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ATOMIC ABSORPTION INSTRUMENT FUNCTIONAL DESCRIPTION

R. I. Bystroff and W. G. Boyle, Jr.
Project Leader: G. W. Barton, Jr.

April 27, 1976

MASTER

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ATOMIC ABSORPTION INSTRUMENT FUNCTIONAL DESCRIPTION

Abstract

This report describes a proposed system for automating atomic absorption analysis. The system consists of two atomic absorption instruments and an automatic sampler that can be attached to either instrument. A computer program controls the sampling and gathers data. The program then uses the data to perform bookkeeping, data processing, and report writing.

System Definition

The atomic absorption spectrophotometer is used to determine metals in water samples. The instrument consists of a characteristic atomic-line source (hollow-cathode lamp) of the metal to be determined, either a flame source or a furnace to produce metal atom vapor from the sample, a monochromator to select light of the appropriate wavelength, and a photomultiplier tube to detect the light. When using the flame source, water samples are aspirated into the flame, which stands between the hollow-cathode lamp and the monochromater-detector. Neutral atoms of the metal of interest absorb the characteristic light from the hollow-cathode source, and the decrease in light energy (absorption) is detected and measured. The concentration of the metal of interest can be calculated from this absorption. The furnace method is similar, differing only in the manner of forming the metal vapor. Trace concentrations of over 25 metals, including the important ones, Ca, Mg, Na, K, and Hg, can be determined reliably and precisely.

The proposal for automating the atomic absorption system has two parts: (1) automating the sampling itself, and (2) automating the gathering and processing of data.

We propose to automate the sampling for the flame method of atomic absorption analysis only. We have no mechanism for automating sampling for the furnace method at this time. Of course, the automatic gathering and processing of data will be done for both the flame method and furnace method of analysis. The proposed implementation is shown in Appendix A. The various blocks shown are explained below.

DESCRIPTION OF AUTOMATED SAMPLING (FLAME METHOD ONLY)

In the automated sampling system, the samples are held in a computer-controlled sampling wheel with 40 positions. A stepping motor rotates the sample arm in either direction and an air piston moves it up and down. The sample arm carries one end of an aspirator tube and the other end is connected to the chamber of the atomic absorption (AA) instrument. The sampling arm can be rotated at a rate of 0.02 s per step, and 0.6 s are required for the arm to raise and clear the sampling bottles before the new step commands are sent to the motor. Thus the sampler can reach any position from any other position very quickly. This device is able to sample 40 plastic bottles of 28 ml capacity.

A computer-controlled solenoid valve aspirates blanks by switching the sampling from the automated sampler to a separate container.* This container can be a flow-through cell if the blank is water, or a larger container of solution if the blank is used to match a matrix. This arrangement allows a blank to be used in any sequence without continually refilling a sample container.

Random Sampling

First, the operator loads the sampling wheel. Then, at the terminal, he enters the positions and concentrations of standards, the positions and identification numbers of samples, and the sequence of base-line checks.

On the sampling wheel, position 0 is for rinse solutions or blanks and has a flow-through filling device. Positions 1 through n (n is the number of standards) are the locations of standards in the order of increasing concentration. Positions n + 1 through n + m (m is the number of unknowns) are the locations of the unknowns.

The operator enters the identification data for the unknowns in the order of their wheel positions. Position n + s is the position of a check standard. (In the computer program, the unknowns will be cross referenced by wheel position.)

The computer program (referred to as the AA program) generates a pseudo-random position on the wheel and samples the standard or unknown. It continues this operation until all the standards and unknowns are read. Before the first run the operator will signal the mode of

*Items that are new and are not part of the existing system are indicated by a bar in the margin, sometimes supplemented by a dashed underline if required for precise indication. If an entire page is new, the page is marked with a dagger in the upper right-hand corner and in the lower left-hand corner.

calculation. After the run the computer calculates the answers. If the precision of duplicates is out of range, they will be redone once and the new precision checked. If they are still out of range, the result will be flagged. The program then waits for the operator to signal rejection or acceptance of the data and a new cycle or an analysis. (Quality control action is delayed until each run is completed.)

See Appendix B for a schematic diagram of the sampler movement. Appendix C shows an example of interaction when the operator sets up a random or sequential sampling routine, and Appendix D shows a sample of automatic random sampling.

Sequential Sampling

The timing and movement of both the aspirator and the sampler are controlled by the computer. The turntable is divided into three sections: a section for a standard calibration curve, a section for a main run of undiluted samples, and one for a supplementary run of diluted samples. The program will halt and wait for operator input at the end of each section of the sample wheel before continuing to the next section.

Blanks are aspirated using the computer-controlled solenoid valve described previously.

Samples and standards are loaded in the main run section of the sampler tray in a predetermined pattern. For example, 20 samples could be loaded in a repeating sequence of 10 samples, one quality control solution, then 10 more samples, etc. The AA program will compute the sampler position from the starting position and will correlate the readings from each sample with the sample number. The operator may load the samples in the order of the sample list to avoid entering sample numbers, or he may load them in any order he chooses, and enter the sample numbers.

The computer halts after the standards have been run. The operator continues with the analysis if he is satisfied with the calibration data. One pass is made on all solutions, and a value for each is returned as it is calculated. If a sample is out of absorbance range, the AA program calculates a concentration and sounds a buzzer to alert the operator that a sample needs to be diluted. The program will automatically look for these samples on the supplementary run for diluted samples. Replicates are checked for acceptable precision, and will be redone once. If they are not acceptable at this point, they are flagged in the data file.

The computer halts at the end of the main run and waits for a command

from the operator before continuing the supplementary run. Before giving the command, the operator prepares dilutions and loads them with the check standards and duplicates the sequence used in the main run.

See Appendix E for an example of sequential-automatic sampling.

DESCRIPTION OF SEMI-AUTOMATIC OR MANUAL SAMPLING (FLAME OR FURNACE METHOD)

Semi-Automatic or Manual Flame Aspiration

The proposed system has a second mode of operation in which the operator has complete or partial control of the sampling process through commands to the AA program. See Appendix F for examples of semi-automatic and manual sampling.

Semi-Automatic Flame Aspiration

The operator loads the sampler, inputs the concentration and position of standards, and inputs the unknown solution positions as in the automatic mode of operation. Solutions are then sampled on command by the operator. For example, if the operator types B, the sampler samples a blank or rinse solution and reads a baseline. If the operator types S1, the sampler locates the first standard and the value for that standard is read. When the AA program receives the command U3, the sampler locates the third unknown on the wheel and the value is read.

Each time, it reads and calculates an absorbance using the last baseline measurement. If a position and number are repeated, the old value is replaced by the average value and precision of all the replicate values.

Computer identifiers will be furnished for check standards and spikes. When the operator is satisfied with the data, he can type C to tell the computer to calculate and print the results. The operator can obtain a report and transfer the data to the Sample File when the work session is completed.

Manual Flame Aspiration

The mode of operation described above is also the one used when manual positioning of the samples is preferred (i.e., no automatic sample changer is used).

Manual Sampling and Semi-Automatic Preprocessing for the Furnace Method

The sample wheel cannot be employed in the furnace (or carbon rod atomizer) method. The solutions are sampled on command by the operator. For example, the operator would sample and insert a blank solution and type B to read a blank absorbance. If the operator types S1Λ1! (Λ is a space, ! is a terminator), a reading is taken and identified as the first

replicate of the first standard. Similarly, C'AA2! identifies the second replicate of the third unknown. If a position and replicate number are repeated, the old value is replaced by the new. An average value and precision for all replicates will be calculated if the operator types an A after the space (e.g., S1AA!). An individual replicate may be excluded from the average by typing E after the space (e.g., S1A1E!). An example of this mode of manual sampling is shown in Appendix E.

After receiving the above commands to take a reading, the computer waits to receive a signal originating from the furnace controller before beginning the preprocessing algorithm. This program searches for a baseline deviation that will activate an integration or peak locating routine. The operator may define the beginning of an integration or peak location by injecting a representative sample. The peak-locator algorithm times each peak, and the operator can indicate which peak is correct and adjust peak location limits accordingly. Subsequently, the computer will begin looking for a single peak within this predetermined interval.

The operator has the option of using the peak value or integrating the curve. The peak-locator algorithm is shown in Appendix G.

DESCRIPTION OF GATHERING AND PROCESSING DATA

The proposed AA program is written in a conversational mode so that the operator may interact with the computer by a series of questions, answers, and commands. The program minimizes operater input and manipulation of numbers, by using algorithms that keep track of sample and calibration data and that transfer data to and from the Sample File Controller.[1]

Data Acquisition

When the mode of operation is a flame with aspirated samples, the computer waits for a predetermined time to reach a plateau and takes an operator-specified number of readings on the plateau, averages them, and outputs the mean.

For ignited samples where the vaporized material is swept into the light path of the hollow cathode source, the operator first specifies a peak height or an integration mode. The computer starts the integration or peak search at a given time, or it

[1] R. W. Crawford and H. S. Ames, Sample File Controller System Definition and Functional Design, Lawrence Livermore Laboratory, Rept. UCRL-52047 (1976).

determines the start time from the signal that activates the strip chart recorder, together with the deviation from the baseline furnished by the operator.

The computer also calculates the concentration of the sample solution and outputs it as the run proceeds.

Quality Control

The concentrations of calibration standards may be entered at the beginning of a run, or they can be stored on a file if the same ones are to be used repeatedly. The operator chooses one of three methods of charting quality control: the Cusum, Shewhart, or Industrial method.

The operator inspects the quality control data as he proceeds with the sample analyses. When a check standard is measured, the operator will be notified if the error is above a warning level. If the result is outside of limits, the operator may choose to rerun the samples and standards, discard the data, or accept the data.

Compliance Limits

The operator enters compliance limits when he logs in. The program will automatically include a report of the compliance limit for each parameter with the work load list if the study type is appropriate. At the operator's request, a buzzer will be sounded for sample results that approach or exceed the limit.

Calculation

Calculations of concentration may be done by first or second degree least square fitting of the standards data, by simple interpolation using the two closest standards as predetermined by the operator, or by the method of additions. The definition of least squares is given in Appendix H, and a schematic of the interpolation routine is given in Appendix I. The method of additions is described in Appendix J.

Sample File Controller

The atomic absorption system is linked to the Sample File Controller. This allows the operator to do any or all of the following: (1) examine the work load by getting a lineprinter listing of all samples requiring analysis for any constituent by the AA instrument; (2) call for a listing of AA samples by constituent; (3) transfer a group of sample identification numbers to the AA analysis algorithm for a computerized run; (4) call for a position map of the 40-position sampler; (5) transfer the results of a computerized run to the Sample File; and (6) quiz the file by sample number to check a particular sample, change a value, or input a value from

manual runs or special situations. A data flow schematic of the Sample File Controller is shown in Appendix K. Examples of the work load listings are shown in Appendices L and M.

Computer Report to the AA Operator

Where applicable, the optical absorbance and/or peak height and sample concentration are calculated and available to the operator as the analysis proceeds. The operator's report is a digital computer printout of the AA signals obtained as solutions (blanks, standards, and samples) are aspirated into the AA flame or ignited into the furnace. Appendix N shows examples of the operator's reports.

The AA signals are also stored for transfer to the Sample File and for generating a final report. At the end of a computerized run, the operator may obtain a report of all analyses in that run in a format suitable for his inspection. He can then transfer the data to the Sample File and clear his program.

System Specifications

INPUT DATA FOR THE AA PROGRAM

In this section we specify all the data that must be supplied to the AA program. The data may be permanently stored if it is to be used repeatedly, or it may be entered from the keyboard terminal for each run.

There are trade-offs between permanently storing the information or entering it from the keyboard as each run is set up. These trade-offs will become clearer as the program is used. The AA program will be written in BASIC, a conversational interpretive language. With such a language it is a simple matter to change variable data to permanent and vice versa.

All data required by the computer is detailed here without specifying which will be permanently stored and which must be entered by the operator.

Information Sent to the Sample File Controller

The following data are input to the Sample File Controller either from a permanent file or by manual entry:

1. The constituent(s) for which the file is to be searched to get a work load listing.

2. The constituent for which identification numbers are to be

transferred from the file to an analysis algorithm.

3. The first and last identification numbers to be transferred from the file to the analysis algorithm.

4. Compliance limits appropriate to the sample and constituent.

5. A command to transfer the results of a run to the Sample File Controller.

Standards Information

The following standards information must be provided as input to the AA program either from a permanent file or by manual entry:

1. The number of standards in a calibration set.

2. The concentration of each standard.

3. The units of concentration for the constituent to be determined.

4. The location of each standard in the analytical sequence.

5. The volume of standard and sample (and when required, the dilution factor of the sample) for the method of additions, and for spikes.

6. Test criteria for baseline deviation to start an integration or for the peak height method.

Quality-Control Information

The following quality control data must be provided to the system as a data base or must be entered at run time:

1. The number and nature of quality control solutions in a run.

2. The concentration of each quality control solution.

3. The location of each quality control solution in the analytical sequence.

4. The number of duplicates and samples that are duplicated.

5. The sequence for baseline checks.

6. Test criteria for acceptance of the analysis results.

7. Test criteria for acceptance of baseline checks.

Sample Information

The AA program must be provided with the following information about the samples in each run (manually or from a file):

1. The number of samples in each run.

2. The identification number of each sample.

3. The location of each sample in the analytical sequence.

4. The dilution factor for any diluted samples.

5. The concentration factor for any concentrated samples.

6. The reporting basis (wet weight, dry weight) of each sample.

7. The weights of solid samples or the volumes of liquid samples taken.

Mode of Calculating Concentrations

The operator will determine the mode of calculation at initial set-up time and enter this information into the computer. For subsequent runs this mode is fixed. The modes are:

1. By first or second degree least-squares fitting of the standards data. See Appendix H for the definition of least-squares.

2. By simple interpolation between the two nearest standards. A schematic diagram of the interpolator routine is shown in Appendix I.

3. By the method of additions. Standards are added to an unknown and the resulting curve is extrapolated to zero signal. See Appendix J.

Operator Interaction during the Course of a Run

The operator must be able to control the run and interact with the system. The AA program should include the following commands for operator interaction:

1. A command to halt a run in case conditions get out of control or there is an equipment failure.

2. A command to restart the run after an interruption. This includes the following input by the operator:

   a. Sampler position.
   b. Identification of the starting solution.

3. Commands that allow the operator to set pause time and integration time, and to tell the computer if the background corrector (Varian AA6) is in use.

4. Analysis command for the Semi-Automatic Sampler mode of operation. The following commands should be available to the operator:

S (sample standard); for example, S1 means read standard 1, and average with the previous readings, if any.

U (sample unknown); for example, U1 means read unknown #1, and average with the previous readings, if any.

B (read the baseline).

C (calculate): CI means interpolate, C1 and C2 mean use first or second degree least square fit, and CA means use the method of addition.

5. Special commands for the preprocessed-sample mode of operation (e.g., using the graphite furnace). The following commands should be provided:

INT! or PK! to integrate or find the peak-height value.

S (sample standard); for example, S1^N means sample the Nth reading of standard 1.

U (sample unknown); for example, U1^N means sample the Nth reading of unknown 1.

A (average the replicates); for example, U1^A means average all replicates of unknown 1.

E (exclude a run); for example, S2^2E means exclude the second replicate run of standard 2.

Multiple commands; for example, U1^S1^N means sample the Nth reading of unknown 1 plus standard 1, U1^S2^N means sample the Nth reading of unknown 1 plus standard 2, and U5^S3^N means sample the Nth reading of unknown 5 plus standard 3.

6. Quality Control Commands that allow the operator to identify standards as follows:

a. Identifiers for check standards; for example SC5 means standard 5 run as a check standard and SC5^N means the Nth reading of standard 5 run as a check standard.

b. Identifiers for spiked unknowns; for example, SP5 identifies spiked unknown number 5 and SP5^N specifies the Nth reading of spiked unknown number 5.

Other Commands

1. Commands that let the operator store, retrieve, change, and display data in the Sample File Controller. The commands are described in UCRL-52047.[1]

2. A command to produce a final report for the operator's files.

INSTRUMENT INPUT REQUIREMENTS

The dynamic range for instrument signals is 10,000 intervals for a -5 V full scale. A change of 500 μV must be detectable. Appendix O shows an example of a typical AA signal.

Requirements for the PE 305B

1. Signal characteristics:

a. Internal sources: 8 V full scale from an operational amplifier.

[1] R. W. Crawford and H. S. Ames, Sample File Controller System Definition and Functional Design, Lawrence Livermore Laboratory, Rept. UCRL-52047 (1976).

b. Sample source is pin 2 of the demodulated signal separation board (A2).

c. Reference source is pin 1 of the demodulated signal separation board (A2).

d. Noise is dependent upon damping switch setting. Time constant varies from 1 to 75 s.

2. Required filter: to be measured.

3. Connector must be provided.

4. The analog signals should be differentially buffered before leaving the chassis.

Requirements for the Varian Techtron AA6

Signal characteristics:

a. 75 Ω output impedance.

b. -5 V full-scale output at pin 11 photomultiplier amplifier circuit.

c. Integration of the signal is required. An integrating voltmeter might be used.

d. The required filtering directly preceding the DVM is an analog low-pass filter, 4-pole roll off at 0.1, 1.0, 10 Hz.

e. Connector must be provided.

f. The signal noise bandwidth is undetermined.

Requirements for the HGA 2000 Power-Supply Controller

The synchronizing signal is supplied via two normally open contacts used to start the strip chart recorder. These are shown in Fig. 1.

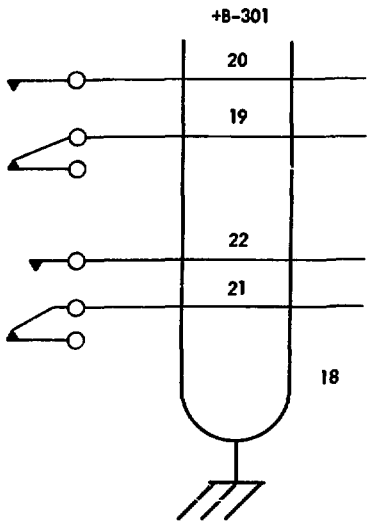


Fig. 1. Contacts used to start the strip-chart recorder.

ELECTRICAL AND MECHANICAL REQUIREMENTS FOR COMPUTER CONTROL

The Solenoid Valve and Sampler

The solenoid valve and sampler will be controlled by the computer, using signals. They do not require mechanical modifications. The following controls are required:

1. A signal from the computer to lower the sample aspirator.

2. A signal from the computer to raise the sample aspirator.

3. A signal from the computer to rotate the aspirator arm of the 40-position sampler one position per signal in the forward direction.

4. A signal from the computer to rotate the aspirator arm of the 40-position sampler one position per signal in the reverse direction.

5. A signal from the computer to open the solenoid valve for a blank.

6. A signal from the computer to close the solenoid valve.

Timing of Events

The system will use a computer clock to control the time that the aspirator is in and out of each test solution and to signal the aspirator to move to the next position each time it is raised. It will also time the pause and integration intervals via a computer clock.

A signal from the programmable graphite furnace control will start the clock to give times of peak heights for specific samples.

DATA ACQUISITION ALGORITHMS

The AA program must retrieve data from the automated system. This interaction is described below:

1. Readings of the detector output signal are taken on the plateau, or at the peak, or by integrating the signal; and the raw data is processed. The raw data is a digital reading (or mean of several readings) of the detector voltage, which is proportional to the constituent of interest.

2. The raw data is transformed to the proper concentrations for samples and quality control standards. The values for standards or standards plus unknowns are transformed into coefficients of an equation that is used to calculate concentrations. The raw data for baseline blanks is used for correcting the samples and standards before making calculations.

3. The mathematical procedure for converting raw data to its final form is either by least-squares fitting of the standards data, by interpolation between the two

closest standards, or by the methods of additions. See Appendices H, I, and J.

4. The criteria for precision and accuracy are based on quality control standards and blanks interspersed with the samples. The criterion for acceptance is established by a quality control charting algorithm chosen by the operator at the beginning of a run.

5. The identification number and dilution factor for off-scale samples is retained and used to request dilutions of the off-scale samples after the initial run is completed. The operator must dilute the solutions and load them with quality control solutions in the same pattern as the initial run. The new dilution factor is entered at this time.

6. Four analysis algorithms are provided to:

a. operate the 40-position sampler in a fully automated mode with random sampling of standards and unknowns,

b. operate the 40-position sampler in a fully automated mode with sequential sampling of standards and unknowns,

c. run samples in a semi-automated mode, and

d. run samples that have been dried and ashed.

Each algorithm (computer program) must allow the operator to transfer identification numbers from the Sample File to the analysis algorithms. Each algorithm runs independently and is accessible to either the 305B or Varian AA6. The algorithms correlate test solution signal readings with their identification numbers and sampler positions, calculate standards calibration data, update the baseline value after each baseline check, test quality-control standards, calculate sample concentrations, convert concentration units, check the sample concentrations against compliance limits if appropriate, and output messages.

DATA STORAGE REQUIREMENTS

During a run with the 40-position sampler, about 500 computer locations are required to acquire and store data (including the identification number, absorbance, concentration value, and off-scale data for the sampler). Approximately 50 locations are required to acquire the raw data, which are processed and stored as single values in real time and cleared before reading the signal from the next solution.

COMPUTER OUTPUT

Work-Load Listings

The operator may obtain a work-load listing of all the samples in the file requiring analysis for any constituent, or of all samples requiring analysis for a specified constituent. This listing can be requested at any time except when an analysis run is in progress. See Appendices L and M. The following information appears on the output:

1. The laboratory identification number of each sample.

2. The project name or number for each sample.

3. The constituent(s) to be determined for each sample.

4. The due date.

5. The study type and sample type.

6. Permit limits in proper units if applicable.

Initial Conditions

The AA program supplies a report of initial conditions. This includes:

1. The baseline reading before starting the sampler.

2. The number of samples in the run.

3. The total number of solutions in the run, including standards, samples, and quality-control solutions.

Standards Calibration Data

The following data is displayed on the operator's terminal:

1. The digital reading as each signal is read.

2. Values of the constants determined for least-squares fit of the standards data.

3. The warning and out-of-limits criteria from the quality-control charting method.

4. The quality-control charting method selected.

Analysis Progress Report

This report is available to the operator during a run:

1. Sample identification number and concentration of samples.

2. Dilution factor and identification number for diluting off-scale samples and dilution or concentration factors used for preprocessed samples.

3. Digital reading of quality control blanks.

4. The concentration found for quality control standards and a message "OK" if it meets the test criteria,

a warning buzzer and message if it is out-of-limits.

5. A warning buzzer and message if an unknown sample concentration exceeds the compliance limit for the sample. The compliance limit check must be specifically requested.

6. The number of diluted samples plus quality-control solutions to be loaded on the sampler in the same sequence as the initial run.

7. For the diluted samples which have been rerun, the following information is given:

a. The concentration of the diluted solution.

b. The dilution factor.

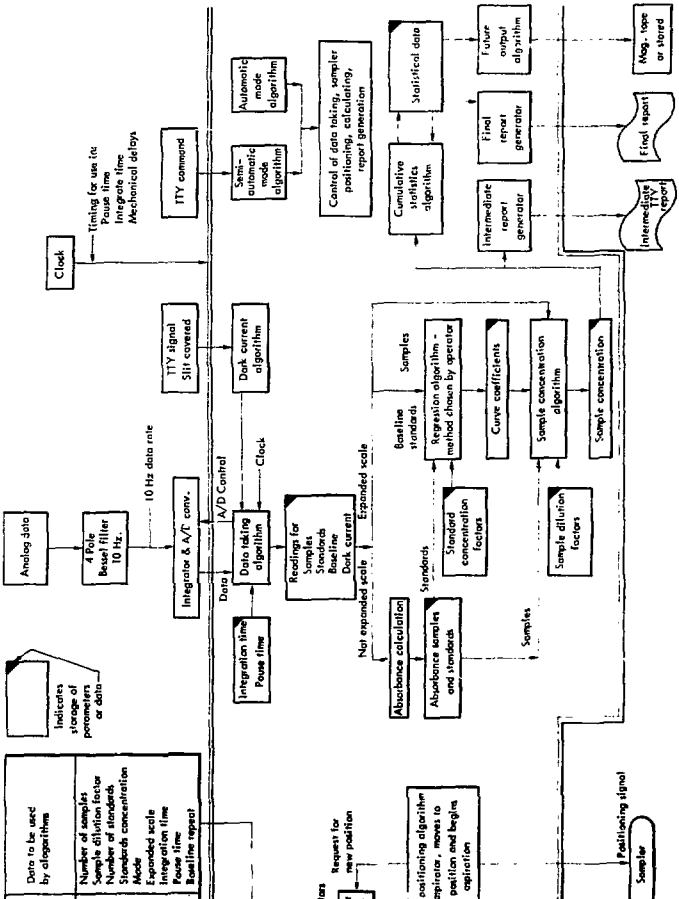
c. The concentration of the original solution.

Analysis Summary Report

A report of a completed run may be listed or saved on files at the end of each run. An example of a computer generated report for the operator's files is shown in Appendix N. The report contains the following information:

1. Title
2. Date
3. Operator's name
4. Instrument conditions
5. Units of concentration
6. The mode of calculation and constants or statistical data
7. The sample number
8. The study name or number
9. The concentration of the constituent determined
10. Results of quality control including operator approval
11. Type of sample

Appendix A
Functional Schematic



Appendix B
Algorithm for Positioning Sampler

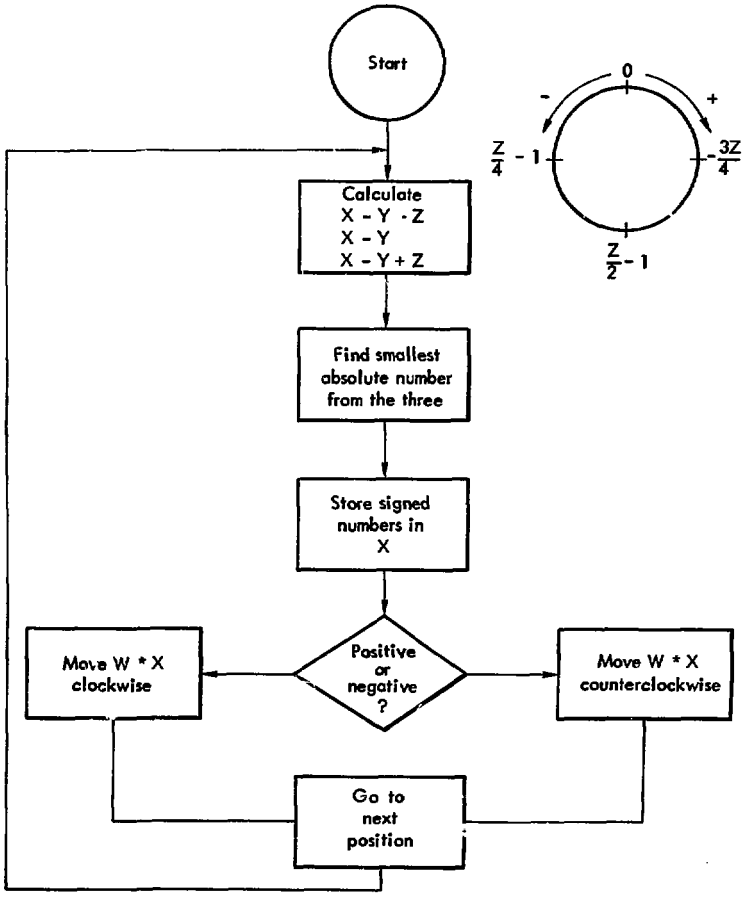
X = Present position (stored)

Y = Next position - calculated from TTY input or random number generator

Z = Total number of positions

W = 40/Z = Number of steps per position. Wheel positions are numbered 0 to Z - 1.

The flow diagram for the sampler is shown in the following figure. The arm movement of the sampler is shown in the upper right-hand corner.


Start
Calculate
X - Y - Z
X - Y
X - Y + Z
Find smallest absolute number from the three
Store signed numbers in X
Positive or negative ?
Move W * X clockwise
Move W * X counterclockwise
Go to next position
0
-
+
Z/4 - 1
-3Z/4 -1
Z/2 - 1

Appendix C
Setting Up a Sampling Routine

The following is an example of the operator-computer interaction required to set up a random or sequential sampling routine. Input by the operator is underlined. The input line ends with a terminator, such as a line feed or carriage return. Comments are given in italics.

```
RUN "RSAA
DATE,TIME OF DAY, OPERATOR'S NAME, AND INSTRUMENT
? 1/14/76 PAT JOHNSON AA6
ELEMENT AND SAMPLE SOURCE
?FE WESTINGHOUSE 2023
BASELINE LIMIT
? 10000
UNITS
? PPM
INTEG. TIME IN SECONDS
? 1
7 POINTS
PAUSE TIME IN SECONDS
? 1
BASELINE AVERAGE: Y/N ?
? N
FREQUENCY OF BASELINE ? 3
MODE OF CALCULATION (C1,C1,C2) C1
INSTRUMENT CONDITIONS ? Ø          None specified.
NO. OF STDS.
? 4
CONC:                              The standards are set up
 1  ? 2.5                          in the first positions.
 2  ? 5.0
 3  ? 7.5
 4  ? 10.0
NO. OF SPIKES ? 2
SPIKE NO.   1     VALUE 2.5
SPIKE NO.   2     VALUE 5.0
```

```
NO. OF SAMPLES?  12
SAMPLE I. D. CODE
 1  ? 76011888                    The operator enters sample
 2  ? 76011889                    numbers next to position
 3  ? 76011890                    numbers.
 4  ? CS3*                        CS3=check standard 3.
 5  ? SP13*                       Read spike No. 1 in sample 3.
 6  ? 76011891
 7  ? 76011892
 8  ? DU6*                        Read the duplicate of sample 6.
 9  ? SP23*
10  ? 76011983
11  ? CS2*
12  ? DU10*
CORRECTIONS Y/N ? Y
NO. OF I.D. CORRECTIONS ? 1
NO. AND I.D. OF SAMPLE ? 5 ? SP12*
SHALL I CALC. D. L. ? YES          The baseline will be sampled n times
                                   to determine the Standard Deviation.
                                   At the end of the calibration run,
                                   D. L. is expressed in concentration
                                   units.  D. L. (conc) = 2 * S. D.
                                   (conc. units).  Thereafter, if
                                   SIGNAL = ϕ assign "<D. L." to VALUE,
                                   where D. L. is a result of the above
                                   calculation.
RANDOM OR SEQUENTIAL ? R           Choose the mode.
```

The above technique can be used for any desired order, or no order. Below is an example of using a stored sequence for a run with prompts for sample numbers only.

```
INSTRUMENT CONDITIONS ? 248.3 NM    Enter any useful information.
DO YOU WANT TO SEE SAVED PATTERN ? Y
4 STANDARDS
```

```
3 UNKNOWNS   1 2 3
  CS3        4
  SP13       5
2 UNKNOWNS   6 7
  DU6        8
  SP23       9
1 UNKNOWNS   10
  CS2        11
  DU10       12
DO YOU WANT TO CHANGE ? N
```

If Y had been typed, the previous example would be used to enter a new pattern.

```
STANDARD CONC = 2.5, 5., 7.5, 10.
CHANGE ? N
```

No change in the values of standards.

```
SPIKES ARE 2.5, 5.
CHANGE ? N
ENTER SAM NO. PREFIX (4 DIGITS) ? 7601
```

This is a device to avoid repeated key-ins. If the response Ø had been typed, the subsequent input would require 8-digit numbers. The prefix is the year and month.

```
ARE SAM NO.'S SEQUENTIAL ? N
    1ST SAM NO. ? 1984
    LAST SAM NO. ? 1989
```

If Y is typed, the program would query and set up a sequential load pattern with the sample numbers 76011984 and 76011989 as limits. The N answer continues as follows:

```
SAMPLE I.D. CODE
 1 ? 1984
 2 ? 1987
 3 ? 1986
 6 ? 1985
 7 ? 1988
10 ? 1989
   :
   :
(as before)
```

The sample numbers are entered in any desired sequence in the positions given by the pattern above.

Appendix D
Random-Automatic Sampling

The following example is used only in the flame mode. The preliminary inputs are shown in Appendix C.

Input by the operator is underlined. An input line ends with a terminator, such as line feed or carriage return.

BASELINE AVERAGE ? N	*A YES answer means the baseline is taken after every reading and averaged with others.*
FREQUENCY OF BASELINE ? 2	*Select the number of standards or unknowns to be read before taking a new baseline.*
CALCULATE CI, C1, C2 OR C3 ? CI	*The mode of calculation is requested. These are: interpolation and least-squares fitting of 1st, 2nd or 3rd degree.*
RANDOM OR SEQUENTIAL ? R	*See Appendix E for sequential.*
TAKE A READING	*The computer displays this each time an integration begins.*

The computer displays the following information after each reading:

POSITION	SAMPLE	SIGNAL	ABSORBANCE
Ø	BL	10000	
3	76011986	9440	0.025
5	SP13	7500	0.125
Ø	BL	10050	
1	76011984	7080	0.150
7	76011988	8020	0.0958
Ø	BL	10020	

The random selection continues until all samples and standards are completed.

An interim quality control report is produced at this point for this run. The report is similar to that in the first part of Appendix N.

HARD COPY ? N	*A line printer output of the interim report can be obtained.*
RECALCULATE ? N	*Another mode of calculation can be requested.*
ACCEPT OR REJECT (A/R) ? A	*If quality control is acceptable the operator decides to proceed.*
ANOTHER RUN ? Y	*The new run will be averaged with the previous if it is accepted, and the report will show the standard deviation of duplicate unknowns.*
ANOTHER RUN ? N	
FINAL REPORT ? Y	*A final operator's summary report is printed on the line printer as shown in Appendix N.*

Appendix E
Sequential-Automatic I/O Examples

The following example is used only in the flame mode. The preliminary inputs are shown in Appendix C, with a baseline frequency of 2.

Input by the operator is underlined. An input line ends with a terminator, such as line feed or carriage return.

RANDOM OR SEQUENTIAL ? S *The following information is displayed.*

POSITION	SAMPLE	SIGNAL	ABSORBANCE
Ø	BL	10000	
1	S1	9440	0.025
2	S2	8910	0.050
Ø	BL	10000	
3	S3	8410	0.075
4	S4	7920	0.100
Ø	BL	10010	

A buzzer sounds when the standards are finished, and the requested mode of calculation is performed.

CALCULATED BY 2ND ORDER LEAST SQUARES FIT
SIGNAL = 0.003 + 0.04 * C + 0.001 * C * * 2
COEFF. OF DETN = 0.9997702
OK ? Y *If the operator is satisfied, the run may proceed.*

POSITION	SAMPLE	SIGNAL	ABSORBANCE
1	76011984	8130	0.090
2	76011985	7900	0.102
Ø	BL	10010	
3	76011986	7100	0.210

*** OVER LIMIT ***

The sample ranges above the compliance limit. The operator can obtain a duplicate on the next run.

POSITION	SAMPLE	SIGNAL	ABSORBANCE
4	76011987	1959	.8041

***** NOT ENTERED *** DF10**

The value is rejected for being too far from the calibration set of values. A dilution factor of 10 is prescribed.

If a QC standard is found to be out-of-limits as follows:

15	CS5	7080	0.15

***** RESTANDARDIZE *** +20%**

The routine signals the 20% error and waits for an operator instruction. It may restandardize before completing the run or start over.

At the end of the run, the routine expects to find diluted samples, in the same quality control pattern.

```
DF  76011987 ? 10                    The dilution factors for the
                                     samples are entered before
                                     proceeding.
OK ?
 0      BL          10090
20      76011987    7900    0.102
ANOTHER RUN ? Y                      If N is typed, summary reports may
                                     be requested.
```

An interim report is printed and a new run begins.

Appendix F
Semi-Automatic or Manual I/O Examples

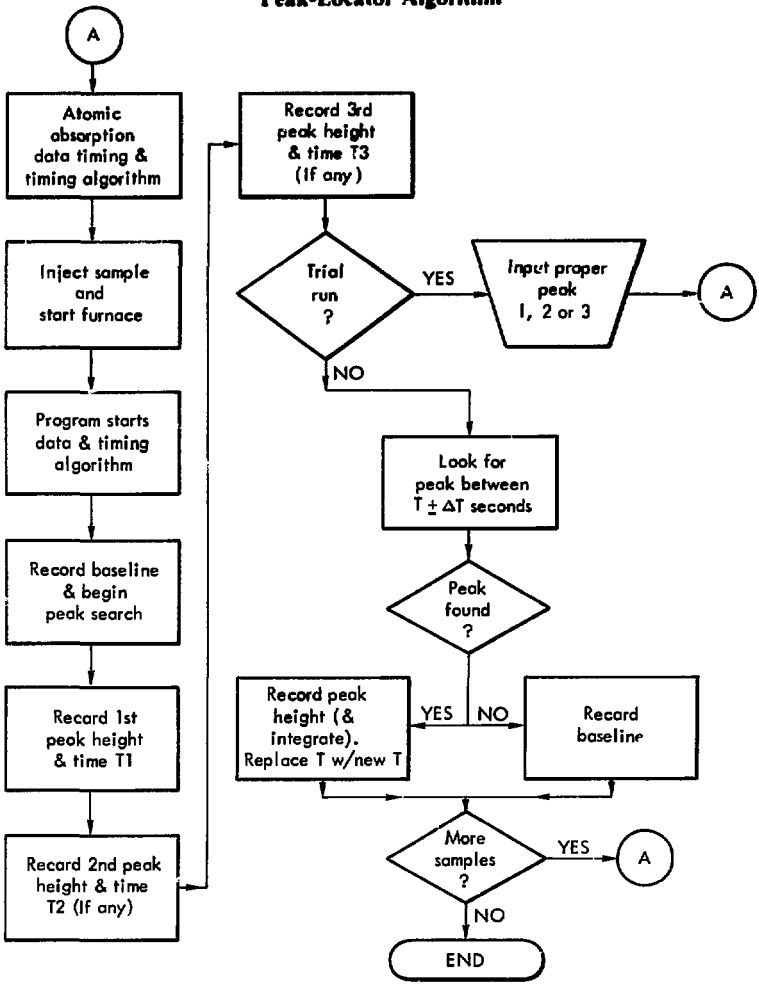
The following is an example of inputs and outputs used for the manual handling of samples in the Furnace (or carbon rod atomizer) Method.

NO. OF STDS ? 3	*The computer is to prompt for three standards.*
CONC OF STD 1 ? 0	
CONC OF STD 2 ? 10	*Entries are in the preassigned units.*
CONC OF STD 3 ? 20	
NO. OF CORRECTIONS ? 1	*The operator is given a chance to*
NO. AND CONC.	*correct typos.*
? 3 ? 25	
NO. OF SAMPLES ? 3	*Enter the number of samples to be run.*
CODE ? 76011987	*Enter the sample number in the*
CODE ? 76011988	*order desired on the output report.*
CODE ? 76011989	
NO. OF CORRECTIONS ? Ø	
TIME FOR TAKING DATA ? 5	*300 points will be taken in a 5 second period after the drying or charring cycle.*
**	*The double asterisk is a prompt for the operator to specify a command. The computer displays values for the signal and absorbance. Examples follow:*
** B 10000	*A blank*
** S1 1 9450 .0246	*The first replicate of the first standard*
** S2 3 9100 .0410	*The third replicate of the second standard*
** U1 1 9420 .0259	*The first replicate of the first unknown*

** SP2 1	9010	.0452	*The first replicate of a spiked solution of the second unknown.*
** CS2 1	9110	.0412	*The first replicate of the second standard used as a check standard (for which a percent recovery is to be calculated).*
** DU2 1	9320	.0310	*The first replicate of a duplicate unknown solution, to be compared to the average result from the replicates of the second unknown.*
** S3 A	9323	.0306	*Average all replicates of the third standard and display.*
** S3 1E	9300	.0290	*Exclude the first replicate and display the average of the remaining replicates for the third standard.*
** C			*Calculate the results using the previously specified mode of calculation.*

The interim report is displayed as shown in Appendix N.

Appendix G
Peak-Locator Algorithm



Appendix H
Least-Squares Definition

The least squares fit of pairs of data assumes that the errors in the measurement of the independent variable are insignificant compared with those of the dependent variable. Therefore, when constructing a calibration curve using standard solutions, data points are presented as concentrations for the independent variable (X) and as an instrumental parameter for the dependent variable (Y).

For a first order polynomial the function values is $y_k = a + bx_k$ and the deviations are $d_k = Y_k - y_k = Y_k - a - bx_k$, where Y_k is a data point (instrumental parameter). The function to be minimized is

$$\sum_{k=1}^{N} d_k^2 = \sum_{k=1}^{N} (Y_k - a - bx_k)^2$$

where N = number of points resulting in the normal equations:

$$aN + b \Sigma x_k = \Sigma Y_k$$

$$a\Sigma x_k + b\Sigma x_k^2 = \Sigma x_k Y_k.$$

The summations all extend from k = 1 to k = N.

Solving these equations for a and b results in an equation for the instrumental parameter dependent on a, b, and the concentration. This equation is solved for x (concentration) when the standard curve is "read". x = (y-b)/a where y is measured as an instrumental parameter for the unknown concentration x.

The coefficient of determination of the curve is

$$\Sigma (y_k - \bar{Y})^2 / \Sigma (Y_k - \bar{Y})^2;$$

it is the ratio of the variation of the predicted values to the total variation and is a measure of the "goodness of fit."

Similarly for a second order polynomial, $y = a + bx + cx^2$, the equations are:

$$aN + b\Sigma x_k + c\Sigma x_k^2 = \Sigma Y_k$$

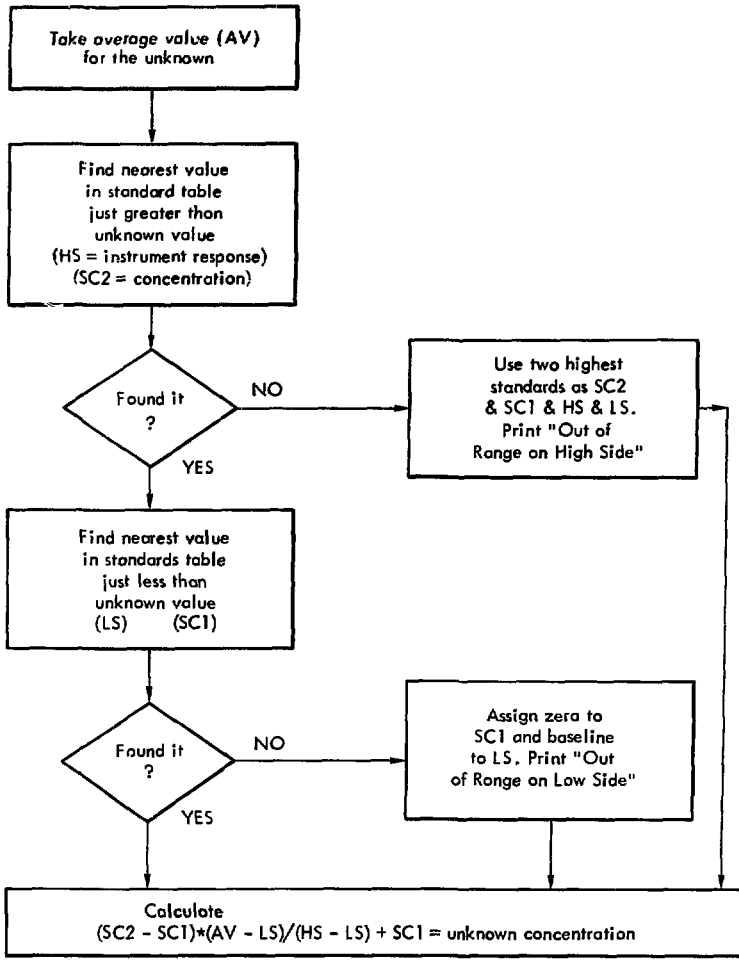
$$a\Sigma x_k + b\Sigma x_k^2 + c\Sigma x_k^3 = \Sigma x_k Y_k$$

$$a\Sigma x_k^2 + b\Sigma x_k^3 + c\Sigma x_k^4 = \Sigma x_k^2 Y_k$$

where the summations all extend from k = 1 to k = N.

The resulting quadratic equation must be solved for the concentration; either by a direct method, $x = (-b \pm (b^2-4ac)^{1/2}) / 2a$ and the correct root selected; or by some approximation procedure.

Appendix I
Interpolation



Appendix J
Method of Additions

1. Take data from a set of solutions in the form:

Sample		Standard	Signal
Unknown	+	Ø	SØ
Unknown	+	C1	S1
Unknown	+	C2	S2
	"		"
	"		"

Where C1, C2, etc. are the concentration of standards added in the same volume and Ø could mean an equal volume of water.

2. Calculate 1st degree linear least squares fit of signal versus concentration and get an equation of the type:

Signal = Slope * Conc + Intercept

3. Set signal = Ø; solve for the concentration.

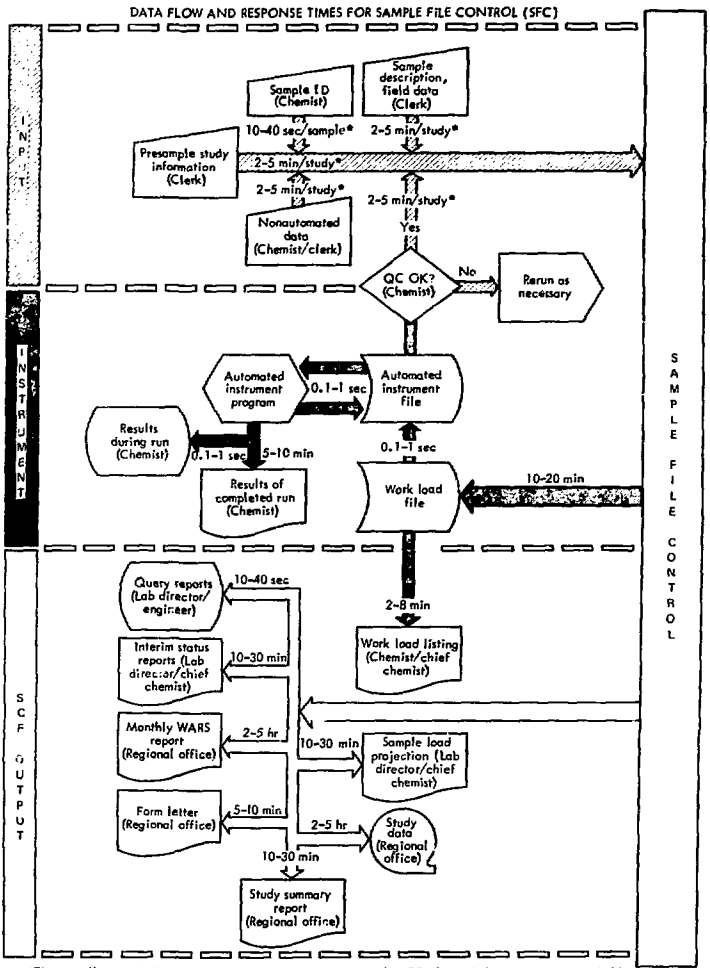
4. Equal volumes of standards and samples are usually used.

5. An unequal (say 1 part sample to 5 parts standard) ratio of volumes may be used.

6. Sample may be diluted (say 1 part sample to 5 parts diluent).

Appendix K

Interaction with the Sample File Controller



*Time on all input is time required for data to be written into the SFC after it is logged into a scratch file.

Appendix L
Work-Load Listing (General)

The following are examples of work load listings for the AA instruments from the Sample File Controller. Operator inputs are underlined and terminated with !, a symbol to indicate a carriage return or line-feed.

RUN REPT!		
FORMAT?	WORK!	
FILE?	SAMPLE!	
METHOD?	AA!	
ANALYSIS?	ALL!	
PROJECT?	ALL!	
OUTPUT?	TERM!	*Send output to the local terminal.*

METHOD AA

PROJECT	SAMPLE	ANALYSIS	DUE DATE
100	75111100	CD	11/23/75
100	75111101	CD	11/23/75
100	75111102	CD	11/23/75
100	75111103	CD	11/23/75
100	75111104	PB	11/23/75
100	75111105	PB	11/23/75
.	.	.	.
.	.	.	.
.	.	.	.

METHOD AA

STUDY	SAMPLE	ANALYSIS	DUE DATE
200	75111200	CD	11/30/75
200	75111201	CD	11/30/75
200	75111202	PB	11/30/75
.	.	.	.
.	.	.	.
.	.	.	.

Alternatively, the operator could proceed from the ANALYSIS prompt as follows:

```
ANALYSIS?    ZN, BE!      Find samples for ZN and BE and give
                          the due date
PROJECT?     ALL!
OUTPUT?      TERM!

METHOD AA
PROJECT      SAMPLE       ANALYSIS     DUE DATE
  100        75111100        BE        11/23/75
  100        75111101        BE        11/23/75
  100        75111104        ZN        11/23/75
  200        75111201        ZN        11/30/75
```

Appendix M
Work-Load Listings with Compliance Limits

The following is an example of a work load listing and a request for compliance limits:

```
? RUN REPT!
  FORMAT?      CM WORK!      Call the program.
  FILE?        SAMPLE!       Request compliance monitoring work
  METHOD?      AA!           schedule.
  ANALYSIS?    FE!
  PROJECT?     ALL!
  OUTPUT?      LINE!         Send output to the line printer.
  CM SAMPLES
```

PROJECT	SAMPLE	ANALYSIS	LIMIT	UNITS	DUE DATE
100	75110101	FE	24.0	PPM	11/23/75
100	75110102	FE	24.0	PPM	11/23/75
100	75110103	FE	24.0	PPM	11/23/75

```
? RUN REPT!
  FORMAT?      CM WORK!      Only samples with study type=CM
  FILE?        SAMPLE!       (Compliance Monitoring) are requested.
  METHOD?      AA6 B!        The sample file is looked at for
  NI,CR,FE                   specified parameters done only by
  PROJECT?     ALL!          the multi-element lamp B.  All
  OUTPUT?      LINE!         studies are searched by study type
  CM SAMPLES                 and output to the line printer.
```

PROJECT	SAMPLE	ANALYSIS	LIMITS	UNITS	DUE DATE
100	75110101	FE	24.0	PPM	11/23/75
100	75110101	NI	5.0	PPM	11/23/75
110	75111502	FE	24.0	PPM	12/2/75
110	75111503	CR	3.0	PPM	12/2/75

Appendix N
Computer-Generated Operator's Report

The following is an example of a report printed at the end of a run on request

* * * AA VARIAN TECHTRON AA6 * * *

OPERATOR: PAT JOHNSON
DATE: 12/14/76 TIME: 4:30
SOURCE: ASL HC 2021
UNIT: MG/KG DRY WT. BASIS
ELEMENT: FE
CALCULATED BY 2ND ORDER LEAST SQUARES FIT
SIGNAL = 0.003 + 0.04 * C + 0.001*C**2
COEFF. OF DETN = 0.9997702

POSITION	SAMPLE NO.	VALUE	AVERAGE	SD
1	76111888	5.816	5.816	0
2	76111889	11.051	11.051	0
3	CS3	7.498	7.498	0
	RECOVERY OF STANDARD 3 7.5 MG/KG is 99.976%			
4	SP1 2	13.502		
	RECOVERY OF SPIKE 2 2.5 MG/KG is 98.04%			
5	DU 1	5.912	5.864(2) *The number of replicates is shown in parentheses.*	0.067
6	DU 1	5.70	5.880(3) *The number of replicates is shown in parentheses.*	0.055
	*** WARNING ***			
7	76111890	17.432*	*This sample must be rerun; it is overrange.*	
8	DU 1	6.5		
	*** OUT OF CONTROL ***		*If OK, print "OK."*	

ANALYSIS REPORT

DATE: 12/16/1975	COPPER PPB
INSTRUMENT: GRAPHITE FURNACE	INSTR CONDITIONS: 3247
STANDARDS SOURCE: WESTINGHOUSE HOLLOW CATHODE	OPERATOR: Pat Johnson
CALCULATED BY 2ND ORDER LEAST SQUARES FIT	STDS IN CALIB SET=4
COEFF OF DETN FOR 1ST DEGREE FIT	.99980329
COEFF OF DETN FOR 2ND DEGREE FIT	.9998775

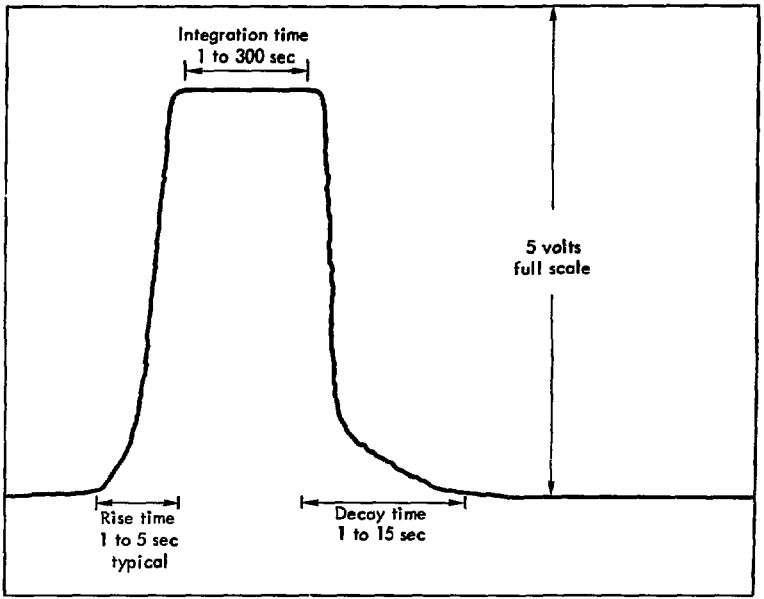
SAMPLE ID	NUMBER OF REPLICATES	AVERAGE CONCENTRATION	STANDARD DEVIATION
76111889	1	4.494	0
76111890	1	8.863	0
76111891	1	25.965	0
76111892	3	48.588	1.167

Note: if the Industrial Chart is used, replicates must be grouped as 2, 4, etc. (paired comparisons).

QUALITY CONTROL DETERMINATIONS

TYPE	AMOUNT TAKEN	AMOUNT FOUND	PERCENT FOUND	OPERATOR CHECK
SPK	5.0	4.9	98.0	OK
CS	10.0	10.1	101.0	OK
CS	20.0	19.8	99.0	WARNING

Appendix O
A Typical AA Signal



SIGN-OFF:

This System Definition and System Specification for the Atomic Absorption Instrument, which is not an Implementation Design, is approved by the undersigned interested parties. It is understood that changes in detail are likely, and that implementation of all features depends upon the availability of funding and manpower.

For Annapolis Field Office:

_____
Head, Field Office

_____
Chief, Laboratory Section

_____
Analyst

For LLL:

_____
Team Leader

_____
Project Leader

For Pilot Automation Project:

_____
Project Leader

PO/gw/1a