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TECHNICON AUTOANALYZERS: FUNCTIONAL DESCRIPTION

Richard W. Crawford
George W. Barton, Jr.

April 1, 1976

Prepared for U.S. Energy Research & Development
Administration under contract No. W-7405-Eng-48

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Printed in the United States of America

Available from

National Technical Information Service

U.S. Department of Commerce

5285 Port Royal Road

Springfield, VA 22161

Price: Printed Copy \$; Microfiche \$2.25

Page Range	Domestic Price	Page Range	Domestic Price
001-025	\$ 3.50	326-350	10.00
026-050	4.00	351-375	10.50
051-075	4.50	376-400	10.75
076-100	5.00	401-425	11.00
101-125	5.25	426-450	11.75
126-150	5.50	451-475	12.00
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TECHNICON AUTOANALYZERS: FUNCTIONAL DESCRIPTION

Abstract

This document describes and specifies a computer automation system for the Technicon AutoAnalyzers (I, II, and CSM-6 colorimeter). Operator inputs and interaction during the analysis run are described.

Computer outputs during and at the end of the run are described and illustrated. The computer calculates concentrations, monitors quality control, and prepares reports.

System Definition

DESCRIPTION OF COMPUTER AUTOMATED SYSTEM

Introduction

Provisions will be made for taking data from five channels of Technicon AutoAnalyzer I, four channels of Technicon AutoAnalyzer II, and six channels of Technicon AutoAnalyzer CSM-6 colorimeters.^a The detector output signal of each colorimeter will be conditioned and interfaced for computer reading. Computer analysis algorithms (programs) will be provided for each analysis train and will automatically time the signal readings, calculate concentrations, and correlate results with sample identifications.

The computer algorithms will also contain a variety of subroutines for bookkeeping, data processing, editing, and report writing.

^a Items that are new and 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.

They will be written in a conversational mode so that the operator may interact with the computer by a series of questions, answers, and commands. Algorithms to keep track of sample and calibration data, to make simple quality checks, and to transfer data to and from the sample file controller will be used to minimize inputs and manipulation of numbers by the operator.

Sample File Controller

The AutoAnalyzer systems will be linked with the sample file controller so that the operator can (1) examine his work load by getting a listing of all samples requiring analyses for any constituent by the AutoAnalyzers; (2) call for a listing of AutoAnalyzer samples by constituent; (3) transfer a group of sample identification numbers to the AutoAnalyzer analysis algorithms for a computerized run; (4) call for a position map for the 40-position sampler; (5) transfer the results of a computerized run to the sample file controller; (6) quiz

the file by sample number to check a particular sample, change a value, or input a value from a manual run or special situation; (7) compare two or more states of the same element (e.g., total Kjeldahl nitrogen and ammonia) while conducting a run; (8) list the concentration of one state of an element (if available) on the work-load listing of another listing (e.g., inorganic phosphorus on the total phosphorus listing).

A functional schematic of the file is shown in Appendix A. Examples of work load listings are shown in Appendices B and C. The sample wheel setup pattern for the operator in Appendix D is produced as shown in Appendices E and F.

Computer Reports to the Operator

The concentration of each sample will be calculated and returned to the operator as the analysis proceeds. It will also be stored for transfer to the data file and for generating a temporary report. At the end of a computerized run, the operator can obtain a report of all analyses in the run in a format suitable for his files, transfer the data to the data file, and clear his program on command. Final results for sediments will be calculated when sample dry weights have been entered. Appendix G shows an example of the operator's report.

Data Acquisition

The system will obtain a digital computer readout of the colorimeter outputs as the AutoAnalyzers aspirate standards, samples, and blanks from the automatic sampler modules. The computer will look for absorption peaks above background at appropriate intervals as samples pass through the colorimeters. The peak reading will be associ-

ated with the particular sample being run and will be used to calculate the concentration of the constituent being determined. A schematic of the peak-locator routine is given in Appendix H.

The sample number and concentration will be reported as the analysis proceeds.

Calculations

Calculations of concentrations will be done by first- or second-degree least-squares fitting of the standard curve or by sample interpolation as desired by the operator. A schematic of the interpolation routine is shown in Appendix I.

Baseline corrections will be made by calculating the slope between instrument blanks and then correcting each sample in between the blanks. The amount of correction will depend on the time elapsed since the last blank and the slope of the baseline.

Calculation of total phosphorus and total Kjeldahl nitrogen from sediment samples requires both the wet weight and percent dry weight in order to calculate the final concentration in milligrams per gram. If either of these values is not available at the time of analysis, the concentration will be reported in milligrams per liter during the run and flagged as temporary.

Phosphorus results can be calculated either as PO_4 or P at the operator's request.

Sampling

Six Technicon AutoAnalyzer samplers will be used (one CSH-6, three TAA-I, and two TAA-II samplers). These are 40-position samplers and are internally timed with a motor and cam. The number of samples per hour can be set by the operator. This rate

varies from 20 to 60 samples per hour, depending on the type of determination.

In the case of the CSM-6 samples, one to six different analyses are run simultaneously from the same sampler. Examples of this are analyses for ammonia, nitrite, phenol, and silica.

Discrete samples are aspirated for 1 to 2 minutes. Ten to thirty minutes are required for the sample to reach the colorimeter detector through the AutoAnalyzer chemical processing systems. Thus there will be a time delay before the first sample solution arrives at the detector; then sample solutions will pass through the detector flow cell at the sampling rate until all samples in the run have been processed. The solutions flow through the flow cell continuously, and the constituent concentration builds up to a peak value as the middle portion of the sample stream passes through the flow cell. The TAA-I and CSM-6 samplers give sharp peaks; the TAA-II sampler gives a plateau. The signal will be read at the peak or on the plateau. Examples of the signal are shown in Appendix J.

DESCRIPTION OF AN AUTOMATED ANALYSIS RUN

A description of a typical automated analysis run is given below. See the following appendices for more details of the system operation:

Appendix D for an example of the sample-wheel pattern output.

Appendix F for an example of the input and output required to initiate and complete a run.

Appendix K for a flow diagram of the AutoAnalyzer timing.

Appendix L for a flow diagram of the quality-control procedure.

Appendix M for a functional schematic of the entire system.

The operator will select a turntable-loading pattern and load standards, blanks, samples, and quality-control solutions according to the pattern selected. The pattern will start with three setup standards, followed by two blanks and the standards for the calibration curve. It then follows the repeating sequence of samples, blanks, and quality-control solutions that was specified at the beginning of the run.

The concentrations of the calibration standards can be entered by the operator at the beginning of the run, or they can be stored if the same ones are always used. The computer will correlate the value of each sample with the sample number. The operator will have the option of loading the samples in the order read from a computer-prepared sample list. This avoids having to enter sample numbers. Alternatively, he can load samples in any order he chooses, but then he must manually enter the sample numbers. The computer can also be instructed to randomly select sample numbers to eliminate bias.

The operator should be able to enter multiple dilutions of the same sample into the sample-wheel pattern. The computer should select the highest on-scale peak for each analyte.

More than one sample-wheel pattern for an analyte may be created and stored in the computer system. This is particularly useful for analyses (e.g., total phosphorus) that require autoclaving or other extended pretreatment. Thus the pattern is created,

the samples and standards put in correct order and pretreated. The pattern is stored and a previously treated set of samples is run using the previously stored pattern.

An option will be available to automatically create two different sample-wheel patterns at the same time for such analytes as the total Kjeldahl nitrogen: one for normal water samples and the other for sediment samples. An option is also available to run all samples as duplicates for such applications as inorganic and total phosphorus analyses.

Occasionally so many samples are entered into a sample-wheel pattern that they cannot be finished in one day. The program will automatically insert a pattern of set-up standards, blanks, and calibration standards at the operator-selected point so that the remaining samples can be run without being reentered on the following day.

The baseline will be established before the calibration standards and will be updated on the basis of blanks in the sample sequence. *The raw digital readings of the baseline and calibration standards will be returned as they are taken, for operator inspection, and stored for calculating the concentration of samples. The calibration data will be processed according to the type of calculation desired (first- or second-degree least-squares fitting, or interpolation). The factors to be used to calculate concentrations will be returned when the last standard solution has been read.*

The operator will examine the calibration data. If he is satisfied with it, the run will continue; if he is not satisfied with the data, he can stop the run and restart.

One pass will be made on all solutions, a value being returned for each. This initial concentration will be an approximation based on the previous instrument blank read. After the next instrument blank is read, all samples between the two blanks will be corrected for any slope in the background. The corrected concentrations may then be displayed. A set standard will be used as the first run of each tray after the first tray. This will be used by the computer to reestablish timing when sample trays are changed. No peak-height information is available from this standard.

Quality-control chart information will be calculated and stored for spikes, check standards, and duplicates. Either the Cusum,¹ Shewhart², or Industrial³ method can be selected. As each quality-control standard is run, it will be checked against the appropriate limits; if the standard is out of limits, a warning will be displayed and a buzzer sounded. The data from the standards must be stored, and when 25 or more new data points are available, the operator will be informed. On command, the computer will create new chart limits from these data.

An approximate concentration and an appropriate dilution factor will be calculated for off-scale samples; a buzzer will sound to alert the operator. The computer

¹ Anon., Laboratory Quality Control Manual, Federal Water Pollution Control Administration, Robert S. Kerr Water Research Center (1969).

² W. A. Shewhart, Economic Control of Quality of Manufactured Products (1931).

³ E. G. Robles, Jr., U.S. Air Force Environmental Health Laboratory, McClellan Air Force Base, Sacramento, Calif., personal communication.

will store the dilution factor and identification number of the off-scale samples and look for them in the sequence reported, at the end of the run, automatically. The computer will also be able to give a listing of all off-scale samples at predetermined points. The operator will prepare dilutions according to the dilution factors suggested and load them in the order found, starting in the next sampler position.

The concentration of the diluted solution, the dilution factor, and the concentration of the original sample will be returned.

The operator can obtain a report suitable for his files and transfer the data to the data files upon completion of the run. The data used to create the appropriate control charts can also be listed for storage.

System Specification

OPERATOR OR FILE INPUTS

The computer must have certain information in order to perform its tasks such as data logging, calculations, or report writing. There are tradeoffs between permanently storing the information or entering it from a keyboard as each run is set up. The first is faster, the second more flexible. All of the information that the computer requires is detailed here without specifying which items will be permanently stored and which must be entered by the operator. Appendix F contains our suggested trade-off. Since the programming is in BASIC, a high-level language, it is easy to make changes as needed.

Interaction with the Sample File Controller (SFC)

1. The constituent(s) for which the file is to be searched to get a work-load listing.
2. The constituent, if any, whose concentration is to be listed on the work-load listing.
3. The constituent for which identification

numbers are to be transferred from the file to an analysis algorithm.

4. The first and last identification number to be transferred from the file to the analysis algorithm.

5. A command to transfer the results of a run to the data file.

Timing Information

1. Three large peaks as the first three samples in the first wheel.
2. One large peak at the start of all subsequent wheels.
3. The number of samples per hour as determined by the sampler cam.

Standards Information

1. The number of standards in a calibration set.
2. The concentration of each standard.
3. The units of concentration for each constituent to be determined.
4. The location of each standard in the sampler.

Quality-Control Information

1. The number 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 sampler.
4. Quality-assurance criteria for signaling the operator.

Sample Information

1. The number of samples in each run.
2. The identification number of each sample.
3. The location of each sample in the sampler.
4. The dilution factor for each diluted sample on the initial run.
5. The number of dilutions of the same sample and the dilution factor of each.

Mode of Calculating Concentrations

1. By first- or second-degree least-squares fitting of the standards data.
2. By simple interpolation between the two nearest standards. A schematic of the interpolator routine is shown in Appendix 1.
3. Concentration as percent dry weight. The appropriate equation is used, taking into account the wet weight of the sample, the volume, and the percent dry weight of the sediment.

Interactions During the Course of a Run

1. A command to halt a run in the event of out-of-control conditions or equipment failure.
2. A command to restart the run in the event of an interruption. The information needed in this command includes the following:
 - a. Sampler position.

- b. Identification of the starting sample, standard or blank.
3. A command to list all samples that must be reanalyzed and the required dilutions, if necessary.

Data for Operator's File at the End of a Run

1. Date.
2. Operator.
3. Instrument conditions.
4. Standards source.
5. The mode of calculation and constants used.
6. The units of concentration.
7. Command to generate a report (an example of a report is shown in Appendix G).

INSTRUMENT INPUTS

Only one input to the computer from each Technicon AutoAnalyzer is needed: the output of the photodiode in the colorimeter. The dynamic range of the signal is 10,000.

Signal Characteristics--AutoAnalyzer 11

The source of the signal is telemetry output. Pin 4 is the signal, pin 3 is the ground, and pin 2 is the guard. Pin 1 is not used.

Signal Characteristics--AutoAnalyzer 1

The source of the signal is a retransmitting slidewire installed on the recorder. The signal is 0 to 10,000 ohms full scale.

Signal Characteristics--CSM-6

The signal is 5 V full scale. Must be able to detect 500 μ V. Noise is typically 0.5-msec, 1-V spikes.

The signal source is telemetry output with 1000-ohm output impedance. Connections are to terminal board (TB) 1. Common is on pin 7. Channels 1 through 6 are on pins 1 through 6, respectively.

Analog filtering can be controlled from 0.1 to 1 Hz before computer input.

Locking controls are needed for signal-conditioner potentiometers on the front panel.

COMPUTER PROGRAMS (ALGORITHMS)

This section describes the various programs that will be provided to automate the Technicon AutoAnalyzer portion of the laboratory. These programs are written in BASIC with a limited number of assembly language patches to take care of such items as data logging and timing.

Sample File Controller

The sample file controller is described elsewhere in this document. This program is to be used by all instruments, as well as for management functions. The operator of the Technicon AutoAnalyzer would use this program to create a workload listing using the report generator and to edit results (see Appendices B and C). The program could be used to create such reports as, for example, all mercury determinations from a particular creek still in the data base.

It will be used to make real-time comparisons of different chemical forms of the same element. The operator should be informed immediately if these checks are unreasonable (e.g., ammonia exceeding total Kjeldahl nitrogen). This will be done

without the sample file controller if necessary.

The sample file controller takes sample numbers and passes them to the setup program. These numbers can be taken as a block, in order as found in the workload listing; they can also be reorganized in smaller blocks or individually (see Appendix E).

Setup Program

The setup program ~~works on the data handed to it by the sample file controller.~~ The computer asks which channel of the analog-to-digital converter is being used by the analyst. Up to six different channels can be used with one set of samples. Dilutions of samples, wet weight of sediments, and concentration of standards are entered if necessary. The operator then chooses a pattern of blanks, quality-control standards, and samples to use for the run.

Once a standardized pattern has been established, it will be stored. It can be recalled as needed to save repeated manual entry.

The setup program then creates a sample-wheel pattern, the standards being interleaved as previously directed by the operator. Since any given run will probably use more than one filling of the 40-position sampler, a printed copy of the pattern will be created on the line printer for operator reference. This pattern must be the same throughout the run. An example of the sample-wheel pattern is shown in Appendix D.

There are three different types of quality-control standards: check standards (standards made up by a different operator), spikes (a known amount of the analyte

added to a sample), and duplicates. The operator will enter the concentration of the control standards. If the computer finds that any of the quality-control standards are outside the limits, a warning will be placed next to the result on output. When multiple determinations are being run simultaneously, quality-control information for each analysis should be displayed.

The computer may ask the operator the units of the standards, such as milligrams per liter. After this the operator has an opportunity to change any of the previous data. When he is satisfied, the sample-wheel pattern will be printed. More than one pattern can be stored for any one analyte.

Data Acquisition

The operator informs the computer when he has started the run. The first three positions on the first sample tray must be three standards. These are used by the operator to set the recorder, if desired, and by the computer to measure the time interval. The peak-detection algorithm records the time for the first three standards and the time between peaks (ΔT). If the time between peaks is not uniform, a buzzer will sound. The program then reads the next blank, stores it, and looks for the first peak. If none is located in the time expected, the reading taken at the proper time ($T + \Delta T$) is recorded.

If an off-scale reading is encountered (10% higher than the highest standard), the datum is tagged. The program will bring this to the operator's attention.

If following samples are to be suspected of contamination by an off-scale peak,

they will either be tagged for repeat running or will be corrected by a special algorithm.

Calculations

The calculations program takes information from the setup program and data acquisition and calculates concentrations and quality-control checks. The values for standards will be transformed into a calibration curve and factors for use in calculating concentrations.

The concentrations in the samples will be calculated by either using a least-squares fitting of the standards data or by interpolation between the two closest standards (see Appendix I). The instrument blank taken before the samples will be used for initial calculations. After a second blank is taken, the slope of the line between the blanks, or baseline drift, will be calculated. All the samples and standards run between these instrument blanks will be recalculated, using the interpolated value of the baseline.

As each concentration is calculated, it will be compared to a previous run of the same element in a different state, if applicable. If the results of the comparison are unreasonable, the operator will be notified. Examples might be the ammonia concentration being higher than the total Kjeldahl nitrogen or the inorganic phosphorus exceeding the total phosphorus.

If the sample is from a sediment, the program will determine whether percent dry weight is available. If it is, results will be reported in milligrams per gram.

The calculations routine will also check the quality-control standards and display

useful information about each. The control standards will be calculated as if they were samples; the differences between the calculated values and the concentration as made by the analyst or another person will then be displayed in absolute values. The spike samples will be calculated as samples, the previously calculated sample value being subtracted and the absolute recovery of the spike displayed. The absolute difference between the duplicates will be displayed. The limits for the appropriate control chart will be calculated and displayed. If the standard is on or beyond the warning limit, a buzzer will sound and a message will be displayed.

This routine will also check the data for off-scale values. Any datum exceeding a predetermined absorbance range will be tagged and an approximate value and a suggested dilution factor calculated and displayed. The operator will do the appropriate dilution and put the sample in the first open location at the end of the sampler tray. If the concentration of a sample exceeds the calibration range by a fixed amount (usually 10%), the same action will be taken as with an off-scale sample.

All results will be displayed on the operator's console immediately after calculation. A symbol may indicate which results have not had the interpolated baseline correction subtracted. When two or more determinations are being run on the same sample, an identifier will be placed in front of each result, and all results will be displayed on the same console. The computer can, at predetermined times, give a listing of all samples need-

ing dilution. This will be displayed on the terminal.

An addition to the calculation program is an algorithm to correct for the contamination of a dilute sample by a concentrated sample run just previously. This could be applied to peak heights differing by a factor of 2 or more.

DATA STORAGE REQUIREMENTS

Approximately 200,000 eight-bit bytes of disk storage will be required to store data during analysis runs in order to operate all 15 channels of the AutoAnalyzers simultaneously. About 200 locations will be required for raw data used by the data acquisition routines for each colorimeter.

COMPUTER OUTPUTS

Introduction

One of the computer's most important tasks is creating useful, timely reports in a variety of formats. Some of these are described in detail in the section entitled "Sample File Controller." This section discusses those that are most important to the TAA operator.

It is important to realize that a time-sharing computer system should have a fast enough response for every user to feel that he has the computer to himself. All calculations and reports will be made in near real time.

There will be two different output media. The operator's console will consist of a cathode-ray tube (CRT) or typewriter-style terminal on which alphanumeric will be displayed. There will also be a moderate-speed printer to produce hard copy. It will be shared by all users.

Work-Load Listings

The operator can obtain a work-load listing of all of the samples in the data file requiring analysis for any constituent by the AutoAnalyzers, or of all samples requiring analysis for a specified constituent, at any time except when an analysis run is in progress (see Appendices B and C). The following information will appear on the output:

1. The sample number of each sample.
2. The date that sample was received.
3. The constituent(s) to be determined for each sample.
4. The due date.
5. The permit limit, if applicable.
6. Concentration of element in different state, if applicable.

Sampler Format Listing

The sampler format listing is a hard-copy list of the samples, standards, and blanks as they should be loaded into the sample tray. It will be broken into groups of 40 to aid the analyst (see Appendix D).

Standards Calibration Data

The standards calibration data will consist of the following:

1. The digital reading as each signal is read.
2. Values of the constants determined for least-squares fit of the standards data.
3. Statistical parameters for the least-squares fit.

Analysis Progress Report

The analysis progress report will con-

tain the following data:

1. Sample identification number and concentration of samples.
2. Dilution factor and identification number for diluting off-scale samples.
3. Digital reading of quality-control blanks.
4. The concentration found for quality-control standards and the message "OK" if they meet the test criteria or a warning buzzer and message if one is out of limits.
5. For the diluted samples that were off-scale in the initial run, the following information is given:

- a. The dilution factor.
- b. The concentration of the original solution.

Analysis Summary Report

A report of a completed run can be generated from the operator's files at the end of each run. An example of a computer-generated report for the operator's file is shown in Appendix G. The report will contain the following information:

1. Title.
2. Date.
3. Operator
4. Instrument.
5. Standards source.
6. Units of concentration.
7. Mode of calculation and constants or statistical data.
8. Sample number.
9. Title of the study.
10. Concentration of the constituent determined.
11. Results of quality-control standards.
12. List of all data used to create control parameters, if requested.

Signoff

These system definition and system specifications for the Technicon Auto-Analyzer, which are not an implementation design, are approved by the undersigned

interested parties. It is understood that changes in detail are likely and that the implementation of all features depends on the availability of funding and manpower.

For Annapolis Field Office:

Analyst

Analyst

Chief, Laboratory Section

Head, Field Office

For LLL:

Team Leader

Project Leader

For Pilot Automation Project:

Project Leader

Appendix A

Data Flow and Response Times for Sample File Control (SFC)

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

Appendix B

Total Work-Load Listing¹

<u>LLL BASIC READY</u>	[BASIC is read]
<u>RUN "REPT"</u>	[Call report generator]
FORMAT? <u>WORK</u>	[Work-load list format]
STUDY TYPE? <u>WATER</u>	
METHOD? <u>TAA</u>	
ANALYSIS? <u>ALL</u>	
OUTPUT? <u>LINE</u>	[Put on line printer]

[A typical output from the line printer is as follows:]

<u>SAMPLE</u>	<u>ANALYSIS</u>	<u>DUE DATE</u>
100101	TP	10/3/76
100102	TP	10/3/76
100103	TP	10/3/76
100104	TP	10/3/76
100105	TKN	10/3/76
100106	TKN	10/3/76
100701	TP	10/9/76
100702	TP	10/9/76
100703	TKN	10/9/76
.	.	.
.	.	.
.	.	.

¹ Explanatory comments are given in brackets.

² Not part of existing software.

Appendix C

Work Load Listing**

<u>LLL BASIC READY</u> <u>RUN 'REPT'</u> <u>FORMAT? WORK</u> <u>STUDY TYPE? WATER</u> <u>METHOD? TAA</u> <u>ANALYSIS? NO2</u> <u>OUTPUT? LINE</u> <u>METHOD? TAA</u> <u>ANALYSIS? NO2</u>	[BASIC ready] [Call report generator] [Work-load list]
---	--

[A typical output from the line printer is as follows:]

<u>SAMPLE</u>	<u>RECEIVED</u>	<u>ANALYSIS</u>	<u>DATE DUE</u>	<u>PERMIT LIMIT</u>
110101	11/01/76	NO2	12/10/76	
110102	11/01/76	NO2	12/10/76	
110103	11/01/76	NO2	12/10/76	
.	.	.	.	
.	.	.	.	
.	.	.	.	
120701	12/07/76	NO2	12/20/76	10.0
120702	12/07/76	NO2	12/20/76	15.0
.	.	.	.	
.	.	.	.	
.	.	.	.	
120737	12/07/76	NO2	12/23/76	
120738	12/07/76	NO2	12/23/76	
.	.	.	.	
.	.	.	.	
.	.	.	.	

* Explanatory comments are given in brackets.
 ** Not part of existing software.

Appendix D

Sample-Wheel Pattern*

TAA CSM-6

12/15/1976

9:15

E. MCPHERSON

CHAN 6 NO3

CHAN 7 NO2

CHAN 8 NH3

CHAN 9 SILICA

CODE	POS	NUMBER	TYPE	DIL	CONC.			SIL
					NO3	NO2	NH3	
1	A 1		SET	{Used to get timing, set gain}				
2	A 2		SET					
3	A 3		SET					
4	A 4		BLK	{Computer needs a blank}				
4'	A 4'		BLK					
5	A 5		STD		2	2	2	10
6	A 6		STD		1.5	1.5	1.5	7.5
7	A 7		STD		1	1	1	5
8	A 8		STD		.5	.5	.5	2.5
9	A 9		STD		.2	.2	.2	1
10	A 10	120701	SMP	1				
11	A 11	120701	SMP	1	{Always run two of First sample}			
12	A 12	120702	SMP	1				
13	A 13	120703	SMP	1				
14	A 14	120704	SMP	1				
15	A 15	120705	SMP	1				
16	A 16	120706	SMP	1				
17	A 17	120707	SMP	1				
18	A 18	120708	SMP	1				
19	A 19	120709	SMP	1				
20	A 20	120705	DUP					
21	A 21	120705	SPK		.5	.5	.5	2.5
22	A 22		BLK	{Completed one pattern}				
23	A 23	120710	SMP	1				
24	A 24	120711	SMP	1				

* Explanatory comments are given in brackets.

Sample-Wheel Pattern (continued)

<u>CODE</u>	<u>POS</u>	<u>NUMBER</u>	<u>TYPE</u>	<u>DIL</u>	<u>N03</u>	<u>N02</u>	<u>NH3</u>	<u>SIL</u>
25	A 25	120712	SMP	1				
26	A 26	120801	SMP	10				
27	A 27	120802	SMP	10				
	.		.	.				
	.		.	.				
	.		.	.				
40	A 40	120913	SMP	1	[End of first sample carrier wheel]			
41	B 1		SET		{Used to establish timing}			
42	B 2	120914	SMP	1				
43	B 3	120909	DUP	1				
44	B 4	120909	SPK		.5	.5	.5	2.5
45	B 5		BLK					
	.	.	.	.				
	.	.	.	.				
	.	.	.	.				

Appendix E

Commands to Transfer Data from the Sample File*†

LLL BASIC READY

RUN "TAA SEL"

[Short for TAA select]

REQUESTOR E. MCPHERSON

[Optional]

ANALYSIS NO3, NO2, NH3, SILICA

SELECT NOS 120701 TO 120712,

[Selects sets of samples from three different days. Could have selected

120801 TO 120825,

individual samples or all samples

120900 TO 120909

needing above analyses (ALL)]

* Explanatory comments are given in brackets.

† Not part of existing software.

Appendix F

Example of the Input/Output (I/O) for the Setup, Data Acquisition, and Calculational Programs*

INSTRUMENT CSM-6

OPERATOR E. MCPHERSON

INST. COND. NEW PUMP TUBES

DATE 12/14/76 TIME 08:45

ALL NORM. COND.? (Y OR N) N

STDs. NORM.? N

NO. OF STDs. 6

[Any comment]

[Computer gives date and time]

[If Y typed, would have skipped to PRINTING
SAMPLE WHEEL PATTERN]

[If Y, next eight lines skipped. If the
normal pattern is to be changed, that can be
done in the BASIC program.]

CODE		<u>NO3</u>	<u>NO2</u>	<u>NH3</u>	<u>SIL</u>
5	STD 1	<u>2</u>	<u>2</u>	<u>2</u>	<u>10</u>
6	STD 2	<u>1.5</u>	<u>1.5</u>	<u>1.5</u>	<u>7.5</u>
7	STD 3	<u>1</u>	<u>1</u>	<u>1</u>	<u>5</u>
8	STD 4	<u>.5</u>	<u>.5</u>	<u>.5</u>	<u>2.5</u>
9	STD 5	<u>.2</u>	<u>.2</u>	<u>.2</u>	<u>1</u>
10	STD 6	<u>.1</u>	<u>.1</u>	<u>.1</u>	<u>.5</u>

QC PATTERN NORM.? N

SAMP	DUP	SPK	CS	BLK
<u>5</u>	<u>1</u>	<u>1</u>	<u>0</u>	<u>1</u>

[If Y, the next 10 lines are skipped]

[This sets the repeating pattern of samples
and standards. The last pattern may have
fewer samples than specified. CS stands for
"check standard."]

SAMP. POSITION DUPD? 3

[The third sample of each set of five samples
will be duplicated]

SAMP. POSITION SPKD? 4

ALL SPKS SAME? N

[If Y, would have asked for the one
concentration]

CODE		<u>NO3</u>	<u>NO2</u>	<u>NH3</u>	<u>SIL</u>
18	SPK 1	<u>.5</u>	<u>.5</u>	<u>.5</u>	<u>2.5</u>
26	SPK 2	<u>.2</u>	<u>.2</u>	<u>.2</u>	<u>1</u>
34	SPK 3	<u>1</u>	<u>1</u>	<u>1</u>	<u>.5</u>
42	SPK 4	<u>.5</u>	<u>.5</u>	<u>.5</u>	<u>2.5</u>

* It is assumed that the steps shown in Appendix E have just been completed. Operator's responses are underlined. Explanatory comments are given in brackets.

Example of the Input/Output (I/O) for the Setup, Data Acquisition, and
Calculational Programs (continued)

[If check standards had been requested, the
concentration would have been asked for at
this point using the same format as spikes]

DILUTIONS? Y

[Are there diluted samples?]

? 120801 TO 120810, 120817; 10, 1

[Both tenfold and not diluted]

? 120820 TO 120831; 5

[Fivefold dilution]

? 0

[No more dilutions]

EDIT? Y

[Chance to correct mistakes]

CODE 34

34 SPK 3

1	1	1	.5
<u>1</u>	<u>1</u>	<u>1</u>	<u>5</u>

[Change 0.5 to 5]

CODE 0

[Done editing]

PRINTING SAMPLE WHEEL PATTERN

EDIT? N

[Another chance after looking at printout]

HIT RETURN WHEN READY TO RUN

[Tells computer to start looking for set
standards]

	<u>NO3</u>	<u>NO2</u>	<u>NH3</u>	<u>SIL</u>
A 4 BLANK 1	00.10%	00.23%	00.17%	00.33%
A 5 BLANK 2	00.10%	00.22%	00.16%	00.31%
A 6 CAL STND 1	49.63%	48.72%	49.91%	47.97%
A 7 CAL STND 2	37.42%	37.39%	37.51%	37.32%
A 8 CAL STND 3	24.87%	24.96%	25.02%	24.67%
A 9 CAL STND 4	12.44%	12.31%	12.55%	12.29%
A 10 CAL STND 5	4.88%	4.76%	5.09%	4.63%
A 11 CAL STND 6	2.42%	2.39%	2.56%	2.23%

LINEAR EQUATIONS

NO3 A/D = +0050.0 + 8174.0 * C, COEFF. OF DETN. = .99987

NO2 A/D = -0063.0 + 8231.0 * C, COEFF. OF DETN. = .99974

NH3 A/D = +0009.5 + 8194.0 * C, COEFF. OF DETN. = .99998

SIL A/D = -0043.2 + 1647.0 * C, COEFF. OF DETN. = .99847

	<u>NO3</u>	<u>NO2</u>	<u>NH3</u>	<u>SIL</u>
A 6 CAL STND 1	1.98 PPM	2.01 PPM	1.99 PPM	10.05 PPM
A 7 CAL STND 2	1.50 PPM	1.49 PPM	1.50 PPM	7.43 PPM
A 8 CAL STND 3	.997 PPM	1.02 PPM	1.00 PPM	5.01 PPM
A 9 CAL STND 4	.512 PPM	.497 PPM	.506 PPM	2.48 PPM
A 10 CAL STND 5	.207 PPM	.195 PPM	.206 PPM	1.01 PPM
A 11 CAL STND 6	.094 PPM	.109 PPM	.101 PPM	.521 PPM

* Existing software can handle only three analytes.

Example of the Input/Output (I/O) for the Setup, Data Acquisition, and Calculation Programs (continued)

		<u>NO3</u>	<u>NO2</u>	<u>NH3</u>	<u>SIL</u>
A 12	120701	13.47%	29.64%	3.42%	9.03%
		.539 PPM	1.18 PPM	.137 PPM	1.80 PPM
		<u>{ignore first result}</u>			
A 13	120701	13.68%	30.51%	3.65%	10.12%
		.547 PPM	1.22 PPM	.146 PPM	2.03 PPM
A 14	120702	35.62%	64.31%	24.19%	21.54%
		1.425 PPM	<u>DIL</u> * <u>2</u>	.968 PPM	4.302 PPM
DILUTE AND PLACE IN NEXT OPEN POSITION		[The sample should be diluted. A buzzer sounds to warn operator]			
A 15	120703	31.29%	20.51%	1.07%	12.04%
		1.25 PPM	.820 PPM	.043 PPM	2.41 PPM
A 16	120704	40.10%	31.11%	2.53%	20.32%
		1.60 PPM	1.24 PPM	.101 PPM	4.09 PPM
A 17	120705	38.21%	26.32%	5.17%	36.17%
		1.52 PPM	1.05 PPM	.207 PPM	6.13 PPM
A 18	120701	31.40%	20.63%	1.16%	12.23%
		1.25 PPM	.825 PPM	.046 PPM	2.44 PPM
DIFFERENCE		+ .004 PPM +	.005 PPM +	.003 PPM +	.036 PPM
INDUSTRIAL		OK	OK	OK	OK
A 19	SPIKE 1	52.42%	1.73 PPM	15.28%	31.51%
		<u>OFF SCALE</u>	1.73 PPM	.611 PPM	6.31 PPM
	RECOVERY	*	98.3%	101.2%	93.2%
	INDUSTRIAL	*	OK	OK	WARNING
		[A buzzer sounds to call operator's attention to the silica spike]			
A 20	BLANK 2	.20%	.37%	.29%	.62%
		[At this point the baseline is extrapolated back to the previous one, and each sample or standard is corrected accordingly. <u>The new numbers are then displayed, much like the above.</u>]			
A 21	120706	21.37%	15.23%	11.21%	20.21%
		.854 PPM	.609 PPM	.448 PPM	4.05 PPM
.	.	.	.	.	.
.	.	.	.	.	.
.	.	.	.	.	.
B 3	BLANK	1.01%	.97%	.53%	1.21%
		[End of regular run]			

Example of the Input/Output (I/O) for the Setup, Data Acquisition, and
Calculational Programs (continued)

	<u>NO3</u>	<u>NO2</u>	<u>NH3</u>	<u>SIL</u>
R I 120702	17.73%	32.14%	12.07%	10.80%
	1.42 PPM	2.57 PPM	.969 PPM	4.30 PPM

[This is a rerun of the diluted sample]

END, PRINTING OPERATOR'S REPORT

READY TO TRANSFER DATA? N [If Y, would have asked for code as in Edit]
 DELETE? Y [Chance to remove bad data]
 CODE 23

	<u>NO3</u>	<u>NO2</u>	<u>NH3</u>	<u>SIL</u>
120709	1.35 PPM	.643 PPM	4.92 PPM	2.60 PPM
	<u>OK</u>	<u>OK</u>	<u>BAD</u>	<u>OK</u>

[The NH₃ number was removed, as an air bubble caused a false reading]

CODE 0 [No more deletions]
 ADD? N [Chance to add manually run data]
 READY TO TRANSFER DATA? Y
 DATA TRANSFERRED
 END TAA
 STOP 1130

Appendix G

Report for Operator's Files*

OPERATOR E. MCPHERSON
DATE 12/14/76 TIME 8:45
INST. COND. NEW PUMP TUBES
LINEAR EQUATIONS

NO3 A/D = +0049.0 + 8175.0 * C, COEFF. OF DETN. = .99989

NO2 A/D = -0064.0 + 8230.0 * C, COEFF. OF DETN. = .99977

NH3 A/D = +0009.7 + 8193.5 * C, COEFF. OF DETN. = .99999

SIL A/D = -0043.5 + 1646.3 * C, COEFF. OF DETN. = .99873

CODE	POS	NAME	NO3		NO2		NH3		SIL†		DIL	COMM
			%	PPH	%	PPH	%	PPH	%	PPH		
STANDARDS												
5	A 5	CAL STD 1	49.60	1.98	48.71	2.01	49.89	1.99	47.92	10.0		
6	A 6	CAL STD 2	37.40	1.50	37.36	1.49	37.48	1.50	37.29	7.48		
.	.	.	.	.	.	.	.	.	.	.		
.	.	.	.	.	.	.	.	.	.	.		
.	.	.	.	.	.	.	.	.	.	.		
SAMPLES												
11	A 11	120701	13.47	.539	29.64	1.18	3.42	.137	9.03	1.803	1	OK
12	A 12	120701	13.68	.547	30.51	1.22	3.65	.146	10.12	2.03	1	OK
13	A 13	120702	35.62	1.42	64.31	*	24.19	.968	21.54	4.30	1	R1
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
40	A 40	120813	38.21	1.52	26.32	1.05	5.17	.207	61.32	1.22	10	OK
44	R 1	120702	17.71	1.42	32.14	2.57	12.07	.969	10.80	4.30	2	OK

[The asterisk is put beside those numbers that are used on repeat runs]

SAMPLES THAT MUST BE RERUN

47 R 4 120805

DIL 100*

OFF SCALE

[Must rerun NO₂ on this one, first dilution was not enough]

BLANKS

4	A 4	BLANK 1	.10		.23		.17		.33			
19	A 19	BLANK 2	.20		.37		.29		.62			
.	.	.	.		.		.		.			
.	.	.	.		.		.		.			
.	.	.	.		.		.		.			

*This is an example of the report that is automatically printed at the end of a run. Explanatory comments are given in brackets.

†Existing program can handle only three analytes.

Report for Operator's Files (continued)

CODE	PDS	NAME	NO3		NO2		NH3		SIL		DIL	COMM
			%	PPM	%	PPM	%	PPM	%	PPM		
Q C STANDARDS												
17	A 17	DUP 1	31.40	1.25	20.63	.825	1.16	.046	12.23	2.44		
	120703		31.29	1.25	20.51	.820	1.07	.044	12.04	2.41		
	DIFF.		+ .004		+ .005		+ .002		+ .036			
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
18	A 18	SPK 1	52.42	*	43.30	1.73	15.28	.611	31.51	6.31		
	120704		40.10	1.60	31.11	1.24	2.53	.101	20.32	4.09		
	ADDED		.5 + 2.10		.5 = 1.74		.5 = .601		2.5 = 6.59			
	RECOVERY		*		97.6%		102.0%		88.8%*			
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
	DUPLICATES		NO3		NO2		NH3		SIL		[The absolute difference in concentration between duplicate pairs is compared to this number.]	
	INDUSTRIAL WARNING		.031		.0352		.0281		.0642			
	INDUSTRIAL OUT OF CONTROL		.0482		.0533		.0422		.0964			
<hr/>												
	DUP 1		.0016		.0030		.022		.0072			
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
	SPIKES		NO3		NO2		NH3		SIL			
	INDUSTRIAL WARNING		.0417		.0521		.0317		.0621			
	INDUSTRIAL OUT OF CONTROL		.0626		.0782		.0476		.0932			
<hr/>												
	SPIKE 1		*		.0120		.0100		.1116*			
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.

***** NOTE *****

THERE ARE 25 OR MORE POINTS IN THE FOLLOWING INDUSTRIAL FILES

NO3

NO2

PLEASE RUN "QC UPDATE"

Appendix H
Peak Locator Flow Chart

Peak Locator Flow Chart (continued)

Appendix I
Interpolation Definition

Appendix J
Example of Signals

Example of TAA-1 Signal

Example of TAA-1 Signal

Example of TAA-1 Signal

Example of CSM-6 Signal

Appendix K

Timing Flow Chart

Appendix L Quality Control

Schematic of the System