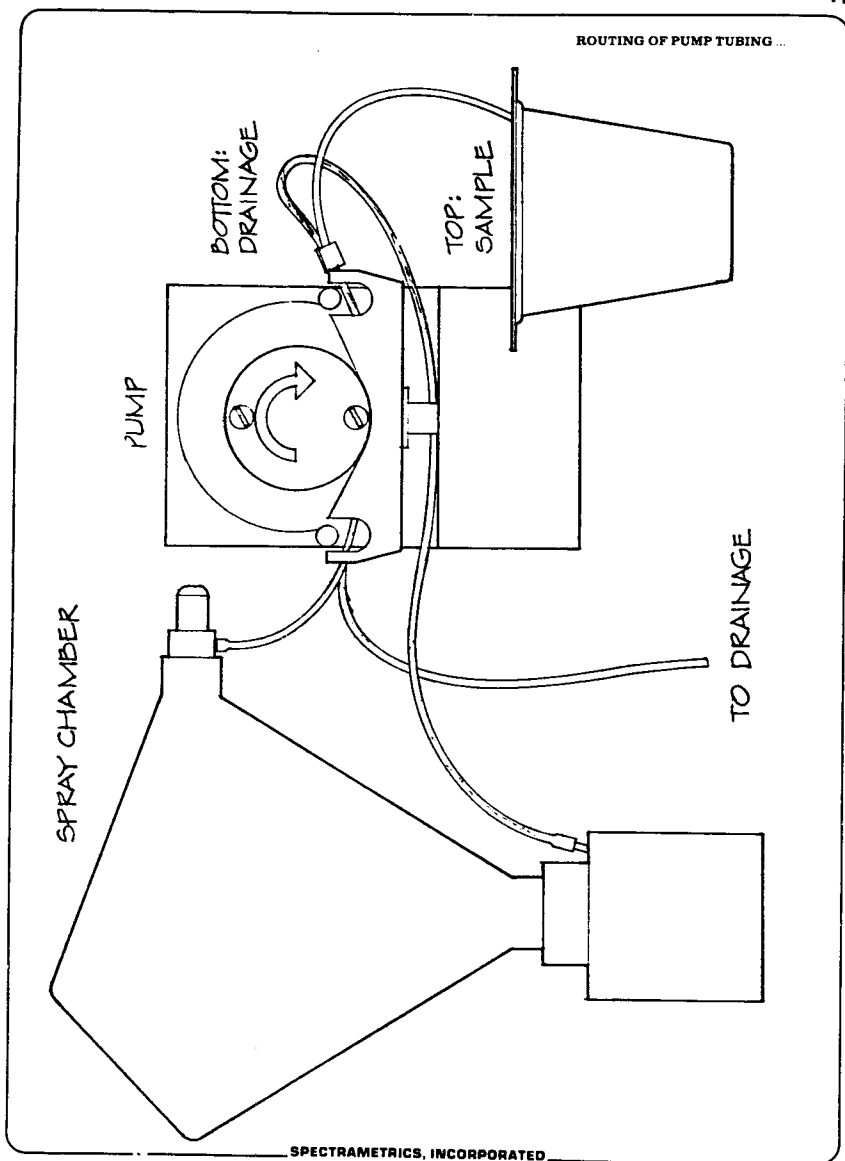
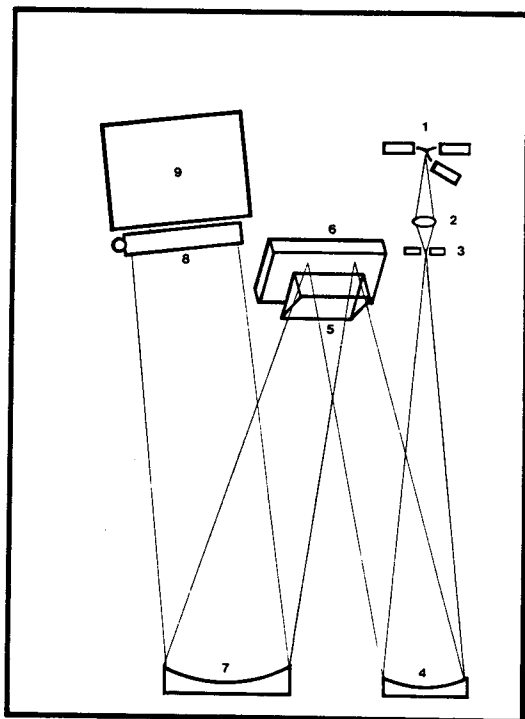


fig.4



SPECTRAMETRICS, INCORPORATED

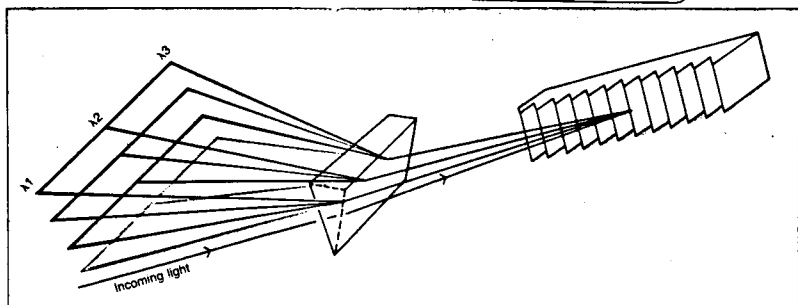
fig. 5



# ECHELLE GRATING SPECTROMETER

- |                       |                        |                  |
|-----------------------|------------------------|------------------|
| 1.) PLASMA JET        | 4.) COLLIMATING MIRROR | 7.) FOCUS MIRROR |
| 2.) LENS              | 5.) PRISM              | 8.) CASSETTE     |
| 3.) ENTRANCE APERTURE | 6.) ECHELLE GRATING    | 9.) DETECTOR     |

SPECTRAMETRICS, INCORPORATED

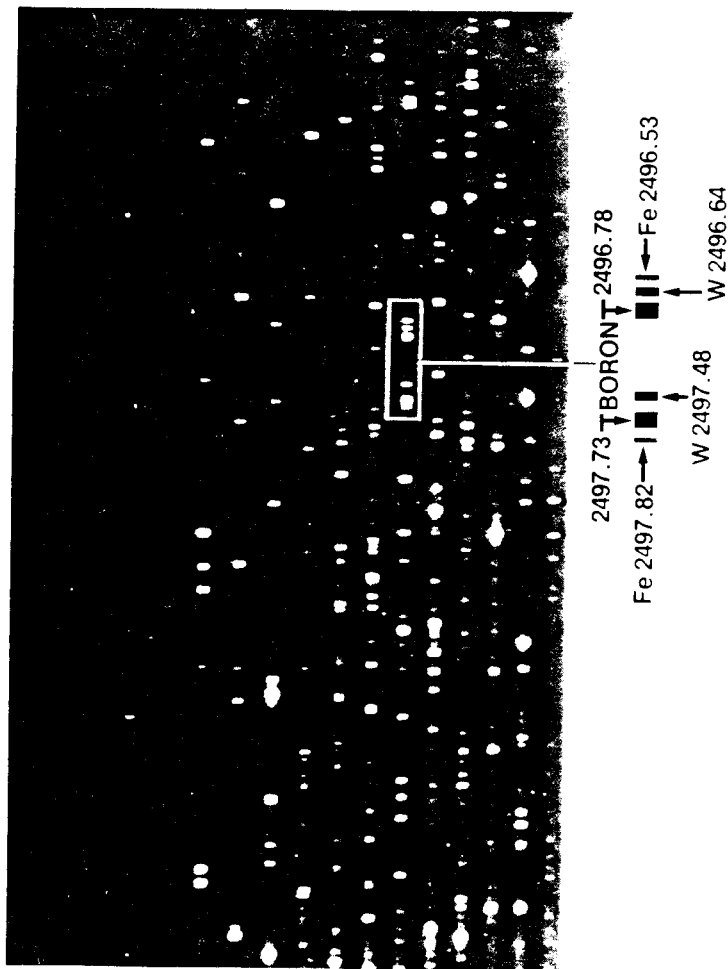


The occurrence of many high orders of diffraction across a small range of diffraction angles makes necessary the performance of order sorting to simplify the spectrum produced. Positioning of a prism ahead of the echelle grating in such a way

that its dispersion is perpendicular to that of the grating sorts the orders into a stacked arrangement. The result is a compact, two-dimensional spectrum consisting of spectral rectangles instead of the conventional lines.

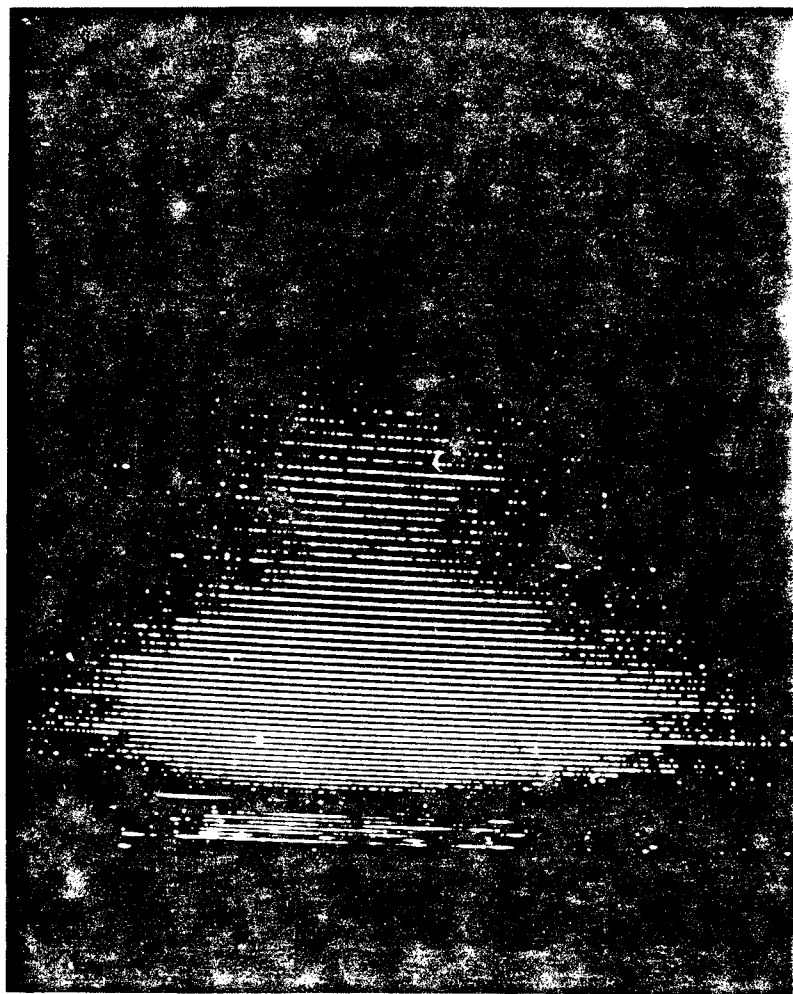
fig. 6

... ENLARGED PORTION OF SAMPLE DETECTOR



SPECTRAMETRICS, INCORPORATED

RASTER SPECTRUM OF THE 100% OVEREXPOSED PHOTOGRAPH OF FIG. 6



SPECTRAMETRICS, INCORPORATED

#### EXPERIMENTAL:

The instrument used in this project was the SpectraSpan IV produced by SpectraMetrics Incorporated, located in Andover, Massachusetts. As mentioned in the introduction this is an emission spectrometer. The SpectraSpan IV incorporates an analytically useful plasma with advanced optics and a powerful on-board computer unit.

There are three electrodes used to generate the plasma. One is a tungsten cathode and the other two are graphite anodes. These electrodes are held in their electrode blocks which allow argon to be passed over them at 50 p.s.i. while the electronics supply the 15 amp current necessary for plasma operation.

The sample delivery system is designed to convert the liquid solutions into an aerosol which can be aspirated into the plasma. The system begins with a peristaltic pump which draws three milliliters of sample per minute. The sample is then introduced to an argon stream of 20 p.s.i. at the nebulizer. The aerosol like sample is then carried into the spray chamber after which it is introduced to the plasma. The same peristaltic pump mentioned works to drain the sample not carried into the plasma.

The overall requirements of the instrument are simple. The power required is normal line voltage of 115 VAC at 15 A. The only gas necessary for operation is argon which is easily handled since it is not toxic or flammable like the gases used for other types of flames. The argon is supplied at

seven liters/minute at 80 psi. The instrument consumes about 17 cubic feet per hour. Lastly, an exhaust system is used to vent gases from the lab. The only other necessity is a supply of cooling water to the power supply unit.

The optics are covered for the most part in the introduction as are the computer controls. Detail about the computer functions is best accomplished by referring to appendix B rather than repeating them here.

The last piece of instrumentation utilized was a data logger. In this case a Texas Instruments Silent 700 was used. The Silent 700 is used basically as a printer to record the "digital counts" measured by the instrument. It is also possible to have the output show the average values and the standard deviations for the ion concentrations.

Samples for the DCP must be in solution form. The main item used to accomplish this was concentrated nitric acid. Other than this the only requirement was analytically pure standards and glassware. As a result, the matrix for all the samples was similar; a nitric acid matrix. The detail for this section is better discussed in the PROCEDURE SECTION and following sections.

In summary, the amount of instrumentation and equipment employed in this project is small yet powerful. The preparation of samples is relatively clean and easy and the DCP is moderately easy to operate while being precise and accurate.



#### PROCEDURE:

This section of the report represents the bulk of the information gained and the thought processes behind the development and testing of the method. The PROCEDURE section will consist of two parts; experimental procedure and operational procedure. As a result, this report will serve not only as a account of what was done and how but, also, as a guide to people who follow in this research.

Since this report will serve as material for the individuals who follow, this is a fitting place for advice. As one will find in the detail to follow, the achievement of ones goal is rarely immediate when it comes to the development of a feasible method. It often takes trial and failure to guide one in the proper direction. This is not to say that nothing in research comes quickly, some things do; rather, one must learn to temper their desire for rapid results. Moreover, to learn to direct their energies towards carefully thought out strategies based on the information gained from the experiences they encounter in the lab. Which leads to the last philosophical point. In investigation like this, one must always pay attention to what the data is revealing and, most importantly, to develop a feel for what is going on in the microcosm one is preparing in a variety of glassware.

#### EXPERIMENTAL PROCEDURE:

The goal of this project was to develop a quantitative method for preparing liquid solutions of silica containing

geological samples. The samples used were the Thorne Smith samples mentioned in the EXPERIMENTAL section. The means pursued was one of digesting the samples in a nitric acid matrix. Furthermore, all standards were prepared using nitric acid to give the same matrix.

The four main elements of interest were calcium, magnesium, iron and aluminum. These elements are present, for the most part, as carbonates in limestone (reported as oxides). Thus, nitric acid is a suitable agent to perform the digestion. There is, however, one complication in that some of the elements are bound to the silica in the form of metasilicates. Older methods called for the removal of the silica using HF. This was to be avoided at all costs in this project; as a result, the route pursued was one that assumed the metasilicate could be broken down by using hot concentrated nitric acid. The calcium and magnesium were not expected to provide any complications since they were present mostly as the carbonates and are not bound to the silica as are the iron and aluminum.

The following procedures are listed in chronological order in which they were attempted. Whether they failed or succeeded will be mentioned here and discussed in later sections of this text.

#### Preparation of Stock Standard Solutions:

The first step required was the preparation of the standard stock solutions; it was decided that one part per

thousand, 1 ppt, would work well. It should be noted from this point on all glassware used was acid washed: see operational procedure. The first stock solution prepared was to be a 1 liter, 1 ppt,  $\text{Ca}^{++}$  solution. Thus, 2.4973g of Thorne Smith (99.8 pure)  $\text{CaCO}_3$  were weighed out. This is 0.02495 moles of Ca which is 1 gram of Ca. This was then placed in a 400 ml beaker. Next, 50 ml of concentrated nitric was slowly added to the sample so as to allow for the initial release of  $\text{CO}_2$  gas to occur without splattering. An additional 25 ml of con nitric acid was then added to the sample. A watch glass was placed on the beaker and the beaker was placed on a hot plate in a hood. The sample was brought just to a boil, while constant agitation was applied to avoided splattering. The sample was then allowed to cool to room temperature. The digested sample was then added to an acid washed one liter volumetric flask. The beaker was washed twice with 10 ml of con nitric acid and the washes were added to the flask. The balance of the volume was taken up with deionized water (DI water). Thus, the first stock solution was prepared. It is worth noting that a 1 ppt stock solution was employed since it was felt that a concentration less than this was facilitate loss of sample due to adsorption onto the glassware.

The other standard stock solutions were prepared basically the same way as the one above. The magnesium standard was prepared by using one gram of pure magnesium metal digested in con nitric. The iron standard employed one gram of

pure iron wire and the aluminum standard utilized one gram of pure aluminum foil. Furthermore, a copper standard was prepared using one gram of pure copper foil. All of the above standard preparations were found to be acceptable and useful.

The next logical direction to describe was the digestion of the Thorne Smith samples. It was hoped that these would behave like the standards had and be digested quantitatively by the nitric acid treatment. The only variation that was predicted was that a filtration method was needed to remove the silica left behind after digestion before the sample could be diluted to volume. This was to be accomplished by using a fine fritted glass filter in conjunction with vacuum filtration. Thus, the first preparation of a Thorne Smith sample could proceed.

#### Experimental Procedure I:

As in the case of the standard stock solutions, a sample was weighed out. Limestone sample number 26 was employed in this prototype run. It was assumed that limestone is about 90%  $\text{CaCO}_3$  and, thus, a 2.5000g sample would give appropriate concentrations of the four elements in question. Thus, 2.3757g of sample 26 were weighed out and added to a 400 ml beaker. Again, 50 ml of con nitric acid were slowly added to the sample and the sample was swirled. Then an additional 25 ml of con nitric were added and the beaker covered and placed on the hot plate. It was important that during heating the

sample was swirled to keep the silica from settling. Settling may cause splattering due to a sudden boiling under the film of silica. The sample was allowed just to achieve a boil. It was then removed from the heat and allowed to cool. After cooling, the vacuum filtration set-up was turned on (NOTE: a trap was employed to prevent and back flow of water). The solution above the silica sediment was added to the filter first to facilitate rapid filtering. Next, the remainder of the contents of the beaker was flushed into the filter using a wash bottle of previously prepared 1 M nitric acid. After the filter had pulled all the solution through, the beaker was washed with 10 ml of con nitric and this was poured over the silica sediment in the filter. This was repeated. Next, four washes with 1 M nitric ensued. The filter flask (previously acid washed) now contained the sought after filtrate. This was poured directly into a one liter volumetric. The filter flask was washed with 20 ml con nitric which was added to the volumetric and then the filter flask was washed twice with DI water and this was added to the volumetric. The balance of the volumetric flask was filled with DI water. The sample was then introduced to the DCP for analysis: this process will be covered in later parts of this section.

Thus, it was hoped that this simple, one and one half hour, procedure had eliminated days of work in the lab involving tedious procedures and corrosive agents. Unfortunately, the results determined proved otherwise. Thus, it was neces-

sary to examine the results obtained and consider what might be going on in the sample preparation which precluded the achievement of agreement with the Thorne Smith results.

First of all, the concentrations of the iron and aluminum were too low for quality determinations; in the region of two to ten ppm. Thus, it was decided to lower the final volume of the samples to 500 ml. Also, the mass of the sample was reduced by ten to twelve percent in order to reduce the silica content so as to allow for more efficient digestion by the nitric acid. Lastly, it was resolved that a longer boiling time was required to help leach to iron and aluminum off of the silica.

#### Experimental Procedure II:

As a result, the following procedure was adopted and carried out on samples 24, 25, 26, 28 and 37. The samples were prepared one at a time. To begin with, the sample was weighed out to be about 2.100 grams. The sample was then added to a 400 ml beaker to which two 10 ml portions of concentrated nitric were added with swirling. The sample was then brought to a volume of 60 ml with concentrated nitric and placed on the hot plate until it boiled. After boiling was achieved, it was continued for the course of an hour. During the boil, concentrated nitric was added when the volume of the sample approached the 50 ml level; usually 25 ml were added each time. At the end of the hour the sample was removed from the hot plate and allowed to cool to room temperature. The remainder of the

procedure is for the most part the same as in experimental procedure I. The sample was filtered and the beaker and the silica in the filter were washed with con nitric. The only real difference is that the volumetric flask used was a 500 ml flask instead of the 1000 ml flask previously used. The sample is now sent to the DCP for analysis.

Again, it was thought that this basic sample treatment would yield accurate results according to the Thorne Smith data. As it turned out, however, this was not to be. The values for the iron and the aluminum were low which indicated that these elements were not being freed from the silica contained in the samples.

So, as before, another plan of attack had to be formulated to get as much of the sample into solution. It was contemplated that perhaps the nitric acid used in the boiling should be renewed periodically. Hence, a new procedure was developed and at this point is considered to be a successful method of sample preparation.

#### Experimental Procedure III:

The concept behind this procedure was to renew the con nitric used in the digestion process. This was to be accomplished by three half hour boils with decanting of the nitric acid supernatant each time.

Samples were prepared not only one at a time using this procedure but as many as three were run at one time using this procedure. Again, the sample weight was reduced to

facilitate digestion. Thus, samples of between 1.0000g and 1.5000g were used; values closer to 1.000g proved better. The sample was again added to a 400 ml beaker and 75 ml of con nitric acid was added slowly to the sample. The sample was then swirled to assure that clumps were broken up. The beaker was covered with a watch glass and then placed on a hot plate. The sample was continuously swirled to prevent "popping". The sample was then allowed to boil for a half an hour while being agitated. At the end of the half hour the sample was removed from the heat and allowed to cool for fifteen minutes. One must be careful not to agitate the sample after cooling has begun in order to allow the silica to settle to the bottom. At this point, the solution above the silica is slowly decanted into the vacuum filter, leaving only the silica in the beaker. When all the solution is pulled through the filter two 10 ml washes with 1 M nitric were used followed by a 10 ml wash with con nitric. Subsequently, another 75 ml of con nitric was added to the beaker containing the silica. The boiling process described above and the subsequent filtration operation was repeated two more times for a total of three consecutive boil/filter steps. Upon completion of the last filtration the beaker and the filter flask were washed as in procedures I and II and the sample was made up to a volume of 500 ml in a volumetric flask. The sample is now ready for introduction to the DCP for analysis. The sample requires no further dilutions.

This last method was the one which proved to be most



effective in correlating with the Thorne Smith data. Thus, it is hoped that upon further testing and possible refinement this procedure will stand effective.

#### OPERATIONAL PROCEDURE:

##### Acid Washing:

All glassware used in this project had to be extremely clean and free of elemental contamination. This is because the DCP is such a sensitive instrument that any residue in the glassware of the elements being analyzed could affect the experimental results. Thus, a process of acid washing was used for all glassware.

Acid washing involves the addition of a small amount of concentrated nitric acid (5 to 15 ml) to the article being washed. This is swirled around the object and then it is allowed to sit. Next, the item is rinsed with five tap water washes and ten washes with deionized water. This is all there is to this vital process.

##### Preparation of HI and LO Standards:

The first step before introducing a sample to the DCP is to prepare standard solutions for the element(s) to be analyzed. Two such standards were required; a HI standard and a LO standard. The concentration of these standards was chosen so that the unknown concentration should fall between the HI and LO standards. These standards were made up to 100 ml in acid washed volumetric flasks. For example, if a 100 ppm HI standard and a 10 ppm LO standard of  $\text{Ca}^{++}$  were required one would pipette 10 ml of the 1 ppt  $\text{Ca}^{++}$  stock solution to the 100 ml volumetric and then dilute up with DI water to create the 100 ppm standard. The LO could be made by using only 1

ml of stock or 10 ml of the 100 ppm HI standard. All standard solutions are prepared in this way. Furthermore, due to the low concentrations of these standard, they must be used on the day they are prepared to avoid absorption loss to the glass.

#### Ignition of the Plasma:

This process is easy to describe in principle; however, in practice it requires a great deal of the "feel" mentioned in the opening of this section. To begin with, the instrument power ("PWR" button) must be turned on along with the argon at 80 PSI from the regulator and a supply of cooling water from the sink behind the instrument. The electrodes must be aligned as shown in figure 2 of the INTRODUCTION with the cathode just touching the back anode. The sleeve argon pressure should be 50 PSI and the nebulizer pressure should be 20 PSI: these settings should not be touched during the running of the instrument. Once the argon is turned on by flipping the "on-off" switch to "on", the pump should be turned on and a sample of DI water should be introduced to the DCP via the sample intake tube.

Following this, the PLS switch should be activated supplying power to the electrodes. A high pitched whine should be heard; if not, adjustment of the electrodes is required. Allow the whine to continue for five seconds then move the "run/ready" switch to the "run" position. The plasma should now be ignited. If the plasma fails to light

one must make adjustments in the positions of the electrodes, argon pressures, and other components and repeat the ignition process. See section 4.2.5.3 of the Instruction Manual for the SpectraSpan IV for further details.

#### Alignment of the Plasma:

Now that the plasma is lit it must be adjusted to make it stable for analytical work. This is done if the plasma makes a popping or whistling sound, indicating too little or too much argon flow, respectively, to the electrodes. Furthermore, one can view the image of the plasma on the input slit. If it is not a symmetric "Y" shape with strait legs alignment is necessary. This is done by first adjusting the needle valves to the back and front anodes in order to straighten the legs of the plasma. Once done the cathode needle valve is adjusted to make the plasma stand straight up when viewed through the protective glass and to eliminate any whistling or popping heard. Once done the plasma should have a smooth consistent sound and have a uniform "Y" shape.

Furthermore, there are a set of knobs on the front of the plasma housing which adjust the X-Y position of the plasma on the input slit. These are used to align the excitation region of the plasma up with the input slit to the monochromator. To accomplish this one should aspirate a concentrated sample of Ca, Mg or a limestone sample into the plasma. These samples give a bright spot in the excitation region which should be adjusted to fall on the input slit.

Note that the adjustment should be made so that the legs of the plasma are clear of the slit with the slit set on its largest opening. Resume the flow of DI water to the plasma. See sections 4.2.5.4, 4.2.6.1. and 4.2.6.2 of the Instruction Manual for another reference. Furthermore, 4.2.6.3. sums the process up by stating:

"Some of these adjustments are interactive and require several iterations in order to achieve the desired level of performance."

#### Peaking of the DCP:

This is the segment of operating the DCP that requires the most feel for the instrument. The purpose of peaking is to get the optics of the instrument to be focused exactly on the line of interest without any interference. If this skill is not mastered the results obtained by the experimenter may be spurious.

Once all the above adjustments have been made one consults the list of orders and wavelenghts available and adjusts the thumbwheels on the front of the instrument to the values required for that element. Next make sure the mode switch is on direct T=1, repeats on 4 or 5, the input slit fully open and PMT voltage set at 800 V or 900 V. Now the HI standard is introduced to the plasma. After hearing the air bubble go through and the sample begin to be aspirated, wait at least 30 seconds before continuing. Now the "A/R" (auto-range) button is pushed and the instrument goes through a gain setting cycle. If stat message #3 comes up turn up the PMT voltage. When the "A/R" light goes out the "SMP" (sam-

ple) push-button is depressed and continual readouts will be given.

Now fine adjustments are made referring to the analog meter as a guide for which way to go. Start by adjusting the bottom thumbwheel up or down to give maximum increase in signal. If in any adjustment the signal goes off scale, turn down the PMT voltage by 100V; do not go below 600 V. Once the bottom thumbwheel is adjusted adjust the top wheel the same way to give a peaked signal. If the PMT voltage is down to 600 V it is possible to drop to 500 V but it is preferable to begin decreasing the size of the input slit by one size at a time. Thus, a good peaking job should end up with a PMT voltage of 600 V and an input slit on the second or third largest size.

Finally, the memory is cleared and the "A/R" button is pressed in order to allow the instrument to set the range to half scale. Moreover, the test of the peaking process is done by introducing a DI water sample and having the signal drop off to below 150 digital counts. If all other conditions are still correct (i.e. alignment and positioning) and the DI water gives a "zero" reading the instrument can be assumed peaked and ready for sample analysis. This is covered in the Instruction Manual section 4.2.5.5..

#### Analysis of an Unknown:

Now that the instrument is up and running one is ready to perform an analysis of an unknown such as the calcium

content of the Thorne Smith limestone number 26. The first step is to switch the instrument over to integrate mode. A time setting of 10 seconds and repeat of 5 are more than enough to get good results. One must also make sure the "PRINT" switch is on, the "AVG ONLY" switch is on and the "DIAG" switch is on. These allow for the hard copy. Also, one should push the "CLR MEM" button to clear any previous memory.

The value for the HI standard should be entered on the keypad and the "ENT/HI" button depressed. The same is done for the LO standard value by entering the value on the keypad and pressing "ENT/LO". The HI standard is introduced as in peaking process, allowing at least 30 seconds for equilibration, and the "A/R" button is pushed. The instrument sets the gain and the scale for the HI standard. When the cycle is complete the light will go out and the value of the HI standard will appear in the digital readout. At this point a small amount of DI water is fed into the instrument. Now the LO standard is introduced to the plasma allowing for equilibration after which the "LO STD" button is pushed. When the light goes out the cycle is done and the standard curve is established. If at any time during the above steps a STAT message comes up and a correction is made the above steps must be repeated.

Again, a small wash of the delivery system is done with DI water and the unknown is introduced into the plasma. Upon equilibration the "SMP" button is depressed and the cycle

precedes until the light goes out and the average value is displayed in the digital readout. Furthermore, the Silent 700 prints out the average value along with the five raw data values. Further samples of the same element can be run immediately.

This process is simple and requires only a few minutes. Thus, it is beneficial to check the results by repeating all of the above at a different line to rule out possible background interference. If the second line data agrees with the first line data then the results are valid. If the data do not agree then a third line must be checked and the two lines which give the same results are taken as valid.

In summary, the operation of the DCP is simple once it is mastered. It is important to develop a feel for the instrument before it can be mastered. Once this level of competence is reached, however, the DCP can become an infinitely powerful tool at ones disposal which is an asset to ones work.



# DATA AND RESULTS:

Note: the following data and results are presented in chronological order of their completion.

TABLE I  
TAP WATER HARDNESS TEST

sample	element	HI STD	LO STD	ppm Ca	ppm CaCO <sub>3</sub>
tap water	Ca	200 ppm	50 ppm	54.8	137

TABLE IIA  
ANALYSIS OF LIMESTONE #26  
USING EXP. PRO. I

element analyzed	comp. sought	HI STD /ppm	LO STD /ppm	ppm of analyzed	ppm of sought
Ca	CaO	1000	500	701	981
Mg	MgO	500	50	105	174
Fe	Fe <sub>2</sub> O <sub>3</sub>	100	10	3.52	5.03
Al	Al <sub>2</sub> O <sub>3</sub>	100	10	3.45	6.51

TABLE IIB  
PERCENT COMPOSITION OF LIMESTONE #26  
USING EXP. PRO. I

sample component	% of sample by DCP	% of sample Thorn Smith	% deviation
CaO	41.3	40.58	1.76
MgO	7.32	7.23	1.30
Fe <sub>2</sub> O <sub>3</sub>	0.212	---	---
Al <sub>2</sub> O <sub>3</sub>	0.274	---	---
R <sub>2</sub> O <sub>3</sub> *	0.486	1.14	57.4

\*R<sub>2</sub>O<sub>3</sub> is Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> since Thorn Smith only reported R<sub>2</sub>O<sub>3</sub>.

TABLE IIIA  
ANALYSIS OF LIMESTONES 24, 25 AND 28  
USING EXP. PRO. II

sample #	ppm Ca	ppm CaO	ppm Mg	ppm MgO	ppm Fe	ppm Fe <sub>2</sub> O <sub>3</sub>	ppm Al	ppm Al <sub>2</sub> O <sub>3</sub>
24	1398	1956	152	252	71.6	102	5.83	11.0
25	1358	1900	196	325	29.0	41.5	6.36	12.0
28	1282	1794	238	395	39.5	56.4	5.69	10.7

NOTE: the standard for these determinations were the same as for table IIA except the Al standards were 10 ppm and 1 ppm. also, all samples made up to 500 ml volume.

TABLE IIIB  
PERCENT COMPOSITION OF LIMESTONES 24, 25 AND 28  
USING EXP. PRO. II

sample # & wt.	sample component	% of sample by DCP	% of sample Thorn Smith	% deviation
24 2.1174g	CaO	44.9	43.38	3.50
	MgO	5.79	5.36	8.02
	Fe <sub>2</sub> O <sub>3</sub>	2.59	---	---
	Al <sub>2</sub> O <sub>3</sub>	0.253	---	---
	R <sub>2</sub> O <sub>3</sub> *	2.59	3.47	25.4
25 2.1757g	CaO	43.7	41.71	4.77
	MgO	7.47	6.88	8.58
	Fe <sub>2</sub> O <sub>3</sub>	0.943	---	---
	Al <sub>2</sub> O <sub>3</sub>	0.276	---	---
	R <sub>2</sub> O <sub>3</sub> *	1.22	1.63	25.2
28 2.1753g	CaO	41.2	40.61	1.45
	MgO	9.07	8.33	8.88
	Fe <sub>2</sub> O <sub>3</sub>	1.29	---	---
	Al <sub>2</sub> O <sub>3</sub>	0.192	---	---
	R <sub>2</sub> O <sub>3</sub> *	1.48	2.05	27.8

TABLE IVA  
ANALYSIS OF LIMESTONES 24, 25, 26 AND 28  
FOR  $R_2O_3$  USING EXP. PRO. III

sample #	sample mass/g	ppm Fe	ppm $Fe_2O_3$	ppm Al	ppm $Al_2O_3$
24	1.5289	66.4	94.9	5.06	9.56
25	1.5210	22.1	31.6	5.10	9.64
26	1.5885	8.20	11.7	5.82	11.0
28	1.7753	19.6	28.0	3.07	5.80

NOTE: all samples are made up to be 500 ml in volume.

TABLE IVB  
PERCENT OF  $R_2O_3$  IN LIMESTONES 24, 25, 26 AND 28  
BASED ON DATA IN TABLE IVA

sample #	% $Fe_2O_3$ by DCP	% $Al_2O_3$ by DCP	% $R_2O_3$ by DCP	% $R_2O_3$ Thorn Smith	% deviation
24	3.10	0.313	3.42	3.47	1.44
25	1.04	0.317	1.36	1.63	16.6
26	0.372	0.346	0.718	1.14	36.4
28	0.789	0.163	0.952	2.05	53.6

TABLE VA  
TEST OF EXP. PRO. III PRECISION AND ACCURACY  
ON LIMESTONE #28

trial #	sample mass/g	ppm Fe	ppm Fe <sub>2</sub> O <sub>3</sub>	ppm Al	ppm Al <sub>2</sub> O <sub>3</sub>
1	1.0016	21.4	30.6	3.13	5.91
2	1.0010	19.8	28.3	3.12	5.90
3	1.0061	21.5	30.7	3.36	6.35
4	1.0034	21.8	31.2	3.33	6.29
5	1.0014	21.1	30.2	3.44	6.50

NOTE: all samples made up to 500 ml.

TABLE VB  
RESULTS OF TEST FOR PRECISION AND ACCURACY  
ON LIMESTONE #28 BASED ON R<sub>2</sub>O<sub>3</sub>

trial #	%Fe <sub>2</sub> O <sub>3</sub> by DCP	%Al <sub>2</sub> O <sub>3</sub> by DCP	%R <sub>2</sub> O <sub>3</sub> by DCP	%R <sub>2</sub> O <sub>3</sub> Thorn Smith	% deviation
1	1.53	0.295	1.83	2.05	10.7
2	1.41	0.294	1.70	2.05	17.1
3	1.53	0.316	1.85	2.05	9.76
4	1.55	0.313	1.86	2.05	9.12
5	1.51	0.325	1.84	2.05	10.2
average	1.51	0.309	1.82	2.05	11.3
avg.dev.	0.0380	0.0110	0.046	----	2.24
average*	1.53	0.312	1.84	2.05	9.95
avg.dev*	0.0100	8.75e-3	0.0100	----	0.505

\* indicates that the values reported are calculated without the data for trial #2.

TABLE VI  
THORNE SMITH DATA ON  
SILICA CONTENT OF SAMPLES

sample	% silica
24	7.58
25	9.63
26	10.78
28	7.83

OTHER DATA COLLECTED:

TABLE VII  
LINEARITY AND DETECTION LIMIT CHECK  
OF DCP USING CALCIUM

ppm Ca as prepared	digital counts	ppm Ca from DCP
10	4082.0	10.0
5	2271.6	5.15
1	728.2	1.02
0.5	537.8	0.505
* 0.1	385.6	0.097
0.05	368.8	0.052
0.02	358.6	0.025
0.01	353.0	0.010

NOTE: these data are plotted on figure A1 and the data from \* down are plotted on figure A2.

Data from work done for Prof. Harlow, CE.  
Winter 1987:

TABLE VIII  
EXAMPLE OF POOR PRECISION AND ACCURACY  
ON COPPER DETERMINATIONS

run	ppm copper
1	0.063
2	0.086

<0.025 is the predicted value in ppm.  
<Sample is a salt mixture.

TABLE IX  
DEMONSTRATION OF INTERFERENCE  
BASED ON SPECTRAL LINE CHOICE

run	spectral line	ppm copper
1	5218.2 nm	0.063
2	5218.2 nm	0.086
3	3247.5 nm	0.025
4	3247.5 nm	0.026

fig. A1

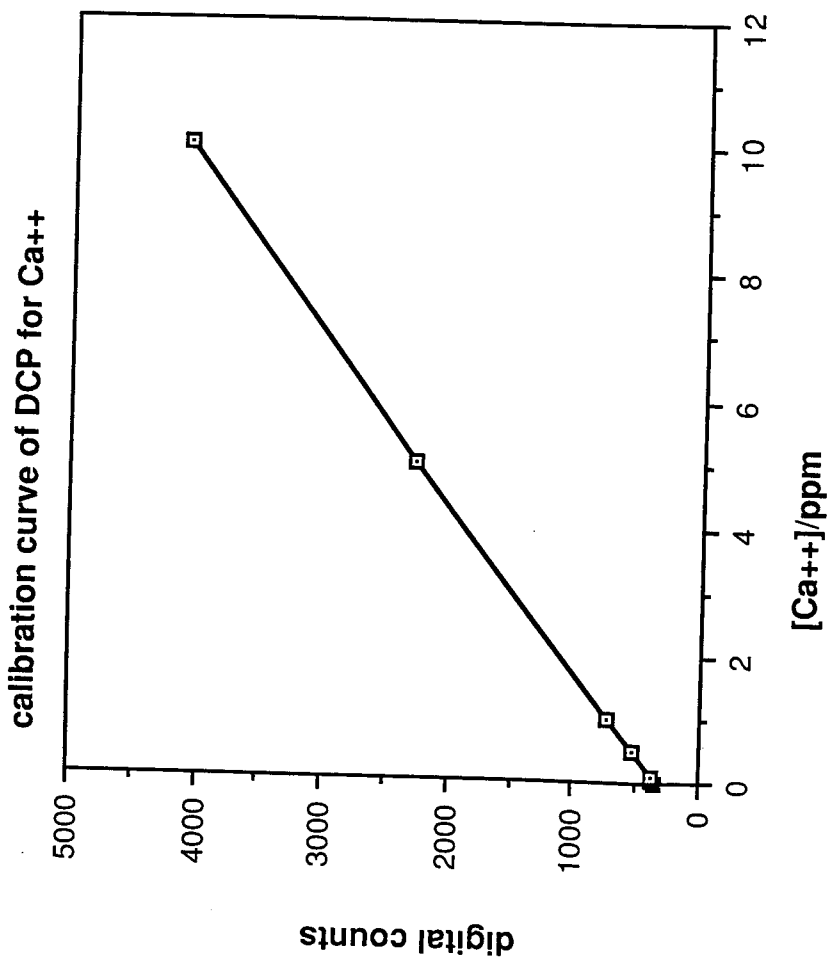
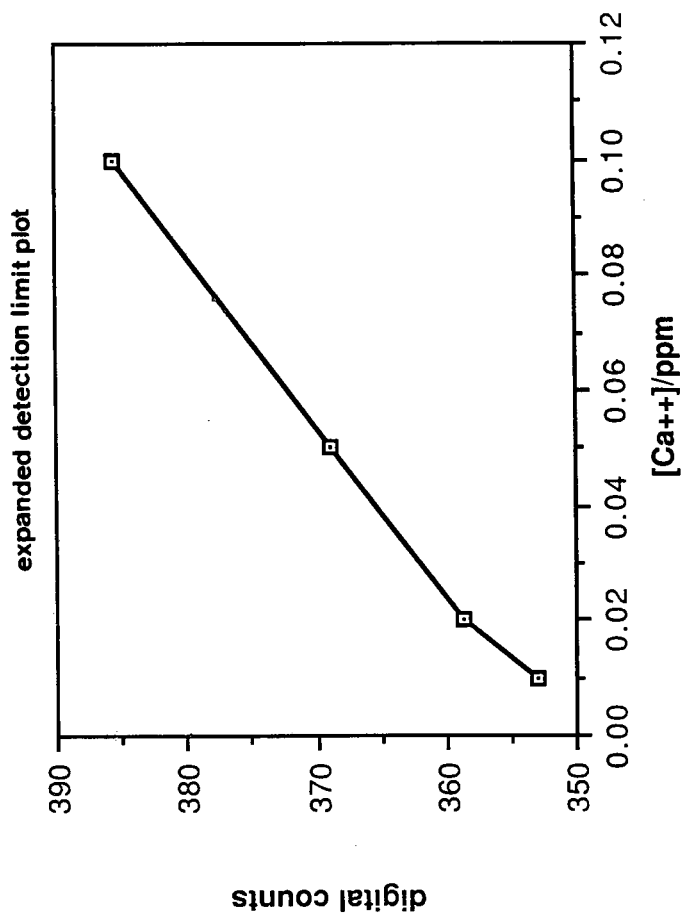


fig. A2





#### DISCUSSION:

Upon completion of the work for this project and review of the data collected a number of observations can be made. These observations relate to both the experimental procedure and the DCP analysis of such samples.

The first experiment done was designed to give the experimenter some experience in working with the DCP. This was a simple test for  $\text{Ca}^{++}$  in Schenectady drinking water. The data from this experiment are found in table I. It was accepted that the drinking water contained an average of 120 ppm of  $\text{CaCO}_3$  which would be 48.1 ppm  $\text{Ca}^{++}$ . The results obtained showed the water to be 137 ppm  $\text{CaCO}_3$  which is 14% higher than the expected value. One possible explanation for this occurrence is that the water was particularly hard on October 10, 1986 due to the lack of rain water at that time of year. Moreover, the high result may have been due to lack of experience with the DCP. As found by later work, some spectral lines, especially higher wavelengths, tend to succumb to interference which falsely increases the signal. This data was taken at 4454 Å which is high compared to some other calcium lines. Furthermore, if the instrument is not peaked and aligned exactly results tend to be increased erroneously.

Thus, some important lessons were learned from this first simple experiment. Primarily, the DCP is a fairly easy instrument to operate and obtain data from. This ease, however, was found to be coupled with other considerations

which must be taken into account to obtain quality data.

The next direction taken was to begin work on the Thorn Smith samples. In order to pursue this it was necessary to prepare standard stock solutions in addition to the 1 ppt Ca stock existing from above. Furthermore, the material for stocks had to be at least 99.8% pure. Thus, magnesium metal was used for a Mg stock, iron wire was used for an Fe stock and aluminum foil found in the stock room was used for the Al stock. These were all prepared using the method described in the procedure section.

Tables IIA and IIB represent the data and results from the preparation of sample #26 using experimental procedure I. This procedure assumed that simply bringing the sample to a boil in hot nitric acid would be enough force to remove all the desired material from the silica and put all the ions in solution. Table IIB shows some interesting results. Primarily, the Ca and Mg are easily solubilized by brief nitric acid treatment. This is based on the close agreement of the DCP data for %CaO and %MgO with the Thorn Smith data. Furthermore, it can be assumed that the Fe and the Al are bound much tighter to the silica based on the 57.4% deviation from the Thorn Smith results for  $R_2O_3$ .

Thus, it can be said that from this point on the goal of this project was to find a method for getting all the iron and aluminum free from the silica. Based on the results, it was assumed that the calcium and magnesium would cause little problem since they are present mostly as carbonates with

little metasilicate.

It was now necessary to investigate what caused the problems with sample 26 and try to develop a new method to overcome the inadequacies of experimental procedure I. First of all, the sample weight was reduced from almost 2.4000g to around 2.1000g in order to reduce the amount of silica present in the sample. Furthermore, since this would reduce the concentrations of the ions in solution the final volume of the sample was reduced to 500 ml as opposed to 1000 ml. In addition, the length of the boil was increased from just bringing the sample to a boil to a constant boil for one hour. Thus, it was hoped that these changes would prove to be effective.

The data and results from experimental procedure II are presented in tables IIIA and IIIB. To begin with, the reduction in sample size and volume proved to be effective. The silica content was reduced and, moreover, the ion concentrations increased due to the actions taken. This is evidenced by the higher metal ion ppm values in table IIIA as opposed to table IIA.

The percentage deviations for CaO range from 1.45 to 4.77 and for MgO they range from 8.02 to 8.88 all of which are fairly consistent. These values are higher than those found in table IIB for sample 26. A possible explanation is that when sample 26 was run experience with the DCP peaking procedures was limited and results may have been recorded as too high. All in all, it can be safely assumed at this point

that quantitative yield of the CaO and MgO can be accomplished.

More important are the values reported for the  $R_2O_3$  percentage deviation. These values are all between 25.2% and 27.8% which shows fairly good precision. Additionally, these results show that the procedure is improving from the 57.4% deviation for procedure I. Furthermore, the results presented in table IIIB show that the changes made were beneficial in improving the  $R_2O_3$  yield; however, these changes were not extreme enough since 25% deviation is still too high.

Based on the above results it was determined that other measures were necessary to make this project fruitful. As one can see, reducing the sample weight and increasing the boiling time had a marked effect on the results. Therefore, it was decided once again to reduce the sample weight and to increase the boil time to one and one half hours. The sample weight was reduced to the area of 1.5000 grams. Moreover, it was contemplated that the con nitric acid employed should be renewed after each boil. Hence, the one and one half hour boil was broken down into three half hour boils. After each boil the solution above the silica sediment was decanted for filtration, washed, and a fresh aliquot of con nitric acid was added to the silica sediment. As a result, three separate physical removals of Fe and Al were accomplished as opposed to the former with only one removal.

The preliminary results of testing procedure III are presented in tables IVA and IVB. Recall, it has been assumed

that the Ca and Mg can be satisfactorily determined by this method since the previous two methods proved reliable. The results presented in table IVB under percent deviation range from an excellent value of 1.44% for sample 24 to an unacceptable value of 53.6% for sample 28. The results for three out of the four samples run do show improvement, however. Most distinct is the deviation of only 1.44% for sample 24 as opposed to 25.4% under experimental procedure II. Sample 25 also showed improvement in recovery of  $R_2O_3$  with a deviation of 16.6% as opposed to 25.2% in table IIIB. Likewise, the percent deviation for sample 26 dropped from 57.4% in table IIB to 36.4% under this method. Sample 28 was the only real disappointment of the four with a deviation of 53.6%. This discrepancy may be due to the fact that during the preparation of sample 28 the glass filter cracked which may have resulted in the loss of some sample and inefficient filtration. In addition, the boiling of the sample was not as smooth as with the preparation of the others. A great deal of "popping" was incurred which may have caused sample loss. Also, the sample weight of 28 was the greatest by more than 0.2 grams which increased the silica content.

In review of table IVA and IVB, a few interesting ideas can be formulated. First of all, one might conclude that the iron is bound more tightly to the silica than the aluminum based on the fact that in table IVB as the percent deviation went up the percent  $Al_2O_3$  also went up and the percent  $Fe_2O_3$  went down. This suggests that the aluminum is being removed

well but the iron is the problem. Furthermore, in review of the data for sample 28 it is reasonable to say that if no sample were lost better results would have been obtained. This deduction is based on table IVA since the ppm data seems to be following the trends one would expect compared to the other samples, being just a bit low. Additionally, going ahead to table VB and comparing the results to table IVB for sample 28 one finds that the %Fe<sub>2</sub>O<sub>3</sub> in table IVB is 48.4% lower than that of VB and the %Al<sub>2</sub>O<sub>3</sub> in table IVB is 47.4% lower than the value in table VB. This seems to indicate a specific amount of sample was lost during preparation since it is assumed that iron and aluminum are not removed equally.

Another disappointment was the lack of agreement among the deviation values in table IVB for the various samples. This is most likely due to the fact that each time the sample was prepared small details such as cooling time and nitric acid volume were not consistent. It was hard to believe that small aspects such as these could result in such deviations.

As a result, it was decided to test the precision of the method stressing the consistency of every detail. Thus, experimental procedure III as stated in the procedure section was followed in every detail. Moreover, since sample 28 caused the problems above the test was run on this sample. It was hoped that this inquiry would prove the refined method accurate as well as just precise.

The data and results from this test are presented in tables VA and VB. After evaluation of the data and results

presented, it was decided that trial 2 was in error and disregarded. Otherwise, the results for the ppm of the components and the percent deviation were in excellent correlation. This is shown by average deviations of  $1.00 \times 10^{-5}$  ppt for the  $\% \text{Fe}_2\text{O}_3$ ,  $8.75 \times 10^{-6}$  ppt for the  $\% \text{Al}_2\text{O}_3$ , and for  $\text{R}_2\text{O}_3$  a value of  $1.00 \times 10^{-5}$  ppt was obtained. Most significant, however, was the average deviation for the percent deviation which was only  $5.05 \times 10^{-4}$  ppt. In summary, this test shows that if the procedure was followed exactly it can be extremely precise.

In regard to trial 2, there were some problems encountered in its preparation similar to those in the preparation of sample 28 in table IVB. The sample did not come to a boil as quickly as the others and it boiled roughly as did sample 28 which may have caused some sample loss. Furthermore, the filter used for trial 2 contained some grey deposits. Even though the filter was soaked in con nitric acid overnight some of the iron or aluminum may have bound to this material. Thus, trial 2 shows that the method is very sensitive to even slight deviations.

Accuracy is a major goal of any quantitative work and this case is no different. The average percent deviation for this method was 9.95%. It would have been nice to have this value down below one percent but the value obtained is superior to any other result obtained to this point except for that of sample 24 in table IVB. Furthermore, out of curiosity it was decided to check and see if any response was found when the instrument was set on a chromium line and the trials were

introduced. All the samples showed a fairly strong response. Thus, some of the  $R_2O_3$  reported by Thorn Smith may have been  $Cr_2O_3$ . This material may account for some of the deviation and should be checked by the next individual who performs this work.

In all, the results of this test were encouraging. This procedure has proved to be very precise and fairly accurate. Moreover, the method must be followed exactly since it has been shown that even slight deviations from the procedure may result in worthless results. Finally, it is hoped that the next person to peruse this work will pick up at this point and quickly refine this method to achieve results with less than two percent deviation. One last area of inquiry was whether or not the percent of silica present in the sample had any effect on the results. Table VI lists the Thorn Smith data for percent silica. In review of the data collected in this project a number of different observations can be made regarding the effect of the silica. It was postulated that as the percent silica increased the percent deviation would increase. According to table IIIB, this is not the case. Sample 25 which had the highest percent silica of the three had the lowest percent deviation. Table IVB, on the other hand, supports this postulate; if sample 28 is disregarded. Furthermore, if data from table VB is substituted for the data for sample 28 in table IVB this trend is followed quite well. Thus, it is confusing as to whether or not the percent silica has any effect. Once more work is done on these samples the true



effect, if any, will become more evident.

The last sets of data presented in the data and results section deal with information collected during the course of the project which helped to further insight into the DCP.

Table VII shows the data used in preparing figures A1 and A2 which show the linearity of the DCP down to the part per billion, ppb, range. These figures helped to instill confidence in the data collected. This is due to the fact that all the data collected fell on figure A1 and higher which shows excellent linear response in that range. Furthermore, figure A2 allows a detection limit of about 30 ppb to be given to the DCP. Again, this is much better than would ever be required for any of the samples run in this project.

During the winter a number of samples were run for Professor Harlow of the Civil Engineering Department. The samples were of a salt based growth medium for begonia clones. It was proposed that somehow copper was contaminating the samples and that a test for copper should be done on the salt solution and the solutions containing plant tissue that had died.

The main benefit from this work was an appreciation of how important proper peaking and line choice were to the achievement of valid results. In the course of this discussion it has been mentioned several times that earlier results may have been high due to lack of experience with the DCP. Those cases were prior to this work. As seen by table VIII, the results were not reproducible nor were they accurate. The expected result was 0.025 ppm and values different and higher

were found. However, when a different spectral line was chosen the results became near ideal.

There are a couple of possible reasons for this sudden correlation which are applicable to the entire project. First of all, as mentioned earlier in regard to the calcium determination in tap water, the higher the wavelength the more interference. This may be due to the fact that with the echelle grating with a prism, as the wavelengths go up the order goes down and the lines become closer together and harder to resolve. Thus, they are subject to interference more readily. This is evidenced in table IX. When the line was switched from 5218.2 A to 3247.5 A, the results became accurate and precise.

Another lesson learned is that a certain wavelengths matrix effects may cause interference which boosts the results. There are a few references which claim that matrix effects cause "signal enhancements".<sup>8</sup> In order to avoid such interference a practice was developed of determining a value at one spectral line then another. If the data from the two lines agreed it was accepted. If, however, they did not agree a third line was checked and if the results from the third line agreed with either of the other lines the value was accepted. This was acceptable since it would be rare that two lines would be subject to the same interferences.

Thus, this side work helped to improve the precision and accuracy of the data and results obtained during the project.

### CONCLUSION:

The goal of this project was to develop a method for quantitatively analyzing geological samples with a moderate amount of silica. Moreover, the final method of preparing the samples, experimental procedure III, in conjunction with the DCP for elemental analysis proved to be fairly successful. The final results of only 9.95% deviation with an average deviation of only 0.505% are quite good. Moreover, it is felt that when work is picked up at this point in the future the method will prove to be extremely accurate, as well as, precise.

Furthermore, this process avoids the time consuming techniques and the use of highly corrosive HF formerly employed in such analyses. The analysis developed required only concentrated nitric acid, clean glassware and the DCP. Moreover, assuming all stock solutions needed were available the entire analysis of a sample from preparation to finish could be done in about four hours.

Another significant gain from this project was a true understanding for one of today's stronger analytical instruments; the DCP. When this project was begun, the experimenter only had experience with the theoretical aspects of the DCP. By the end of the project both the theoretical and operational facets of the DCP was understood quite thoroughly. As a result, this thesis serves not only as a report on how to analyze mineral samples, but also as a guide

to the use of the DCP for any analysis. The DCP has been referred to as a "laboratory workhorse". After completion of this work there is no doubt that this is true.

In summary, attainment of this success was not always simple. As seen in the procedure section, three different preparation methods had to be run and tested before a viable technique was developed. This frustration at first was taken as failure; however, in retrospect it was the impetus for original thought and development of thought patterns. This development after each set-back helped to speed the recovery from later delays.

Thus, more was gained from this project than just a successful analytical technique. Rather, a number of more subtle learning experiences were aquired. One of which was an appreciation for the time and skill required for any development process. Moreover, the development of some of these skills was felt. Most important of which were patience and a sense of feel for what goes on in the microscopic aspects of research and life in conjunction with the macrocosm.

## APPENDIX A

#### 2.4.3.16 STATUS MESSAGES

**STAT** A lighted pushbutton. When lit, it should alert an operator to incorrect or potentially degrading conditions or instrument parameters. Pushing this switch when lit causes the computer to display up to four integers corresponding to the various status messages. These are:

- 1 **OVERRANGE** Signal input to channel amplifier is too large. Analog to Digital converter is off scale. Reduce PMT voltage. Calculation of concentration will be inhibited.
- 2 **HIGH BACKGROUND** Background exceeds 50% of High Standard. Check source alignment and standard solutions.
- 3 **HIGH GAIN** Gain 50. Input to electronics is very weak. Automatic gain adjust is near maximum. One possible action is to increase PMT voltage.
- 4 **IMPROPER SEQUENCE** Operational error. Necessary information is missing. For instance, a Low Standard cycle must be performed before a sample cycle can be done. Calculation of concentration will be inhibited.
- 5 **HIGH STD CONC LOW STD CONC** High standard value is less than or equal to the low standard value. Calculation of concentration will be inhibited.
- 6 **HIGH STD INT LOW STD INT** Intensity of high standard solutions signal is less than or equal to the intensity of the signal produced by the low standard solution.
- 7 **ONE OR BOTH STD CONC NOT ENT** One or both standard concentration values not entered. Calculation of concentration will be inhibited.
- 8 **LOW GAIN** Gain 11. Input to electronics is quite high. Automatic gain adjust is near minimum. One possible action is to decrease PMT voltage.

APPENDIX B

### 2.4.3.1 ANALYZE SECTION

**DIRECT** This mode of operation allows signals to be processed in a "real time" situation with variable sampling of 1, 3 or 10 second time constants. All calibration functions are operable in this mode.

**INTEGRATE** The information is processed by accumulating the input signals across an appropriate capacitor.

**TIME** In the INTEGRATE mode, the signal is integrated for a period of time (seconds) set on these thumbwheels—01 to 99 seconds. These have no effect when in DIRECT mode.

**REPEAT** In DIRECT mode this switch instructs the processor to accumulate a number (1-9) of ANALOG to digital conversions as requested from the A/R, LO STD, or HI STD cycles.

While in the INTEGRATE mode, this switch will instruct the processor to automatically repeat integration periods for the set number of times (1-9).

#### 2.4.3.1.3 FUNCTION (CYCLE) PUSHBUTTONS

**A/R** Initiating this function will cause the instrument to automatically select the electronic gain necessary to amplify the input signal to a level corresponding to 50% full scale.

Following this, the appropriate mode operations are performed. The high standard value is displayed upon completion.

**LO STD** This cycle will handle incoming data and assign the resulting number to the low standard value calibration point. The stored low standard value concentration will be displayed upon completion. If, after a sample cycle, the "DIS LO" key is held down and "LO STD" switch is pressed momentarily, the low standard calibration will be updated. See Section 4.1.2.11.

**HI STD** The HI STD function is essentially a calibration update. If it becomes desirable or necessary at any time to recalibrate the instrument, this can be done using the HI STD pushbutton. The HI STD does not perform any auto-ranging. There are no gain changes. It is therefore necessary that the signals can still be accommodated with the previously set gain. Again, the high standard value will be displayed when completed. If, after a sample cycle, the "DIS HI" key is held down and the "HI STD" switch is momentarily pressed, the high standard calibration will be updated. See Section 4.1.2.11.

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### 2.4.3.1 MAIN CONTROL PANEL

The main panel control can be considered as subdivided in two subsections, the one to the left dealing with power switches and a standard value keyboard, and the one to the right dealing with the computational process and displaying the unknown concentration of the element under analysis.

All pushbutton switches are momentary except the latching PWR and PLS pushbuttons.

#### 2.4.3.1.1 STANDARD VALUE SECTION

**PWR** Power on/off switch for the computer electronics. This switch is located in the upper left-hand corner of the front panel.

**PLS** Power on/off switch for the SpectraJet excitation source. This switch is located in the lower left-hand corner of the front panel.

#### KEYBOARD:

**0-9** Used for entering data

**'** Decimal point

**C** Clear keyboard register

**ENT HI** Pressing this keyboard switch causes the computer to store the contents of the keyboard register as the HIGH STANDARD VALUE. The display shows the contents of the keyboard register whenever data is entered.

**DIS HI** This key requests the computer to display the current stored value of the HIGH STANDARD VALUE. Holding this key down and then momentarily pressing the "HI STD" pushbutton after a sample cycle will update the high standard calibration. See Section 4.1.2.11.

**ENT LO** Pressing this keyboard switch causes the computer to store the contents of the keyboard register as the LOW STANDARD VALUE.

**DIS LO** This key requests the computer to display the current stored value of the LOW STANDARD VALUE. Holding this key down and then momentarily pressing the "LO STD" pushbutton after a sample cycle will update the low standard calibration. See Section 4.1.2.11.

**SMP**

After the calibration curve has been set (defined by a high and a low standard), the SMP function is used to analyze unknown sample concentrations. NOTE: In DIRECT, once this cycle is initiated, it will continue to loop continuously converting, calculating and updating the display until interrupted by the initiation of another function switch.

The INTEGRATE mode will display the average result in concentration.

**RST**

This switch interrupts any of the function or cycle operations and resets them to their beginning. It does not affect previously completed cycles or calibration data.

**2.4.3.1.4 DISPLAY METER**

**ANALOG**

This meter is calibrated to follow the analog signal output of the channel card. The primary function of this meter will be for "peaking", i.e., maximizing signal throughout while locating spectral lines, optically aligning the spectrometer, or optimizing source position and parameters.

#### FOOTNOTES

<sup>1</sup>Douglas A. Skoog, Principles of Instrumental Analysis Third Edition (Philadelphia: Saunders College Publishing, 1985), p. 254.

<sup>2</sup>Andrew T. Zander, DC Plasma Emission Spectrometry Speeds Elemental Analysis (Barrington: Industrial Research and Development, February 1982), p. 149.

<sup>3</sup>Skoog, Principles of Instrumental Analysis Third Edition, p. 300.

<sup>4</sup>SpectraSpan IV Emission Spectrometer Operating Manual, (Andover: SpectraMetrics, Incorporated), section 2.1.2.

<sup>5</sup>Ibid., 2.1.2

<sup>6</sup>Ibid., 2.1.2.

<sup>7</sup>Skoog, Principles of Instrumental Analysis Third Edition, p. 303.

<sup>8</sup>SpectraMetrics, PlasmaLine, Vol. II No. 3, January 1982, (Andover: SpectraMetrics, Incorporated), p. 3.

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