

Water Quality Analysis of Calcium and Magnesium in the Great Smoky Mountains National Park

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R. Bruce Robinson, Ph.D, P.E

James L. Smoot, Ph.D, P.E.

John Shubzda, Research Assistant

Thomas W. Barnett, Graduate Research Assistant

**Dept. of Civil and Environmental Engineering
73 Perkins Hall, University of Tennessee, Knoxville, TN 37996
Office: 423/974-2530, FAX: 423/974-2669, E-Mail: rbr@utk.edu**

**Report Prepared For:
The National Park Service**

Cooperative Agreement No.: 1443-CA-5460-98-006 (Amendment 4)

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ABSTRACT

Water quality is monitored in the Great Smoky Mountains National Park by taking quarterly samples from many stream sites and seeps in the Park and by 15-minute measurements and weekly sampling at the Noland Divide watershed, which is a high elevation site sensitive to acid deposition. All samples are analyzed for pH, conductivity, acid neutralizing capacity and major anions and cations. The Noland Divide site also records flow, pH, and conductivity at 15-minute intervals in two small streams. The water quality monitoring program is integral to the Park's efforts to protect and manage its natural resources.

As part of the water quality monitoring, calcium and magnesium have been analyzed in all water samples because they are major dissolved species in the water and are important to vegetation and aquatic species. In September 1993, the previous investigators began using ion chromatography (IC) to analyze calcium and magnesium and began to realize that these analyses were suspect for several reasons including a poor ion balance. The current investigators evaluated the use of IC for calcium (Ca) and magnesium (Mg) analysis and have concluded that a different method of analysis is warranted. A search of relevant literature have shown both success and questions with using IC for Ca and Mg. Other researchers were contacted and were found to have similar problems with IC that this project experienced. The instrument manufacturer's representatives were not able to resolve the problem. Additionally, IC is not currently approved by the U.S. Environmental Protection Agency for Ca and Mg analyses in drinking water nor is it an approved method in *Standard Methods for the Examination of Water and Wastewater*. Extensive laboratory experiments identified a serious pH effect with IC analysis of Ca and Mg that could not be overcome. For these reasons, the current investigators have decided to use the more commonly used method of atomic absorption (AA) spectrophotometry.

Archived samples for the Noland Divide streamlets were re-analyzed by AA. Regrettably, there were insufficient Park-wide samples available for meaningful re-analysis. The AA analysis of Noland Divide samples underwent rigorous quality assurance/quality control (QA/QC) procedures, and indeed the AA values for Ca and Mg brought the ion balances into line. The re-analyzed samples showed little correlation with the previous IC measured Ca and Mg. Consequently, those IC values can not be sanctioned for use except as order of magnitude values. The re-analyzed Noland Divide samples were used to construct a regression model that was used to estimate missing values of Ca and Mg for Noland Divide. These models had adjusted r-squared values of 0.66 to 0.68. Ion balances using the regression based values of Ca and Mg were also close to zero as they should be.

Time trend analyses were performed with the AA values of Ca and Mg and showed declining calcium and magnesium concentrations of from 4.7% to 16.6% over ten years for the two streamlets at Noland Divide. The reason for this decline were not the subject of this paper but may be partly due to vegetation regrowth in the watershed, which would be consistent with declines seen in nitrate, but may also be partly due to acidification processes.

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INTRODUCTION

This report is an evaluation of problems that occurred previously with the analysis of calcium and magnesium by ion chromatography. The report also discusses relevant literature, dialogue with other investigators and instrument manufacturer's representatives, and extensive laboratory experiments that led to a switch in methodology to atomic absorption spectrophotometry. The results of re-analysis of available historical samples for calcium magnesium and mathematical modeling to predict missing values are also included as well as an analysis of time trends in calcium and magnesium concentration using the new, more accurate values at the Noland Divide (ND) watershed monitoring site.

History and Purpose of Project

The Little River in the Great Smoky Mountains National Park (GSMNP) is reported to be one of the top 100 best trout streams in the U.S. Also, several waters within the park are classified as Outstanding Natural Resource Waters (ONRWs) including the Little River, Abrams Creek, West Prong Little Pigeon River, and the Little Pigeon River. These resources need to be protected and the National Park Service is required by law to protect and preserve resources unimpaired for present and future generations. Regrettably, it appears that the water quality (especially pH) in high elevation streams has declined in the last 25 years and may now be threatening native brook trout populations. For example, brook trout are no longer found in some higher elevation stream reaches today which were populated earlier in the 20th century. This is part of a general concern that chronic and episodic stream acidification has progressed from the Northeast to the Southeast and pose threats to the resources of the Park. For these reasons, the Park established a long term monitoring site in a high-altitude, sensitive area of the Park, i.e., the Noland Divide site, in order to detect changes in acid deposition and to establish a data base that can be used in other efforts such as evaluation of impacts on vegetation and nutrient fluxes, and as an early warning of potential changes in other parts of Park. The Park also established water quality monitoring sites throughout the Park that are currently sampled quarterly. These monitoring sites provide a data base of stream quality which can be used to detect long term trends and changes in water quality that can harm native aquatic species and assist the Park in making decisions about managing its resources, e.g., best and worst locations to try to reintroduce lost native species.

Originally when the Park-wide monitoring program started in 1993, 160 sites were sampled monthly and 360 sites were sampled biannually. This was eventually reduced to 90 sites sampled quarterly with samples analyzed for pH, conductivity, acid neutralizing capacity (ANC), sulfate, chloride, nitrate, calcium, magnesium, sodium, potassium, and ammonium. Water quality monitoring at Noland Divide started in 1991 and consists of 15-minute readings of pH, flow, conductivity, and temperature, and weekly grab samples that are analyzed for the same constituents as Park-wide samples.

Until September, 1993, the United States Geological Survey (USGS) was contracted to analyze the dissolved ions noted above. The University of Tennessee investigators purchased a

Dionex ion chromatograph (IC) and began doing these analyses themselves in September, 1993. This was probably done in order to save money. As discussed below, quality assurance/quality control (QA/QC) problems occurred with this method. In February, 1998, cation samples were acidified to partially mitigate the QA/QC problems. For various reasons, the principal investigators for the project changed in January, 1999 to Dr. James L. Smoot and Dr. R. Bruce Robinson of the Civil and Environmental Engineering Department at the University of Tennessee. After lengthy evaluations of the QA/QC problems and evaluation of the suitability of the ion chromatograph for calcium and magnesium analyses, the decision was made in the summer of 2000 to use atomic absorption spectrophotometry for calcium and magnesium analyses. The report below documents the efforts and rationale behind this decision.

QA/QC Problems with Calcium and Magnesium Determination by Ion Chromatography

Ion chromatography (IC) is commonly used for analyses of anions, but is not commonly used for cations. There is a 1986 EPA method for cation analysis by IC, Method 300.7 - Dissolved Sodium, Ammonium, Potassium, Magnesium, and Calcium in Wet Deposition by Chemically Suppressed Ion Chromatography (EPA 1986), however, IC is not approved by EPA for cation analysis of drinking water nor is it an approved method in *Standard Methods* (APHA et al., 1998). Method 300.7 is fairly general, and the previous and present investigators have chosen to follow the recommendations of the instrument manufacturer's manual and the manufacturer's representatives. One significant difference between Method 300.7 and the manufacturer's methodology, is in the choice of eluents. Method 300.7 recommends using a hydrochloric acid:meta phenylenediamine dihydrochloride (mPDA 2HCl)(0.0015 N:0.0030 N) eluent for divalent cations, whereas the manufacturer has recommended using methanesulfonic acid (MSA). The use of mPDA 2HCl requires two sets of guard and suppressor columns, one for monovalent cations and one for divalent cations, because the divalent eluent is strongly retained in the column making it unsuitable for monovalent cations. The instrument manufacturer has on at least four different occasions by at least four different people reviewed the present and the previous investigator's methods including eluent and indicated it was satisfactory. (We may still at some time incur the extra expense and try the mPDA 2HCl eluent.)

Poor analytical results using IC for divalent cations in Smoky Mountains project is evidenced by poor ion balances, by apparent step increases in calcium and magnesium when IC was first implemented, and by poor results from round robin interlaboratory comparison samples. Figure 1 shows ion balances versus date for the northeast streamlet at Noland Divide. Results for the southwest streamlet are similar. For the period of September 1993 until February 1998 when unacidified samples were run by IC, the ion balances averaged 14.1% too high, i.e., the cations exceeded the anions. Figures 2 and 3 show calcium and magnesium concentrations versus time and show an approximate step increase in calcium concentration in September 1993 when IC analyses began and a step decrease in February 1998 when acidification of the IC samples began. Changes in magnesium are visually less apparent. Further evidence of poor analytical results for calcium and magnesium is the scores received from analysis of USGS round robin samples. These are natural water samples collected by USGS and sent to interested laboratories who then analyze

them and send their results back to USGS. USGS assigns a score depending on how close the analyses were to USGS's most probable results. The results for all analytes have generally been very good for UT except that calcium and magnesium have consistently received the lowest grades when unacidified samples were run by IC. Acidification of IC samples commenced February and did improve the ion balance and brought the calcium results back into line with historical values. But the reasons for this and whether a specific pH was required were unknown.

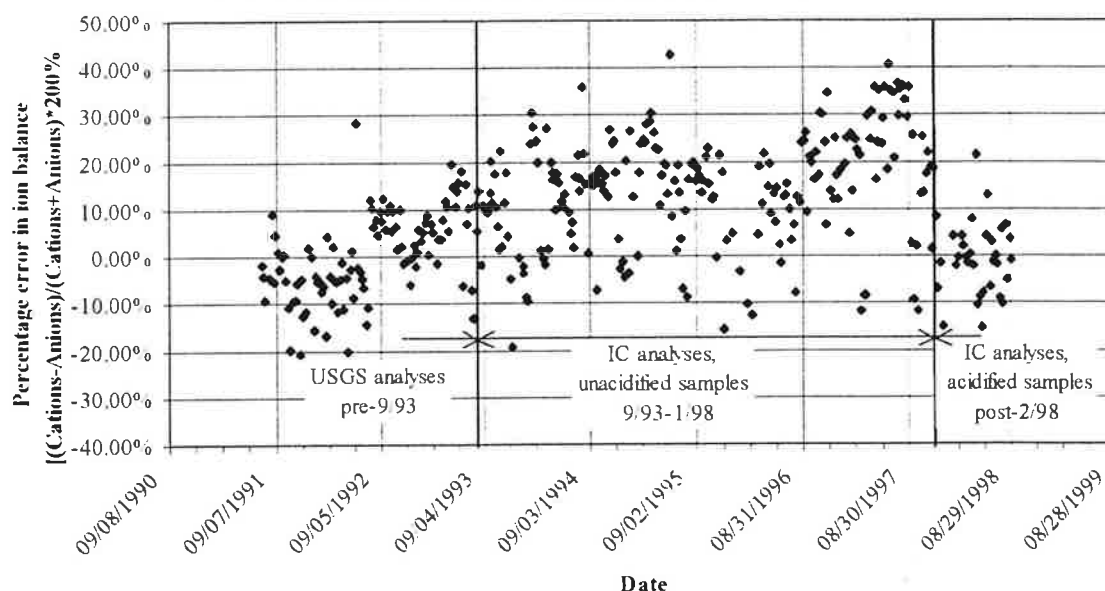


Figure 1. Percentage error in ion balance in NE streamlet of Noland Divide

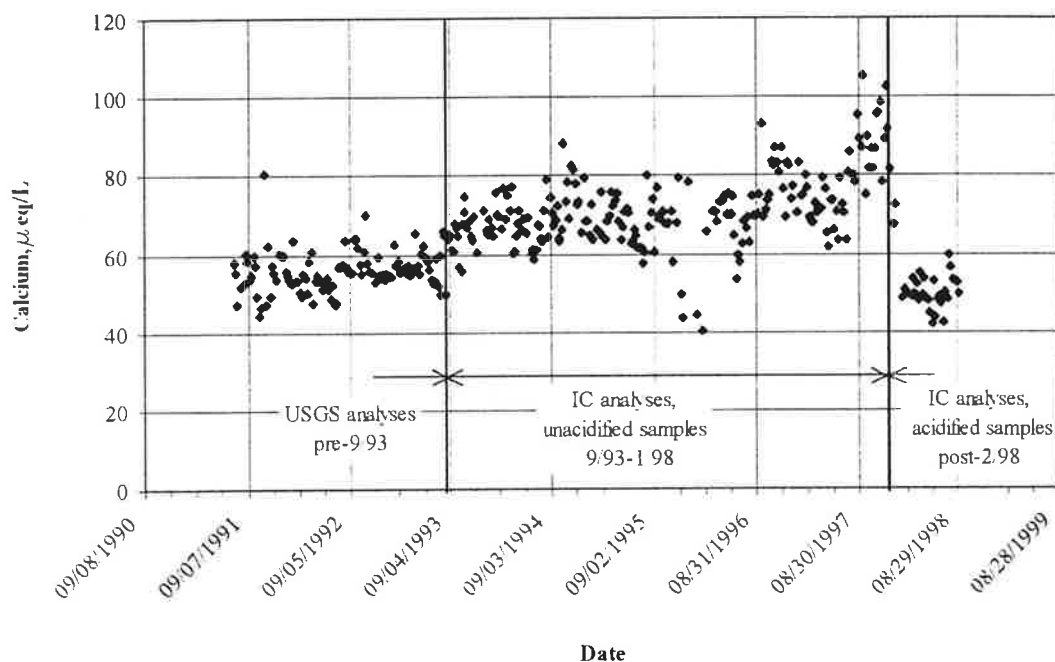


Figure 2. Calcium concentration in NE streamlet of Noland Divide

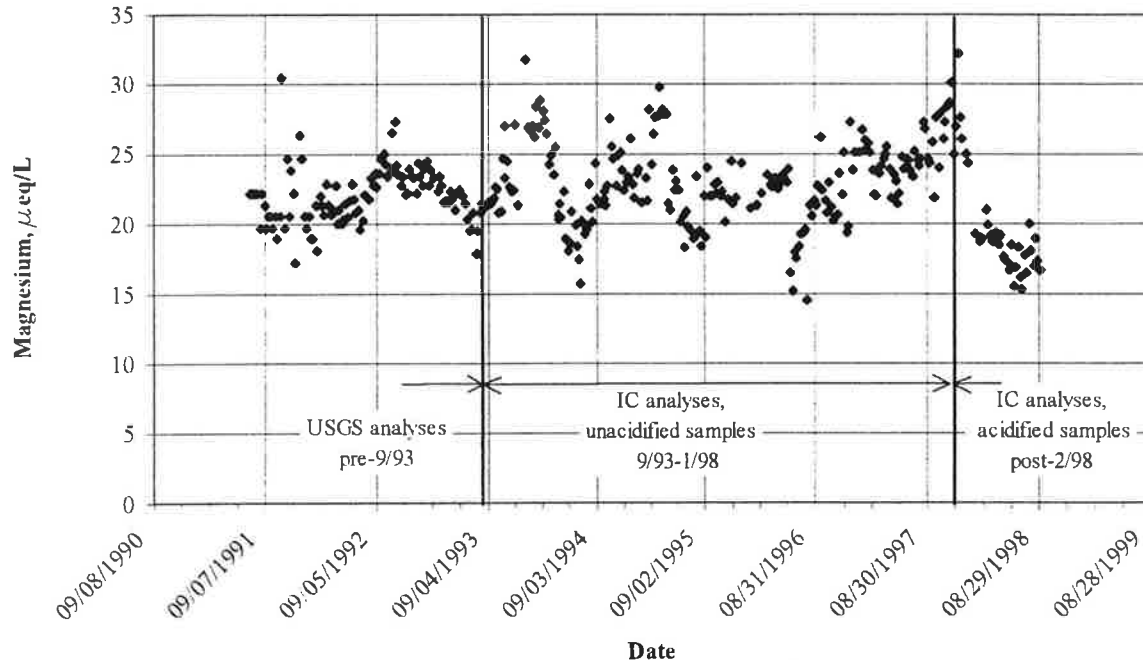


Figure 3. Magnesium concentration in NE streamlet of Noland Divide

The experiences of at least two other researchers, John Maben at the University of Virginia and Ed Drake of the USGS, have been identical to our experience and are discussed in more detail later.

Objectives

When the present investigators assumed responsibility for this project, the Park Service requested an evaluation of the methodology and QA/QC for calcium and magnesium. Specifically, the goals were:

- To evaluate QA/QC issues for calcium and magnesium
- To adopt revised sampling and analysis protocols if necessary
- To correct previous values of calcium and magnesium if possible

EVALUATION OF IC METHODOLOGY FOR CATIONS

Several investigations were pursued in order to resolve and improve calcium and magnesium analyses. These included:

- Use of an inductively coupled plasma instrument (ICP) in another lab on campus
- Assistance from the instrument manufacturer
- Discussions with other researchers experiencing similar problems
- Discussions with analytical chemists
- Literature search on IC analyses of cations and on pH effect of such analyses
- Extensive laboratory experiments to identify, quantify, and resolve the problem

ICP Analyses

There is one ICP instrument on the University of Tennessee campus, albeit an older model, operated by another department. The advantage of ICP analyses is that over a dozen metals and some other inorganics can be analyzed simultaneously. Several archived samples were analyzed by ICP, but regrettably the QA/QC samples submitted did not show acceptable results for reproducibility and accuracy.

Assistance from the Instrument Manufacturer

Four different representatives from the instrument manufacturer were consulted at various times beginning in summer 1999. The technical support group was first contacted and information about the problem, instrument, and protocols transmitted. The representatives ultimately decided that the problem was contamination of the sample loop, which was the same diagnosis given a couple of years earlier under the previous investigators. The entire sample loop was replaced upon the first diagnosis but no improvement was seen. Later contacts with one of the manufacturer's research chemists ultimately ended up with the same diagnosis but that person was relying on the previous technical memorandum. The last contact in October of 2000 produced a recommendation of operating the IC in chemical mode. The representative was kind enough to supply us with the equipment, but the experiments would take a couple of days and we have not had time to pursue this, especially since the results are very uncertain.

Discussions with Other Researchers Experiencing Similar Problems

The IC issue was discussed with John Maben in June, 2000 (Department of Environmental Sciences, Clark Hall, University of Virginia, Charlottesville, Virginia 22903, Tel: 804/924- 0590; Fax: 804/982-2300, jrm@virginia.edu). John has also been working on analysis of Appalachian waters. His group had tried for some time to get IC to work but eventually gave up and now use AA. Their waters are similar to ours - trout waters with conductivity about 10-30 $\mu\text{mhos/cm}$. The instrument manufacturer was not much help to them and only talked about dirty connections,

etc., identical to our discussions with the manufacturer. John said that many other people have experienced the same problems. John did try adjusting samples to a higher pH with NaOH and Na_2CO_3 and saw higher calcium with higher pH which again parallels our results.

The problem was also discussed with Ed Drake of the USGS laboratory in Atlanta in September, 1999. Ed's comments were similar to John Maben's comments and much more critical of the manufacturer. Ed said that a manufacturer's representative finally worked with Ed in his laboratory and left convinced that there was a problem with the manufacturer's instrument or methods. Ed was the source of the suggestion to acidify samples.

Discussions with Analytical Chemists

In March, 2000, Dr. James Chambers, analytical chemist with Chemistry Department at the University of Tennessee, was consulted. Dr. Chambers thought that the pH of the samples and of the standards should be at the same pH otherwise there might be a matrix affect. This comment was consistent with our group's thoughts. An experiment to adjust samples and standards was attempted but proved very difficult to get all samples at the same pH unless sufficient acid was added to lower the pH to less than 2. Adjusting samples and standards to close the same pH <2 did not resolve the problem. Dr. Chambers did not believe that the type of acid, i.e., HCl vs HNO_3 , should make a difference in acidification unless there was significant complexation between the calcium and chloride, but this seems unlikely. Nor did he think that there was an ionic strength matrix effect. Dr. Chambers did agree that plots of measured calcium versus standard additions calcium should yield a slope of one. Dr. Chambers did believe that IC should be adequate for analysis of cations. But he also did not have an explanation for why a lower pH should give lower calcium values especially since higher pH levels can lead to more complexation and precipitation of calcium. Dr. Chambers did remark that he thought we "knew what we were doing."

Literature Search on IC Analyses of Cations and on pH Effects

Chemical Abstract Service's electronic data base was searched to identify literature papers on cation analysis by IC and on pH effects on IC analysis. Several papers were obtained and reviewed, but none specifically targeted pH effects or analysis of divalent cations such as calcium and magnesium.

Waterworth (1997) used IC to measure inorganic cations and anions in pharmacopoeial samples. Methods were similar to our own. Methanesulphonic acid (MSA) was used as the eluent for cation analyses and the instrument was a Dionex DX500. Indeed MSA is used by most researchers. The concentrations of calcium and magnesium analyzed were 2.0 mg/L and 1.0 mg/L (100 and 100 $\mu\text{eq/L}$) respectively which are slightly higher but still in the same order of magnitude as Park samples. Waterworth reported recoveries of 98.3% and 98.9% of the expected concentration for calcium and magnesium respectively. The relative standard deviations for

replicates were 2.0% and 0.9% for calcium and magnesium respectively.

Döscher et al. (1995) used IC to analyze high-alpine snow-melt samples. They used MSA as the eluent and a Dionex instrument. In contrast to Waterworth's good results, Döscher et al. showed a figure comparing calcium analyzed by ICP with calcium analyzed by IC. The graph appeared to show that the IC results were about 15% higher than the ICP results which is consistent with our results. Attempts to contact the authors were unsuccessful.

Marchetto et al. (1995) compared the precision, i.e., the variance or scatter in the analyses of duplicate samples, of IC and AA for simulated rainwater samples and concluded that the precisions were comparable. This did not include a comparison of accuracy, i.e., how close were the analyses to the expected concentration. Tartari et al. (1995) also investigated IC precision and found relative standard deviations of 2-15% for cations. They used MSA as the eluent and a Dionex instrument.

Jauhianinen et al. (1999) used IC for analysis of ice core samples. They used MSA as the eluent and a Waters instrument. They did not report finding any problems in analysis of calcium or magnesium but did not appear to do investigations of accuracy.

Nguyen (1996) reported using IC for analysis of 93 ng/L of calcium (4.65 neq/L) and magnesium (7.65 neq/L) with good accuracy. An ion exchange column was used to preconcentrate the ions. They used MSA as the eluent and a Dionex instrument. Nguyen et al. (1999) reported similar positive results.

Gros and Gorenc (1997) evaluated calcium and magnesium at concentrations roughly 50 times higher than Park waters. They used MSA as the eluent and a Dionex instrument.

In summary, the literature is somewhat inconclusive on the issue of validity of using IC for cations and especially divalent cation such as calcium and magnesium. Two papers, Waterworth (1997) and Nguyen (1996), reported good agreement between expected and measured calcium and magnesium. Our laboratory protocol is nearly identical with Waterworth's. We use the same eluent (20 mM MSA) and the same guard and suppressor columns. Our instrument is older and his standards were made from 1000 ppm MgCl_2 and CaCl_2 whereas ours were purchased and made from $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ but this should make no difference. Döscher et al. (1995) appear to show a high bias in their measurements similar to our and other investigator's experiences. Other papers suspiciously only report precision and not accuracy of measurements.

Extensive Laboratory Experiments to Identify, Quantify, and Resolve the Problem

All the experiments were conducted by the current investigators at the University of Tennessee. All the experiments were entered into a laboratory notebook and any relevant information was placed into Excel spreadsheets along with the data.

Precision. To test the precision of the IC analysis, three natural samples representing high, medium, and low concentrations were chosen to represent the variability in Noland Divide and Park-wide samples. Five aliquots from each type of sample were prepared for a total of 15 samples. All samples were analyzed on the IC for sodium, potassium, calcium, magnesium, sulfate, and chloride. To minimize bias, the samples were analyzed in random order.

Results of the experiments indicate that the IC shows relatively good precision with the repeated measurements of the individual samples. Table 1 shows the calculated mean and relative standard deviation for each analyte and each sample. A sample with very low relative standard deviation percent indicates very little variation was detected in the repeated measurements and hence very good precision (Table 1). The IC responded with good precision over all three ranges of the experiment, except for potassium in the medium concentration range, where one outlier was detected.

Table 1. Precision results for selected analytes run on the IC. Mean results are give in $\mu\text{eq/L}$.

	Statistical Variables	Cl^-	SO_4^{2-}	Na	K	Mg	Ca
High Concentration Sample	Mean	17.20	99.42	31.23	5.31	79.82	206.95
	Relative Standard Deviation in %	4.2%	0.7%	0.9%	4.7%	0.7%	1.2%
Medium Concentration Sample	Mean	14.56	45.08	33.36	8.61	24.22	67.91
	Relative Standard Deviation in %	6.3%	0.7%	9.03%	19.6%	2.5%	2.2%
Low Concentration Sample	Mean	16.8	20.37	42.14	12.75	12.86	29.02
	Relative Standard Deviation	3.6%	0.5%	0.92%	3.2%	2.8%	4.6%

pH Effect on IC Ca and Mg response. Several experiments were performed to test the effect of sample pH (i.e., hydrogen ion concentration) and IC Mg and Ca response. A sample stock solution containing 1 ppm Ca, 0.6 ppm Mg, 0.57 ppm sodium and 0.39 ppm potassium was prepared using reagent grade standard solutions (i.e., 1000 ppm stock solutions). From this stock solution, three replicate samples were prepared for each pH. The samples were placed in 30 mL polyethylene bottles and acidified using 1.0 or 0.1 N ultra pure hydrochloric acid depending on the desired pH. The pH of the samples were 1.38, 1.7, 2.14, 2.59, and 3.06 after acidification.

Results from the experiments showed that the IC Mg and Ca had a negative response to

increasing hydrogen ion concentration, i.e. as the pH decreased, the IC Ca and Mg response decreased (Figure 4 and 5). Potassium also showed a slight negative response to increasing hydrogen ion concentrations (Figure 6). Only sodium did not show a change with pH (Figure 7). Therefore, as the pH of the sample decreased the ratio of measured divided by expected Ca and Mg significantly decreased indicating the pH of the sample does have an effect on the accuracy of the IC measurements. Based on these results, it was decided if the samples could be consistently acidified to a certain pH, the IC response should be valid, but achieving this was not possible in practice because of weakly-buffered, low-ionic-strength waters.

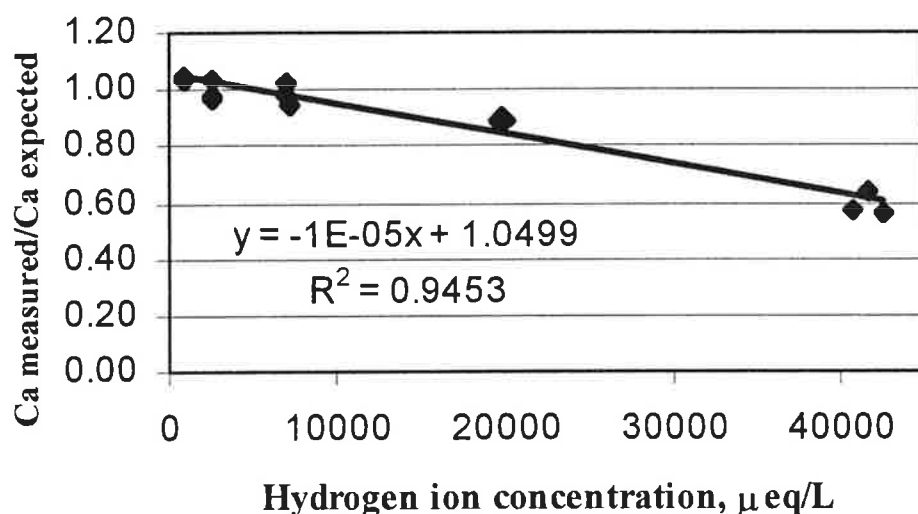


Figure 4. IC Calcium response with increasing hydrogen ion concentration.

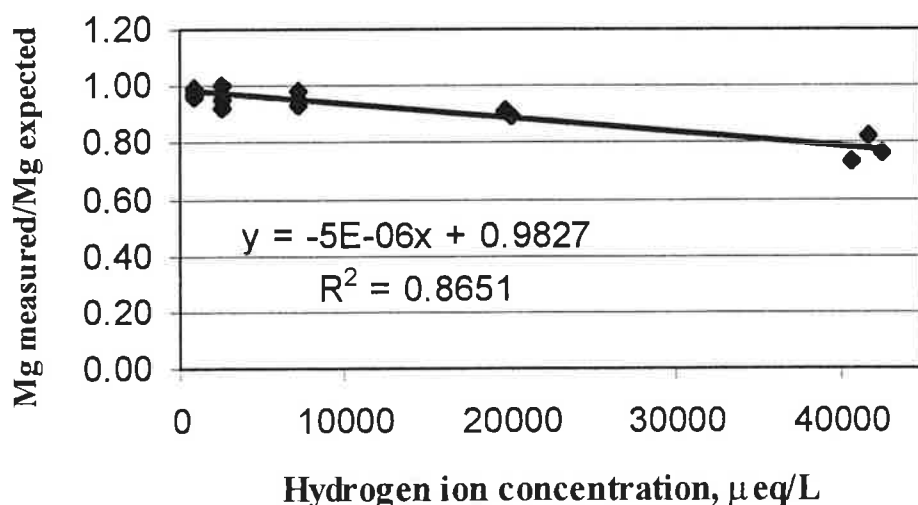


Figure 5. IC Magnesium response with increasing hydrogen ion concentration.

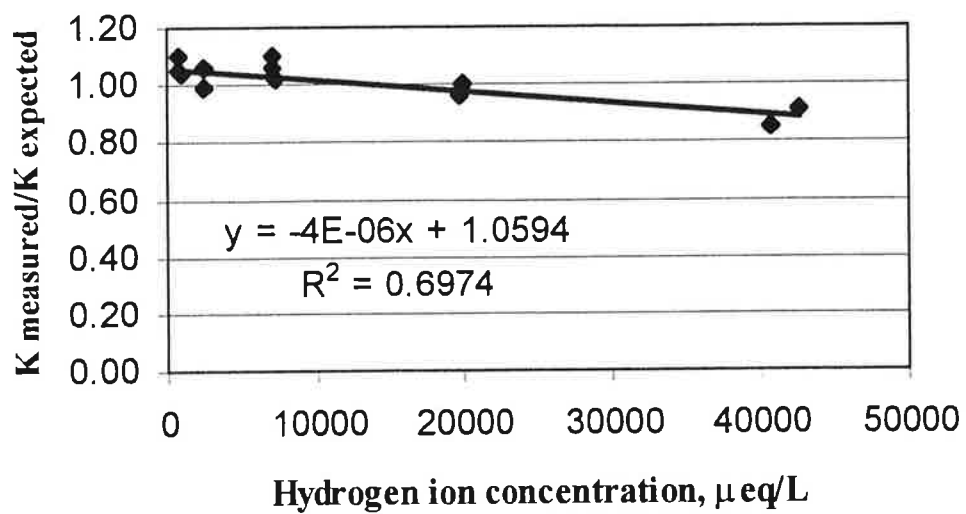


Figure 6. IC potassium response with increasing hydrogen ion concentration.

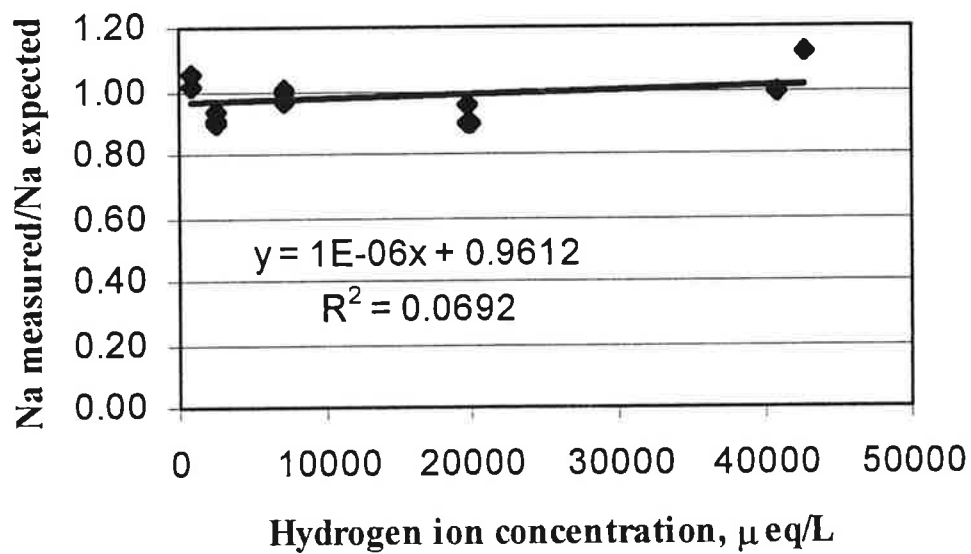


Figure 7. IC sodium response with increasing hydrogen ion concentration.

Accuracy/bias experiment. In order to assess the accuracy of certain analyte measurements made on the IC, a series of standard additions experiments were performed. A standard addition experiment is a QA/QC laboratory procedure to determine the most accurate value. A considerable amount of time and effort goes into sample preparation, analysis, and computation of results. Because of the time required for these experiments, nitrate and sulfate experiments were performed because of the interests in those analytes, and calcium and magnesium experiments were performed based on the poor inter-laboratory comparisons for those analytes.

Standard addition samples are performed by adding a series of known certified standard amounts of an analyte to a sample and measuring the instrument response. The instrument's response should be the sample concentration plus the known additions. The range of added concentrations must be around the sample concentration. Also the maximum concentration of analyte and added standard must be in the linear range of the instrument, and within the calibration of the instrument. By performing a linear regression on the results of the measured analyte verses the amount of analyte added to the sample the slope of the line should be around one (i.e. a one to one relationship), and the absolute value of the x-intercept should be the best estimate of the true concentration of the original sample. Any slopes for the regressions under 1 represent an underestimate of the true value, and any slopes over 1 represent an overestimate of the true value.

Anion Accuracy. Because nitrate and sulfate are very important to many people using these data, the accuracy of the IC measurements was tested for these anions. The slopes of the regressions for the standard addition experiments were very close to one, indicating IC was measuring the values very close to the "true" concentration within that sample (Figure 8 and 9). The highest mark available was also achieved, indicating excellent accuracy on those anions during an inter-laboratory experiments conducted with the USGS. Based on results of these experiments, and the results of the inter-laboratory comparisons, the anion data should not be in question.

Cation Accuracy. Since the measurements of the cations are in question with respect to divalent cations (i.e. Mg and Ca), a series of standard addition experiments were performed to test the accuracy of the divalent cation measurements made on the IC. The following is a list of the experiments and results:

- The first experiment involved a series of standard additions added to samples with relatively high and low concentrations of cations, similar to the range of concentrations associated with the Noland Divide and Park-wide samples (These samples were also the two samples used in the nitrate and sulfate standard additions experiments discussed earlier). The first standard addition received 15 μ L of 1000 ppm Ca and 15 μ L of 1000 ppm Mg to each 30 mL sample. The second standard addition sample received 30 μ L of 1000 ppm Ca and 30 μ L of 1000 ppm Mg, and so on. Therefore, for every 15 μ L added to the sample during the additions, 25 μ eq/L of Ca and 41.15 μ eq/L of Mg was added. The results of the experiment revealed a poor relationship with the added verses measured

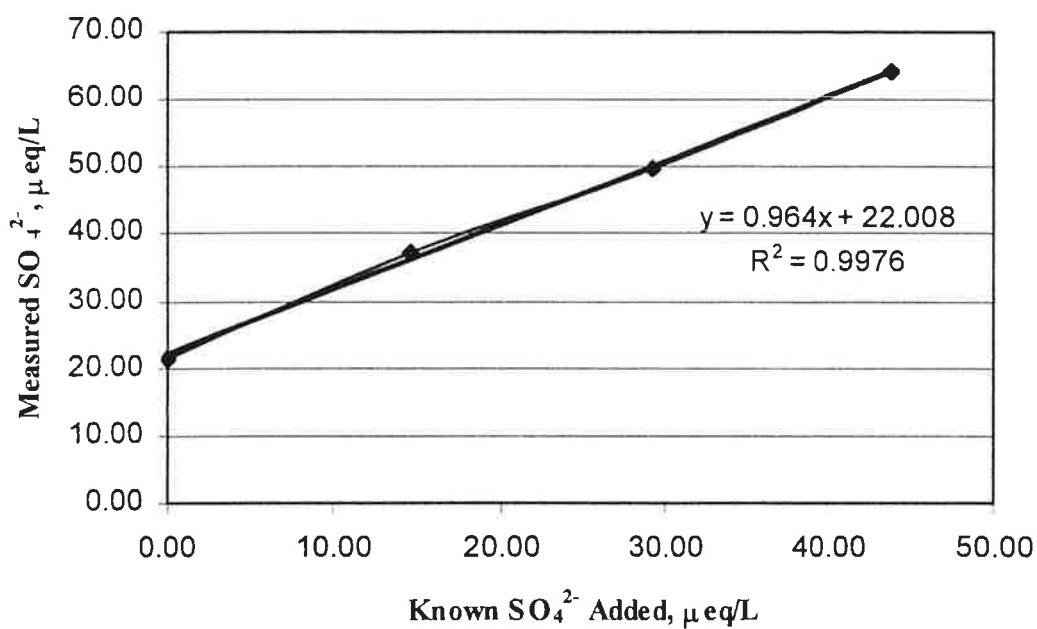


Figure 8. IC response to the sulfate addition experiments.

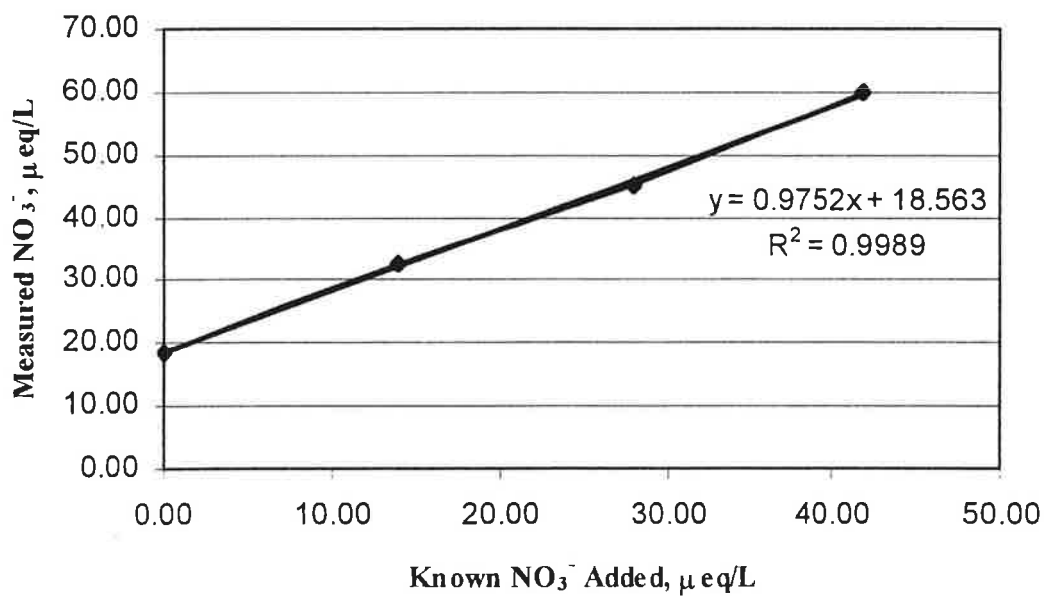


Figure 9. IC response to the nitrate addition experiments.

Ca and Mg additions, i.e., the slope of the regressions were not equal to one (results not shown). The method used in the experiment was questioned by the investigators, because 15 μ L of 1000 ppm of Ca and Mg were added to the samples. It was thought that using a micro-pipetter to deliver such a small amount of volume would cause some bias in the results.

- In the second experiment, a different method was chosen. For this experiment, two separate standard addition stocks were prepared for calcium and magnesium. The standard stocks were prepared by adding 8 mL of 1000 ppm of Ca and 12 mL of 1000 ppm of Mg. To each standard addition sample, 1 mL of Ca stock and 1 mL of Mg stock was added to 15 mL of sample plus 13 mL of deionized water. For the second addition sample, 2 mL of Ca stock and 2 mL of Mg stock was added to 15 mL sample plus 11 mL of deionized water, and so on. These series of one to one dilution experiments was thought to minimize the possible bias of adding such low volumes to the samples. Therefore, for every 1 mL of Ca and 1 mL of Mg stock added to each sample should have added 13.36 μ eq/L of Ca and 32.92 μ eq/L of Mg, respectively. The outcome of the results were the same, i.e., the slopes regressions were not equal to one (Figure 10 and 11). The bias in the results were attributed to the sample's pH, since it was determined sample pH has a significant influence on IC response to Ca and Mg measurements made on the IC (See Section on pH effects on IC response).
- For the third experiment, the same method of additions described above was applied to this experiment, in addition, the samples received equal amounts of 0.1 N hydrochloric acid. The results of these experiments also showed a poor relationship with the added versus measured Ca and Mg additions. Based on the results of the pH experiments, it was decided that the standards and sample additions were not acidified to a low enough pH.
- For the fourth experiment, the same methods were applied, but the pH of the standards and addition samples were adjusted to a pH low enough that it could be achieved by adding the same volume of acid to each sample and would swamp any variation in the original sample conditions. The pH was determined by the experiments described earlier. The results also revealed a poor relationship.
- Finally for the last experiment on the IC, the same procedures were followed as in the previous experiments except a different eluent suggested by Dionex was used. The outcome of the experiment was the same, poor accuracy with Ca and Mg measurements from the IC.

The same type of standard addition samples were analyzed on the AA to test the methodologies used during the IC experiments. The results of the experiment revealed a very good relationship with the added versus measured Ca additions, i.e., the slope of the regression was close to one (Figure 12). At this point in time, it was decided to change the protocols and start using the AA for divalent cation analysis.

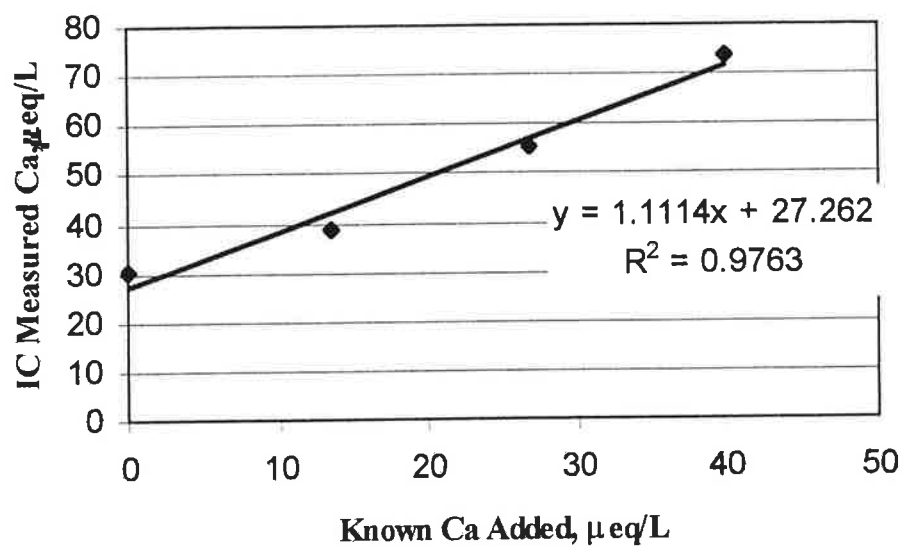


Figure 10. IC response to calcium addition experiments.

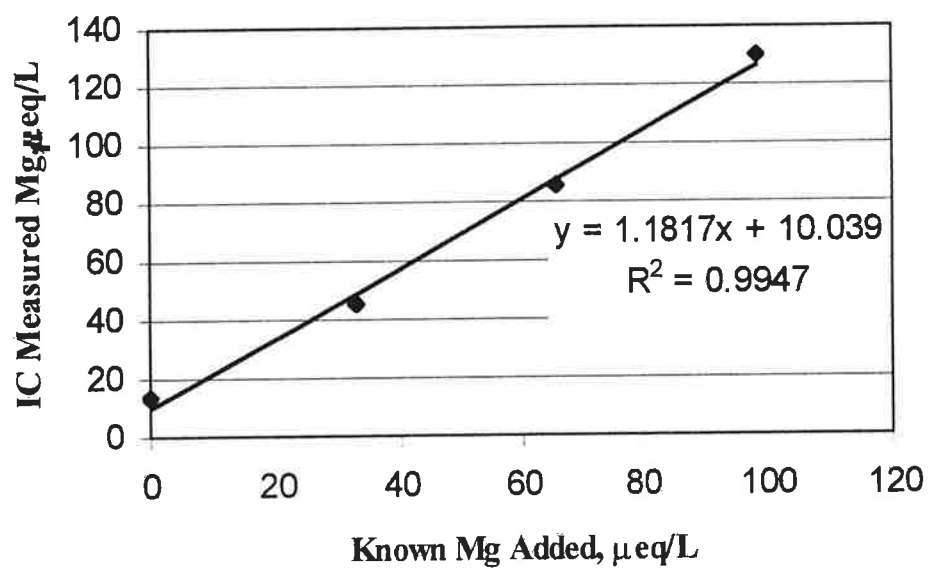


Figure 11. IC response to the magnesium addition experiments.

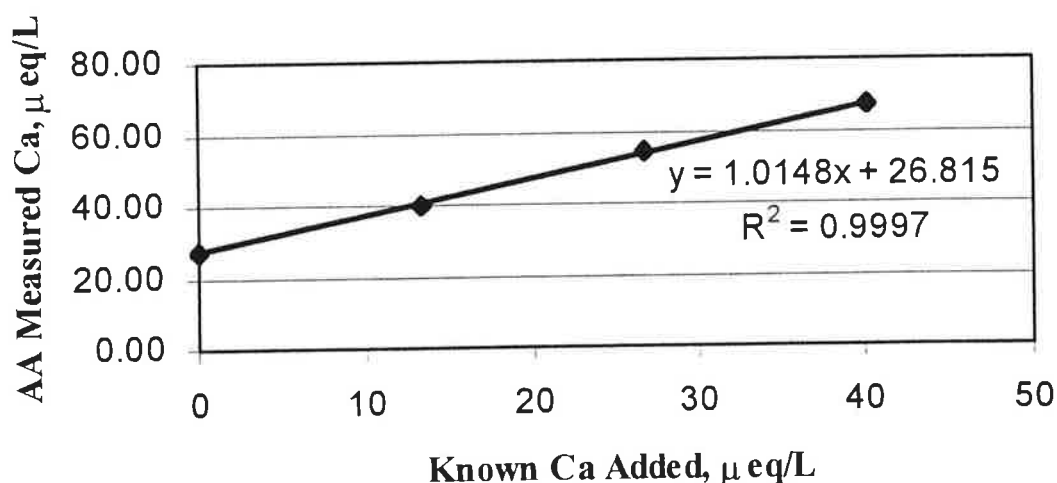


Figure 12. AA response to the calcium addition experiments.

Conclusion on Appropriateness of IC Measurement of Calcium and Magnesium

There is considerable conflicting information about whether IC is a viable choice for analysis of low concentrations of calcium and magnesium. The results of our own work, the experiences of investigators with the USGS and University of Virginia, results of Döscher et al. (1995), comments made by the instrument manufacturer's representatives and their lack of being able to identify any problem with our methods, lack of wide use of IC for cation analyses (few analytical labs use IC for this purpose) lead to a conclusion that IC is not suitable for calcium and magnesium. However, there are several papers in the literature that do report good results.

The experiments with IC showed significant QA/QC problems. Experiments with the method of standard additions showed that the IC measured more calcium and magnesium than what was added in the additions. Experiments also showed significant pH effects, i.e., the lower the pH of the sample, the lower the calcium or magnesium measured by the instrument. Attempts to remedy this pH effect by adjusting samples and standards to the same pH were impractical because of the weak buffering of the samples.

Based on the evidence and experience available and the need to move forward, the decision was made to use atomic absorption spectrophotometry for calcium and magnesium analyses. AA is widely used by analytical laboratories for these cations, and extensive QA/QC experiments on a sample Park water has shown excellent results. The experimental protocol is included in the appendix.

RE-ANALYSIS OF HISTORICAL CALCIUM AND MAGNESIUM SAMPLES

Most of the samples taken at Noland Divide over the years were taken in duplicate and the duplicate sample stored. This allowed them to be re-analyzed by AA. The results of the re-analyses could then be used to evaluate trends in calcium and magnesium concentration over time. The results might also be combined with other measurements to build a mathematical model capable of estimating missing values at Noland Divide and in the Park Wide monitoring program. Regrettably, some of the stored samples had been previously subsampled or otherwise sacrificed in attempting analyses by ICP. This limited the samples available for re-analysis. Also, very few Park Wide samples had been saved over the years.

Methodology for Re-analysis of Ca and Mg

Only samples that had clearly not been sub-sampled before were analyzed because there was concern that previously sub-sampled samples had not been acidified and materials may have precipitated or sorbed to the bottle walls. A total of 187 samples were chosen from the NE and SW streamlets. The dates of these samples ranged from May 18, 1993 to August 25, 1998. Storage samples prior to May, 1993, were previously sampled by the previous investigators and were not included in the analysis. Initially, only 20 samples were analyzed to test the methodology of the experiment. The initial experiment had very good results, and the rest of the samples were then analyzed.

The samples were prepared by acidifying the entire bottle to $\text{pH} < 2$ with ultra pure nitric acid. For every 125 mL sample, 0.2 mL of acid was added using a micro-pipetter. The samples were placed on a shaker overnight to maximize the amount of Ca and Mg placed back into solution that might have precipitated or sorbed to the walls of the sample container.

All sample preparation and analysis followed previously developed AA protocols by the current investigators and which are included in the appendix.

Results of the Experiment

A series of QA/QC samples were used during the experiments and closely monitored throughout the entire run of samples. Some of the QA/QC samples included; reagent blanks, sample acidification blanks, replicates, and spiked samples. The sample acidification blanks and reagent blanks showed no traces of Mg or Ca. Therefore, the samples were not contaminated by the acidification process or the ionization suppressant (Table 2). Replicates and spiked samples were also analyzed during the experiments. A spike sample is a procedure where a known concentration is added to a sample and the difference between the unspiked and spiked sample is measured. The difference divided by the expected is the % recovery. A replicate sample is a QA/QC procedure where a sample is collected or processed separately from the original. The replicate sample results are compared to the original and % difference is calculated. Table 2

shows very good QA/QC results.

Table 2. Average QA/QC results of the AA analysis for magnesium and calcium.

QA/QC Procedure	Mg	Ca
R-squared of the calibration curve	0.9987	0.9994
Acidification Blanks	0.0	0.0
Reagent Blanks	0.0	0.0
Absolute Average Value of % Spike Recoveries,	99.57% (n=12)	101.52% (n=8)
Absolute Average Value in % Difference in Replicates	2.20% (n=7)	0.06% (n=17)

In the original data set there appeared to be a step trend and increasing Ca concentrations over time (Figure13). After plotting the results of the AA measurements against the original Ca concentrations the apparent trends no longer exist (Figure13). The Mg concentrations didn't show a similar step trend over time and the reanalysis revealed lower Mg concentration measured on the AA (Figure 14). Long term trends in the Ca and Mg concentrations are discussed in detail in a later section of this report.

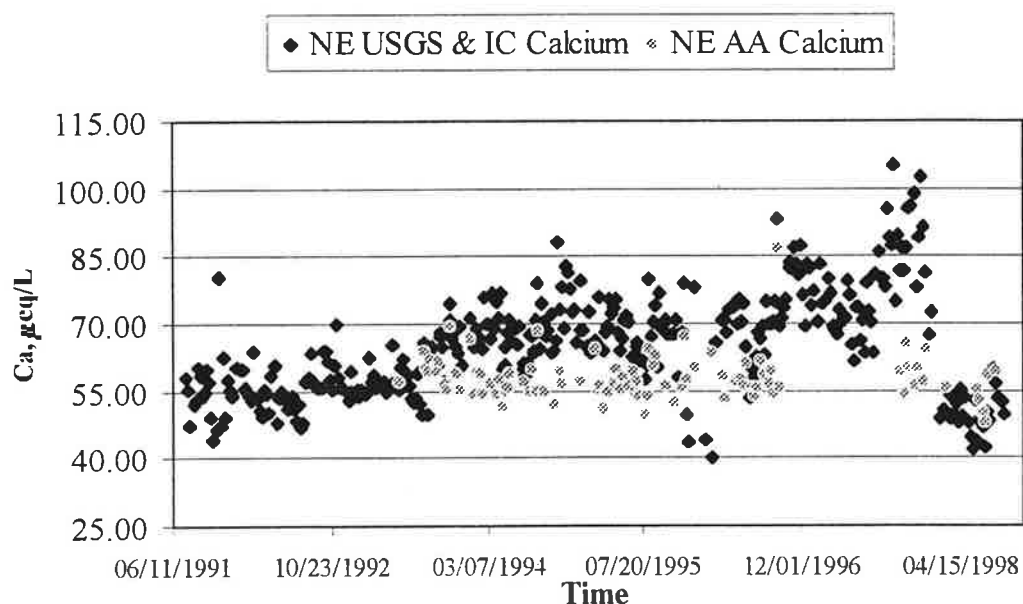


Figure 13. Ca by IC and AA versus time.

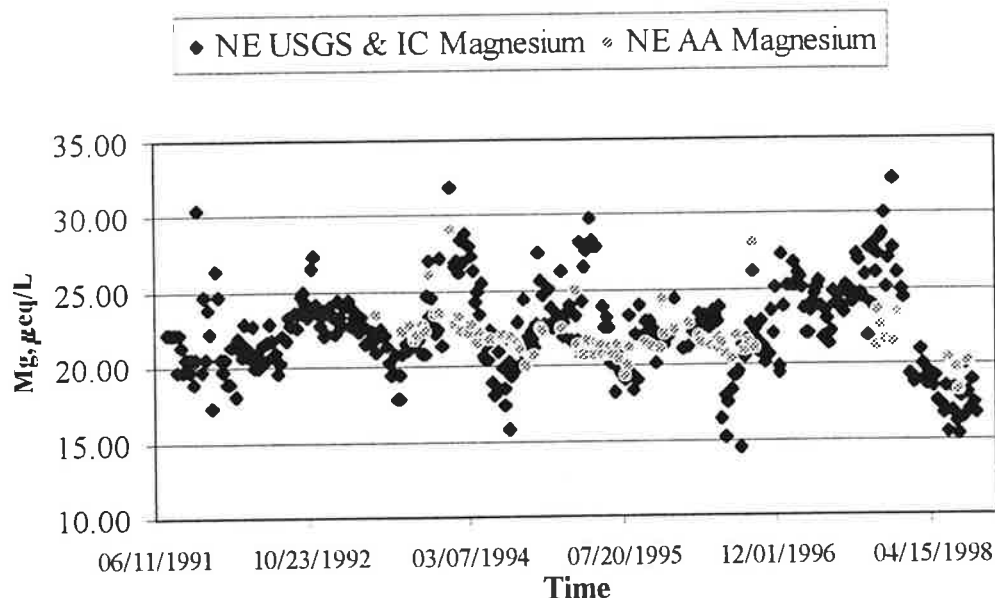


Figure 14. Mg by IC and AA versus time.

Estimation of Missing Calcium and Magnesium Values

Because many of the samples taken at Noland Divide and in Park Wide sampling were either no longer available or were deemed unsuitable for re-analyses, mathematical models were constructed in order to predict these missing values of calcium and magnesium in order to assist researchers needing weekly values. Two types of models were investigated: 1) multiple linear regression (MLR) and 2) artificial neural networks (ANN's).

Multiple linear regression methodology. Several regression modeling approaches were tried including separate models on each streamlet, i.e., the NE or SW, a combined model on both streamlets, forward selection regression, backward elimination regression, and stepwise regression. Based on the preliminary results, stepwise regression on the NE and SW combined database was chosen. Variables entered the stepwise regression at an F value ≤ 0.05 and left at an F value ≥ 0.1 . The dependent variable of the MLR was either the AA calcium concentration or the AA magnesium concentration in $\mu\text{eq/L}$. The independent variables that the stepwise MLR could chose from were cumulative day, $\sin(\theta)$, $\cos(\theta)$, conductivity, temperature, sodium, potassium, ammonium, calcium measured by IC, magnesium measured by IC, sulfate, chloride, nitrate, hydrogen ion, and total anions. The terms $\sin(\theta)$ and $\cos(\theta)$ reflect seasonal effects with θ ranging from 0 to 2π as the days progress from January 1 to December 31. Regression of the log transform of these variables was also tried but did not show an improvement. SPSS (SPSS 1999) was the statistical package chosen to run on a desktop computer.

In order to have an acceptable regression model in the stepwise regression, several criteria had to be met. Cook's Distance Measure was used to evaluate high leverage records. Here, record refers to all the variable values associated with a specific sample. According to one reference (Anderson et al., 1993), if Cook's Distance Measure > 1, then there is a possible influence problem due to that record. In this case, no record exceed 1.0. Collinearity was evaluated with condition indices calculated by SPSS. If the condition index exceeded 30, then serious collinearity was considered to exist (SPSS 1999). The model with the highest adjusted r-square that did not exceed a condition index of 30 for any variable was used. Residual plots for each independent variable in the model plotted were inspected as whether the residuals were scattered randomly about zero indicating no biases in the model. DfBetas were also inspected for each record to determine if any one record would greatly alter the regression coefficients if omitted.

The detailed SPSS regression results for calcium and magnesium are given in the appendix. The tables below summarize the coefficients, i.e., β 's, for the calcium and magnesium regressions. The adjusted r-square for the calcium model is 0.683 and for magnesium is 0.657. The tables also give statistics on the β 's as well as the 95% confidence bounds. The last column gives an indication of the leverage associated with the two records giving the highest Cook's Distance Measure. These two records were deleted and the model rerun. The last column gives the β 's without these records and shows some, but not significant change in the β 's. Plots of residuals are also included in the appendix and show a reasonable scatter of residuals about zero for all variables and do not show any clear biases.

Table 3. Regression results for calcium (adjusted r-square = 0.683).

Variable	β	Standard Error	t	p	95% CI Lower Bound	95% CI Upper Bound	β w/o leverage points
Constant	45.754	2.698	16.959	0	40.43	51.077	43.713
SO ₄ ²⁻	0.148	0.05	2.935	0.004	0.049	0.248	0.177
Sin(θ)	-1.869	0.365	-5.125	0	-2.589	-1.149	-1.728
Flow, L/s	0.33	0.055	6.016	0	0.222	0.438	0.283
Stream ID (0 = NE, 1=SW)	-3.906	0.825	-4.735	0	-5.533	-2.278	-3.359
Cumulative day (1/1/91 = 1)	-0.00185	0	-3.888	0	-0.003	-0.001	-0.00205
Conductivity	0.469	0.146	3.22	0.002	0.182	0.757	0.560

Table 4. Regression results for magnesium (adjusted r-square = 0.657).

Variable	β	Standard Error	t	p	95% CI Lower Bound	95% CI Upper Bound	β w/o leverage points
Constant	17.2	0.902	19.058	0.000	15.419	18.980	16.181
IC Magnesium	0.135	0.027	4.962	0.000	0.0810	0.188	0.129
Cumulative day (1/1/91 = 1)	-0.000866	0.000	-5.218	0.000	-0.001	-0.001	-0.000895
Conductivity	0.0156	0.048	2.253	0.001	0.061	0.251	0.237
Stream ID (0 = NE, 1=SW)	-1.678	0.200	-8.410	0.000	-2.072	-1.284	-1.464
Flow, L/s	-0.09564	0.015	6.278	0.000	0.066	0.126	-0.07526

It is significant that the variables in the model tend to be physical and not chemical. For example, the previous calcium concentrations measured by IC were not selected by stepwise regression as significant. Indeed, the Pearson correlation coefficient, r_{xy} , between AA and IC measured calcium is only 0.373 which is consistent with the poor results by IC. The low correlation also indicates that IC was not in error by a consistent amount or percentage. Regrettably, it must be concluded that the previous IC calcium measurements are of little value except as order of magnitude estimates. The Pearson correlation coefficient, r_{xy} , between AA and IC measured magnesium is higher at 0.523 and was selected in the magnesium regression. Because flow and stream ID appear in the model as significant variables, which would not be available for Park Wide data, and because the readily available chemistry data did not appear in the regression models, it was concluded that developing calcium and magnesium predictions for Park Wide data should not be attempted. Indeed, a regression model based just on the chemistry variables (sodium, potassium, ammonium, calcium measured by IC, magnesium measured by IC, sulfate, chloride, nitrate, hydrogen ion, and total anions, and conductivity) and cumulative day produced a regression model with only three significant variables, i.e., sulfate, conductivity, and cumulative day, and with an adjusted r-square of 0.576. The investigators do not have such a model would adequately represent water quality conditions outside the Noland Divide streamlets.

Point estimates and confidence interval estimates were made for all the records used in the regression. The confidence interval is not constant but is larger for points farther away from the mean. However, as an indication of error, the average upper and lower 95% confidence levels for these point estimates is 6.8 $\mu\text{eq/L}$ (12.5%) for calcium and 2.29 $\mu\text{eq/L}$ (11.2%) for magnesium. Note that the confidence interval for the point estimates is not the same as the confidence interval for the mean expected values from the regression, but instead is larger due to the variance of individual measurements. The regression equation was applied to all the Noland Divide samples and a table is included in the appendix. Users are cautioned not to use the estimated values of

calcium and magnesium for time trend analyses but rather should use the AA determined values of calcium and magnesium only.

Artificial Neural Networks. The calcium and magnesium in the streamlets at Noland Divide are functions of many complex interactions including rainfall, the hydrologic interactions associated with runoff, interflow and groundwater flow, the chemical kinetics and equilibria interactions between water and soil and organic materials, and seasonal effects. It is reasonable to believe that this constitutes a highly non-linear system. Multiple linear regression is limited on how well it can accurately depict such systems. Artificial Neural Networks (ANN's) are very useful for modeling such nonlinear systems.

ANN's can be viewed as function approximators. By fine-tuning a set of parameters known as weights ($w_1, w_2, \dots, w_l$) and biases (b), the network searches for the relationship between a given set of input variables ($p_1, p_2, \dots, p_l$) and output variables ($a_1, a_2, \dots, a_l$). The multi-layer perceptron (MLP) with as few as one hidden layer and a nonlinear activation function has proved to be a universal function approximator. Therefore, it was the type of network employed in this research. In order to let a network learn to map inputs to outputs, the learning algorithm, a procedure that a network uses to adjust its weights and biases, is implemented. Typically, the data set is divided into three fractions. One fraction is used to train the network, i.e., find the values of weights and biases. To prevent overtraining and mere memorization of the input-output relationship, another fraction of the data set is used to validate the network, i.e., the neural network is tested against these data and when the predictions begin to worsen, the training ceases. Finally, the last fraction is used to test how well the resultant network predicts the data it has not seen before. The development of the best ANN requires art and experience because there are many choices the user can make including choice of activation function, number of hidden layers, number of perceptrons in each layer, and the training rate.

Two different ANN packages: Neural Connection 2.0 (SPSS, 1997) and Clementine (Integral Solutions Limited, 1998). Clementine gives the user fewer options on the choice of ANN and gives no information on what type of activation function is used. Neural Connection gives the user more flexibility and information about its methodology. Several different networks were tried with each package. Graphs of actual versus predicted calcium are shown in the figures below along with the root mean square (RMS) error for an ANN generated from each package and for multiple linear regression discussed above.

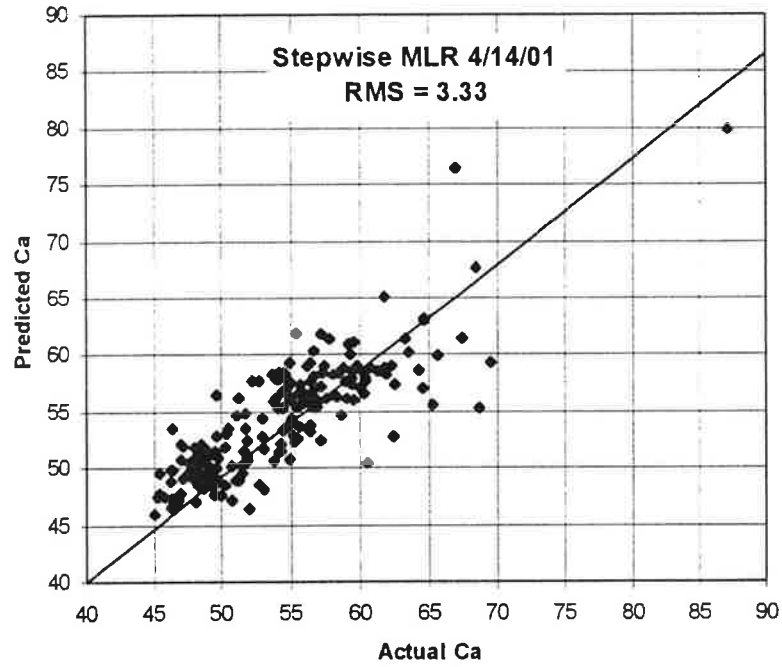


Figure 15. Actual vs predicted calcium from multiple linear regression

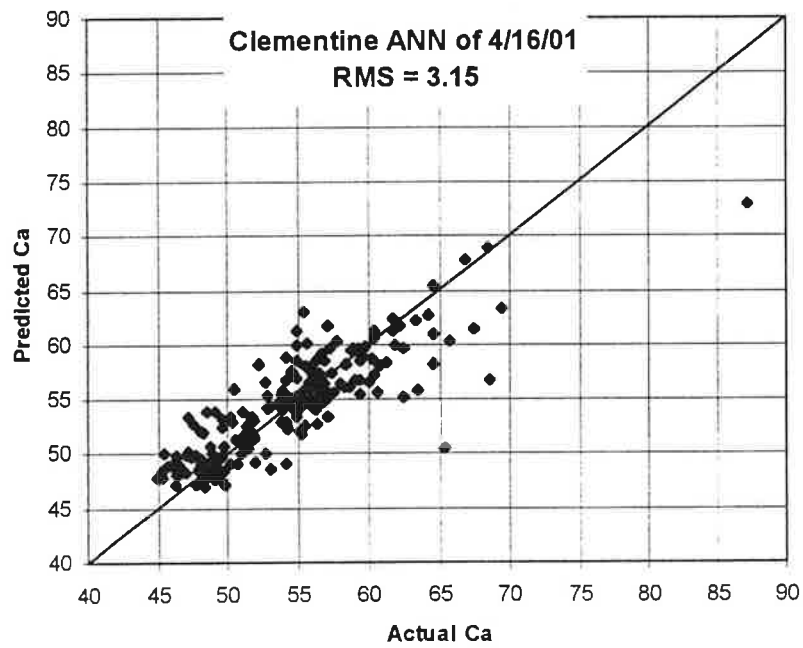


Figure 16. Actual vs predicted calcium from Clementine ANN

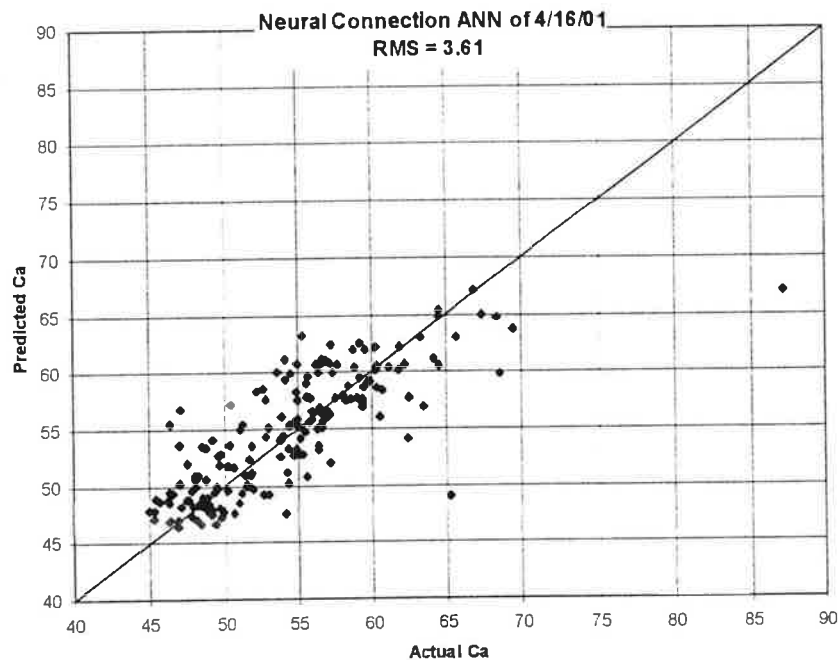


Figure 17. Actual vs predicted calcium from Neural Connection ANN.

Graphs of predicted and actual calcium versus case number are shown in the figures below for the best ANN and the MLR and show that predicted versus actual track each other well.

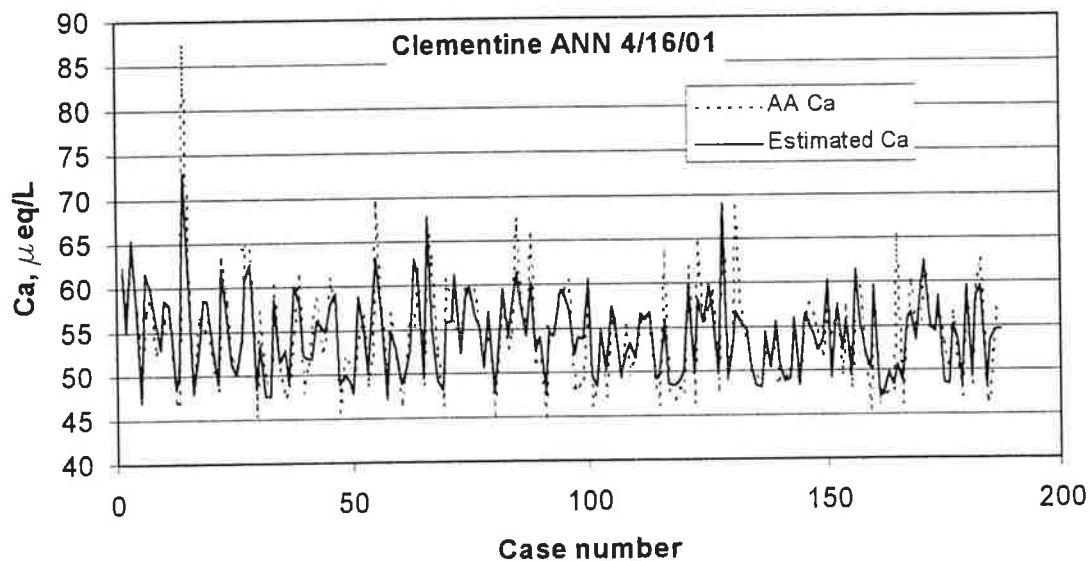


Figure 18. Clementine ANN predicted and actual calcium versus case number.

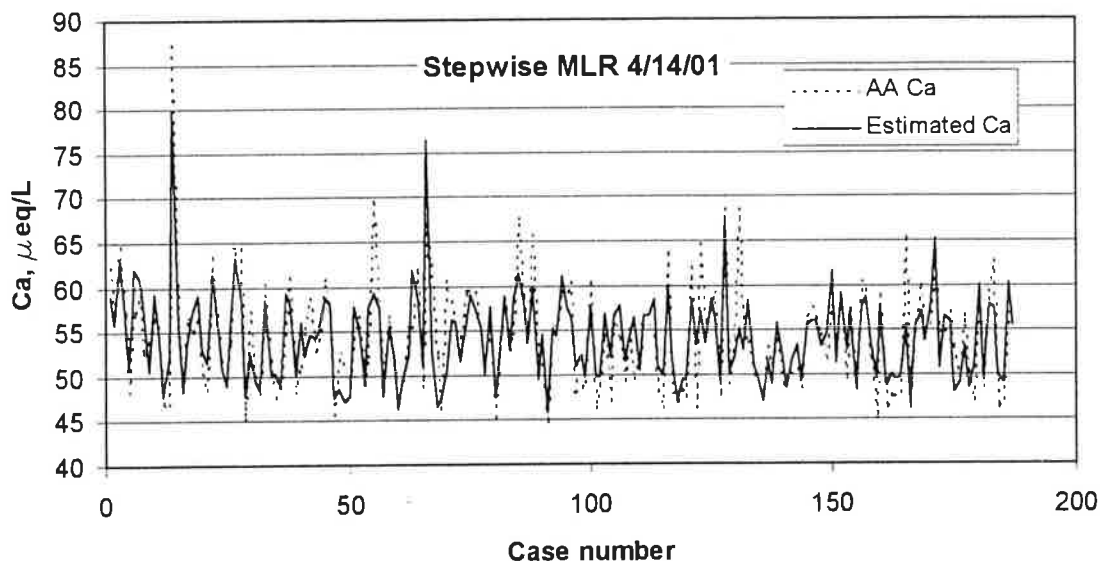


Figure 19. MLR Predicted and actual calcium versus case number.

It was decided not to use ANN's for prediction because they did not significantly improve the prediction for calcium and valuable statistical information and insight on the most important variables would be lost. Also, the ANN would not be easily used by other researchers. Instead, the MLR models were used.

Improvement in ion balances. The multiple linear regression models given earlier were used to estimate calcium and magnesium concentrations for all ND samples from September 1993 through October 30, 1998 which were all the records available at the writing of this report. The table below summarizes ion balances for samples analyzed by the USGS prior to September 1993, ion balances using IC values for calcium and magnesium and ion balances using calcium and magnesium estimated from the regression models. The ion balance is the difference between the sum of all cations in $\mu\text{eq/L}$ minus the sum of all anions expressed as a percentage of the average cation and anion concentration. The ion balance is theoretically zero because there must be as many positive charges as negative charges in water. As can be seen in the table, the IC based balances are significantly off whereas the ion balances based on USGS analyses and the ion balances based on estimated values of calcium and magnesium are close to zero.

Table 5. Summary of ion balances.

Ion balance basis	NE streamlet at ND	SW streamlet at ND
USGS analyses (pre-9/93)	0.63%	1.89%
IC values of Ca and Mg	12.37%	18.14%
AA values of Ca and Mg	2.26%	5.72%
Estimated Ca and Mg	-1.18%	2.39%

TIME TRENDS FOR CALCIUM AND MAGNESIUM

The calcium and magnesium concentrations obtained from the atomic absorption spectrophotometer were modeled to determine if long-term time trends and seasonal variations exist. Two types of models were investigated: 1) a simple linear regression model and 2) a multiple linear regression model.

A simple linear regression model, with the cumulative Julian day as the independent variable, was used to investigate the existence of long-term trends in calcium and magnesium concentrations. The regression results for each streamlet and constituent can be found in table 6. Also, the calcium and magnesium time trends for the southwest streamlet can be viewed in figures 20 and 21, respectively. The results from this modeling exercise indicate that a decreasing concentration trend does exist for both calcium and magnesium in both the northeast and southwest streamlets.

Table 6. Regression time trend analysis results (simple linear regression).

Variable	Coefficient	Standard Error	t	p	95% CI Lower Bound	95% CI Upper Bound
Southwest Streamlet (calcium, adjusted r-square = 0.0809)						
Constant	54.929	1.499	36.628	2.937E-56	51.950	57.908
Cumulative Julian Day	-0.00250	0.00083	-3.0164	.00332	-0.00414	-0.00085
Southwest Streamlet (magnesium, adjusted r-square = 0.1035)						
Constant	20.874	0.491	42.525	7.787E-62	19.898	21.848
Cumulative Julian Day	-0.00092	0.00027	-3.4098	0.00097	-0.00146	-0.00038
Northeast Streamlet (calcium, adjusted r-square = -0.0042)						
Constant	59.217	1.757	33.705	1.464E-53	55.728	62.706
Cumulative Julian Day	-0.00077	0.00099	-0.7819	0.43627	-0.00273	0.00119
Northeast Streamlet (magnesium, adjusted r-square = 0.1167)						
Constant	23.482	0.522	45.012	1.858E-64	22.446	24.518
Cumulative Julian Day	-0.00107	0.00029	-3.6454	0.00044	-0.00165	-0.00049

A multiple linear regression model, using cumulative Julian day, $\sin(\theta)$, and $\cosine(\theta)$ as the independent variables, was utilized to determine if seasonal variations in calcium and magnesium concentrations are present. The results of this modeling are presented in table 7. The results indicate that there are significant seasonal effects on calcium and magnesium in both streamlets.

Table 7. Regression time trend analysis results (multiple linear regression).

Variable	Coefficient	Standard Error	t	p	95% CI Lower Bound	95% CI Upper Bound
Southwest Streamlet (calcium, adjusted r-square = 0.1412)						
Constant	54.916	1.450	37.862	1.154E-56	52.034	57.3798
Cumulative Julian Day	-0.00247	0.00080	-3.0683	0.00285	-0.00407	-0.00087
$\sin(\theta)$	-1.6347	0.6198	-2.6376	0.0099	-2.8662	-0.4033
$\cosine(\theta)$	0.6760	0.6167	1.0960	0.2760	-0.5495	1.9074
Southwest Streamlet (magnesium, adjusted r-square = 0.1685)						
Constant	20.830	0.473	44.038	3.279E-62	19.890	21.770
Cumulative Julian Day	-0.00085	0.00026	-3.2471	0.00164	-0.00137	-0.00033
$\sin(\theta)$	-0.0421	0.2021	-0.2083	0.8354	-0.4437	0.3595
$\cosine(\theta)$	0.6034	0.2011	3.0002	0.0035	0.2038	1.0031
Northeast Streamlet (calcium, adjusted r-square = 0.0845)						
Constant	59.380	1.681	35.315	1.589E-54	56.040	62.721
Cumulative Julian Day	-0.00085	0.00096	-0.8869	0.3775	-0.00274	0.00105
$\sin(\theta)$	-2.0872	0.7193	-2.9019	0.0047	-3.5162	-0.6583
$\cosine(\theta)$	1.1030	0.7359	1.4989	0.1374	-0.3590	2.5649
Northeast Streamlet (magnesium, adjusted r-square = 0.3189)						
Constant	23.407	0.459	50.976	3.493E-68	22.495	24.320
Cumulative Julian Day	-0.00093	0.00026	-3.5481	0.00062	-0.00144	-0.00041
$\sin(\theta)$	-0.1821	0.1964	-0.9269	0.3565	-0.5723	0.2082
$\cosine(\theta)$	1.0663	0.2010	5.3061	7.9746E-7	0.6671	1.4655

The regression models obtained show that calcium is decreasing by 0.913 $\mu\text{eq/L}$ and 0.281 $\mu\text{eq/L}$ per year for the southwest and northeast streamlets, respectively. This equates to a 16.6 % and a 4.7 % decrease over ten years. Magnesium is found to decrease by 0.336 $\mu\text{eq/L}$ and 0.391 $\mu\text{eq/L}$ per year, which represents a 16.1 % and a 16.6 % decrease over ten years in the southwest and northeast streamlets, respectively. The findings of this analysis indicate significant long-term decreases and significant seasonal variations in both calcium and magnesium concentrations in streamwater from the Noland Divide watershed. The reason for this decline were not the subject of this paper but may be partly due to vegetation regrowth in the watershed, which would be consistent with declines seen in nitrate, but may also be partly due to acidification processes.

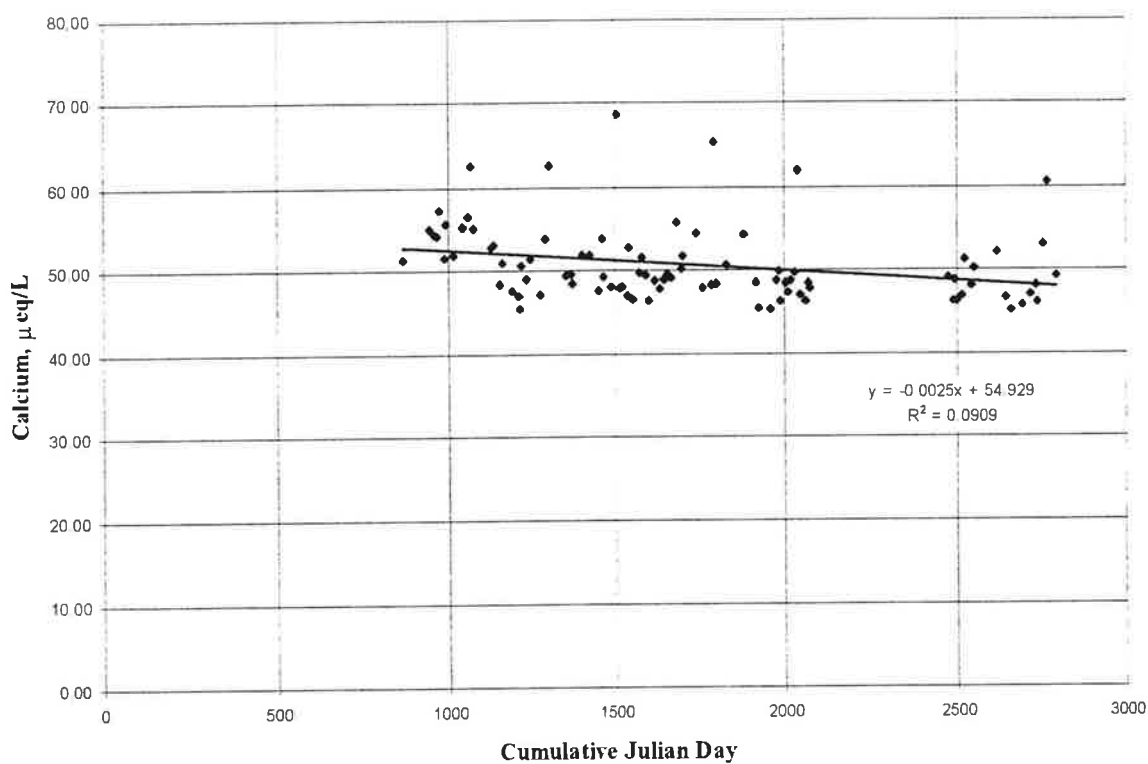


Figure 20. AA calcium time trend (SW streamlet).

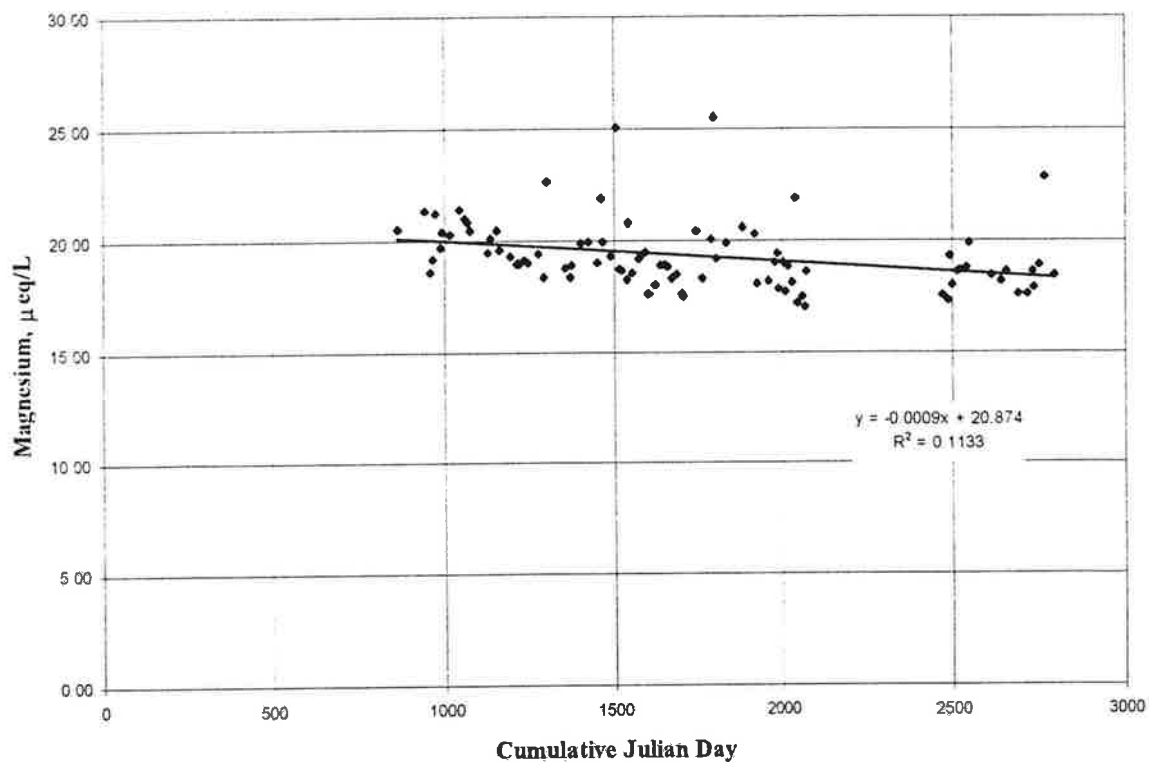


Figure 21. AA magnesium time trend (SW streamlet).

CONCLUSIONS

1. Poor analytical results using IC for cations in Smoky Mountains project is evidenced by poor ion balances, by apparent step increases in calcium and magnesium when IC was first implemented, and by poor results from round robin inter-laboratory comparison samples.
2. There is considerable conflicting information about whether IC is a viable choice for analysis of low concentrations of calcium and magnesium. The results of our own work, the experiences of investigators with the USGS and University of Virginia, results of Döscher et al. (1995), comments made by the instrument manufacturer's representatives and their lack of being able to identify any problem with our methods, lack of wide use of IC for cation analyses (few analytical labs use IC for this purpose) lead to a conclusion that IC is not suitable for calcium and magnesium. However, there are several papers in the literature that do report good results.
3. The experiments with IC showed significant QA/QC problems. Experiments with the method of standard additions showed that the IC measured more calcium and magnesium than what was added in the additions. Experiments also showed significant pH effects, i.e., the lower the pH of the sample, the lower the calcium or magnesium measured by the instrument. Attempts to remedy this pH effect by adjusting samples and standards to the same pH were impractical because of the weak buffering of the samples.
4. Based on the evidence and experience available and the need to move forward, the decision was made to use atomic absorption spectrophotometry for calcium and magnesium analyses. AA is widely used by analytical laboratories for these cations, and extensive QA/QC experiments on a sample Park water has shown excellent results.
5. The Pearson correlation coefficient, r_{xy} , between AA and IC measured calcium is 0.373 which is consistent with the poor results by IC. The low correlation also indicates that IC was not in error by a consistent amount or percentage. Regrettably, it must be concluded that the previous IC calcium measurements are of little value except as order of magnitude estimates. The Pearson correlation coefficient, r_{xy} , between AA and IC measured magnesium is 0.523.
6. Because flow and stream ID appear in the Noland Divide calcium and magnesium regression models as significant variables, which would not be available for Park Wide data, and because the more available chemistry data did not appear in the regression models, it was concluded that developing predictions for calcium and magnesium for Park Wide data should not be attempted.
7. Point estimates and confidence interval estimates were made for all the records used in the regression. As an indication of error, the average upper and lower 95% confidence levels for these point estimates is 6.8 $\mu\text{eq/L}$ (12.5%) for calcium and 2.29 $\mu\text{eq/L}$ (11.2%) for

magnesium. This can be used as an error of the estimates for the missing calcium and magnesium values. Users are cautioned not to use the estimated values of calcium and magnesium for time trend analyses but rather should use the AA determined values of calcium and magnesium only.

8. Two different neural network software packages were used to predict calcium concentrations but did not improve the predictions enough to warrant using them.
9. The regression models using the AA values of calcium and magnesium show that calcium is decreasing by 0.913 $\mu\text{eq/L}$ and 0.281 $\mu\text{eq/L}$ per year for the southwest and northeast streamlets, respectively. This equates to a 16.6 % and a 4.7 % decrease over ten years. Magnesium is found to decrease by 0.336 $\mu\text{eq/L}$ and 0.391 $\mu\text{eq/L}$ per year, which represents a 16.1 % and a 16.6 % decrease over ten years in the southwest and northeast streamlets, respectively. The findings of this analysis indicate significant long-term decreases and significant seasonal variations in both calcium and magnesium concentrations in streamwater from the Noland Divide watershed. The reason for this decline were not the subject of this paper but may be partly due to vegetation regrowth in the watershed, which would be consistent with declines seen in nitrate, but may also be partly due to acidification processes.

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APPENDIX

CALCIUM AND MAGNESIUM ATOMIC ABSORPTION PROTOCOL

Protocol for the AA Analysis of Mg and Ca

Prepared by:

John Shubzda, Research Assistant
Dr. R. Bruce Robinson, Professor
Dr. James. L. Smoot, Professor

**The Department of Civil and Environmental Engineering
The University of Tennessee**

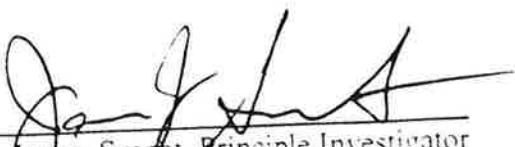
January 2001

QA/QC PLAN SIGNATURE SHEET

Protocol for the AA Analysis of Mg and Ca

Great Smoky Mountains Water Quality Project

Approval for Project Investigators:


Dr. James Smoot, Principle Investigator
Department of Civil and Environmental Engineering
University of Tennessee

1/11/01
Date


Dr. Bruce R. Robinson, Co-Principle Investigator
Department of Civil and Environmental Engineering
University of Tennessee

1-16-01
Date


John Shubzda, Research Assistant
Department of Civil and Environmental Engineering
University of Tennessee

1-10-01
Date

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- B. Atomic Absorption Spectrophotometer Calibration
- C. Magnesium Method
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- E. Glassware and Plastic Cleaning
- F. The AA Step by Step

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Date

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Department of Civil and Environmental Engineering
University of Tennessee

Date

John Shubzda, Research Assistant
Department of Civil and Environmental Engineering
University of Tennessee

Date

1.0 Scope:

This document discusses analytical and QA/QC procedures to be used in analyzing magnesium (Mg) and calcium (Ca) in water samples for the Great Smoky Mountains Water Quality Project. Sample collection and transfer methods are discussed elsewhere.

2.0 Analysis Plan:

One aliquot of 25 mL will be taken from each sample collected from the Noland Divide Watershed (NDW) and Park Wide Stream Monitoring samples. The samples will be hand shaken and sub-sampled using a clean 25 mL volumetric pipette. If suspended solids are present in sufficient amounts to clog the nebulizer, the samples may be allowed to settle and the supernatant liquid sampled directly (U.S. EPA, 1992). The samples will then be placed in a clean 30 mL polyethylene bottle and acidified to a $\text{pH} < 2$ (using a micro-pipetter, 40 μL of ultra pure nitric acid (HNO_3 , 12 M) acid will be added to every 25 mL sample). Samples will be stored in the dark at 4°C until analysis are performed. Maximum holding time for these samples will be 6 months (U.S. EPA, 1983). Atomic absorption (AA) spectrophotometer will be used to determine the Mg and Ca concentration of these samples according to Standard Methods (1998).

3.0 Sample Preparation:

A mixture of lanthanum chloride will be added to the samples just prior to analysis. Lanthanum chloride is used as an ionization suppressant for analysis of Mg and Ca according to Standard Methods (1998). To each 25 mL volume of calibration standard and sample alike, 2.5 mL of the lanthanum chloride will be added.

3.1 Lanthanum Solution

To make the lanthanum solution as per Standard Methods (1998) Dissolve 58.65 g lanthanum oxide, La_2O_3 , in 250 mL concentrated HCl (Caution: Reaction is violent). Add acid slowly until the material is dissolved and dilute to 1000 mL with deionized water.

4.0 Calibration Procedure:

The AA instrument will be calibrated with a minimum of 5 standards which includes one of zero concentration. It is planned to operate in the linear range of the instrument and make dilutions of samples accordingly (e.g. samples from the Cades Cove region of the Park). The standards will be run at the beginning to calibrate the instrument and again at the end. A standard (#3) will be run after every 10 samples to monitor instrumental drift. If drift is detected, the instrument will be recalibrated and the prior 10 samples will be rerun.

4.1 Standards and Stock Solutions

A standard stock solution will be made from high quality calibration standards. The stock solution will be made by taking 10 mL of 1000 ppm Ca and 2 mL of 1000 ppm Mg and bringing the total volume up to 1000 mL. Clean volumetric pipettes and a 1000 mL volumetric flask will be used to make this dilution. This will provide a stock solution of 10 ppm Ca and 2 ppm Mg. From this stock solution, 4 standards will be made in addition to one of zero concentration (Table 1). The standards will also be acidified using ultra pure nitric acid, and an ionization suppressant (lanthanum chloride) added as described above.

Table 1. Recipe for making the AA standards

Standard	Ca	Mg	Amount of	D1 water	Nitric Acid	Lanthanum	Total
	Conc.	Conc.	Stock	Added	Added (mL)	Added (mL)	Volume
	(ppm)	(ppm)	Added (mL)	(mL)			(mL)
1	0	0	0	25	0.04	2.5	27.54
2	0.5	0.1	1.25	23.75	0.04	2.5	27.54
3	1	0.2	2.50	22.50	0.04	2.5	27.54
4	1.5	0.3	3.75	21.75	0.04	2.5	27.54
5	2.0	0.4	5	20	0.04	2.5	27.54

5.0 Operational Parameters:

The atomic absorption spectrophotometer will be operated within the instrument's manual recommended parameters (Table 2). The instrument will be allowed to "warm up" for a period of 30 minutes after igniting the burner before samples are run.

Table 2. Standard Atomic Absorption Conditions for Magnesium and Calcium Determination by Flame Atomization

Parameters	Magnesium	Calcium
Light Source	Hollow Cathode	Hollow Cathode
Lamp Current	3 mA	7 mA
IL Lamp No.	62968	62610
Wavelength	285.2 nm	422.7 nm
Slit Width	320 μ m	320 μ m
Bandpass	1 nm	1 nm
Burner Head	Single Slot	Single Slot
Flame Description	Air-Acetylene	Air-Acetylene
	Oxidizing. Fuel Lean. Blue	Oxidizing. Fuel Lean. Blue

If samples are outside the current standard range (Table 1), they will be diluted to within the range and rerun. In this case, an additional aliquot will be taken from the original sample, diluted with deionized water, and processed according to procedures discussed herein. Typical operational parameters are listed in Table 3.

Table 3. Operational Parameters for Magnesium and Calcium Determination by Atomic Absorption.

Parameters	Magnesium	Calcium
Detection Limit	0.08 $\mu\text{eq/L}$	0.5 $\mu\text{eq/L}$
Sensitivity	0.58 $\mu\text{eq/L}$	4.0 $\mu\text{eq/L}$
Optimum Concentration	8.23-247 $\mu\text{eq/L}$	10-350 $\mu\text{eq/L}$
Range according to EPA		
Current Standard Range	6-95 $\mu\text{eq/L}$	10-160 $\mu\text{eq/L}$

6.0 QA/QC Section:

To insure high quality work during the experiments the following QA/QC samples will be prepared and analyzed.

6.1 Reagent blanks

The purity of the reagent grade water will be tested each day the AA analysis are performed to make sure its conductivity is less than 0.1 $\mu\text{mho/cm}$. The purity of the ionization suppressant (lanthanum chloride) will be tested each time the AA is in use. The suppressant will be added to the reagent grade water and analyzed for magnesium and calcium. If contamination is indicated, then new suppressant salts will be obtained and the reagent grade water system tested and repaired respectively.

6.2 Field blanks

Field blanks are currently being collected during the Park Wide Stream Monitoring efforts.

Therefore, no additional field blanks will be added. If the field blanks show significant contamination, either the source of the contamination will have to be identified and adjustments made to the analytical results, or the analytical results may be disregarded.

6.3 Replicates

Field replicates are currently being collected during the Park Wide Stream Monitoring efforts. Therefore, no additional replicates will be added. If results from the two samples differ by more than 20%, the source of the discrepancy will be evaluated and the samples possibly rerun depending on the findings.

6.4 Sample preservation blank

Nitric acid will be added to the reagent grade water and tested for contamination. If contamination is indicated, then new ultra pure nitric acid will be obtained and the reagent grade water system tested and repaired respectively.

6.5 Spiked samples

Four matrix spikes samples will be performed on a second 50 mL aliquot taken from the original samples. Basically, it will be an analytical split from the original sample, to which a known quantity of magnesium and calcium will be added. Two samples will be Ca spikes and 2 samples will be Mg spikes. Two of the 50 mL samples will receive 0.038 mL of 1000 ppm Ca and two will receive 0.038 mL of 157.89 ppm Mg (Take 3.947 ml of 1000 ppm Mg and bring the total up to 25 ml with D.I. water to make the Mg spike stock). Therefore, each Ca sample spike will receive 0.76 ppm Ca and every Mg sample spike will receive 0.12 ppm Mg. The volume of the spike added must be negligible (less than or equal to 0.001 of the sample aliquot volume). A percent recovery of the spike will be calculated as follows:

$$\% \text{ spike recovery} = \{(\text{measured concentration of sample plus spike} - \text{measured concentration of unspiked sample}) / (\text{actual concentration of spike added})\} \times 100$$

The spike recovery must be 100 ± 15 percent. If the recovery is out of this range, rerun the sample and check for contamination within the spiking solutions.

6.6 Analysis Schedule

After every 10 samples a check sample, standard (≈ 3), will be run to determine instrumental drift. If no drift is detected, those same samples will be run again to produce a second concentration value. If the check sample differs by more than 10% from the expected concentration, the AA will be recalibrated and all suspect analysis, typically the last 10 analysis, rerun. If the instrument is re-zeroed, it will also be recalibrated. After the results are entered into a spreadsheet, the duplicate analyses will be checked to see if the results of the two analyses differ by more than 15%. If the results differ by more than 15%, they will be rerun in triplicate. If the results differ by more than 20%, the source of the discrepancy will be evaluated and the samples rerun depending on the findings.

6.7 Corrective Action

The chemical analyst will measure a control standard at the beginning and end of each analytical session on the AA. The values will be plotted on a control chart. The control standard will have a concentration in the upper part of the working range of the AA instrument for Mg and Ca. This sample should be consistently measured within $\pm 10\%$ of the mean value (Standard Methods (1998) suggests a $\pm 4\%$ range, however $\pm 10\%$ is more realistic for our low concentration waters). Failure to do so will be cause for repeating the instrument set up, optimization, and calibration procedures.

Any of the following problems will cause corrective actions (in all cases, Dr. Smoot and Dr. Robinson will be notified).

- Failure to measure control standard to within $\pm 10\%$ even after repeating the instrument set up, optimization, and calibration procedures: initiate review of analytical procedure, and/or more extensive instrument maintenance and diagnostic procedures
- Detection of contamination in reagent blanks: purchase and test new reagents
- Detection of contamination in field blanks: confirm analytical result, try to determine source of contamination and whether all samples were similarly contaminated; determine if the samples at that field site should be considered invalid or whether the contamination will not significantly affect the results or whether the results can be adjusted
- Failure to recover field spikes to within 85-115% of the expected concentration: confirm analytical results; evaluate why recovery was not achieved; determine best course of action that preserves integrity of the data including the possibility of considering the field samples from the site invalid
- Analytical results outside the working range of the AA: re-dilute and re-analyze (Dr. Smoot and Dr. Robinson need not be notified)
- Duplicates and replicates: If the results of duplicate and replicate analyses are significantly outside the expected precision of the instrument, i.e., outliers, the source for the difference will be sought and the samples rerun. Unless justifiable reasons are found for disregarding data, the data must be retained. If data are more than three standard deviations outside the mean, then they may be disregarded depending on the situation.

6.8 Precision and Accuracy

Standard methods reports the following relative standard deviation and relative errors from an interlaboratory precision and bias evaluation (Table 4). Because of the significantly

Table 4. Results from interlaboratory precision and bias evaluation in determining Mg and Ca concentrations in surface water using atomic absorption spectrometer (data taken from Standard Methods, 1998)

	Concentration	Relative Std.	Relative Error	No. of
	(mg/L)	Deviation (%)	(%)	participants
Calcium	5.0	4.2	0.4	8
Magnesium	1.1	10.5	10.0	8
Magnesium*	0.2	10.5	6.3	42

* A second lower magnesium concentration was also used in the evaluation.

lower concentrations of Mg and Ca in the Park samples, the relative standard deviation and relative error are expected to be higher than the values given in Table 4.

7.0 Data Handling:

7.1 Data Processing

The results of the AA analysis will be printed out from the instrument as the samples analyses are analyzed. The sample ID number will be recorded on the printout after each sample is run. The AA results will be entered directly from the instrument printouts into a spreadsheet. The spreadsheet file will be stored on a computers hard disk drive and a back-up copy on a floppy or zip diskette. After each set of data is entered, a copy of the spreadsheet file will also be given to Dr. Smoot and Dr. Robinson. After 2 or more days, the original operator will check that all data were entered correctly by comparing the entered values with the hard copies of the data. Dr.

Smoot or Dr. Robinson will review the data for obvious errors. No data can be changed without approval after this point. Any corrections to data values will be noted on the hard copy and spreadsheet files along with the reason.

7.2 Data Quality Assessment

Dr. Smoot and Robinson will review all data including any calculations and results of various blanks and agreement between duplicates and replicates.

7.3 QA/QC Statistical Data Analysis

Statistical analysis of the data itself will determine if the QA/QC objectives were met and will calculate the mean value of concentrations of samples. The following data analyses are planned:

- Calculate percentage recoveries and mean percentage recoveries and laboratory spikes:
this will be done by simple ratio of the difference between the spiked sample and unspiked sample compared to the expected difference.
- Calculation of the mean and standard deviation of each set of duplicate and replicate samples

8.0 Preventive Maintenance and Scheduling:

The following are the manufacturer's recommended maintenance and check activities for our IL Video 12 atomic absorption spectrophotometer:

Daily:

- Clean the lenses
- Clean the burner
- Aspirate deionized water for 2 minutes
- Check and drain the compressor manifold

Weekly:

- Brush out accumulated dry residue
- Clean the single burner slot
- Disassemble and clean premix chamber (weekly or as needed)

Monthly:

- Clean the compressor filter
- Clean the fan filter in the electronics drawer

Semi-Annual:

- Replace the oil-removing air filter

Annual:

- Replace the standard air filter

Because the AA unit is used infrequently, we plan to perform all of these maintenance items before we use the AA for the first time. The filters will only be replaced if needed.

In addition to the above, we have also performed additional checks and maintenance:

- Check performance of electronics and lamps daily by placing "known" metal screen in the light path and observe reading
- Check deuterium lamp initially and then weekly to determine if it is producing enough energy
- Clean and inspect nebulizer head initially and then weekly
- Optimize flow rate on nebulizer and check absorbance of a known concentration and compare with expected value daily. Low absorbance would trigger a search the cause.

A. Atomic Absorption Spectrophotometry Methodology

The AA Step by Step

Open hood- to first mark.

Make sure burner, water, and nebulizer are all in place.

Make sure high voltage is turned all the way down and make sure the "Hollow Cathode" is turned all the way to the left or counter clockwise.

Set the Oxidant to maximum-It is all the way in for maximum or clockwise.

Turn the machine on, give it a minute to warm up, then turn the "Operate" button on.

Set Current to 7 Ma for Ca (3 Ma for Mg).

Set the wavelength to 422.7 and set bandwidth to 1.0 for Ca settings (285.2 Wavelength and 1.0 bandwidth for Mg).

Rotate the lamp and set screws.

Now turn the "High Voltage" to 460, make sure the needle is in the "green".

Leave the injection line out before you light the machine.

Turn the Acetylene tank on, and set at 15 psi (for the machines' pressure) (**Caution:** Don't let the tank go below 100 psi!, internal tank pressure).

Turn the Air tank on to 60 psi (for the machines' pressure)(**Caution:** Don't let the tank go below 500 psi).

Press I/O button, again

Change the Date

Press "Int".

Set to Auto mode;

Change time to 4 to 5 seconds:

Delay 0.0;

Ready to Start Sampling.

Press "Std".

Select Normal Calibration

Select Instrument

Type in standards in ppm.

Put intake in standards

Hit "Read"

Press except (the enter button) after each standard.

Look at the standard curve, if you accept it, now the results will be in ppm.

Run Samples.

Shutdown:

Turn the "Air/fuel" to off.

Shut off the acetylene. Turn back to "Air/fuel" to bleed the line.

Turn back "Air/fuel" to off

Then turn air tank to off

Turn on the "air" button.

Make sure oxidant level is between 12 & 16.

Turn to "Air Fuel"

Make sure fuel is between 3 & 6.

Hit the "Pilot" button to turn on the burner.

Check the nebulizer. Make sure the intake is between 5 and 6 ml/per minute. Rotate nebulizer nob clockwise to increase the flow.

Go to the menu:

Press Mode:

Hit 1	then select Ca or Mg	
2	Optics	AA, DB
3	Background	Needs to be off
4	Results	concentration
5	Statistics	on 3 (average)

Turn on Printer (Press the online button)

6	Flame
7	Auto-Sampler-Off
8	

Check Press I/O button

Check the printer 4568

Go to location 2 (Printer)

Auto Graphic-Off

Select All Data

Turn back to "Air" to bleed the lines, then back to the off position.

Turn "operate" button to "restart standby".

Turn all the nobbs to the left

Turn power off and printer off

Shut the hood.

Bill Long

Allied Analytical Systems, April 1983/122913

Operator's Manual IL Video 11 & 12

AA/AE Spectrophotometers

Serial Number: 1857

Date Installed:

By:



**ALLIED Analytical
Systems**

One Burn Road/Andover, MA 01810/USA/Tel (617) 470-1790/Telex 95 1096

SECTION THREE

INSTRUMENT DESCRIPTION

3.1 FRONT PANELS

Figures 3-1 and 3-2 are detailed close-up views of the displays and controls located on the front panels of the spectrophotometer. The numbers in parentheses below refer to the numbers called out in these figures.

3.1.1 Burner Controls

- (1) PILOT: ignites flame.
- (2) FUEL/OXIDANT CONTROL: initiates delivery of fuel and oxidant to the burner/premix chamber; also used for converting to N_2O /acetylene and for extinguishing the flame.
- (3) FUEL FLOWMETER: indicates the rate of fuel flow. This meter has a scale of 20 SCFH (standard cubic feet per hour) graduated every one SCFH.
- (4) FUEL FLOW KNOB: controls flow rate of fuel delivery to the premix chamber.
- (5) OXIDANT FLOWMETER: indicates the amount of oxidant flow. This meter has a scale of 30 SCFH, graduated every two SCFH.
- (6) OXIDANT FLOW KNOB: controls flow rate of oxidant delivered to the nebulizer/premix chamber.

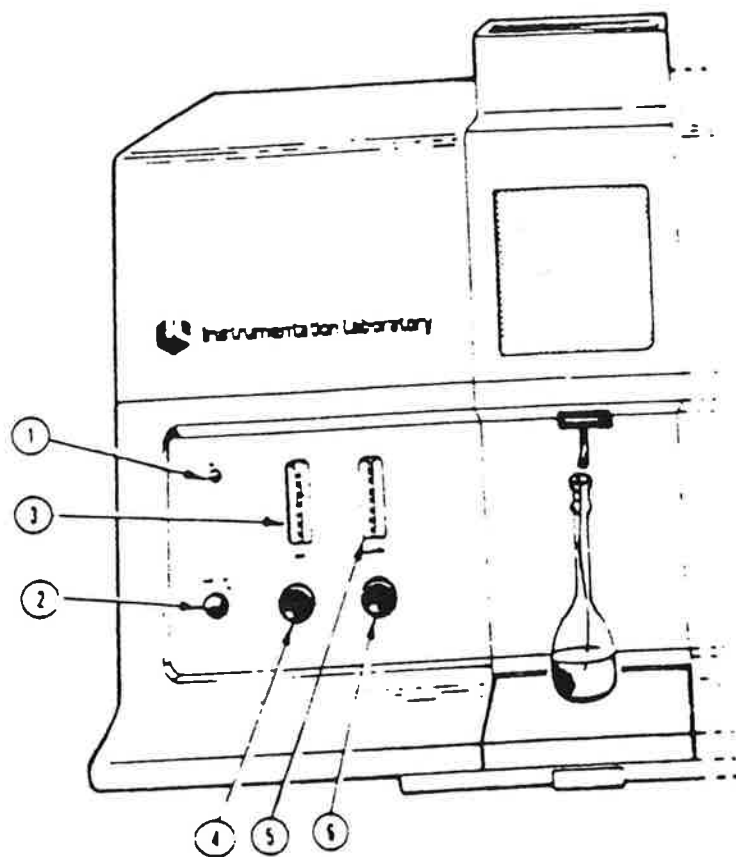
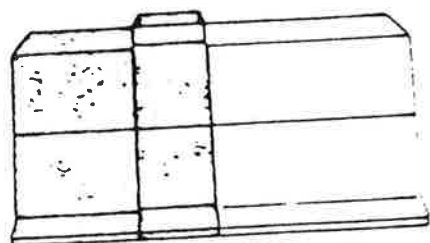


FIGURE 3-1: CONTROLS AND DISPLAYS, LEFT SIDE

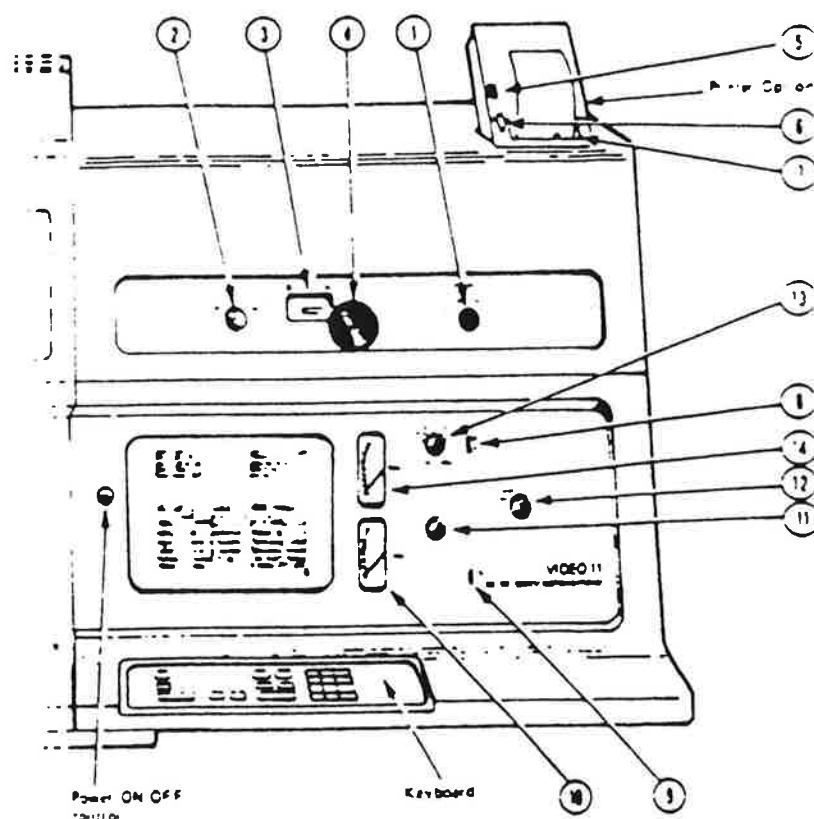
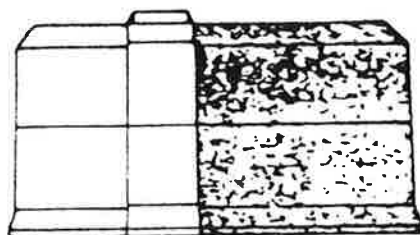


FIGURE 3-2: CONTROLS AND DISPLAYS, RIGHT SIDE

3.1.2 Wavelength and Bandwidth Controls

- (1) Bandwidth selects bandwidth in nm.
- (2) Wavelength Scan (optional) activates the wavelength scanning motor to drive the monochromator to longer wavelengths.
- (3) Wavelength Indicator indicates wavelength in nm.
- (4) Wavelength Selector dials the desired wavelength in nm.

3.1.3 Optional Printer Controls

(5) **Printer ON/OFF Switch** turns the printer on and off.

(6) **Manual Paper Tape Feed Control** threads paper tape when reloading.

(7) **Print Head Lever** removes the print head from contact with the paper tape.

3.1.4 Other Controls

(8) **I/I₀** selects either incident or transmitted light intensity reading for the Energy indicator. On the Video 11, I and I₀ are the same.

(9) **Signal/Background** selects either the low cathode or D₂ arc intensity reading respectively for both the energy and current indicators when employing D₂ arc background correction. In the S/H mode, signal selects monitoring of the low current pulse, while background selects monitoring of the high current pulse on the energy and current indicators.

(10) **Current** indicates the current (0 to 20 mA) of either the signal or background source as monitor-! r, the switch in step 9 above.

(11) **Hollow Cathode** controls current for the hollow cathode lamp. Signal current (small diameter knob) does not operate if the turret is in place, but in either case the large diameter dial controls S/H background current. Small dial controls the signal current when turret is not in place.

(12) **Restart/Sdby-Operate-Format Lock-Battery Off** is a four position switch that controls the operation of the microcomputer. RESTART/SDBY powers down the hollow cathode lamps, CRT and the operational electronics, while the calibration programs stored in microcomputer memory are retained. Additionally, RESTART/SDBY resets the microcomputer's program counter to equal 0000 which can correct certain operational errors. OPERATE is used when entering an analytical program. FORMAT LOCK protects a program from accidental disruption while the spectrophotometer is in use. Only A/Z, A/C, READ, & ENTER are engaged in this mode. BATTERY OFF turns off the battery which comes on automatically if line power is lost.

(13) **High Voltage** sets the voltage in eight increments for the photomultiplier. Vernier dial varies voltage within each increment.

(14) **Energy** indicates the minus log of intensity (0 to 3.4 Abs) reaching the photomultiplier tube for the mode selected in steps 8 and 9 above.

3.2 KEYBOARD

NOTE: In the following descriptions, optional printer messages are given for the sake of completeness. However, the messages displayed by the CRT are standard.

The spectrophotometer keyboard is organized by rows. There are three rows of function keys located on the panel, with a separate number pad to the right.

NOTES: (1) Throughout this manual, the following conventions will be used for keyboard entries:

BOLDFACE entries are typed in;
Entries in < > represent single keystrokes.

(2) * indicates the default condition which results if no numeric entry is made but the <ENTER> key is pressed.

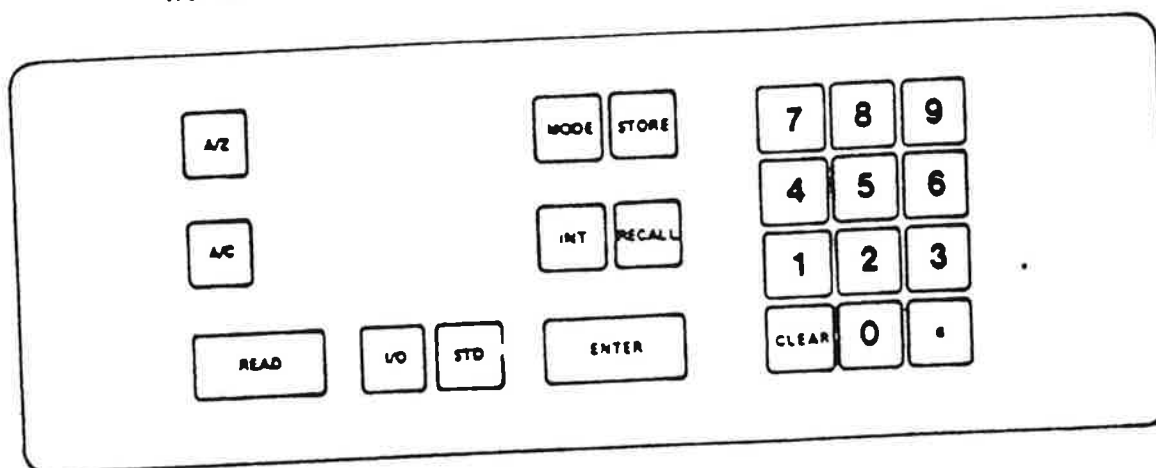


FIGURE 3-3: KEYBOARD

3.2.1 A/Z (Auto Zero)

When pressed, this key instructs the microcomputer to set the absorbance or concentration to zero, or to the specified concentration of standard 0, as indicated on the CRT display. This function will not proceed until the READ key is subsequently pressed. The function is terminated in the statistics mode only after the number of readings selected in statistics has been completed or by keying <ENTER>.

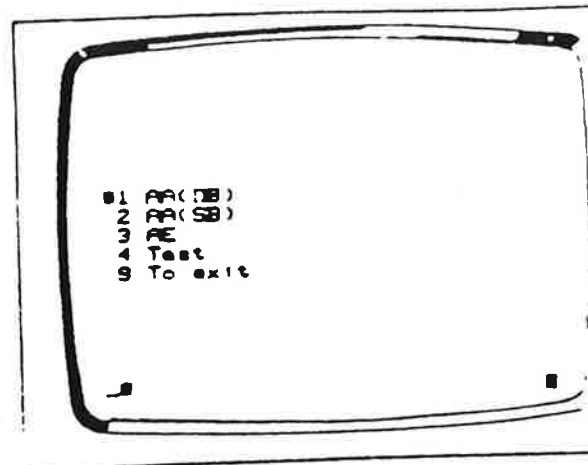
3.2.2 A/C (Auto Cal)

When pressed, this key initiates the automatic calibration routine which compensates for slope changes in the calibration curve by comparing the computed concentration of the first standard to the actual concentration. The microcomputer automatically compensates for changes in the slope of the calibration curve which would result in a discrepancy between the computed and actual values. This function will not proceed until the READ key is pressed. The function is terminated in the statistics mode only after the number of readings selected in statistics has been completed or by keying <ENTER>.

3.2.3 MODE

When <MODE> is keyed on the VIDEO 12, the display appears as shown. The asterisk beside the number 1 signifies that the microcomputer will default to mode 1 (double beam AA) and will remain in mode 1 unless the operator keys mode 2 or 3. If mode 1 is desired, the operator need only key <ENTER>.

When mode is keyed on the VIDEO 11, the double beam option is not displayed.



Mode
1 AA (DB) Double beam
(I, I₀) atomic absorption.
2 AA (SB) Single Beam
(I) atomic absorption.
3 AE- atomic emission.
4 Test- initiates the
microcomputer self-
check procedure.
9 To exit- returns the
operator to the
operating program.

NOTE: Keying <MODE> initiates the parameter selection sequence
(See Section 4.3.1).

3.2.4 STORE (See also Section 4.3.4.)

When pressed, this key allows you to store up to ten calibration curves and operating parameters (i.e., integration time, mode, etc.) in microcomputer memory. The microcomputer's registers (memory locations), are designated by single integers from 0 to 9. To keep electronics and lamps in warm-up state while the spectrophotometer is not in use, set the RESTART/SDBY - OPERATE - FORMAT LOCK - BATTERY OFF switch to RESTART/SDBY. This switches off the operational electronics while maintaining power to the microcomputer. (See the description of the RECALL key.)

- NOTES: (1) If line power to the spectrophotometer is interrupted, the microcomputer memory will be protected for at least five minutes by means of the battery backup system. The battery backup will only maintain memory for a period of time, dependent on its state of charge. The memory is immediately erased only if the battery is turned off by using the switch position BATTERY OFF.
- (2) If the operator attempts to store a curve in a memory register which already is holding a curve, the CRT will display:
"Occupied
ENTER to Overwrite
CLEAR to Exit"
At this point the operator may select a different storage location by keying <CLEAR>, then <STORE>, and a different integer, leaving the previously stored curve intact. To replace (i.e., overwrite) the previously stored curve with the new calibration curve, key <ENTER>.

3.2.5 RECALL (See also Section 4.3.5.)

The microcomputer can store up to ten calibration curves and operating parameters (i.e., integration time, mode, etc.) in ten separate storage registers designated 0 to 9. Keying <RECALL> and the appropriate integer recalls the stored calibration curve.

The RECALL key is also used to recall "cookbook" pages. This is done for flame methods by keying <RECALL>, entering a two-digit atomic number, and keying <ENTER>. If the atomic number is not known, key <RECALL>, enter the digits 00, and key <ENTER>. A list of all elements and their atomic numbers will appear on the display.

For furnace methods, any digit followed by a two-digit atomic number will yield furnace conditions for that element. If the atomic number is not known key <RECALL>, enter any digit followed by 00 and key <ENTER>. The list of elements with atomic numbers will appear. Entering the two digit number will yield the furnace conditions.

3.2.6 INT (Integration)(See also Section 4.3.2)

When INT is keyed, the CRT displays the following four selections:

- 1) Auto: automatic (or continuous) integration.
- 2) Manual: single integration.
- 3) Pk Area: peak area (P/A)
- 4) Pk Height: peak height (P/H)

NOTES:(1) P/A and P/H are usually used with furnace atomizers or other devices in which transient signals are generated.

- (2) When P/A is selected calibration curves are generated in peak area (absorbance .sec) but peak height absorbances are displayed simultaneously.

3.2.7 READ

When pressed, the READ key initiates integration. In the manual, P/H and P/A modes, one reading is initiated each time <READ> is keyed. In the automatic mode, readings start when <READ> is keyed and stop when <READ> is keyed again. When statistics are used, the readings will stop automatically after the designated number of repeats.

3.2.8 STD (Standard)

The STD key is used to:

- o Enter calibration standards (Section 4.3.3).
- o Correct a calibration program error (Section 4.3.7).
- o Enter an additional standard (Section 4.3.8).

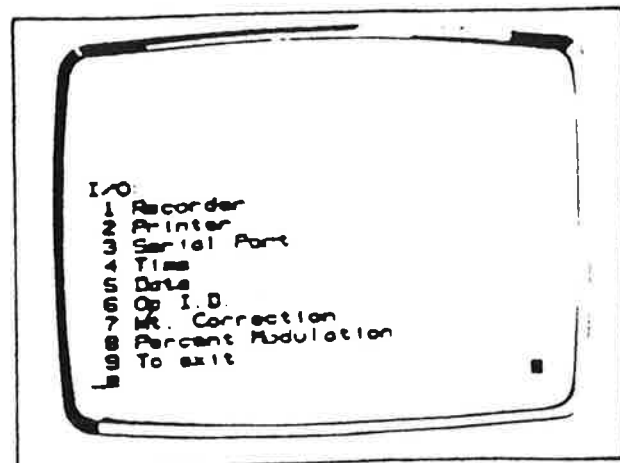
3.2.9 ENTER

When pressed, this key executes the keyed command.

3.2.10 I/O (Input/Output)

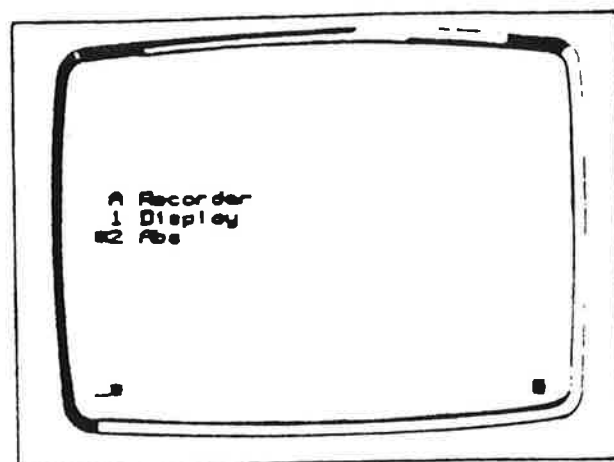
This key formats the input and output functions of the spectrophotometer.

oThe CRT displays:



- A. <I/O> 1 <ENTER>
enables the formatting
of the recorder output.

oThe CRT displays:



NOTE: In place of the letter A, the element and background correction technique (if selected) will be displayed; for example Pb-D for D₂ arc or Pb-S for Smith-Hieftje.

1. If "Display" is selected, the recorder output will track the digits as they appear on the video display. The format of the recorder (display) signal will also track the integration time. If auto integration time is <4 seconds, the recorder signal will be real time; if auto integration time is ≥4 seconds, a square bar (⌌) format will result. This square bar format will occur after the integration has occurred. The recorder pen will move to the corresponding signal level, remain there for 3 seconds, then be reset to baseline.

SECTION FOUR

INSTRUMENT OPERATION

4.1 FLAME IGNITION, OPTIMIZATION, AND SHUTDOWN

4.1.1 Air/Acetylene Flame Operation(Aqueous)

A. Ignition

1. Insert the long path air/acetylene burner head (IL121534-02).
2. At the air cylinder, set the oxidant regulator pressure to 50 psig (3.5 kg/cm²).
3. At the acetylene cylinder, set the external fuel pressure to 15 psig (1.1 kg/cm²).

NOTE: Ascertain that the vent over the flame compartment is on and open.

4. Turn the gas control selector switch to the AIR position.
5. Turn the oxidant flow control knob counter-clockwise to reduce the oxidant flow until the ball in the oxidant flowmeter stops dropping. At this point, oxidant is being supplied to the premix chamber only through the nebulizer, and the auxiliary oxidant supply is off.

NOTES:(1) When taking flow readings, sight in the middle of the ball in the flowmeter.

(2) With the auxiliary oxidant supply turned off, and when using the IL43005-02 Long Path Air/Acetylene Burner, the burner system is optimized for best sensitivity. When maximum sensitivity is not desired (i.e., for wider dynamic range calibration curves), it is advisable for the operator to supply auxiliary oxidant to the burner system by adjusting the oxidant control knob clockwise until the oxidant flowmeter indicates 20 to 22 SCFH. Fuel flow should be set to 4 to 6 SCFH. This procedure decreases sensitivity 20 to 30% and increases the optimal working range.

6. Place the aspirator tube in a graduated cylinder containing deionized water.
7. To set the aspiration (uptake) rate, proceed as follows (keeping the gas control selector switch at the AIR position):
 - a. Rotate the knurled knob of the nebulizer assembly counter-clockwise until bubbles (blow-back) exit the aspiration tubing.
 - b. Gradually rotate the knurled knob clockwise until the bubbles just stop.
 - c. Rotate the knurled knob between one-quarter and one-half of a turn clockwise; the oxidant flowmeter should indicate 12 to 14 SCFH.

- d. Measure the aspiration rate with a graduated cylinder.
- e. Optimal aspiration rate is 4 to 6 mL/min. If necessary, re-adjust the knurled knob to achieve optimal aspiration. (Clockwise rotation increases aspiration rate; counter-clockwise rotation decreases it.)

NOTES: (1) Excessive amounts of water sprayed into the burner head when the flame is out will cause the slot in the burner head to clog.

(2) The oxidant flow and aspiration rate generally require adjustment only when the instrument is installed, when a different solvent is used, or if the nebulizer has been dismantled.

(3) After setting the aspiration rate, steps a to e, observe the gas flowrate on the oxidant flowmeter. Later, if a change occurs, simply reset the aspiration rate by adjusting the nebulizer control until the original gas flowrate is obtained. Although for precise reproduction the aspiration rates should be measured and matched.

8. Place the gas flow selector switch to the AIR/FUEL position.

9. Set the fuel flowmeter to a setting of 3 to 5 SCFH with the fuel flow control.

CAUTION: DO NOT DISCHARGE AN EXCESSIVE AMOUNT OF ACETYLENE.

10. Return the switch to AIR for 15 seconds in order to flush out any remaining unburned acetylene.

11. Turn the gas selector switch to AIR/FUEL, then press and hold the PILOT switch to ignite the flame.

12. Aspirate water continuously as long as the flame is burning.

B. Optimization

1. Measure the aspiration rate with a graduated cylinder.

2. Optimal aspiration rate is 4 to 6 mL/min. If necessary, re-adjust the knurled knob to achieve optimal aspiration while aspirating an aqueous standard. (Clockwise rotation increases aspiration rate; counter-clockwise rotation decreases it.)

3. Optimize the stoichiometry of the flame for maximum sensitivity by adjusting the fuel flowrate while aspirating a standard. Most air/acetylene elements are optimized under fuel-lean (oxidizing) conditions. A fuel-rich flame produces a reducing atmosphere. See Section 4.1.7 for complete premix chamber/burner optimization procedure.

NOTE: Be sure to periodically reset the baseline with a blank during the flame optimization process to compensate for potential baseline shift.

C. Flame Shutdown

1. Aspirate water for about 15 seconds.
2. Turn the gas flow selector switch from FUEL/AIR to AIR.
3. Wait for the flame to go out, then remove the capillary from the distilled water.
4. Wait ten seconds, then switch the gas flow selector to OFF.

4.1.2 Air Acetylene Flame Operation (Organic)

Often in trace analysis, extraction of metals into an organic solvent is a useful technique for separating and concentrating the metal of interest. In addition to the increase in the metal concentration by extracting from a large aqueous volume into a smaller non-aqueous volume, the inherent sensitivity in an organic solvent matrix is typically greater because the nebulization efficiency is increased.

A. Ignition

1. If the solvent is non-miscible with water, replace the contents of the drain cup with the solvent.
2. When using organic solvents such as ketones, perform the following steps:
 - a. Replace the standard O-rings (IL44179) with ketone resistant O-rings (IL44180).
 - b. Replace the tubing leading to the drain cup with polyethylene tubing. If the tubing is not replaced, it will swell and stiffen because of contact with the ketones. Because polyethylene tubing is normally stiff, run the drain line from the premix chamber towards the front of the instrument, around the gas control drawer, and connect it to the drain cup.
3. Turn the oxidant flow control knob clockwise to increase the oxidant flow to 20 SCFH.

4. Set the aspiration rate to 5 to 6 mL/min.

NOTE: Ascertain that the vent over the flame compartment is on and open.

5. Set the acetylene flow to 5 to 6 SCFH.

NOTE: When taking the readings, sight on the middle of the ball in the flowmeter.

6. Ignite the flame and allow the burner to warm up for a few minutes.

B. Optimization

1. Lean the flame out as much as possible without extinguishing it by reducing the acetylene flow to 2 to 3 SCFH.
2. Dip the capillary into the organic solvent. A somewhat yellow flame will result. If an excessively luminous flame results, reduce the aspiration rate of the nebulizer. Be sure to enrich the flame with fuel temporarily while reducing the aspiration rate.
3. Optimize the stoichiometry of the flame for maximum sensitivity by adjusting the fuel flowrate while aspirating a standard. Most air/acetylene elements are optimized under fuel-lean (oxidizing) conditions. A fuel-rich flame produces a reducing atmosphere. See section 4.1.7 for complete premix chamber/burner optimization procedure.

NOTE: Be sure to periodically reset the baseline with a blank during the flame optimization process to compensate for potential baseline shift.

C. Flame Shutdown

1. Increase fuel flow to 4 to 5 SCFH and aspirate air for 30 seconds.
2. Turn the gas flow selector from FUEL/AIR to AIR.
3. Wait for the flame to go out, then switch the gas flow selector to OFF.

NOTE: Higher gas flows (7 SCFH fuel/27 SCFH oxidant) with auxiliary oxidant will result in a larger, stiffer flame that will not be adversely affected by the organic solvents. If the best possible sensitivity is not absolutely necessary, the use of increased fuel/oxidant settings should be employed. With higher gas flows, precisions obtained with organic solvents typically improve, but sensitivities will be reduced by 20 to 30%.

4.1.3 Nitrous Oxide/Acetylene Operation(Aqueous)

NOTE: There are two microswitches on the burner head collar of the premix chamber. The switch closer to the head aperture is the interlock switch which enables flow of acetylene. The outer switch enables nitrous oxide flow. The collar ring on the nitrous oxide burner head is wide enough to contact both switches, which activates the nitrous oxide conversion circuitry.

4.1.7 Premix Chamber/Burner Optimization

NOTE: Prior to optimization, ensure that all parameters, have been set as desired. See Section 4.3 for program selection. Use 1-second auto integration during optimization.

A. Bead Position (See Figure 3-8)

1. Aspirate an element which is nonsensitive to flame stoichiometry (e.g., copper).
2. Slowly move the bead away from the nebulizer.
3. Observe the readout and note the maximum absorbance.
4. Next, pull the bead back toward the nebulizer and peak on the maximum absorbance observed in step 3 above.

NOTE: These adjustments are necessary only if the bead has been removed, or if a new nebulizer has been installed.

B. Flame Condition and Burner Position (See Figure 4-1)

Before igniting the flame, align the burner as described in Section 3.4.3, then proceed as follows:

1. Aspirate a blank solution that represents the matrix of the samples and standards. The blank solution may be deionized, distilled water.
2. Key <A/Z>, and <READ>; 0000 appears on the CRT display.
3. Optimize flame conditions by aspirating a standard that gives approximately 0.1 absorbance units.
4. Optimize the stoichiometry of the flame for maximum sensitivity by adjusting the fuel flow while aspirating a standard.
5. Make the following burner adjustments for maximum absorbance. See Figure 4-1.
 - a. Burner height: 1 to 2 mm (nominal) below the optical beam. Use burner control No. 4.
 - b. In/Out movement: Use burner alignment control, No. 2.
 - c. Rotational movement: Use burner rotation control, No. 5.

- (1) Horizontal Position Locking Bar
- (2) Horizontal Adjustment Knob
- (3) Vertical Adjustment Locking Bar
- (4) Vertical Adjustment Knob
- (5) Rotation Adjustment Lever
- (6) Nebulizer. (The uptake rate is adjusted using the knurled nut on the nebulizer.)
- (7) Burner Identification Collar (This collar actuates the appropriate microswitches on the premix chamber.)

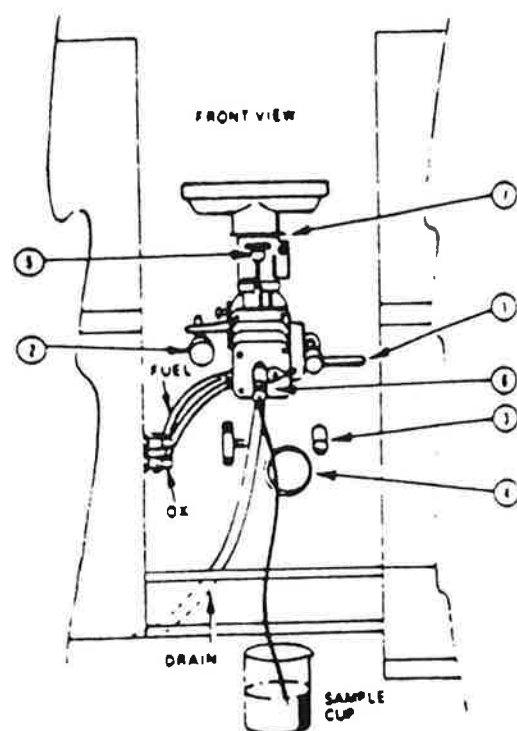


FIGURE 4-1: BURNER SYSTEM CONTROLS

NOTE: Be sure to periodically reset the baseline with a blank during the optimization process to compensate for potential baseline shift.

4.3. PROGRAM SELECTION AND OPERATION

The VIDEO 12 is a microcomputer-controlled, single channel, double beam atomic absorption/atomic emission spectrophotometer with a CRT display and optional D₂ arc background corrector. The IL VIDEO 11 is a single beam version of the VIDEO 12. Both are capable of operating in a wide variety of modes. Operation is simple because a microcomputer controls the various functions of the instrument. The operator selects the desired mode on the built-in CRT screen located on the front panel of the instrument. Additionally, the Smith-Hieftje background correction technique is a standard feature of the VIDEO 11/12.

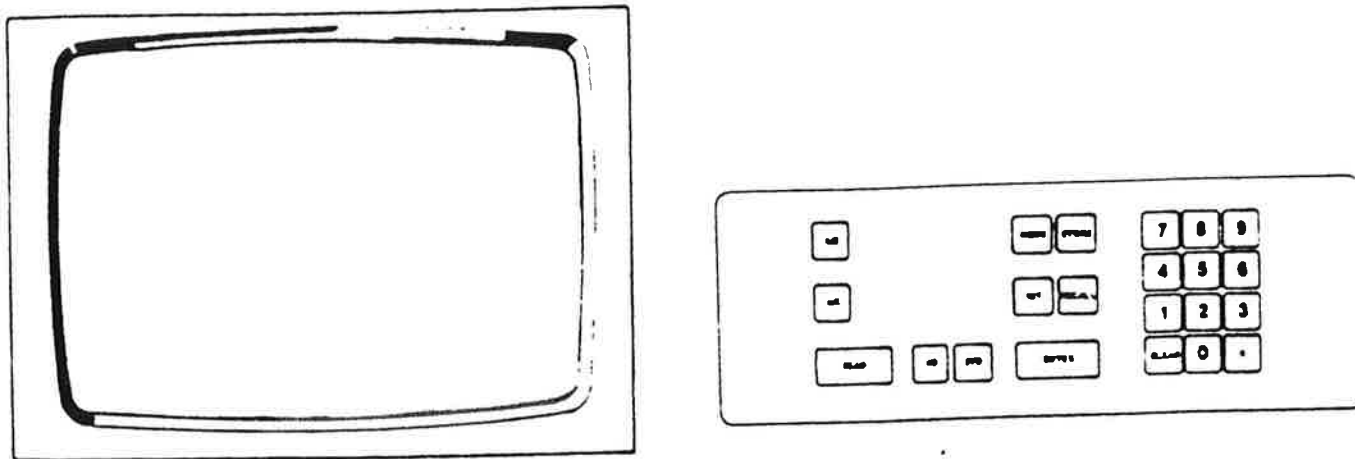


FIGURE 4-5: THE CRT DISPLAY SCREEN AND THE KEYBOARD

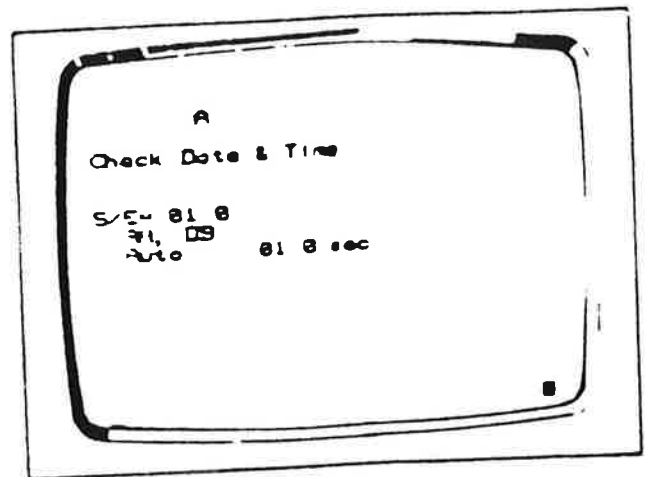
- NOTES: (1) The VIDEO 11/12 microcomputer will automatically initiate the selection that is marked with an asterisk on the CRT (this is termed the default condition). The operator need only key <ENTER> for these default conditions to be initiated. To select any of the other options displayed on the CRT, the operator must first press the appropriate key, then key <ENTER>. To exit the current routine, key 9 <ENTER>.
- (2) If an incorrect entry is made, the error message **INVALID ENTRY** will be displayed on the CRT. Verify that a legal selection is keyboarded in the proper format.
- (3) **BOLDFACE** entries are typed in; Entries in < > represent single keystrokes.
- (4) Throughout this section, CRT displays will be those found on the VIDEO 12, unless otherwise specified. These will be identical to the VIDEO 11 displays with one exception; since the VIDEO 11 is a single beam AA, its CRT will not display "SB" or "DB" (for single beam or double beam respectively) as will the VIDEO 12.

4.3.1 Mode Selection

1. Insert the desired light source as described in Section 4.2.
2. Press the POWER button (Figure 3-2).
3. Set the RESTART/SDBY-OPERATE-FORMAT/LOCK switch to OPERATE (Figure 3-2).

oThe red POWER button lights.

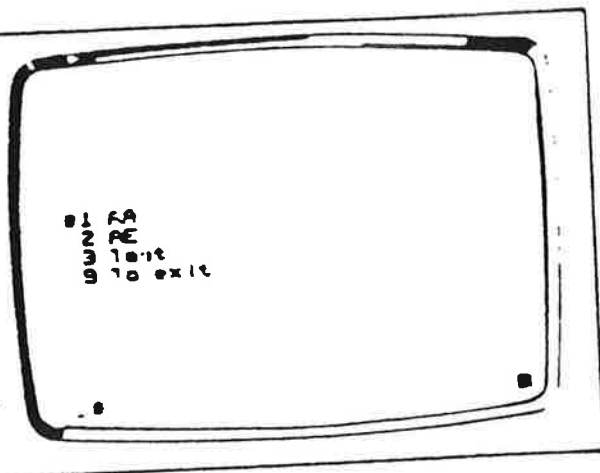
oThe CRT displays:



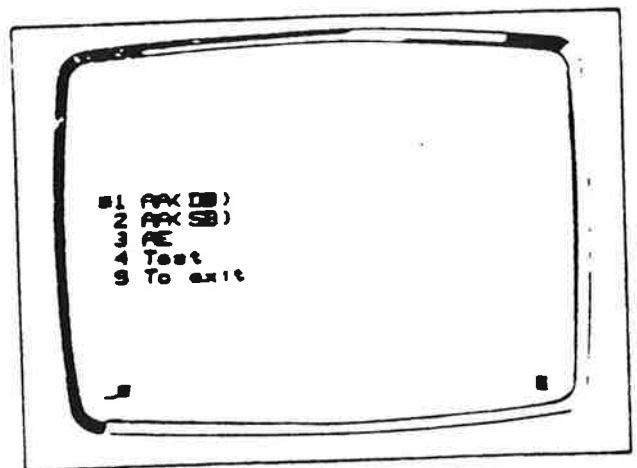
NOTE: The memory-stored date and time should be checked for accuracy at this time using the A/Z key and corrected through the I/O key if necessary.

oThe CRT displays:

4. Key <MODE>.



VIDEO 11



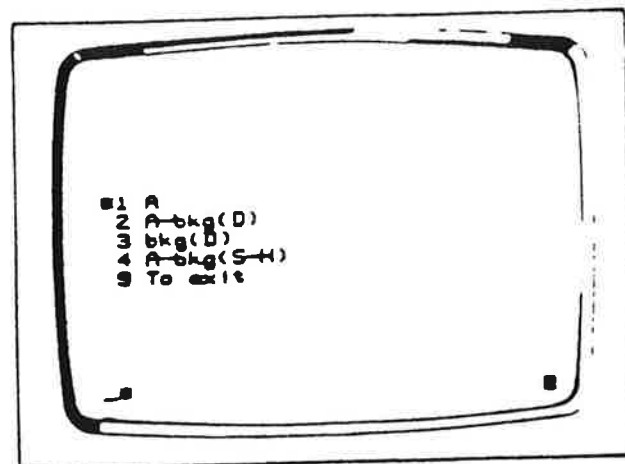
VIDEO 12

5. Key the appropriate number for the desired mode, or key 9 to exit routine.

NOTE: When <MODE> is keyed, the asterisk appears in front of the number 1 as shown in the above CRT display. Mode selection 1 (double beam AA for the VIDEO 12, and single beam AA for the VIDEO 11) is the default selection; to retain this selection, simply key <ENTER>. The asterisk will indicate the default solution as the selection last made for this screen. Alternately, select single beam atomic absorption for the VIDEO 12 AA(SB), atomic emission AE, or the microcomputer self-test function Test.

6. Key <ENTER>.

oIf, for example, mode 1 is selected, the CRT displays:



7. Key the appropriate digit as described below.

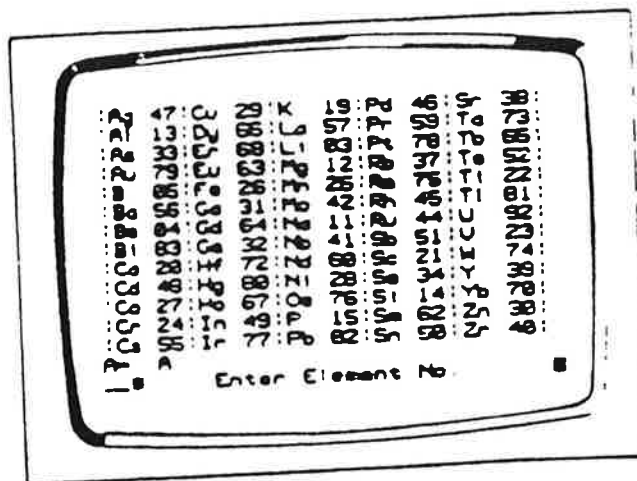
SELECTION

- | | |
|---|---|
| 1 | Uncorrected absorbance
(default selection as
indicated by asterisk) |
| 2 | D ₂ arc corrected
absorbance |
| 3 | D ₂ arc background
absorbance only |
| 4 | Smith-Hieftje corrected
absorbance |
| 9 | To exit current routine |

NOTE: If D₂ background correction (or background only) has been selected, the CRT will display "D₂ Warmup" for a few seconds prior to the subsequent display. (See Section 4.3.14 for deuterium arc background correction procedure.)

8. Key <ENTER>.

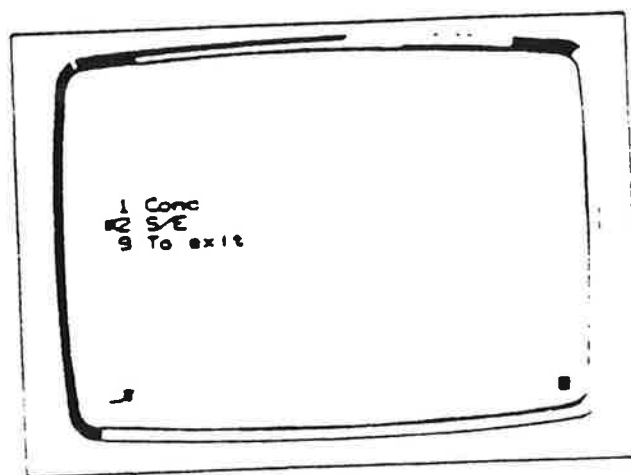
oThe CRT displays:



9. Select the element of interest by keying the appropriate two-digit number.

oThe atomic symbol of the element of interest appears in the bottom line of the CRT display (A=).

10. Key <ENTER>.



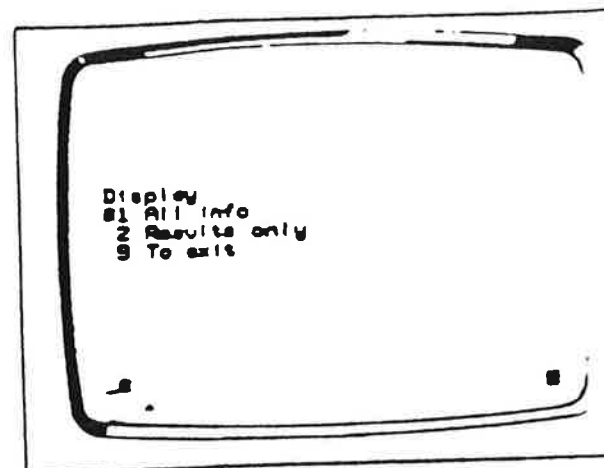
11. To select concentration,
key 1 <ENTER>.

To select scale expansion,
key 2 <ENTER>.

Enter the scale expansion
factor (from 0.1 to 99.9)
and key <ENTER> when the
CRT displays:
"A S/E 1.000".

To obtain results in
units of concentration,
key 1 <ENTER>.

oThe CRT displays:



12. Format the CRT display by keying
the appropriate number and <ENTER>.

SELECTION

DESCRIPTION

- | | |
|----------------|---|
| 1 All info | Displays concentrations,
integrations, mode, and
concentration of calibration
standards |
| 2 Results only | Displays element symbols as
headings and concentrations
(if a curve is entered) or
absorbances (if in the scale
expansion mode) |

B. Atomic Absorption Spectrophotometry Calibration

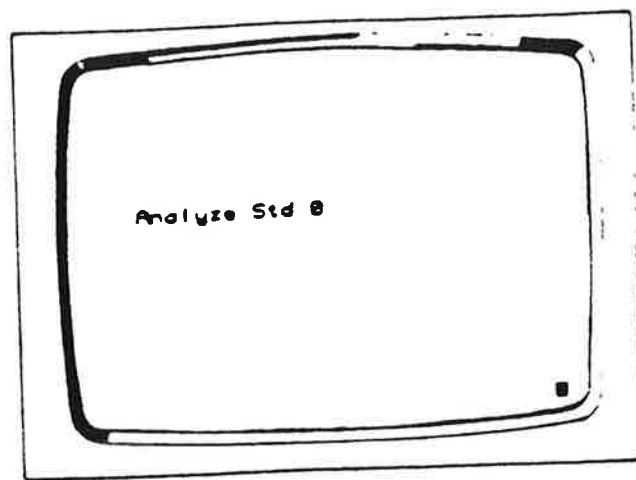
4.3.3 Calibration Procedure

NOTE: This procedure applies both to AA and AE determinations.

1. Perform steps 4-14 (Section 4.3.1), selecting AA mode of operation CONC mode, and statistics as desired. Also, perform steps 1 to 5 in Section 4.3.2.

2. Key <STD>.

oThe CRT displays:

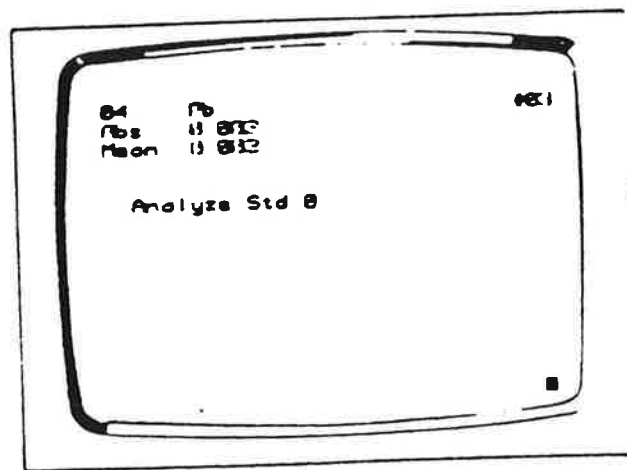


3. Aspirate standard 0.

NOTE: If the operator wishes to use the bracketing technique (i.e., standard 0 is not a reagent blank), refer to the note at the end of this section.

4. Key <READ>.

oThe CRT displays:



5. After the desired number of replicate readings, key <READ> to stop.

6. Key <ENTER>.

NOTE: This step automatically zeroes the absorbance reading of standard 0.

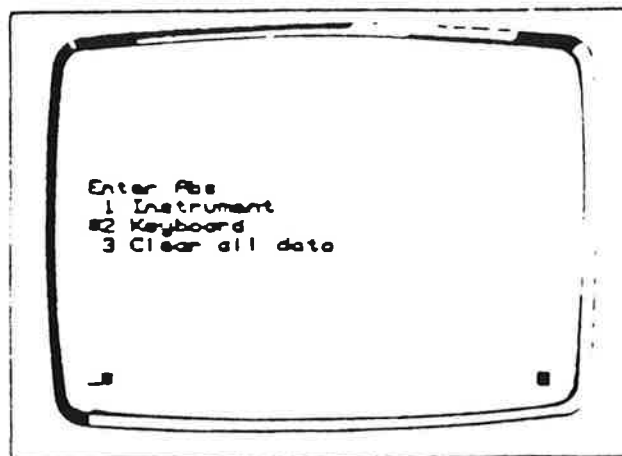
oThe CRT displays:

Select 1 Instrument
when aspirating standard solutions.

Select 2 Keyboard
when manually entering concentrations and absorbances.

Select 3 Clear all data
to clear the previous calibration table prior to entering new CONC and absorbance values.

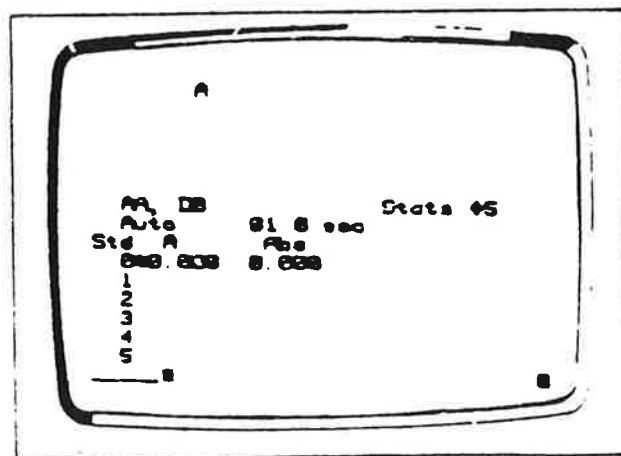
If option 3 is entered, any calibration curves not stored in one of the storage registers will be erased. The operator must then select option 1 or 2.



7. Key the desired option and <ENTER>, or simply key <ENTER> to default to manual (keyboard) entry of concentration and absorbance values. In this case, key 1 <ENTER>.

oIf 1 or 2 is selected, the CRT typically displays:

If manual entry is desired, refer to Section 4.3.6.



The asterisk marks the standard concentration to be entered from the keyboard.

8. Enter the concentration value of element in standard 0. If concentration equals 0.000, omit this step and proceed to step 9.

NOTE: Standard 0 or standard 1 will format the decimal point (i.e. 0010, 010.0, 10.00) for the subsequent standards entered. Before standard entry the decimal format for standard 0 is either the default format (0.000) or the format established by the previous calibration curve.

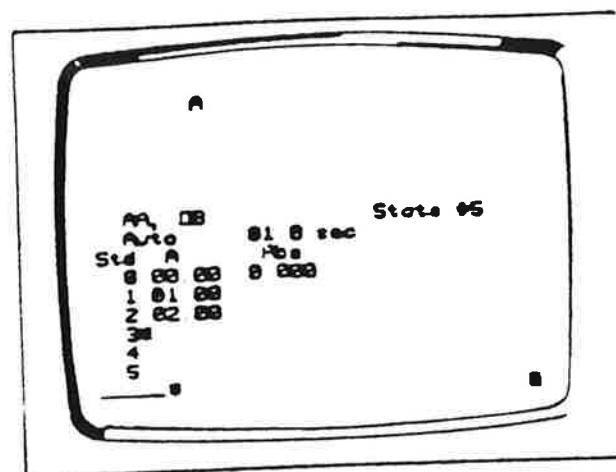
9. Key <ENTER>.

10. Key the concentration of standard 1 and <ENTER>.

NOTE: The auto-cal standard should be midrange in the calibration curve or at the point in the calibration curve where most of the samples are expected to fall.

11. Key the concentrations of the remaining standards (to a maximum of five) and key <ENTER> after each.

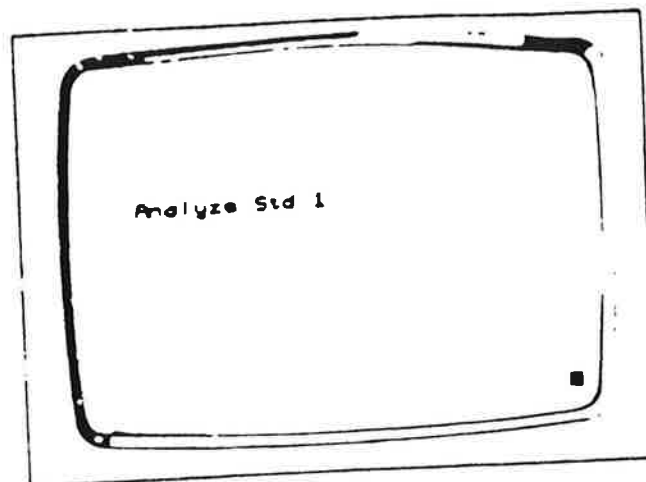
The CRT displays:



NOTE: If five standards are entered, the microprocessor automatically advances to step 13. If fewer than five standards are entered, proceed to step 12.

12. Key <STD>.

oThe CRT displays:

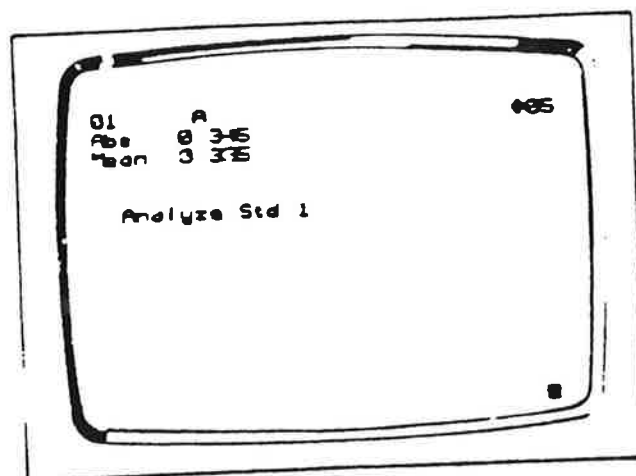


13. Aspirate the first (auto-cal) standard.

14. Key <READ>.

15. After the desired number of replicate readings, key <READ> to stop.

oThe CRT displays:

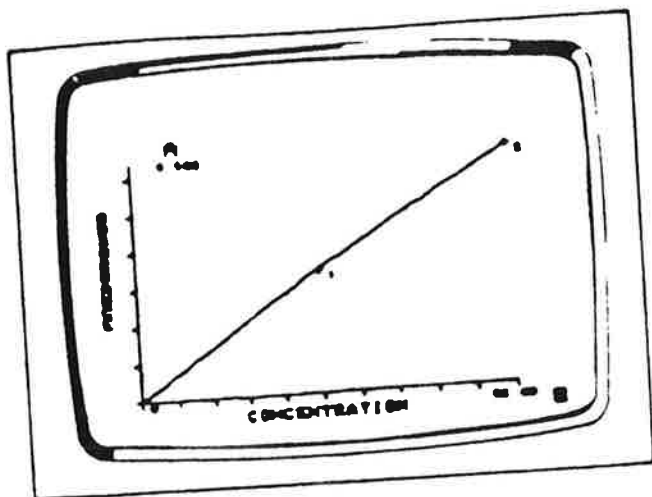


16. Key <ENTER>.

cThe mean absorbance is entered into the microcomputer.

17. Repeat steps 13-16 for the remaining standards.

NOTE: The microcomputer will automatically begin the calculation of the calibration curve after the last standard solution is aspirated and entered.



18. Key <ENTER> to return the CRT to the sample analysis screen.

oWith the graphics option the CRT will display CURVE CALC and the axes of the calibration curve.

oThe CRT will display the plot of absorbance vs. concentration when the calibration curve is completed.

oAccuracy of the curve fit can be determined by the proximity of the dashed line to the + marking standard absorbance points.

oThe optional printer will produce the following tape:

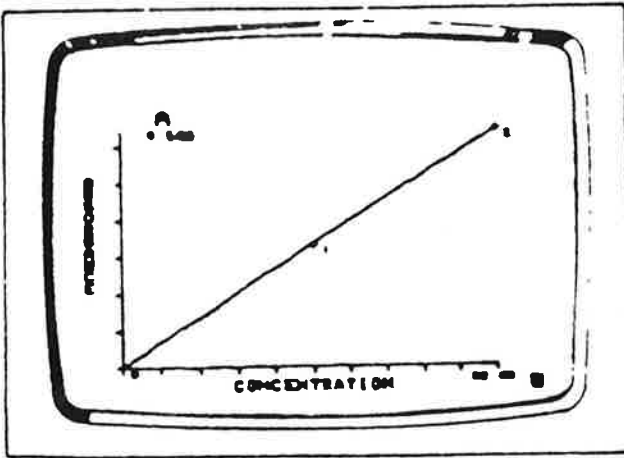
```

CALIBRATE
STD  CONC      MEAN
0      00.00    0.000
1      01.00    0.335
2      02.00    0.679
*** CONC
STD 0      00.00
STD 1      01.00
STD 2      02.00
  
```

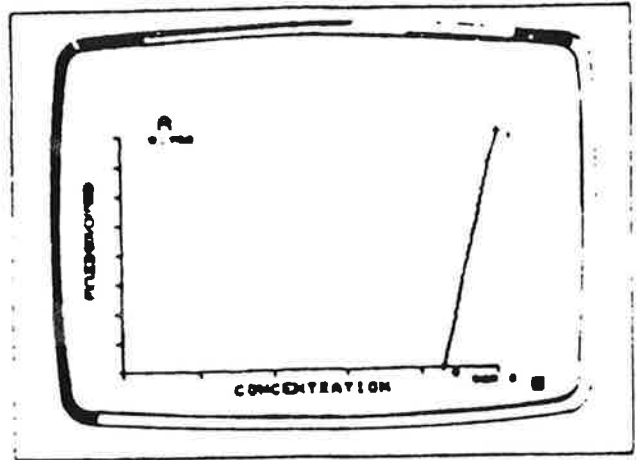
NOTES:(1) After step 18, the microcomputer will read out in direct concentration units. Proceed with analysis by aspirating unknown solutions and keying <READ>.

(2) The bracketing technique may also be used in the calibration procedure. To closely bracket a sample with two standards, the calibration curve need not originate at 0 concentration but may start at an operator-defined concentration. For example, two alloys are used for the calibration. Alloy 1 is 21.5% Ni and Alloy 2 is

25.0% Ni. Using the bracketing approach, 21.5% would be entered as standard 0 (step 8) and its absorbance automatically set to zero during calibration. Alloy 2 would be entered as standard 1. In this manner, the curve need be accurate only over a portion of the calibration curve rather than over the entire range, thus ensuring maximum accuracy. (See screen 2 below.)



SCREEN 1: Normal Calibration



SCREEN 2: Bracketing Technique

THE CRT DISPLAYS:	THE PRINTER DISPLAYS:	CAUSE/CORRECTIVE ACTION:
Invalid Entry	(no listing)	Incorrect data entry (illegal entry or incorrect format). Verify that the entry that was keyboarded is a valid selection in the specified format.
NO STD	NO STD	Readings taken in concentration mode without entering a calibration curve.
MAX AT CONC XXXX or FLEX AT C= XXXX	MAX CURVE FLEX CURVE	Inflection point in the calibration curve. Select standards properly. (Refer to Sections 4.3.7.)
NEG CURVE	NEG CURVE	Calibration curve has an erroneous point less than zero absorbance. Recheck standards and recalibrate.

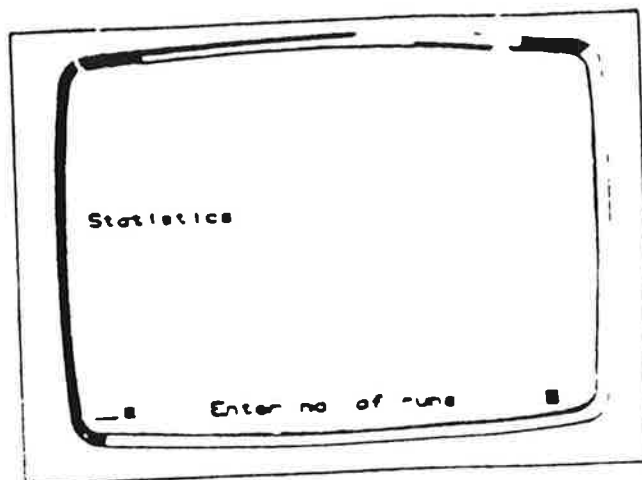
4.3.10 Statistics Program for the Determination of the Mean, Standard Deviation and Relative Standard Deviation

After a curve calibration procedure has been completed, the CRT displays the measured concentration based on the computed calibration curve. A running count of the concentration determinations is displayed on the CRT and reproduced on the optional printer. If statistical evaluation of repetitive determinations is desired, use the following procedure.

- NOTES:(1) Statistics are initiated in the mode selection procedure when the CRT displays:
STATISTICS, ENTER NO. OF RUNS
- (2) Any number of repeats from 2 to 99 may be selected. Keying 1 or 0 results in no statistical evaluation.

1. Perform steps 4-12 in Section 4.3.1.

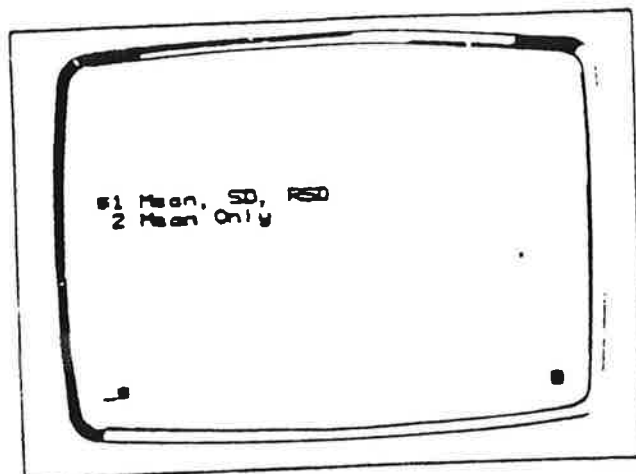
oThe CRT displays:



2. Key the desired number of replicate readings (2-99) and <ENTER>.

NOTE: This number represents both the number of replicate readings for statistical analysis and the number of readings upon which the auto-cal and auto-zero functions are performed.

oThe CRT displays:



3. Key 1 <ENTER> for display of Mean, SD and RSD, or key 2 <ENTER> for display of Mean Only.

TYPICAL PRINTER TAPES FOR:

Full Statistics

```
      A
MODE: AA, DB
STATS #5
      A
SN= 800005
CONC  1  01.62
MEAN   01.62
CONC  2  01.61
MEAN   01.61
CONC  3  01.61
MEAN   01.61
CONC  4  01.62
MEAN   01.61
CONC  5  01.62
MEAN   01.61
      A
MEAN   01.61
SD      00.01
RSD     00.43
```

Mean Only

```
      A
MODE: AA, DB
STATS #5
      A
SN= 800003
CONC  1  01.60
MEAN   01.60
CONC  2  01.61
MEAN   01.60
CONC  3  01.61
MEAN   01.60
CONC  4  01.62
MEAN   01.61
CONC  5  01.61
MEAN   01.61
      A
MEAN   01.61
```

NOTES:(1) If the spectrophotometer is in the automatic integration mode, the selected number of readings will be taken, readings will stop automatically, and the CRT will display the statistics. If the spectrophotometer is in the manual integration mode, the CRT will display the statistics after the selected number of replicate readings have been taken.

- (2) An alternate method is to key <ENTER> after the desired number of readings have been taken. This action will stop the readings automatically and display the statistics on the CRT and optional printer.

C Magnesium Method

STANDARD ATOMIC ABSORPTION CONDITIONS
Mg DETERMINATION BY FLAME ATOMIZATION

Mg

MAGNESIUM

INSTRUMENTAL PARAMETERS

Light Source	<u>Hollow Cathode</u>	IL Lamp No.:	<u>62968</u>
Lamp Current	<u>3</u> mA		
Wavelength:	<u>285.2</u> nm		
Slit Width:	<u>320</u> μ m	Bandpass:	<u>1</u> nm
Burner Head:	<u>Single Slot</u>	IL No.:	<u>43005-02</u>
Flame Description:	<u>Air-Acetylene</u> <u>Oxidizing, Fuel Lean, Blue</u>		
Photomultiplier Voltage (HV):	Once the lamp current, wavelength, and slit width have been set, adjust the HV control until the log intensity meter reads between 0.2 and 0.8 Volt.		
NOTE: 1. For a more thorough discussion of the above instrumental parameters, please consult the appropriate heading in this manual. 2. The recommended lamp current is for a single element lamp.			

Sensitivity

The sensitivity (at 0.0044 Absorbance = 1% Absorption) is about 0.003 μ g/ml for the instrumental parameters described above.

A standard containing 0.1 μ g/ml of Mg will give a reading of approximately 0.1 A.

Linear Range

The working range for Mg is linear up to a concentration of approximately 0.4 μ g/ml (when using an aqueous solution and the instrumental parameters described above).

STANDARD ATOMIC ABSORPTION CONDITIONS

Mg DETERMINATION BY FLAME ATOMIZATION

Preparation of Standard Solution:

Dissolve 1.0000 gram of magnesium ribbon in 50 ml of 1:1 hydrochloric acid and dilute quantitatively to a volume of 1 liter. Final concentration is 1000 $\mu\text{g/ml}$ Mg.

Alternate Analytical Lines:

<u>Wavelength (nm)</u>	<u>Approximate Sensitivity ($\mu\text{g/ml}$)</u>	<u>Slit Width (μm) SBW (nm)</u>
285.2	0.003	320/1
202.5	0.08	320/1

Interferences:

Aluminum, titanium, zirconium and silicon have been shown to depress magnesium absorption in an air/acetylene flame. These interferences can be corrected by the addition of a known excess of a releasing agent such as strontium (1000 to 5000 $\mu\text{g/ml}$ Sr) or lanthanum (1000 to 10,000 $\mu\text{g/ml}$ La).

Flame Emission:

The most sensitive emission wavelength for Mg is 285.2 nm. A nitrous oxide-acetylene flame is recommended. Alternate emission wavelengths for Mg are 333.7 nm and 382.9 nm, respectively. An air-acetylene flame can also be used, but with reduced sensitivity.

D. Calcium Method

STANDARD ATOMIC ABSORPTION CONDITIONS
Ca DETERMINATION BY FLAME ATOMIZATION

Ca

CALCIUM

INSTRUMENTAL PARAMETERS

Light Source:	<u>Hollow Cathode</u>	IL Lamp No.:	<u>62610</u>
Lamp Current:	<u>7</u> mA		
Wavelength:	<u>422.7</u> nm		
Slit Width:	<u>320</u> μ m	Bandpass	<u>1</u> nm
Burner Head:	<u>Single Slot</u>	IL No.:	<u>43005-02</u>
Flame Description:	<u>Air-Acetylene</u> <u>Oxidizing, Fuel Lean, Blue</u>		

Photomultiplier Voltage (HV):

Once the lamp current, wavelength, and slit width have been set, adjust the HV control until the log intensity meter reads between 0.2 and 0.8 Volt.

- NOTE:
1. For a more thorough discussion of the above instrumental parameters, please consult the appropriate heading in this manual.
 2. The recommended lamp current is for a single element lamp.

Sensitivity

The sensitivity (at 0.0044 Absorbance = 1% Absorption) is about 0.05 μ g/ml for the instrumental parameters described above.

A standard containing 1.1 μ g/ml of Ca will give a reading of approximately 0.1 A.

Linear Range

The working range for Ca is linear up to a concentration of approximately 3 μ g/ml (when using an aqueous solution and the instrumental parameters described above).

NOTE: Optimum Flame Conditions for Ca determinations require the use of auxiliary oxidant. Typical oxidant flow should be 18 to 20 SCFH.

Ca DETERMINATION BY FLAME ATOMIZATION

Preparation of Standard Solution:

Disperse 2.497 grams of dried calcium carbonate (CaCO_3) in 50 ml of water. Add drop-by-drop a minimum volume of HCl (approximately 10 ml) to effect complete solution of the CaCO_3 . Dilute the resulting solution quantitatively to a volume of 1 liter. Final concentration is 1000 $\mu\text{g/ml}$ Ca.

Alternate Analytical Lines:

<u>Wavelength (nm)</u>	<u>Approximate Sensitivity ($\mu\text{g/ml}$)</u>	<u>Slit Width (μm)/SBW (nm)</u>
422.7	0.05	320/1
239.9	6.0	40/0.15

Interferences:

Silicon, aluminum, phosphate and sulfate depress calcium's sensitivity. Titanium and zirconium have also been observed to depress calcium's sensitivity. Lanthanum or strontium at concentrations of 0.1 to 1% (w/v) can be added to sample and standards to control these interferences, and simultaneously control a slight ionization interference which occurs when calcium is determined in an air-acetylene flame.

Other Flames:

The use of a nitrous oxide-acetylene flame for the determination of Ca appears to be free from chemical suppressions. This flame is preferable for samples containing large amounts of silicon. When employing the nitrous oxide-acetylene flame, ionization interferences must be controlled by adding a large amount of alkali salt (such as potassium chloride or potassium nitrate) to give a final concentration of 2000 $\mu\text{g/ml}$ K to the samples and standards.

Flame Emission

The most sensitive emission wavelength for Ca is 422.7 nm. A nitrous oxide-acetylene flame having a red feather height of 5 mm is recommended. An alternate emission wavelength for Ca is at 239.9 nm. An air-acetylene flame may also be used, but with reduced sensitivity.

E. Glassware and Plastic Cleaning

as Pyrex, Corex, or Kimax, the stock number of the particular item, and the capacity of the vessel. If the vessel contains a ground-glass connection, this will also be included along with the TD or TC symbol. An example of the markings usually found on volumetric ware is shown in figure 4-1. Class A glassware need not be recalibrated before use. However, if it should become necessary to calibrate a particular piece of glassware, directions may be found in texts (4) on quantitative analysis.

4.5 Cleaning of Glass and Porcelain

The method of cleaning should be adapted to both the substances that are to be removed, and the determination to be performed. Water-soluble substances are simply washed out with hot or cold water, and the vessel is finally rinsed with successive small amounts of distilled water. Other substances more difficult to remove may require the use of a detergent, organic solvent, dichromate cleaning solution, nitric acid, or aqua regia (25 percent by volume concentrated HNO_3 in concentrated HCl). In all cases it is good practice to rinse a vessel with tap water as soon as possible after use. Material allowed to dry on glassware is much more difficult to remove.

Volumetric glassware, especially burets, may be thoroughly cleaned by a mixture containing the following: 30 g of sodium hydroxide, 4 g of sodium hexametaphosphate (trade name, Calgon), 8 g of trisodium phosphate, and 1 l of water. A gram or two of sodium lauryl sulfate or other surfactant will improve its action in some cases. This solution should be used with a buret brush.

Dichromate cleaning solution (chromic acid) is a powerful cleaning agent; however, because of its destructive nature upon clothing and upon laboratory furniture, extreme care must be taken when using this mixture. If any of the solution is spilled, it must be cleaned up immediately. Chromic acid solution may be prepared in the laboratory by adding 1 l of concentrated sulfuric acid slowly, with stirring, to a 35-ml saturated sodium dichromate solution. This mixture must be allowed to stand for approximately 15 min in the vessel that is being cleaned and may then be returned to a storage bottle. Following the chromic acid wash, the vessels are rinsed thoroughly with tap water, then with small successive portions of distilled water. The analyst should be cautioned that when chromium is included in the

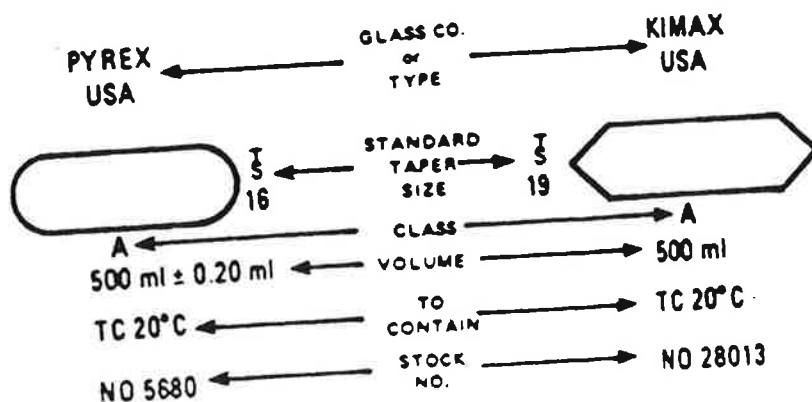


Figure 4-1. Example of markings on glassware.

scheme of analysis, it is imperative that the last traces of dichromate be removed from the apparatus. To this end, a substitute for dichromate cleaning solution, called Nochromix,* is available and may be used to advantage. Fuming nitric acid is another powerful cleaning agent, but is disagreeable to handle. As with dichromate, when the acid becomes dilute, the cleaning mixture is no longer effective. A mixture of concentrated sulfuric and fuming nitric acids is even more efficient but is also hazardous to use. A persistent greasy layer or spot may be removed by acetone or by allowing a warm solution of sodium hydroxide, about 1 g per 50 ml of water, to stand in the vessel for 10 to 15 min, after rinsing with water, dilute hydrochloric acid, and water again, the vessel is usually clean. Alcoholic potassium hydroxide is also effective in removing grease. To dry glass apparatus, rinse with acetone and blow or draw air through it.

4.6 Special Cleaning Requirements

Absorption cells, used in spectrophotometers, should be kept scrupulously clean, free of scratches, fingerprints, smudges, and evaporated film residues. The cells may be cleaned with detergent solutions for removal of organic residues, but should not be soaked for prolonged periods in caustic solutions because of the possibility of etching. Organic solvents may be used to rinse cells in which organic materials have been used. Nitric acid rinses are permissible, but dichromate solutions are not recommended because of the adsorptive properties of dichromate on glass. Rinsing and drying of cells with alcohol or acetone before storage is a preferred practice. Matched cells should be checked to see that they are equivalent by placing portions of the same solution in both cells and taking several readings of the transmittance (T , percent) or optical density (OD) values.

For certain determinations, especially trace metals, the glassware should also be rinsed with a 1:1 nitric acid-water mixture. This operation is followed by thoroughly rinsing with tap water and successive portions of distilled water. This may require as many as 12 to 15 rinses, especially if chromium is being determined. The nitric acid rinse is also especially important if lead is being determined.

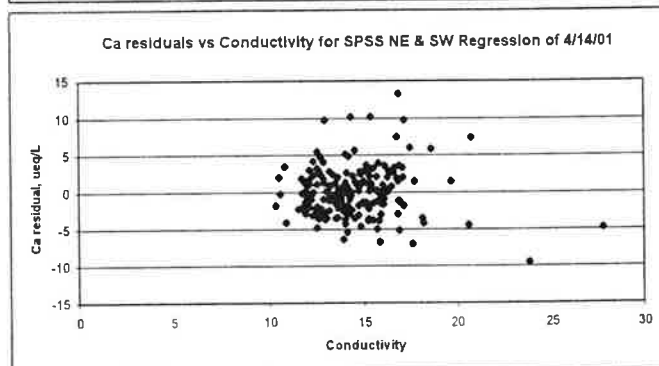
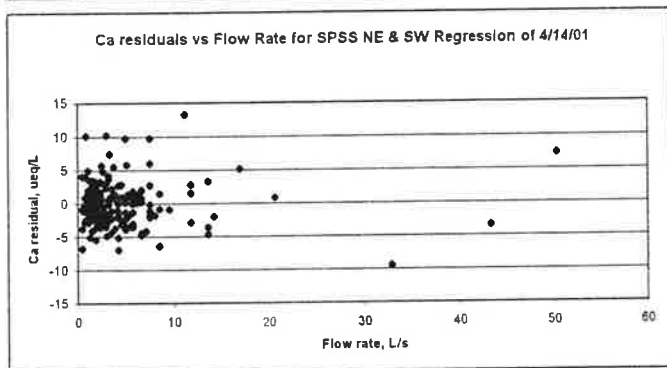
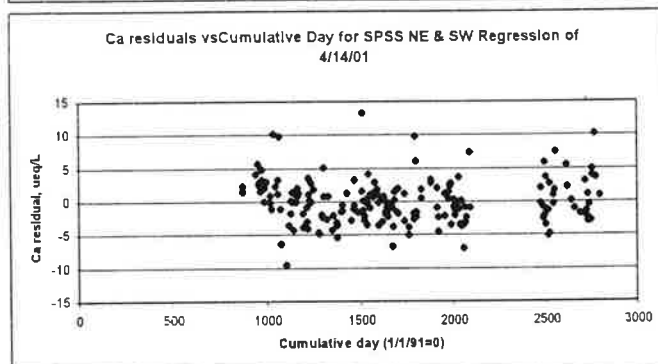
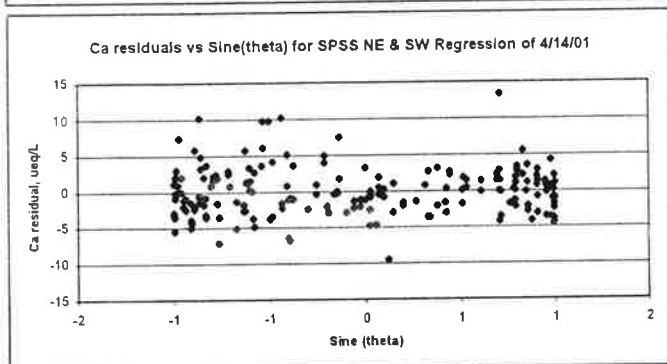
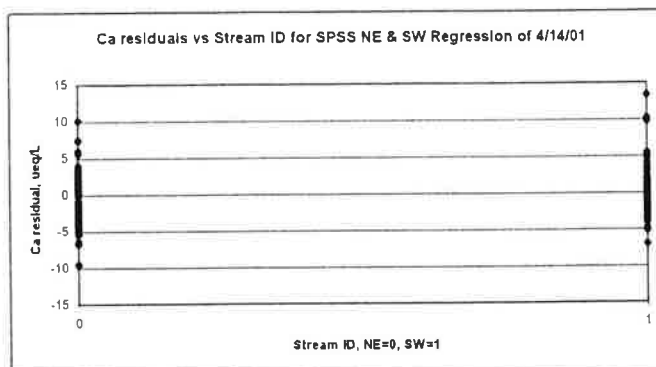
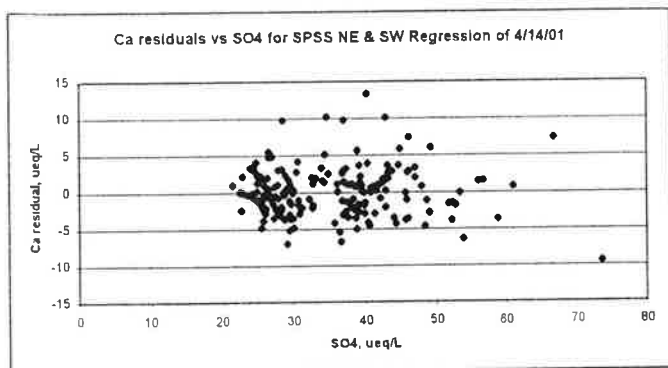
Glassware to be used for phosphate determinations should not be washed with detergents containing phosphates. This glassware must be thoroughly rinsed with tap water and distilled water. For ammonia and Kjeldahl nitrogen, the glassware must be rinsed with ammonia-free water. (See ch. 2.)

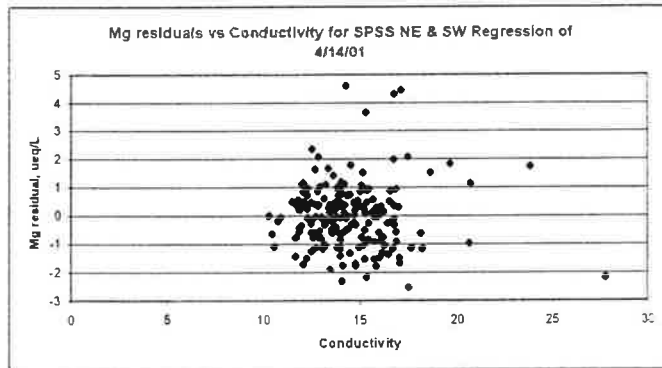
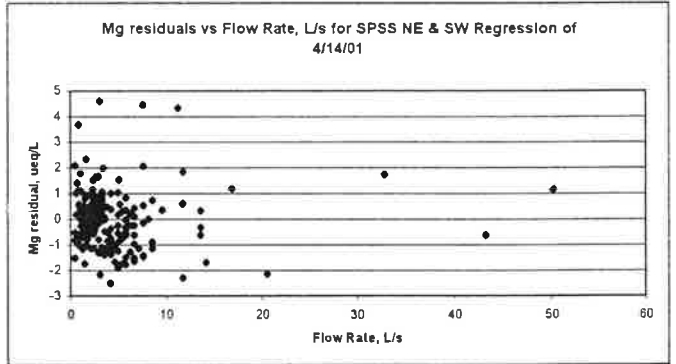
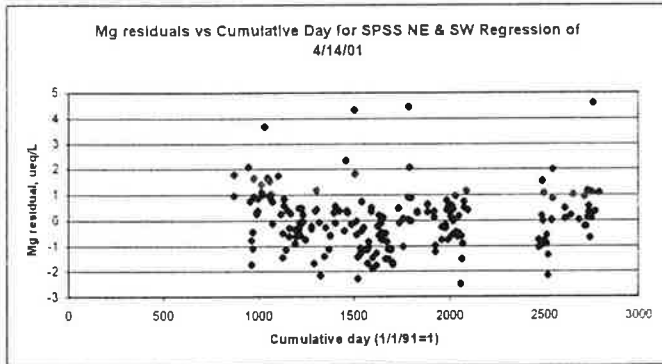
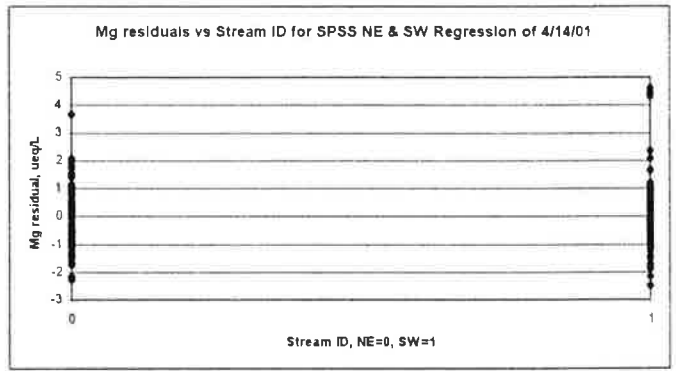
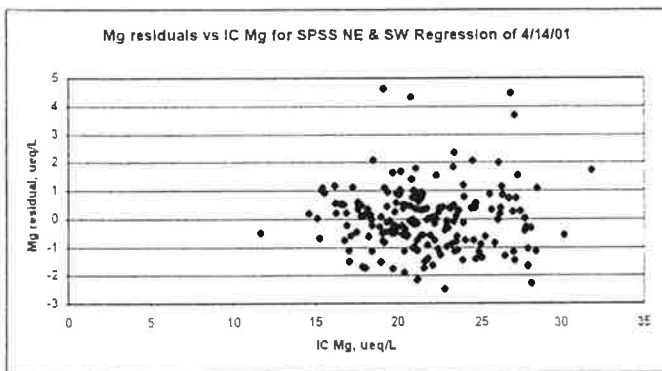
Glassware to be used in the determination of trace organic constituents in water, such as chlorinated pesticides, should be as free as possible of organic contaminants. A chromic acid wash of at least 15 min is necessary to destroy these organic residues. Rinse thoroughly with tap water and, finally, with distilled water. Glassware may be dried for immediate use by rinsing with redistilled acetone. Otherwise glassware may be oven dried or drip dried. Glassware should be stored immediately after drying to prevent any accumulation of dust and stored inverted or with mouth of glassware covered with foil.

Bottles to be used for the collection of samples for organic analyses should be rinsed successively with chromic acid cleaning solution, tap water, distilled water, and, finally, several times with a redistilled solvent such as acetone, hexane, petroleum ether, or chloroform. Caps are washed with detergent, rinsed with tap water, distilled water, and

* Available from Godax Laboratories, 6 Varck Street, New York, N.Y. 10013.

CALCIUM AND MAGNESIUM RESIDUALS FOR REGRESSION ANALYSES





NE DATA - 4/26/01

PLEASE BE AWARE OF THE FOLLOWING NOTES AND CAUTIONS:

1) At some zoom levels, the EXCEL worksheet may show units of microequivalents/L as milliequivalents/L due to font displays.

The correct unit is microequivalents/L.

2) Values for Mg and Ca for the period 9/93-10/98 were analyzed by ion chromatography, IC. These values were found to have QA/QC problems and their use can not be sanctioned except as order of magnitude estimates. Users are advised to use estimated values of Ca and Mg which were based on regression models using atomic absorption (AA) analyses of available archived samples except where AA analyses are available. The user is referred to a report titled "Water Quality Analysis of Calcium and Magnesium in the Great Smoky Mountains National Park," by Robinson, Smoot, Shubzda, and Barnett, University of Tennessee, Knoxville 2001. Contact Dr. R. Bruce Robinson at rbr@utk.edu or John Shubzda at jshubzda@utk.edu for further details. The set of AA analyzed values are included below.

Name	date	NE cfs	NE L/s	pH	Cond	Alk, µeq/L	Cl µeq/L	NO3-N µeq/L	SO4 µeq/L	Na µeq/L	NH4-N µeq/L	K µeq/L	Ca µeq/L (USGS analysis pre- 9/93 IC analysis 9/93 10/98)	Mg µeq/L (USGS analysis pre- 9/93, IC analysis 9/93 10/98)	H-ion conc µeq/L	Al, µmol	Si µmol	AA Mg in µeq/L	AA Ca, µeq/L	Estimated Ca, µeq/L (Based on regression models)	Estimated Mg, µeq/L (Based on regression models)
NE1	07/19/1991			5.76	21.50	4.86	12.13	47.12	48.95	20.00	0.00	11.01	57.98	22.22	1.74						
NE1	07/26/1991			5.59	24.00	7.22	13.54	50.69	42.70	20.87	0.00	10.75	55.48	22.22	2.57						
NE1	08/02/1991			5.61	20.40	12.13	13.25	49.98	37.08	22.17	0.00	10.24	47.48	22.22	2.45						
NE1	08/16/1991			5.49	27.10	4.00	12.97	52.12	41.45	20.44	0.00	11.01	51.98	22.22	3.24						
NE1	08/23/1991			5.76	11.95	7.96	11.84	50.69	36.24	23.04	0.00	21.50	52.87	19.75	1.74						
NE1	08/30/1991			5.62	13.80	8.19	11.28	51.41	50.62	20.44	0.00	12.03	60.35	22.22	2.40						
NE1	09/06/1991			5.83	12.40	5.37	11.84	52.84	38.12	23.04	0.00	10.50	58.36	21.40	1.48						
NE1	09/13/1991			5.89	12.40	5.87	12.13	52.84	36.04	23.91	0.00	10.50	53.87	19.75	1.29						
NE1	09/20/1991			5.79	11.65	12.10	12.97	51.41	36.87	23.91	0.00	11.01	54.87	20.58	1.62						
NE1	09/27/1991			5.96	11.80	6.96	11.28	51.41	42.70	21.74	0.00	10.24	59.86	20.58	1.10						
NE1	10/04/1991			5.88	12.25	8.36	11.84	52.84	37.08	23.48	0.00	9.98	57.36	19.75	1.32						
NE1	10/11/1991			5.87	11.80	7.09	13.62	52.84	34.79	23.04	0.00	9.98	49.48	20.58	1.35						
NE1	10/18/1991			5.77	11.80	8.44	15.51	51.41	32.70	23.04	0.00	10.24	44.48	18.93	1.70						
NE1	10/25/1991			5.90	11.80	24.91	16.07	51.41	31.66	23.91	0.00	10.50	46.48	20.58	1.25						
NE1	11/01/1991			5.59	16.70	22.26	40.04	59.98	56.45	28.26	0.00	23.04	80.47	30.45	2.57						
NE1	11/12/1991	0.010	0.269	5.77	11.40	7.86	15.23	56.41	29.58	23.91	0.00	8.19	47.48	19.75	1.70						
NE1	11/19/1991	0.020	0.577	5.59	15.30	5.04	26.23	57.12	47.08	26.96	0.00	13.57	62.48	24.69	2.57						
NE1	11/26/1991	0.104	2.958	5.41	14.20	-1.20	16.07	62.83	48.24	18.70	0.00	11.26	49.48	20.58	3.89						
NE1	12/03/1991	1.264	35.787	5.03	16.40	-4.27	13.25	44.27	65.82	14.78	0.00	16.90	57.48	23.87	9.33						
NE1	12/10/1991	0.266	7.538	5.36	14.40	5.01	15.23	54.98	49.78	18.70	0.00	13.31	55.48	22.22	4.37						
NE1-1	12/17/1991	0.176	4.986	5.53	13.20	0.91	14.38	61.40	39.58	20.87	0.00	11.01	53.87	17.28	2.95						
NE1-1	12/30/1991	0.219	6.197	5.43	13.60	-2.32	14.10	61.40	43.33	20.44	0.00	11.78	60.35	26.34	3.72						
NE1-1	01/07/1992	0.204	5.779	5.47	13.40	-1.11	18.38	60.69	40.83	20.87	0.00	11.26	59.86	24.69	3.39						
NE1-1	01/15/1992	0.176	4.986	5.45	16.89	-0.36	28.20	60.69	42.91	20.87	0.00	10.50	59.86	20.58	3.55						
NE1-1	01/22/1992	0.067	1.897	5.61	15.47	2.83	15.51	59.98	34.79	22.17	0.00	10.50	55.87	19.75	2.45						
NE1-1	01/28/1992	0.104	2.958	5.52	15.52	0.89	14.66	61.40	37.70	21.74	0.00	11.01	54.87	20.58	3.02						
NE1-1	02/04/1992	0.059	1.689	5.62	15.37	2.50	14.95	60.69	34.79	22.17	0.00	11.78	53.87	18.93	2.40						
NE1-1	02/10/1992	0.038	1.070	5.68	15.10	2.34	14.66	61.40	33.12	22.61	0.00	8.98	52.87	18.93	2.09						
NE1-1	02/18/1992	0.234	6.629	5.67	16.70	-0.92	12.13	62.83	49.78	19.57	0.00	11.26	63.85	21.40	2.14						
NE1-1	02/26/1992	0.782	22.146	5.23	17.73	-3.54	10.43	55.69	56.87	18.09	0.00	12.29	53.37	18.11	5.89						
NE1-1	03/03/1992	0.126	3.576	5.66	15.37	-3.08	13.25	59.26	35.62	24.17	0.00	10.98	53.57	21.97	2.97						
NE1-1	03/12/1992	0.283	8.014	5.60	16.17	-2.83	12.69	59.98	39.99	21.52	0.00	11.96	50.73	21.32	2.51						
NE1-1	03/17/1992	0.138	3.907	5.67	12.95	6.19	13.25	59.26	36.66	22.39	0.00	11.57	49.48	20.74	2.14						
NE1-1	03/24/1992	0.190	5.375	5.57	12.20	-0.34	13.25	59.26	37.91	23.44	0.00	10.96	55.27	22.88	2.69						
NE1-1	03/31/1992	0.266	7.538	5.48	13.25	-0.93	10.72	54.26	48.12	19.00	0.00	11.70	54.17	21.40	3.31						
NE1-1	04/07/1992	0.126	3.576	5.65	12.70	8.87	13.25	59.98	36.24	22.65	0.00	11.21	50.28	20.74	2.24						
NE1-1	04/14/1992	0.169	4.797	5.76	13.75	4.38	12.69	57.83	42.08	20.87	0.00	11.37	58.36	20.99	1.74						
NE1-1	04/22/1992	0.300	8.504	5.62	13.60	0.94	11.56	55.69	47.70	20.31	0.00	10.68	60.75	22.80	2.40						
NE1-1	04/28/1992	0.104	2.958	5.74	10.00	3.08	12.97	58.55	35.83	20.74	0.00	10.27	47.74	20.00	1.82						
NE1-1	05/05/1992	0.094	2.671	5.88	10.10	5.72	12.97	57.83	37.08	23.31	0.00	10.82	53.57	20.99	1.32						
NE1-1	05/12/1992	0.104	2.958	5.77	11.40	22.92	12.69	57.12	40.20	22.57	0.00	11.01	54.67	20.48	1.70						
NE1-1	05/19/1992	0.104	2.958	5.86	11.40	2.05	12.97	55.69	39.58	22.74	0.00	10.65	53.52	20.61	1.38						
NE1-1	05/26/1992	0.067	1.897	5.90	12.30	1.26	13.62	55.69	36.04	23.91	0.00	9.22	53.42	21.48	1.25						
NE1-1	06/02/1992	0.163	4.612	5.77	16.23	1.60	12.41	56.41	40.20	20.39	0.00	9.09	51.23	20.49	1.70						
NE1-1	06/10/1992	0.300	8.504	5.66	18.08	-2.64	15.23	57.83	41.00	21.39	0.00	11.06	52.72	21.64	2.19						
NE1-1	06/16/1992	0.300	8.504	5.57	16.53	-0.07	12.13	57.83	42.28	22.35	0.00	10.16	54.12	22.88	2.69						
NE1-1	06/23/1992	0.104	2.958	5.78	15.53	2.71	12.69	58.55	35.83	23.44	0.00	9.75	51.23	21.81	1.74						
NE1-1	06/30/1992	0.051	1.455	5.78	16.20	3.61	13.82	57.12	34.58	24.87	0.00	9.78	48.63	20.82	1.66						
NE1-1	07/07/1992	0.085	2.399	5.69	15.88	4.22	12.13	54.98	41.04	22.83	0.00	8.78	47.19	19.58	1.86						
NE1-1	07/14/1992	0.051	1.455	5.73	15.39	13.10	12.69	54.98	35.20	24.52	0.00	8.78	47.19	19.58	1.86						
NE1-1	07/21/1992	0.035	0.983	5.72	15.18	10.35	13.25	54.98	33.95	23.87	0.00	8.99	47.83	20.25	1.91						
NE1-1	07/28/1992	0.051	1.455	5.73	14.98	7.79	10.72	48.41	35.42	24.66	0.43	9.46	56.94	22.14	1.86	1.19	65.34				
NE1-1	08/04/1992	0.026	0.745	6.12	15.41	9.53	12.41	51.41	34.79	26.36	5.57	8.77	57.09	21.97	0.76	0.89	68.09				
NE1-1	08/11/1992	0.032	0.900	5.85	16.03	9.75	11.28	50.69	35.83	26.01	0.36	8.72	57.83	21.81	1.41	0.96	67.55				
NE1-1	08/18/1992	0.138	3.907	5.93	16.05	6.05	11.00	53.55	42												

NE1-1	05/02/1995	0.126	3.578	5.60	15.80	4.38	15.24	43.20	46.87	23.87	0.00	9.01	68.33	21.45	2.51	4.48	52.97	58.71	18.63
NE1-1	05/09/1995	0.087	1.897	5.79	14.00	5.81	14.17	48.72	37.73	28.58	0.00	12.71	63.88	21.05	1.92	4.30	59.15	54.10	18.70
NE1-1	05/16/1995	0.266	7.538	5.67	16.06	2.88	13.27	42.17	45.61	25.60	0.93	9.55	66.98	23.85	2.14	4.30	54.98	58.23	18.57
NE1-1	05/23/1995	0.183	4.612	5.58	11.80	3.62	13.34	43.33	42.74	21.13	1.49	9.36	71.02	22.45	2.53	4.22	57.05	54.99	18.58
NE1-1	05/30/1995	0.115	3.260	5.67	14.70	4.71	20.21	40.51	46.02	23.26	0.00	8.50	71.84	23.12	2.14	4.30	58.58	58.56	18.84
NE1-1	06/06/1995	0.219	6.197	5.67	16.20	4.19	10.42	35.24	29.88	22.29	0.00	8.90	70.63	22.48	2.14	4.37	63.35	58.03	18.49
NE1-1	06/13/1995	0.178	4.988	5.72	16.48	7.18	11.62	39.75	47.95	26.47	0.00	8.69	62.59	20.21	1.91	4.26	55.16	58.82	18.30
NE1-1	06/20/1995	0.085	2.399	5.73	16.02	6.49	15.21	45.20	39.08	27.28	3.19	10.38	83.25	20.58	1.56	3.74	60.96	56.45	18.59
NE1-1	06/27/1995	0.115	3.260	5.83	16.82	2.03	17.30	45.12	48.47	21.98	0.00	7.90	66.08	18.29	1.48	3.85	59.90	58.72	18.20
NE1-1	06/30/1995	0.115	3.260	5.82	15.95	3.9	14.30	45.20	40.73	27.88	3.04	9.77	64.97	20.88	1.51	3.82	60.96	57.25	18.53
NE1-1	07/05/1995	0.059	1.689	5.89	15.27	4.09	15.11	45.59	38.51	27.45	0.00	9.51	61.74	19.84	1.29	3.82	62.60	56.23	18.53
NE1-1	07/11/1995	0.032	0.900	5.85	15.52	0.48	14.70	53.23	42.14	25.92	0.00	7.41	61.61	19.72	1.41	3.78	65.02	56.81	18.59
NE1-1	07/18/1995	0.026	0.745	5.98	15.41	6.72	17.04	54.56	46.35	27.22	0.00	7.89	61.55	19.53	1.05	3.59	65.84	57.54	18.57
NE1-1	07/25/1995	0.017	0.478	5.94	15.8	5.03	14.27	46.76	36.57	28.81	0.00	7.69	57.57	18.02	1.15	3.59	67.73	56.39	18.52
NE1-1	08/01/1995	0.017	0.478	5.98	15.5	11.55	15.47	52.53	45.64	27.44	0.00	7.31	60.70	19.17	1.55	3.67	68.66	57.78	18.53
NE1-1	08/08/1995	0.300	8.504	5.46	17.66	1.13	12.53	44.42	55.99	21.68	0.00	9.78	80.03	23.36	3.47	3.85	55.94	57.14	18.35
NE1-1	08/15/1995	0.085	2.399	5.71	14.41	5.27	15.05	42.52	39.96	26.20	0.00	12.90	67.10	19.48	1.35	3.63	62.57	57.39	18.36
NE1-1	08/22/1995	0.076	2.141	5.88	16.74	5.06	11.37	41.00	42.52	25.55	0.00	8.11	70.38	18.43	1.32	3.71	51.95	58.91	18.28
NE1-1	08/29/1995	0.234	6.629	5.6	17.09	5.64	13.23	44.36	46.97	23.65	0.00	10.05	74.19	22.02	2.51	4.71	50.57	61.34	18.33
NE1-1	09/05/1995	0.059	1.689	5.74	12.5	14.85	11.07	39.92	26.98	27.11	0.00	5.60	60.36	19.11	1.62	4.63	71.43	54.69	18.34
NE1-1	09/12/1995	0.219	6.197	5.55	20.6	1.24	17.54	48.24	53.96	23.97	0.00	19.60	76.76	24.02	2.22	4.93	57.30	64.04	18.55
NE1-1	09/19/1995	0.234	6.629	5.74	16.77	4.71	13.60	44.71	45.06	23.59	0.00	9.33	69.06	22.00	1.52	4.74	59.25	61.12	18.31
NE1-1	09/26/1995	0.234	6.629	5.55	16.53	4.92	18.02	44.53	44.35	24.56	0.00	15.07	70.22	21.95	2.24	7.37	61.93	66.92	18.29
NE1-1	10/03/1995	0.104	2.958	5.75	16.77	7.54	17.05	41.50	41.34	26.59	0.00	12.63	71.01	22.88	1.78	7.49	61.68	59.37	18.76
NE1-1	10/10/1995	0.163	4.612	5.55	15.88	2.44	15.17	44.01	40.11	26.92	0.00	11.84	67.89	22.18	2.82	7.41	63.21	59.28	18.49
NE1-1	10/17/1995	0.085	2.399	5.67	18.20	13.44	14.43	44.73	40.74	26.32	5.02	10.39	67.78	22.96	2.14	7.49	64.03	59.67	18.84
NE1-1	10/25/1995	0.044	1.255	5.73	15.71	10.21	14.30	47.31	38.78	25.72	0.00	9.64	67.85	22.02	1.86			57.73	18.77
NE1-1	10/31/1995	0.067	1.897	5.58	15.48	7.17	15.42	46.92	43.17	24.70	0.00	10.18	70.92	22.33	2.63			58.39	18.75
NE1-1	11/07/1995	5.020	142.159	4.91	18.18	-8.42	17.10	40.90	55.51	13.29	0.00	13.26	57.89	20.19	12.30			107.62	5.08
NE1-1	11/21/1995	0.104	2.958	5.52	14.72	-2.84	15.01	45.77	39.90	23.31	0.00	9.04	67.93	21.79	3.02			57.42	18.54
NE1-1	11/28/1995	0.266	7.538	5.39	17.46	2	43.40	49.30	49.16	25.98	0.00	42.73	79.40	24.45	4.67			61.39	18.50
NE1-1	12/05/1995	0.115	3.260	5.38	15.06	-0.19	27.87	61.20	51.69	29.29	0.00	18.98	49.99	21.45	4.17			59.02	18.46
NE1-1	12/14/1995	0.067	1.897	5.65	16.14	4.73	16.27	47.33	37.62	32.34	0.00	11.40	43.95	21.94	2.24			56.71	18.67
NE1-1	01/04/1996	0.204	5.773	5.43	16.78	8.03	57.93	50.32	43.19	27.46	10.09	27.45	78.18	24.41	3.72			58.41	18.62
NE1-1	01/31/1996	0.266	7.538	5.43	15.34	2.39	12.87	46.81	42.77	27.23	0.00	8.45	44.45	21.18	3.72			57.38	17.97
NE1-1	02/23/1996	0.479	13.570	5.25	17.03	-7.61	10.84	52.60	47.03	23.72	0.00	8.63	40.32	21.32	5.82			60.20	17.42
NE1-1	03/07/1996	1.774	50.228	5.15	17.23	5.43	81.94	44.67	48.47	18.61	2.05	31.62	65.91	22.24	7.08			72.37	14.03
NE1-1	03/27/1996	0.234	6.629	5.66	15.67	2.53	23.79	50.05	42.94	21.64	0.00	9.14	70.72	23.47	2.19			56.24	18.32
NE1-1	04/05/1996	0.234	6.629	5.6	20.6	1.97	29.20	47.14	40.57	24.75	0.00	25.73	71.03	22.88	2.51			58.19	18.31
NE1-1	04/12/1996	0.094	2.671	5.53	14.86	0.08	22.44	47.94	38.89	23.06	0.00	8.68	68.23	22.69	2.95			53.96	18.57
NE1-1	04/19/1996	0.104	2.958	5.68	14.82	4.06	13.40	46.74	40.15	24.85	0.00	8.65	73.40	23.34	2.99			54.27	18.62
NE1-1	05/01/1996	0.375	10.611	5.50	15.96	1.23	15.53	46.82	42.16	18.02	0.00	8.91	73.83	22.51	3.16			57.76	17.79
NE1-1	05/08/1996	0.219	6.197	5.90	14.74	1.53	19.00	46.25	42.13	22.95	0.00	12.10	74.70	22.90	1.26			55.84	18.24
NE1-1	05/15/1996	0.572	16.198	5.37	15.37	-0.44	18.43	44.80	51.48	23.40	0.00	8.37	70.20	23.53	4.27			60.96	17.37
NE1-1	05/22/1996	0.104	2.958	5.73	21.90	4.74	27.21	44.52	37.31	22.82	0.00	8.89	75.33	23.27	1.86			57.71	18.70
NE1-1	05/29/1996	0.085	2.399	5.84	18.81	2.48	23.46	45.88	42.58	21.25	0.00	8.81	70.24	22.94	1.45			56.08	18.62
NE1-1	06/04/1996	0.051	1.455	5.84	14.08	7.17	27.34	44.90	36.79	25.19	1.75	9.17	74.71	23.92	1.45			53.79	18.79
NE1-1	06/11/1996	0.266	7.538	5.69	16.56	0.74	13.51	46.33	45.95	17.63	6.00	6.29	64.88	16.52	2.04			58.51	17.24
NE1-1	06/19/1996	0.094	2.671	5.62	14.27	2.74	15.14	46.09	38.33	18.77	7.61	5.51	53.59	15.17	2.40			54.94	17.49
NE1-1	06/25/1996	0.067	1.897	5.70	15.69	4.29	12.93	42.32	39.53	20.83	7.39	6.78	59.76	18.00	2.00			55.71	17.96
NE1-1	07/02/1996	0.032	0.900	5.61	15.72	0.83	15.66	44.33	36.83	21.22	8.51	6.24	58.03	17.56	2.45			55.20	17.99
NE1-1	07/09/1996	0.038	1.073	5.82	15.74	1.97	14.67	52.17	39.84	23.21	15.74	6.76	62.78	18.38	1.51			55.93	18.08
NE1-1	07/16/1996	0.104	2.958	5.97	17.65	9.70	10.71	46.73	45.06	19.19	10.36	6.79	68.34	19.29	1.07			58.43	18.04
NE1-1	07/23/1996	0.115	3.260	5.78	16.87	3.96	29.29	47.04	44.64	21.23	10.97	11.14	66.72	19.37	1.66			58.30	18.01
NE1-1	07/30/1996	1.124	31.833	5.89	19.90	7.03	11.66	41.64	49.88	14.97	5.06	8.85	69.45	19.62	2.04			70.11	15.35
NE1-1	08/06/1996	0.176	4.988	5.70	16.27	2.72	12.82	49.89	40.73	16.41	0.00	4.07	63.07	14.57	2.00			58.37	17.17
NE1-1	08/13/1996	0.415	11.751	5.73	16.29	6.78	10.72	48.34	47.97	23.62	0.00	9.58	74.90	21.36	1.88			62.79	17.47
NE1-1	08/20/1996	0.204	5.773	5.76	18.12	8.26	99.18	50.32	44.02	38.17	0.00	98.03	69.81	20.55	1.74			60.29	17.92
NE1-1	08/27/1996	0.300	8.504	5.65	16.06	-2.44	11.09	47.35	42.11	24.99	0.00	9.36	69.87	21.69	2.24			60.07	17.78
NE1-1	09/03/1996	0.085	2.399	5.89	14.38	3.72	12.49	45.72	38.51	27.81	0.00	9.26	70.24	21.36	1.29			56.83	18.28
NE1-1	09/10/1996	0.076	2.141	5.81	18.27	5.60	20.66	47.48	39.74	30.27	0.00	19.97	75.17	22.81	1.55			58.82	18.56
NE1-1	09/16/1996	1.774	50.228	5.07	20.70	-0.89	10.19	60.88	66.69	17.69	0.00	13.73	93.36	26.25	8.51			79.87	14.46
NE1-1	09/24/1996	0.067	1.897	5.79	14.24	5.44	11.84	46.58	38.35	26.68	0.00	7.98	69.						

SW DATA - 4/26/01

PLEASE BE AWARE OF THE FOLLOWING NOTES AND CAUTIONS:

1) At some zoom levels the EXCEL worksheet may show units of microequivalents/L as milliequivalents/L due to font displays.

The correct unit is microequivalents/L.

2) Values for Mg and Ca for the period 9/93-10/98 were analyzed by ion chromatography (IC). These values were found to have QA/QC problems and their use can not be sanctioned except as order of magnitude estimates. Users are advised to use estimated values of Ca and Mg which were based on regression models using atomic absorption (AA) analyses of available archived samples except where AA analyses are available. The user is referred to a report titled "Water Quality Analysis of Calcium and Magnesium in the Great Smoky Mountains National Park," by Robinson, Smoot, Shubzda, and Barnett, University of Tennessee, Knoxville, 2001. Contact Dr. R. Bruce Robinson at rbr@utk.edu or John Shubzda at jshubzda@utk.edu for further details. The set of AA analyzed values are included below.

Name	date	SW cfs	SW L/s	pH	Cond	Alk µeq/L	Cl µeq/L	NO3-N µeq/L	SO4 µeq/L	Na µeq/L	NH4-N µeq/L	K µeq/L	Mg µeq/L (USGS analysis pre- 9/93, IC analysis 9/93- 10/98)	Ca µeq/L (USGS analysis pre- 9/93, IC analysis 9/93- 10/98)	H ion conc, µeq/L	Al µmol	Si µmol	AA Ca µeq/L	AA Mg µeq/L	Estimated Ca, µeq/L (Based on regression models)	Estimated Mg, µeq/L (Based on regression models)
SW1	07/19/1991			5.52	25.40	17.96	10.72	38.56	33.12	20.44	0.00	7.17	18.11	45.98	2.40						
SW1	07/26/1991			5.96	19.60	13.10	10.43	36.41	29.58	20.87	0.00	6.91	18.11	44.98	1.10						
SW1	08/02/1991			5.83	21.90	14.20	11.00	39.27	25.00	21.74	0.00	7.17	18.93	42.98	1.48						
SW1	08/16/1991			5.80	25.30	15.51	9.87	39.27	31.66	20.44	0.00	7.68	18.93	44.48	1.58						
SW1	08/23/1991			5.82	10.00	12.00	9.59	41.41	26.66	23.48	0.00	8.96	16.46	48.38	1.51						
SW1	08/30/1991			5.73	11.20	11.00	36.94	39.98	35.62	23.48	0.00	8.96	18.11	62.35	1.86						
SW1	09/06/1991			5.97	10.40	18.68	11.00	40.70	25.66	23.91	0.00	8.19	18.11	50.38	1.07						
SW1	09/13/1991			6.06	10.50	18.46	9.87	42.84	24.79	23.48	0.00	7.94	16.46	44.89	0.87						
SW1	09/20/1991			5.75	10.20	13.00	10.15	43.55	26.04	25.22	0.00	8.45	27.98	52.37	1.78						
SW1	09/27/1991			5.96	11.80	14.15	10.43	45.70	30.20	23.48	0.00	8.45	18.93	50.88	1.10						
SW1	10/04/1991			5.96	10.30	20.90	10.15	44.98	25.20	23.48	0.00	7.42	17.28	46.89	1.10						
SW1	10/11/1991			5.92	10.00	19.21	11.28	44.27	23.12	22.61	0.00	7.42	18.11	40.98	1.20						
SW1	10/18/1991			5.64	10.40	20.21	13.25	44.98	22.91	23.04	0.00	8.45	19.75	43.48	2.29						
SW1	10/25/1991			5.90	10.50	26.87	12.97	45.70	23.33	22.61	0.00	7.42	17.28	38.48	1.26						
SW1	11/01/1991			5.85	16.70	26.41	54.43	63.55	52.91	30.87	0.00	25.86	32.10	81.97	1.41						
SW1	11/12/1991	0.010	0.269	5.75	10.10	16.99	12.97	49.98	21.04	22.61	0.00	7.42	18.93	42.48	1.78						
SW1	11/19/1991	0.015	0.420	5.52	14.25	20.22	22.00	58.55	35.41	26.09	0.00	12.29	23.87	55.98	3.02						
SW1	11/26/1991	0.067	1.897	5.33	13.00	2.55	15.79	62.12	33.54	20.44	0.00	9.98	21.40	49.98	4.68						
SW1	12/03/1991	0.930	26.333	5.15	14.20	-6.40	12.13	44.27	53.32	13.91	0.00	13.06	19.75	47.48	7.06						
SW1	12/10/1991	0.204	5.779	5.38	12.30	5.52	14.66	49.98	38.33	17.83	0.00	12.03	18.11	42.98	4.17						
SW1-1	12/17/1991	0.150	4.252	5.57	11.50	2.39	11.84	52.12	31.25	20.87	0.00	9.73	16.46	53.87	3.80						
SW1-1	12/30/1991	0.204	5.779	5.42	12.30	8.02	11.84	54.98	35.20	20.87	0.00	8.19	16.46	53.37	3.39						
SW1-1	01/07/1992	0.204	5.779	5.47	11.75	5.77	11.84	55.69	32.70	20.87	0.00	8.19	17.28	54.87	3.80						
SW1-1	01/15/1992	0.190	5.375	5.42	14.67	7.61	12.13	56.41	32.91	20.44	0.00	8.19	17.28	54.87	3.80						
SW1-1	01/22/1992	0.085	2.399	5.67	13.53	16.40	11.56	55.69	25.83	21.74	0.00	10.24	21.40	53.37	2.14						
SW1-1	01/28/1992	0.115	3.260	5.52	13.68	10.64	10.72	54.98	27.70	21.74	0.00	7.68	16.46	47.39	3.02						
SW1-1	02/04/1992	0.067	1.897	5.66	13.50	13.15	11.00	55.69	25.41	22.61	0.00	7.17	16.46	45.99	2.19						
SW1-1	02/10/1992	0.038	1.070	5.73	13.22	13.80	10.43	52.84	23.95	22.61	0.00	6.91	15.64	49.38	1.86						
SW1-1	02/18/1992	0.204	5.779	5.82	14.06	7.52	10.72	60.69	34.79	19.57	0.00	9.22	18.93	57.36	1.51						
SW1-1	02/26/1992	0.673	19.057	5.41	14.80	1.46	6.77	47.12	43.12	15.22	0.00	9.47	15.64	51.88	3.89						
SW1-1	03/03/1992	0.126	3.576	5.95	12.99	6.14	10.15	49.98	26.25	24.74	0.00	9.04	18.19	47.74	1.12						
SW1-1	03/12/1992	0.250	7.076	5.85	13.60	6.86	9.59	47.12	31.66	22.22	0.00	10.19	18.60	50.88	1.41						
SW1-1	03/17/1992	0.163	4.812	5.98	10.80	17.19	9.87	51.41	25.83	21.57	0.00	8.83	17.69	42.65	1.05						
SW1-1	03/24/1992	0.176	4.986	5.86	10.20	14.32	9.59	47.84	26.45	22.96	0.00	8.63	18.44	47.14	1.38						
SW1-1	03/31/1992	0.275	7.774	5.75	11.50	7.09	8.46	49.98	35.62	18.96	0.00	8.93	19.01	49.18	1.78						
SW1-1	04/07/1992	0.126	3.576	5.88	10.90	14.26	9.87	54.26	25.41	23.65	0.00	8.22	19.18	48.23	1.32						
SW1-1	04/14/1992	0.176	4.986	6.08	11.60	15.00	9.59	49.98	29.16	20.74	0.00	8.73	17.86	45.59	0.83						
SW1-1	04/22/1992	0.266	7.538	5.88	12.50	11.66	9.02	47.12	35.62	21.17	0.00	9.27	19.09	54.32	1.32						
SW1-1	04/28/1992	0.115	3.260	5.90	9.00	22.73	9.59	49.27	26.04	23.13	0.00	7.19	18.44	45.74	1.26						
SW1-1	05/05/1992	0.085	2.399	6.03	8.60	18.61	9.87	47.12	25.62	24.70	0.00	9.14	18.27	48.28	0.93						
SW1-1	05/12/1992	0.094	2.671	5.91	9.60	19.10	10.72	49.27	27.91	23.00	0.00	8.50	17.61	46.24	1.23						
SW1-1	05/19/1992	0.104	2.958	6.11	9.40	12.99	10.43	45.70	27.29	22.57	0.00	6.78	20.08	53.47	0.78						
SW1-1	05/26/1992	0.067	1.897	6.08	10.20	18.98	9.87	44.98	25.00	24.52	0.00	6.53	18.68	46.24	0.83						
SW1-1	06/02/1992	0.138	3.907	5.94	13.65	14.09	9.59	44.98	31.04	23.70	0.00	6.94	19.26	51.28	1.15						
SW1-1	06/10/1992	0.300	8.504	5.65	13.64	6.97	11.92	41.29	45.09	20.81	0.00	4.90	19.90	63.72	2.24						
SW1-1	06/16/1992	0.300	8.504	5.83	13.71	14.43	8.74	44.27	33.95	22.74	0.00	8.01	19.51	52.72	1.48						
SW1-1	06/23/1992	0.094	2.671	6.16	12.70	18.92	9.31	44.98	25.41	23.96	0.00	6.58	17.45	42.10	1.17						
SW1-1	06/30/1992	0.044	1.255	5.93	12.73	19.50	10.15	46.41	24.16	25.39	0.00	6.99	18.44	47.24	1.58						
SW1-1	07/07/1992	0.104	2.958	5.80	13.22	19.85	9.59	44.27	28.75	23.26	0.00	6.99	18.35	44.64	1.02						
SW1-1	07/14/1992	0.044	1.255	5.99	12.82	25.07	9.87	44.27	24.37	24.78	0.00	5.89	17.78	42.45	1.38						
SW1-1	07/21/1992	0.038	1.070	5.86	12.66	42.41	10.72	44.98	23.95	23.70	0.00	5.89	21.23	53.59	1.35	1.00	71.15				
SW1-1	07/28/1992	0.067	1.897	5.87	13.42	20.88	10.15	42.84	27.71	24.23	0.50	6.83	18.93	48.90	0.83	0.56	76.06				
SW1-1	08/04/1992	0.032	0.900	6.08	12.99	20.28	9.31	45.70	21.67	27.54	0.36	6.75	19.83	50.20	1.26	0.59	73.00				
SW1-1	08/11/1992	0.032	0.900	5.90	13.55	23.86	9.02	44.98	22.29	26.19	0.79	7.26	19.83	55.59	0.89	0.93	72.11				
SW1-1	08/18/1992	0.163	4.812	6.05	14.14	15.98	8.18	42.84	31.46	24.84	0.29	7.93	20.24	55.29	1.86	1.22	68.94				

SW1-1	03/25/1993	0.525	14.855	5.66	12.20	6.21	5.64	41.41	29.79	19.01	0.86	8.44	20.74	56.84	2.19	1.85	47.36		
SW1-1	03/30/1993	0.621	17.598	5.26	14.70	6.75	6.49	37.84	28.33	20.05	0.00	8.06	20.41	55.04	5.50	1.74	50.96		
SW1-1	04/06/1993	0.283	8.014	5.58	16.30	10.49	8.46	50.69	32.29	23.49	0.86	7.78	22.05	57.14	2.63	0.85	58.22		
SW1-1	04/13/1993	0.318	9.009	5.58	13.20	9.01	12.29	45.04	32.67	28.32	3.88	10.23	20.16	53.87	2.63	9.87	55.47		
SW1-1	04/20/1993	0.176	4.986	5.97	11.90	10.75	13.56	44.55	28.27	23.72	3.92	6.75	20.09	52.19	1.07	11.16	61.62		
SW1-1	04/29/1993	0.150	4.252	6.04	12.70	13.08	7.55	44.05	28.75	23.66	2.84	6.40	20.12	53.62	0.91	8.94	59.14		
SW1-1	05/04/1993	0.457	12.949	5.70	13.30	8.70	6.94	38.64	43.06	21.08	7.44	7.39	21.27	60.27	2.00	7.32	47.52		
SW1-1	05/11/1993	0.085	2.399	6.07	11.30	13.74	7.85	42.25	26.07	24.63	3.37	6.08	19.17	49.83	0.85	11.17	63.52		
SW1-1	05/18/1993	0.051	1.455	6.15	12.30	15.16	7.90	43.51	25.18	26.29	3.83	6.18	20.15	52.65	0.71	6.76	65.70	51.20	20.49
SW1-1	05/25/1993	0.150	4.252	5.92	12.60	17.54	30.68	37.21	33.54	24.94	3.25	6.87	21.69	57.18	1.17	9.89	57.35		
SW1-1	06/01/1993	0.126	3.576	5.78	12.50	13.77	6.85	40.46	33.19	23.21	6.35	6.06	20.68	57.04	1.66	7.38	61.41		
SW1-1	06/08/1993	0.059	1.669	6.01	11.70	17.68	7.23	43.48	25.55	26.10	2.80	6.01	20.03	53.02	0.98	9.02	64.15		
SW1-1	06/15/1993	0.044	1.255	6.06	14.30	18.79	31.86	41.10	26.74	37.30	4.02	5.84	21.89	58.09	0.87	6.56	66.29		
SW1-1	06/22/1993	0.026	0.745	6.08	12.20	17.17	7.82	43.13	24.91	27.23	3.45	5.54	20.13	52.81	0.83	6.70	67.15		
SW1-1	06/30/1993	0.021	0.604	6.10	13.64	17.60	7.79	42.95	24.73	25.22	2.04	5.56	18.85	48.94	0.79	9.04	152.34		
SW1-1	07/06/1993	0.021	0.604	6.12	12.43	18.35	7.96	43.74	24.76	25.92	1.99	5.80	19.02	50.95	0.76	9.10	65.64		
SW1-1	07/13/1993	0.021	0.604	6.07	13.00	16.10	8.65	43.20	26.88	26.77	3.35	6.26	20.61	55.59	0.85	9.01	54.66		
SW1-1	07/20/1993	0.026	0.745	6.06	12.14	16.51	7.61	43.26	27.62	24.93	2.28	5.51	20.09	55.54	0.87	9.51	68.52		
SW1-1	07/27/1993	0.021	0.604	6.14	12.98	16.59	30.07	42.07	23.25	25.12	0.00	4.73	17.85	49.39	0.72	5.87	69.32		
SW1-1	07/31/1993	0.017	0.478	6.10	12.85	19.57	30.06	43.65	24.85	29.92	23.96	5.32	20.95	49.71	0.79	6.03	68.89	54.93	21.32
SW1-1	08/03/1993	0.017	0.478	6.13	14.07	18.04	16.79	43.59	22.86	29.02	0.00	5.32	20.95	63.19	0.74	6.24	64.42		
SW1-1	08/10/1993	0.104	2.958	5.96	12.10	9.71	15.00	52.37	34.35	23.85	0.00	5.43	18.11	57.13	1.10	6.26	64.47		
SW1-1	08/17/1993	0.059	1.669	6.09	12.60	12.65	7.45	40.90	24.49	26.95	0.00	5.30	19.08	57.18	0.81	3.91	65.50	54.33	
SW1-1	08/24/1993	0.044	1.255	6.14	14.40	15.92	15.60	42.46	22.74	26.27	0.00	5.33	19.25	57.99	0.72	3.32	65.49	54.25	
SW1-1	08/31/1993	0.094	2.571	6.09	12.70	15.22	7.46	40.86	26.41	26.54	0.00	6.00	19.70	59.75	0.81	3.89	66.02	57.18	21.19
SW1-1	09/07/1993	0.150	4.252	6.05	12.70	14.78	14.70	39.64	28.85	26.90	0.00	6.31	19.16	57.36	0.89	3.95	64.82		53.38
SW1-1	09/14/1993	0.067	1.897	6.11	12.30	16.95	7.35	41.32	22.43	27.89	0.00	5.39	19.78	56.27	0.78	3.49	65.64	51.53	19.67
SW1-1	09/21/1993	0.104	2.958	6.04	12.10	14.51	7.69	38.23	27.77	29.27	0.00	6.06	20.06	57.65	0.91	1.56	67.84	55.60	20.37
SW1-1	09/28/1993	0.104	2.958	6.02	11.10	10.27	14.81	41.51	29.64	27.25	0.00	6.43	19.44	56.24	0.95	1.56	64.22		52.43
SW1-1	09/30/1993	0.094	2.671	6.06	11.50	12.42	14.64	42.63	25.76	28.03	0.00	5.96	19.25	57.25	0.87	6.19	68.13		51.95
SW1-1	10/05/1993	0.059	1.669	6.08	11.34	25.15	14.82	44.38	21.82	45.58	0.00	6.09	19.75	55.10	0.83	5.47	68.82		50.94
SW1-1	10/12/1993	0.038	1.070	6.14	12.00	13.53	8.90	43.11	21.41	26.78	0.00	6.63	19.18	51.94	0.72	3.19	66.30	51.85	20.29
SW1-1	10/19/1993	0.026	0.745	6.20	12.60	14.72	16.45	43.88	20.79	31.74	0.00	7.43	20.98	55.41	0.63	4.03	67.41		50.96
SW1-1	10/26/1993	0.021	0.604	6.03	13.24	20.51	20.09	40.60	29.40	34.68	0.00	13.54	21.18	60.91	0.93	9.48	68.67		52.40
SW1-1	10/31/1993	0.038	1.070	5.90	13.43	12.41	16.38	47.81	35.30	26.29	2.32	8.21	25.43	60.35	1.26	9.85	63.74		53.43
SW1-1	11/02/1993	0.038	1.070	5.99	13.13	14.51	10.96	43.68	24.76	27.80	0.00	7.41	20.21	59.22	1.02	4.12	64.61		51.69
SW1-1	11/09/1993	0.104	2.958	5.89	13.34	13.89	19.35	49.56	28.79	26.19	0.00	6.70	20.23	60.87	1.29	9.50	63.91	55.18	21.36
SW1-1	11/16/1993	0.085	2.399	6.05	12.78	11.89	16.79	46.91	27.47	25.19	0.00	6.93	20.28	61.35	0.89	5.57	66.27		52.87
SW1-1	11/23/1993	0.085	2.399	5.97	16.60	4.34	15.10	45.99	23.83	26.10	0.00	5.93	19.92	59.29	1.07	5.53	67.41	56.43	20.99
SW1-1	11/30/1993	0.176	4.986	5.95	12.91	9.04	11.26	47.55	28.38	25.54	1.53	7.60	20.12	62.34	1.12	5.59	64.37	62.45	20.82
SW1-1	12/07/1993	0.266	7.538	5.71	13.20	2.87	14.65	62.68	45.80	25.46	1.50	8.66	23.90	68.75	1.95	6.08	61.66	54.95	20.45
SW1-1	12/14/1993	0.176	4.986	5.84	13.90	6.97	14.52	41.06	33.38	23.85	0.00	6.89	24.35	78.25	1.45	6.46	3.49		53.50
SW1-1	01/07/1994	1.158	32.800	5.52	15.50	6.99	17.43	29.34	57.36	21.47	2.05	9.66	26.63	80.44	3.02	7.01	39.95		66.16
SW1-1	01/14/1994													#####					
SW1-1	01/20/1994	0.104	2.958	5.84	13.75	5.83	13.12	50.96	28.84	28.34	3.42	8.78	22.74	69.92	1.45	6.21	59.48		50.85
SW1-1	01/24/1994	0.104	2.958	5.96	13.66	10.57	18.80	44.18	27.62	27.06	0.00	7.33	21.23	56.67	1.10	5.90	64.10		50.50
SW1-1	01/31/1994	0.204	5.779	5.78	14.31	5.62	12.73	35.87	36.18	20.85	0.00	5.93	19.83	57.54	1.66	6.27	57.42	52.88	16.87
SW1-1	02/07/1994	0.183	5.179	5.81	11.84	13.38	13.95	65.01	39.23	23.92	0.00	5.82	19.88	56.85	1.55	6.53	62.04	53.05	20.12
SW1-1	02/14/1994	0.250	7.076	5.83	16.80	11.57	15.88	44.67	26.65	36.14	1.28	10.21	25.59	64.25	1.48	6.59	61.20		52.59
SW1-1	02/21/1994	0.502	14.205	5.63	12.70	3.61	13.89	38.20	33.09	26.29	0.00	8.05	25.02	69.32	2.34	7.47	49.74		53.81
SW1-1	02/28/1994	0.150	4.252	5.80	11.75	12.08	12.26	45.31	22.91	29.80	0.00	7.30	24.62	61.53	1.58	6.58	63.97	48.30	20.45
SW1-1	03/07/1994	0.234	6.629	5.85	10.50	12.64	11.31	44.38	26.20	29.35	0.00	7.93	25.20	65.03	1.41	6.73	60.20	51.00	19.55
SW1-1	03/14/1994	0.184	5.218	5.80	11.40	9.81	14.63	45.73	24.96	30.12	0.00	9.38	25.36	62.33	1.58	7.14	63.30		48.99
SW1-1	03/21/1994	0.085	2.399	6.01	12.36	10.59	11.77	49.51	28.84	24.73	3.31	6.86	22.30	64.99	0.98	7.09	64.96		48.70
SW1-1	03/31/1994	0.234	6.629	5.82	11.90	11.64	14.45	49.53	37.15	25.73	0.00	7.28	24.29	70.03	2.40	7.27	60.04		51.05
SW1-1	04/05/1994	0.150	4.252	5.95	13.70	11.39	46.86	37.16	25.44	24.32	0.00	6.10	19.58	53.68	1.12	7.27	63.36	47.60	19.30
SW1-1	04/12/1994	0.250	7.076	5.75	11.40	9.25	11.55	38.75	34.05	21.57	3.08	6.37	21.93	66.96	1.74	6.53	58.87		49.37
SW1-1	04/19/1994	0.176	4.986	5.96	10.90	8.18	11.25	38.29	24.69	23.86	0.00	5.66	19.89	60.79	1.10	7.13	64.24		50.52
SW1-1	04/26/1994	0.067	1.897	5.84	12.00	10.18	12.69	42.98	24.30	31.24	0.00	5.88	20.43	61.59	1.45	7.06	66.27	46.93	18.93
SW1-1	04/30/1994	0.051	1.455	6.03	10.90	9.71	11.76	24.96	40.38	25.36	0.00	5.85	20.67	63.12	0.93	5.94	63.06	45.38	19.01
SW1-1	05/03/1994	0.055	1.560	5.81	10.80	11.51	10.53	40.73	24.31	24.59	0.00	5.82	20.93	63.99	1.55	4.18	47.72	50.68	
SW1-1	05/10/1994	0.063	1.781	6.01	12.80	10.59	10.93	42.25	27.78	25.12	0.00	6.71	20.85	67.36	0.98	4.22	48.07		48.81
SW1-1	05/17/1994	0.076	2.141	5.95	12.30	13.63	11.49	40.46	28.49	23.31	0.00	5.81	19.49	64.98	1.12	4.48	52.06	48.88	19.14
SW1-1	0																		

SW1-1	03/01/1995	0.266	7.538	5.55	11.70	2.33	10.35	42.98	32.92	23.50	0.00	7.16	24.65	62.38	5.34	35.54	48.08	18.64	50.23	16.99
SW1-1	03/08/1995	1.450	41.054	5.25	13.00	-2.39	7.40	27.72	42.48	16.77	0.00	9.00	22.68	55.02	5.93	35.89			63.24	13.54
SW1-1	03/15/1995	0.115	3.260	5.91	10.60	6.71	10.07	41.13	25.11	27.24	0.00	7.27	23.54	58.44	4.92	63.78	46.90	18.23	47.13	17.22
SW1-1	03/21/1995	0.115	3.260	5.92	12.30	7.82	10.32	43.52	30.52	26.59	0.00	8.10	26.67	65.06	4.74	62.74	52.68	20.74	48.52	17.67
SW1-1	03/31/1995	0.044	1.255	5.92	13.10	7.82	10.37	43.34	24.99	30.43	0.00	7.40	24.83	60.24	4.71	67.27	46.38	18.52	47.37	17.62
SW1-1	04/05/1995	0.038	1.070	5.86	10.00	9.04	11.76	48.17	25.03	30.76	1.00	7.40	26.78	66.18	4.89	63.45			45.85	17.84
SW1-1	04/12/1995	0.032	0.900	5.82	16.00	10.80	13.39	52.88	34.11	31.05	0.00	10.08	33.64	82.87	4.61	61.48			49.97	18.87
SW1-1	04/19/1995	0.138	3.907	6.00	14.00	12.03	14.79	46.98	27.18	36.57	1.23	8.90	26.93	67.84	4.19	64.45	49.75	19.18	49.04	17.64
SW1-1	04/26/1995	0.138	3.907	5.86	14.00	10.64	10.89	40.89	34.20	27.26	0.97	7.59	25.82	68.21	4.37	59.15	51.50	19.34	50.16	17.49
SW1-1	05/02/1995	0.150	4.252	5.89	12.10	7.85	11.28	40.83	33.41	25.02	0.00	7.05	17.77	56.21	4.59	58.62			49.33	16.33
SW1-1	05/09/1995	0.076	2.141	6.04	12.10	10.58	12.08	42.24	25.79	30.61	3.53	7.21	20.28	60.41	4.08	0.00	49.40	19.47	47.62	16.87
SW1-1	05/16/1995	0.176	4.986	5.80	13.48	7.96	10.09	35.76	29.47	25.85	2.25	7.30	20.39	61.54	4.34	61.57	46.30	17.57	49.88	16.63
SW1-1	05/23/1995	0.150	4.252	5.88	14.20	11.24	10.71	37.47	28.83	24.84	0.00	5.93	20.25	59.84	4.26	63.74			50.04	16.68
SW1-1	05/30/1995	0.104	2.958	5.95	11.80	10.48	10.29	35.92	27.75	24.38	0.00	6.40	21.39	67.47	4.11	64.10			48.49	16.92
SW1-1	06/06/1995	0.204	5.779	5.75	15.90	4.21	12.17	35.38	29.38	23.38	0.00	6.81	19.67	58.73	4.34	63.64	46.75	18.02	51.77	16.47
SW1-1	06/13/1995	0.204	5.779	5.95	13.43	9.92	10.38	35.35	32.60	24.81	0.00	7.73	19.75	60.05	4.45	61.78			51.29	16.44
SW1-1	06/20/1995	0.085	2.399	6.03	13.68	17.26	15.26	41.66	28.16	24.87	3.62	5.21	16.24	51.17	3.78	67.84	47.90	18.65	49.84	16.29
SW1-1	06/27/1995	0.094	2.671	6.03	13.02	10.07	12.91	41.53	30.57	22.25	3.12	5.46	14.21	44.57	3.74	68.73			50.18	15.97
SW1-1	06/30/1995	0.094	2.671	6.04	15.15	12.67	12.93	40.70	26.87	29.12	0.00	6.85	19.32	60.80	3.66	68.51	46.95	18.89	49.79	16.66
SW1-1	07/05/1995	0.059	1.669	6.00	15.13	12.49	12.02	41.46	25.05	29.66	0.00	6.18	22.14	70.58	3.85	69.08	48.93	18.85	50.27	17.16
SW1-1	07/11/1995	0.038	1.070	5.86	13.45	6.94	12.06	48.51	28.82	25.99	0.00	4.72	17.84	54.34	3.74	70.15	49.63	18.81	49.99	16.61
SW1-1	07/18/1995	0.026	0.745	6.13	14.92	13.37	13.21	49.56	26.93	26.75	0.00	14.23	18.16	57.38	3.63	69.26			50.96	16.70
SW1-1	07/25/1995	0.017	0.478	6.17	13.73	14.17	14.94	46.51	26.66	31.22	0.00	7.64	13.04	59.67	4.26	69.83	49.15	18.31	50.04	16.82
SW1-1	08/01/1995	0.021	0.604	6	15.01	13.19	14.92	55.85	32.76	28.19	0.00	6.26	19.69	61.50	3.83	70.47			51.78	16.91
SW1-1	08/08/1995	0.234	6.629	5.62	15.30	9.37	9.66	37.42	41.55	24.37	2.34	7.64	21.56	78.61	3.62	61.85	55.58	18.48	55.38	16.58
SW1-1	08/15/1995	0.085	2.399	5.87	12.55	13.84	10.46	36.95	28.46	27.45	0.00	5.93	16.69	57.98	4.11	69.19			50.91	16.28
SW1-1	08/22/1995	0.085	2.399	5.81	13.85	17.28	10.03	37.07	25.64	26.97	0.00	5.74	17.00	58.49	3.63	69.05	50.20		51.83	16.34
SW1-1	08/29/1995	0.190	5.375	5.80	14.14	11.04	11.11	38.17	32.74	25.34	0.00	7.25	18.03	60.10	4.71	66.84	51.73		53.53	16.19
SW1-1	09/05/1995	0.067	1.897	5.76	14.44	11.10	13.36	44.57	37.58	25.80	0.00	8.56	21.08	84.51	4.71	62.78			53.34	16.93
SW1-1	09/12/1995	0.163	4.612	5.70	16.52	5.72	10.83	40.78	40.75	24.81	0.00	7.59	20.20	65.20	4.71	67.23			55.75	16.58
SW1-1	09/19/1995	0.176	4.986	5.80	14.32	15.46	12.37	38.89	33.58	27.57	2.65	8.62	19.19	67.27	4.78	63.64			53.82	16.37
SW1-1	09/26/1995	0.176	4.986	5.77	15.25	14.98	11.08	37.69	31.57	26.76	0.00	7.07	18.91	60.75	4.77	70.37			53.98	16.34
SW1-1	10/03/1995	0.126	3.576	5.84	15.40	14.87	15.19	40.33	29.42	27.78	0.00	8.71	23.30	71.29	4.45	74.33	54.38	20.37	53.26	17.06
SW1-1	10/10/1995	0.115	3.260	5.72	13.79	7.53	11.76	37.00	27.99	28.68	0.00	7.41	19.46	60.43	4.79	70.72			52.15	16.54
SW1-1	10/17/1995	0.094	2.871	5.88	14.60	16.34	12.59	40.13	28.27	27.51	3.62	7.22	20.17	59.94	4.32	73.4	70.79		52.32	16.70
SW1-1	10/25/1995	0.059	1.669	5.96	15.21	17.95	19.92	42.40	25.69	36.37	3.80	10.61	20.88	62.03	4.10		47.90	18.31	51.79	16.89
SW1-1	10/31/1995	0.104	2.958	5.83	13.18	12.07	14.19	42.82	28.41	26.95	0.00	8.14	20.97	64.03	4.48			51.57	16.75	
SW1-1	11/07/1995	2.726	77.184	5.13	15.14	-1.73	14.86	36.18	39.86	15.29	0.00	13.36	18.25	52.17	4.41			78.54	9.30	
SW1-1	11/21/1995	0.115	3.260	5.76	12.84	4.78	15.52	46.20	27.76	26.42	2.70	8.05	21.25	64.66	4.74		48.225	20.04	50.94	16.73
SW1-1	11/28/1995	0.266	7.538	5.58	17.16	5.69	13.12	47.98	36.95	43.01	0.00	9.16	26.81	46.23	2.63		65.3	25.43	55.54	17.14
SW1-1	12/05/1995	0.126	3.576	5.63	12.72	8.5	13.28	29.24	28.32	36.38	0.00	14.80	21.68	42.16	2.24		48.375	19.18	50.86	16.75
SW1-1	12/14/1995	0.085	2.399	5.76	17.3	13.72	14.37	44.41	26.15	35.83	0.00	10.71	22.05	43.78	1.74			51.82	16.97	
SW1-1	01/04/1996	0.115	3.260	5.56	13.8	11.88	36.69	46.97	28.94	25.30	0.00	11.52	23.59	72.69	2.75		50.65	19.88	50.17	17.03
SW1-1	01/31/1996	0.204	5.779	5.55	13.16	13.5	12.84	43.87	28.77	32.27	0.00	7.00	20.24	37.73	2.82			49.80	16.30	
SW1-1	02/23/1996	0.415	11.751	5.58	13.17	5.23	9.74	49.80	30.38	28.92	0.00	6.44	21.18	45.81	2.63		54.20	20.53	51.42	15.84
SW1-1	03/07/1996	0.930	26.333	5.31	12.89	13.35	8.03	37.15	34.12	26.09	0.00	6.81	18.54	37.08	4.90			56.42	14.07	
SW1-1	03/27/1996	0.338	9.528	6.04	12.86	7.48	10.76	42.87	25.65	23.01	0.00	5.87	23.11	71.51	0.91		48.50	20.25	49.42	16.27
SW1-1	04/05/1996	0.176	4.986	5.89	12.49	10.80	25.05	41.57	25.66	23.31	0.00	6.86	22.45	70.19	2.04		45.33	18.07	47.73	16.61
SW1-1	04/12/1996	0.138	3.907	5.94	12.73	10.24	20.67	43.30	25.63	24.45	0.00	5.85	22.73	71.36	1.15			47.50	16.74	
SW1-1	04/19/1996	0.104	2.958	6.13	11.38	16.86	27.37	42.44	25.27	24.28	0.00	7.60	23.73	73.80	0.74			46.55	16.94	
SW1-1	05/01/1996	0.176	4.986	5.79	12.33	6.55	9.50	38.52	26.28	23.14	0.00	6.85	21.42	66.74	1.52			47.95	16.44	
SW1-1	05/08/1996	0.150	4.252	6.07	11.72	7.71	20.67	37.72	26.06	24.40	0.00	6.67	21.11	66.47	0.85		45.28	18.15	47.50	16.45
SW1-1	05/15/1996	0.436	12.343	5.82	12.67	9.85	17.15	34.64	32.50	20.06	0.00	5.58	23.62	75.28	1.51			51.70	16.03	
SW1-1	05/22/1996	0.104	2.958	5.64	15.14	15.83	23.35	38.18	25.24	24.43	2.55	5.93	21.31	65.73	2.29			48.84	16.65	
SW1-1	05/29/1996	0.085	2.399	5.91	13.62	17.65	23.19	38.24	26.38	23.61	0.00	5.26	22.13	73.13	1.23		48.70	18.97	48.28	16.78
SW1-1	06/04/1996	0.067	1.897	6.15	12.71	21.74	13.36	39.58	24.90	25.98	0.00	8.06	22.64	72.52	0.71		49.90	19.42	47.63	16.88
SW1-1	06/11/1996	0.190	5.375	5.84	12.94	7.44	10.58	36.58	29.96	18.19	5.61	4.09	16.75	56.17	1.45		46.28	17.82	49.83	15.75
SW1-1	06/19/1996	0.104	2.958	5.84	11.84	12.11	18.21	39.28	26.85	23.46	9.59	5.27	17.32	56.80	1.45			48.29	16.03	
SW1-1	06/25/1996	0.085	2.399	6.05	13.75	10.41	12.78	38.77	27.78	20.19	0.00	4.06	17.61	57.98	0.85		48.53	19.01	49.32	16.15
SW1-1	07/02/1996	0.044	1.255	5.93	13.58	5.64	10.52	38.94	31.20	20.69	5.13	3.40	17.13	55.58	1.17		47.45	17.74	49.58	16.19
SW1-1	07/09/																			

SW1-1	05/20/1997	0.067	1.897	6.05	11.71	12.63	9.72	37.43	26.92	13.48	0.00	3.90	20.07	79.14	0.89	46.39	16.21
SW1-1	05/28/1997	0.457	12.949	5.59	13.59	2.11	8.72	31.87	41.05	21.91	3.80	8.90	20.09	71.58	2.57	53.15	15.18
SW1-1	06/02/1997	0.502	14.205	5.54	12.21	1.57	7.58	34.75	36.16	19.11	0.00	5.27	22.56	78.96	2.88	52.37	15.37
SW1-1	06/09/1997	0.250	7.076	5.79	11.91	7.93	8.32	35.76	29.50	24.22	0.00	6.56	21.91	71.55	1.62	49.08	15.95
SW1-1	06/16/1997	0.266	7.538	5.86	12.34	3.04	9.45	35.31	31.27	23.44	0.00	6.63	21.78	74.29	1.38	49.89	15.89
SW1-1	06/23/1997	0.115	3.260	6.03	11.86	5.57	9.22	38.34	27.15	25.28	0.00	6.03	23.88	71.53	0.93	47.85	16.57
SW1-1	06/30/1997	0.204	5.779	5.80	13.14	6.69	9.55	35.69	30.84	23.16	0.00	6.21	23.09	72.38	1.58	50.04	16.24
SW1-1	07/07/1997	0.104	2.958	5.66	12.20	8.16	9.72	37.62	25.85	25.54	0.00	4.92	23.58	80.41	2.19	48.15	16.55
SW1-1	07/14/1997	0.067	1.897	6.03	11.76	12.59	9.47	36.54	25.94	26.16	0.00	4.72	21.41	60.55	0.91	47.71	16.39
SW1-1	07/21/1997	0.051	1.455	6.04	12.12	11.84	9.53	38.47	23.76	26.64	0.00	4.72	21.41	60.55	0.91	47.71	16.39
SW1-1	07/28/1997	0.059	1.669	5.99	12.70	19.96	6.32	37.46	24.20	26.45	0.00	5.26	22.24	62.52	1.02	48.32	16.48
SW1-1	08/04/1997	0.038	1.070	5.83	13.39	14.96	10.15	39.71	23.98	28.33	0.00	5.57	22.94	79.75	1.48	48.59	16.64
SW1-1	08/11/1997	0.044	1.255	5.90	12.42	18.08	8.71	37.28	24.57	27.00	0.00	6.09	23.07	71.56	1.25	48.46	16.62
SW1-1	08/18/1997	0.038	1.070	5.95	12.50	14.23	12.55	40.15	25.89	27.09	0.00	5.37	22.42	72.52	1.12	48.78	16.54
SW1-1	08/25/1997	0.033	0.941	5.91	12.34	21.69	28.55	38.80	22.67	31.74	0.00	6.02	23.95	77.24	1.23	48.32	16.75
SW1-1	09/02/1997	0.047	1.331	6.05	13.41	20.99	9.15	40.57	27.95	30.82	0.00	7.64	23.20	73.58	0.89	49.85	16.63
SW1-1	09/09/1997	0.043	1.215	6.12	12.65	14.27	35.52	41.29	26.34	26.31	0.00	6.63	22.66	82.43	0.76	49.30	16.56
SW1-1	09/16/1997	0.024	0.672	6.33	11.34	15.46	64.25	41.74	24.95	28.42	0.00	8.20	25.29	90.15	0.48	48.35	16.93
SW1-1	09/23/1997	0.020	0.568	5.35	12.04	19.77	10.87	37.16	22.07	30.10	0.00	5.58	21.25	84.17	1.12	48.25	16.40
SW1-1	09/30/1997	0.098	2.789	5.98	13.04	8.89	31.56	36.65	28.73	26.09	0.00	6.95	23.01	75.43	1.05	50.45	16.43
SW1-1	10/07/1997	0.051	1.457	6.17	13.20	12.90	27.25	38.47	24.04	28.15	0.00	6.37	22.35	71.13	0.68	49.13	16.48
SW1-1	10/14/1997	0.035	1.004	6.14	14.75	16.20	18.27	36.98	25.93	31.04	0.00	11.02	22.03	62.57	0.72	49.16	16.48
SW1-1	10/21/1997	0.029	0.808	5.70	13.14	5.61	11.79	38.49	22.57	27.70	0.00	5.49	20.98	57.53	2.00	46.25	17.33
SW1-1	10/28/1997	0.100	2.841	5.81	13.82	24.84	38.44	35.97	30.96	24.17	0.50	11.55	26.02	84.25	1.55	48.78	19.26
SW1-1	11/04/1997	0.104	2.958	5.88	13.03	14.25	32.56	37.35	27.08	26.00	0.00	8.41	23.47	71.73	1.32	46.35	18.02
SW1-1	11/11/1997	0.126	3.576	5.89	12.31	24.54	46.56	42.43	32.26	25.87	0.75	8.06	21.60	71.47	1.29	50.36	16.12
SW1-1	11/18/1997	0.150	4.252	5.91	16.88	13.68	60.20	44.46	29.38	26.33	0.00	16.35	23.17	70.25	1.23	46.58	18.60
SW1-1	11/25/1997	0.109	3.077	5.24	27.80	3.04	12.57	41.55	25.44	25.22	0.00	7.31	21.10	62.27	5.75	51.23	16.33
SW1-1	12/02/1997	0.133	3.758	5.94	13.58	-1.64	66.13	45.35	29.72	25.14	0.70	14.52	22.74	72.55	1.15	50.07	16.25
SW1-1	12/10/1997	0.266	7.534	5.84	15.20	-11.37	42.79	44.03	36.70	24.48	0.00	9.82	22.42	78.78	1.45	52.86	16.14
SW1-1	12/16/1997	0.083	2.341	5.98	14.33	2.14	20.50	42.99	23.49	31.24	6.14	8.75	22.20	65.24	1.05	48.18	18.77
SW1-1	12/23/1997	0.083	2.360	5.86	12.84	-12.33	79.58	47.42	29.15	25.12	0.00	14.57	25.51	86.56	1.38	50.25	19.84
SW1-1	01/06/1998	0.443	12.542	5.38	20.30	-12.53	38.56	47.52	41.74	20.32	0.00	10.83	25.50	84.25	4.17	48.50	16.73
SW1-1	01/13/1998	0.188	5.310	5.68	13.50	-13.79	48.77	42.09	30.47	21.53	0.00	9.16	23.72	74.59	2.05	56.75	15.86
SW1-1	02/06/1998	0.017	0.478	5.91	13.70	11.49	10.65	42.65	24.76	24.79	0.00	5.94	16.51	42.39	1.23	49.27	16.20
SW1-1	02/19/1998	0.220	5.229	5.61	12.67	6.25	11.53	39.43	30.19	21.93	0.00	5.91	17.18	45.58	2.45	46.19	15.67
SW1-1	02/26/1998	0.134	3.804	5.65	12.50	11.32	9.52	40.15	26.42	24.12	0.00	5.99	17.75	47.58	2.24	48.07	15.19
SW1-1	03/12/1998	0.266	7.538	5.76	12.60	6.31	18.50	41.51	26.59	23.60	0.00	6.08	17.08	44.31	1.74	51.98	15.49
SW1-1	03/17/1998	0.138	3.907	5.83	13.46	1.18	13.41	40.79	26.78	29.54	5.39	8.00	18.66	48.44	1.48	47.56	15.03
SW1-1	03/26/1998	0.219	6.197	5.79	11.90	9.43	9.61	38.70	24.75	21.36	0.00	5.70	16.94	41.36	1.62	46.74	15.60
SW1-1	04/01/1998	0.709	20.080	5.88	12.94	2.32	9.96	29.76	35.69	19.31	0.00	7.03	19.91	57.71	1.32	46.39	15.10
SW1-1	04/09/1998	0.149	4.215	5.78	12.20	11.53	14.29	37.89	25.61	25.61	0.00	6.40	15.37	41.27	1.66	53.06	14.20
SW1-1	04/15/1998	0.148	4.189	5.80	12.05	9.67	13.855	38.3315	27.689	26.5692	4.5553	7.1228	16.1234	43.1638	1.58	44.98	18.60
SW1-1	04/21/1998	0.267	7.572	5.80	12.21	6.98	12.321	35.8758	28.392	23.0672	0	7.1302	14.956	41.0696	2.51	46.24	15.18
SW1-1	04/28/1998	0.162	4.579	5.83	11.60	7.93	14.123	37.5329	26.344	24.9726	0	6.1927	15.8465	41.1576	1.48	47.58	14.70
SW1-1	05/05/1998	0.282	7.406	6.20	11.50	9.83	13.684	36.0644	29.274	21.947	0	5.3914	15.4202	41.7642	0.63	46.08	15.09
SW1-1	05/12/1998	0.285	8.076	5.77	10.30	9.39	16.964	35.2939	30.715	24.8043	0	6.6107	15.1015	42.6783	1.70	47.49	14.75
SW1-1	05/19/1998	0.095	2.689	5.84	11.10	12.9	17.276	37.2408	25.902	28.4351	0	6.8609	14.9221	40.5921	1.45	47.49	14.62
SW1-1	05/26/1998	0.054	1.518	5.76	11.70	17.41	15.211	37.4039	25.971	26.505	5.5825	6.0238	15.7212	42.2502	1.74	45.51	15.12
SW1-1	06/02/1998	0.156	4.418	5.36	12.80	9.66	17.416	40.8592	36.524	22.0105	0	7.1279	19.9078	54.905	4.37	45.58	15.34
SW1-1	06/09/1998	0.087	2.475	5.63	12.50	18.37	19.141	42.6309	42.856	23.1144	5.3676	8.7078	18.4315	52.5808	2.34	48.79	15.64
SW1-1	06/16/1998	0.107	3.022	5.81	12.60	12.41	18.524	36.1402	27.391	23.9684	0	5.5858	15.426	42.5645	1.55	49.14	15.62
SW1-1	06/23/1998	0.083	2.362	5.88	12.10	16.06	21.617	34.4155	27.674	35.0281	12.291	10.123	16.1658	46.0825	1.32	47.28	15.15
SW1-1	06/30/1998	0.041	1.153	5.95	12.20	15.71	17.038	37.8567	25.722	28.7574	6.9452	6.5393	17.5557	44.9368	1.12	48.13	18.60
SW1-1	07/07/1998	0.037	1.038	5.68	14.70	5.83	21.7	42.3165	37.732	30.2586	0	10.136	17.1843	48.8399	2.09	46.20	17.86
SW1-1	07/14/1998	0.038	1.070	5.84	14.18	15.36	19.307	39.1066	26.806	30.6847	0	7.1245	17.2628	47.9333	1.45	49.77	15.59
SW1-1	07/21/1998	0.025	0.722	5.94	12.10	14.07	44.702	39.2543	25.016	31.4503	0	33.842	14.7702	42.8644	1.15	53.03	18.13
SW1-1	07/28/1998	0.108	3.053	5.53	14.30	11.8	20.609	42.6718	34.629	25.2958	5.7602	5.8628	19.17	56.9034	2.95	46.98	15.25
SW1-1	08/04/1998	0.049	1.382	5.92	13.10	14.68	14.778	40.6116	28.857	25.4883	0	5.088	15.9168	45.5726	1.20	50.39	15.65
SW1-1	08/11/1998	0.040	1.122	5.68	12.70	16.61	14.598	39.2007	25.45	27.3546	0	8.1557	15.7455	44.8827	2.09	48.61	15.34
SW1-1	08/18/1998	0.040	1.141	5.57	13.20	16.35	14.412	40.3831	27.934	27.0531	0	6.9948	16.5251	47.1305	2.69	48.00	15.33
SW1-1	08/25/1998	0.026	0.745	5.64	13.20	16.7	16.355	40.724	25.822	28.8187	0	5.7778	15.4213	44.4232	2.29	48.76	15.44
SW1-1	09/01/1998	0.021	0.604	5.74	22.10	16.48	153.37	39.7228	24.424	49.5197	0	77.822	15.7122	43.0671	1.82	49.30	18.40
SW1-1	09/09/1998	0.013	0.366	5.93	15.98	21.00										52.47	15.50
SW1-1	09/17/1998	0.013	0.366	5.82	12.28	16.59											
SW1-1	09/25/1998	0.013	0.366	5.99	14.60	21.93	20.807	35.6061	23.239	33.6552	6.563	13.437	15.34	44.7569	1.02	48.89	15.34
SW1-1	10/02/1998	0.010	0.269	5.84	14.00	18.75											

