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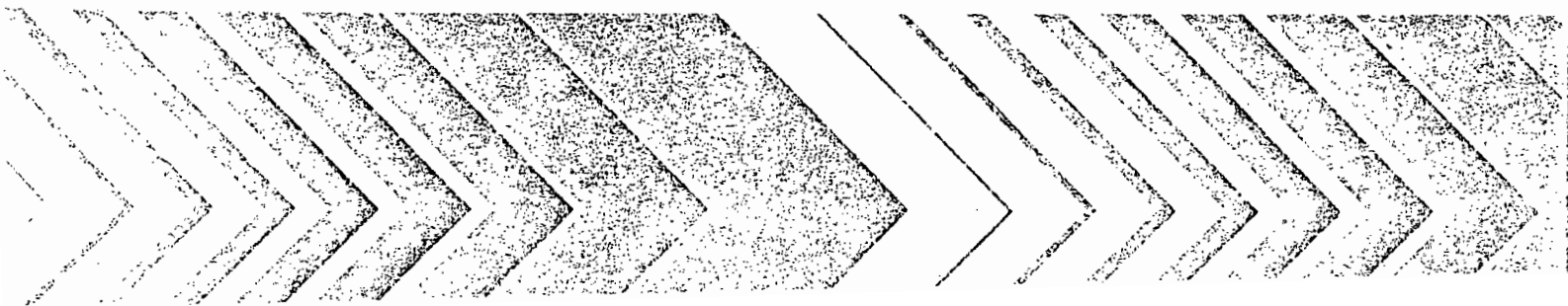
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Research and Development

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# Proceedings:

## National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources



EPA-600/9-84-001  
January 1984

~~PROCEEDINGS: NATIONAL SYMPOSIUM ON RECENT ADVANCES IN~~

POLLUTANT MONITORING OF AMBIENT AIR  
AND STATIONARY SOURCES

Raleigh Hilton Hotel

May 3-6, 1983

Environmental Monitoring Systems Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency

NOTICE

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## FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has the responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Pesticides and Toxic Substances and the Office of Solid Waste and Emergency Response.

This symposium is part of a continuing effort to explore recent advances in pollutant monitoring of ambient air and stationary sources. It serves as a forum for exchange of ideas and scientific information. In response to the Agency regulatory needs, this symposium focused on acid deposition, personal exposure and toxic substances. This publication is intended to assist those researchers interested in furthering the science of air monitoring.

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## INTRODUCTION

The third annual national symposium sponsored by EPA's Environmental Monitoring Systems Laboratory was held May 3-6, 1983 in Raleigh, North Carolina. In seven sessions over four days, papers and discussions focused on state-of-the-art systems for monitoring source emissions, ambient air, acid deposition, hazardous emissions and personal monitoring. The sessions were categorized as follows:

SESSION I	Inorganic Pollutants
SESSION II	Particulate Pollutants
SESSION III	General and Source Oriented Monitoring
SESSION IV	Personal Monitoring
SESSION V	Acid Deposition
SESSION VI	Organic Pollutants
SESSION VII	Panel Discussion

The papers are in the same order as presented by the speakers. Several papers are omitted because the speakers did not submit them in time for the agency's peer review.

AUTOMATED ACQUISITION, FILTERING AND

REDUCTION OF

ION CHROMATOGRAPHIC DATA

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In the past several years, few problems have received the national and international attention that acid precipitation has received (1,2). For informed decisions about pollution control strategies to be reached by policymakers, large amounts of data on the chemical composition of precipitation must be amassed. This data must address and be able to define trends in chemistry and hopefully to delineate sources of pollution from which acid is derived. Trends in the spatial and temporal variability of precipitation are being addressed by national networks such as the National Atmospheric Deposition Program, the MultiState Atmospheric Precipitation Sampling Program, and the Canadian Sampling Program (3). In addition to these deposition oriented networks, a need exists to sample a storm from beginning to end on a systematic basis such as reviewed by Robertson et. al. (4). An intensity weighted sampler used by the Science Research Laboratory at the US Military Academy collects one sample of 7 ml volume every 0.01" of precipitation. For each sample collected a rather complete ionic chemistry workup is desired so as to obtain pH, concentration of major cations (monovalent and divalent) and major anions. With average precipitation of 47" per year at West Point, it became obvious early in our effort that we must

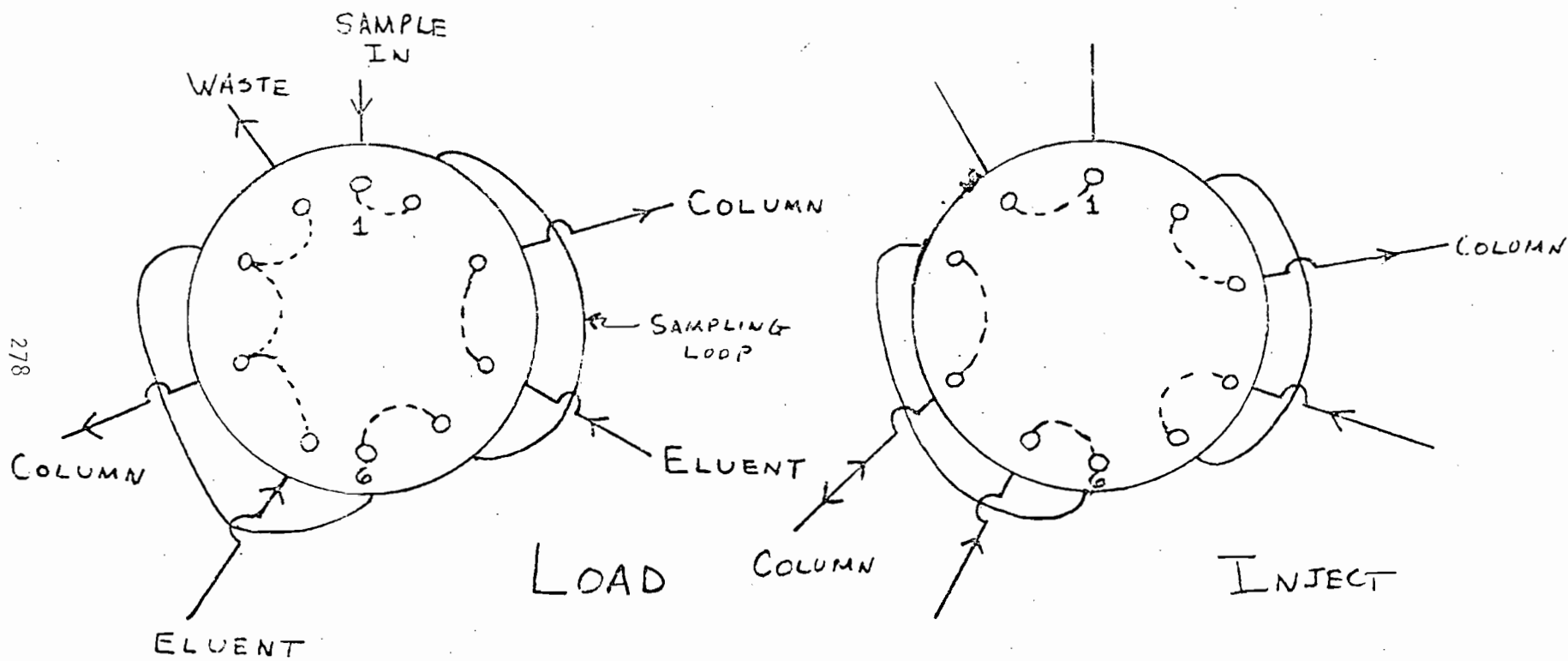


automate as much as possible every aspect of our data collection, storage, and processing effort. We chose to begin our automation effort with the ionic chemistry analysis since this would represent the largest savings of time.

#### INSTRUMENTATION

Since the originally designed DIONEX Model 14 was initially only capable of determining either anions or cations, a second detector and associated circuitry were obtained from DIONEX and the system replumbed to allow for use of both sets of columns at the same time. Anion analyses are performed using the 500 mm x 3 mm or two 250 mm x 3 mm separator column(s) followed by a 6 x 250 mm suppressor column. The eluent is the 0.0024 M  $\text{NaHCO}_3$ /0.003M  $\text{Na}_2\text{CO}_3$  prepared by diluting 2 gms of each anhydrous salt to 8 liters using > 15 megohm-cm deionized water. Monovalent cation ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ) analysis was performed using a 6 x 250 mm separator column followed by a 9 x 250 mm suppressor column. A 0.007 M  $\text{HNO}_3$  eluent is prepared by dilution of 55 ml 1 N  $\text{HNO}_3$  solution to 8 liter using > 15megohm-cm deionized water. Deionized water is obtained from a Millipore water treatment system consisting of a reverse osmosis column, carbon adsorption column, two mixed bed strong ion exchange resins and a 0.2 micron particulate filter.

A Varian 8055 liquid chromatographic autosampler was added to enhance the DIONEX capabilities. A Valco ACV-10-UHPa-N60 10 port sampling valve with two 100 microliter sampling loops was used to allow the simultaneous injection of a single sample onto each of the sets of columns on the ion chromatograph. The sampling valve is plumbed as in Figure 1.



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The original sampling loop as supplied by DIONEX was left in the eluent flow line as the ion chromatograph is used both for research and for teaching.

## OBJECTIVES

The objectives defined at the outset of the project were as follows:

1. To provide a physical link between the DIONEX and a microcomputer.
2. To provide a link between the Varian Autosampler and a microcomputer.
3. To convert the analog signal from the DIONEX to a digital signal for input to the microcomputer.
4. To have the autosampler signal the microcomputer when a sample is injected.
5. To read the rack and vial number of the sample being analyzed.
6. To provide a sample control system.
7. To store the digital information for later processing.
8. To smooth the digital data by an accepted technique.
9. To process the smoothed data to obtain peak height, peak area and retention time of each peak.
10. To sort the output file from objective 9 to include sample identification data from the sample control system.
11. To transfer the sample data from the microcomputer to a mainframe computer for archival, statistical analysis, etc.

To date all but objectives 6, 10 and 11 have been fully implemented.

Programming efforts on the remainder are continuing. We are also pursuing a means to accomplish objective 9 simultaneously with the acquisition of the analog data which will require a foreground/background programming effort.

The overall system is shown as block flow charts in Figure 2 and 3. The program operation can be divided into four sections -- Administrative, Data Acquisition, Data Storage, and Data Processing. Each of the subsystems will be discussed in subsequent paragraphs.

#### Administrative

The administrative portion of the code is an interactive session allowing the analyst to enter run conditions, date, number of samples to be analyzed, number of wash vials, source of sample, etc. The answers to the questions asked during the session control the naming of two types of data storage files -- a file containing the sample identification, run conditions, etc. and a second which contains the digital chromatographic data. It is anticipated that as the software continues to develop that the header file will be accessed to determine if the sample being analyzed is a standard or not, and then using the standards for construction of calibration charts. If the sample is an unknown, then the peak height will be converted to concentration. At this time, the conversion of peak heights to concentration still requires some "manual" manipulations of the data files. Work is ongoing to fully automate this process. The data files are dynamically created during the run as the rack and vial number are read at the autosampler.

#### Data Acquisition

To write the computer code for the acquisition of data from the ion chromatograph and from the autosampler, the internal workings of the

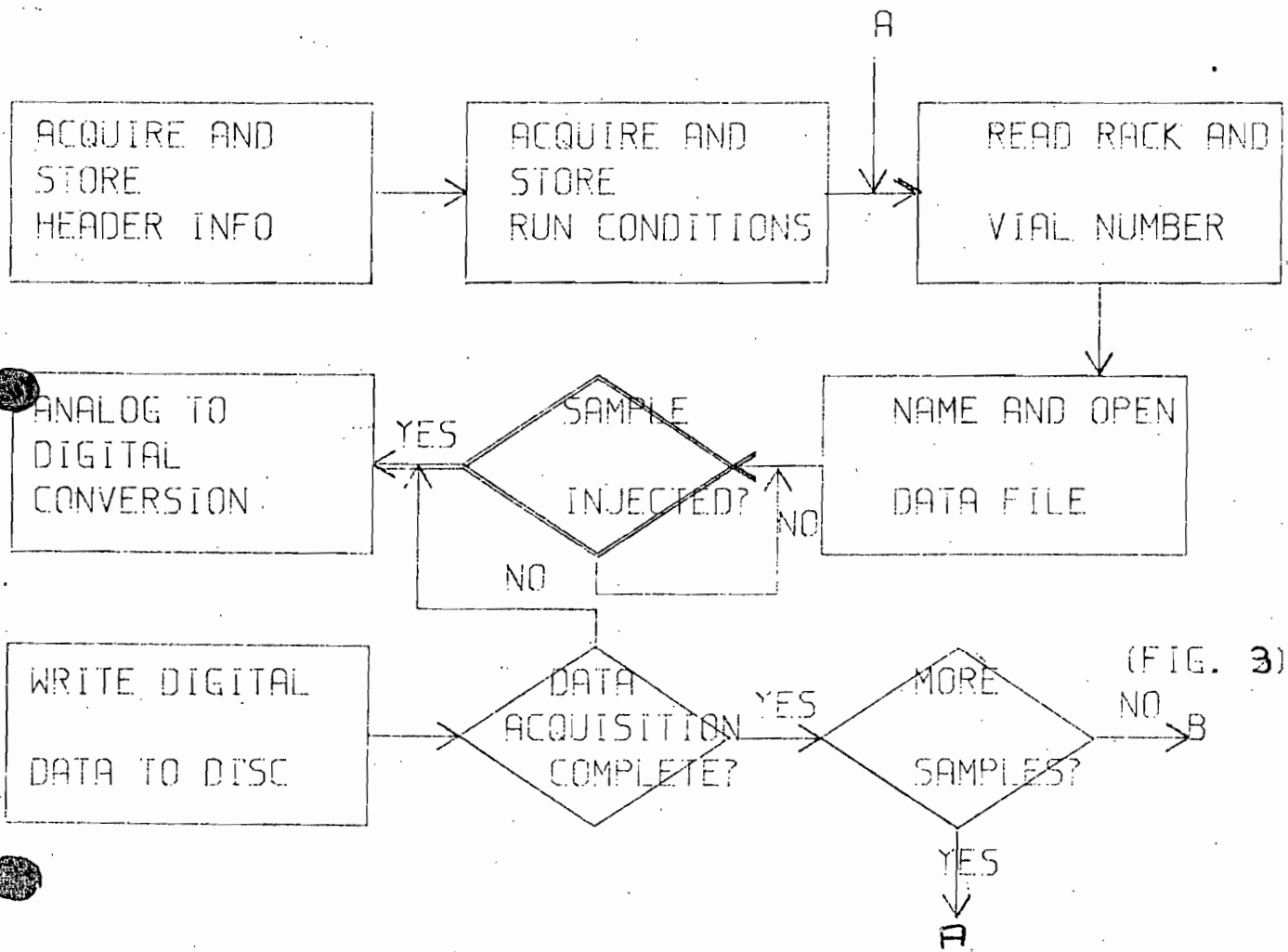


FIGURE 2. FLOW CHART FOR ADMINISTRATIVE, DATA ACQUISITION, AND DATA STORAGE

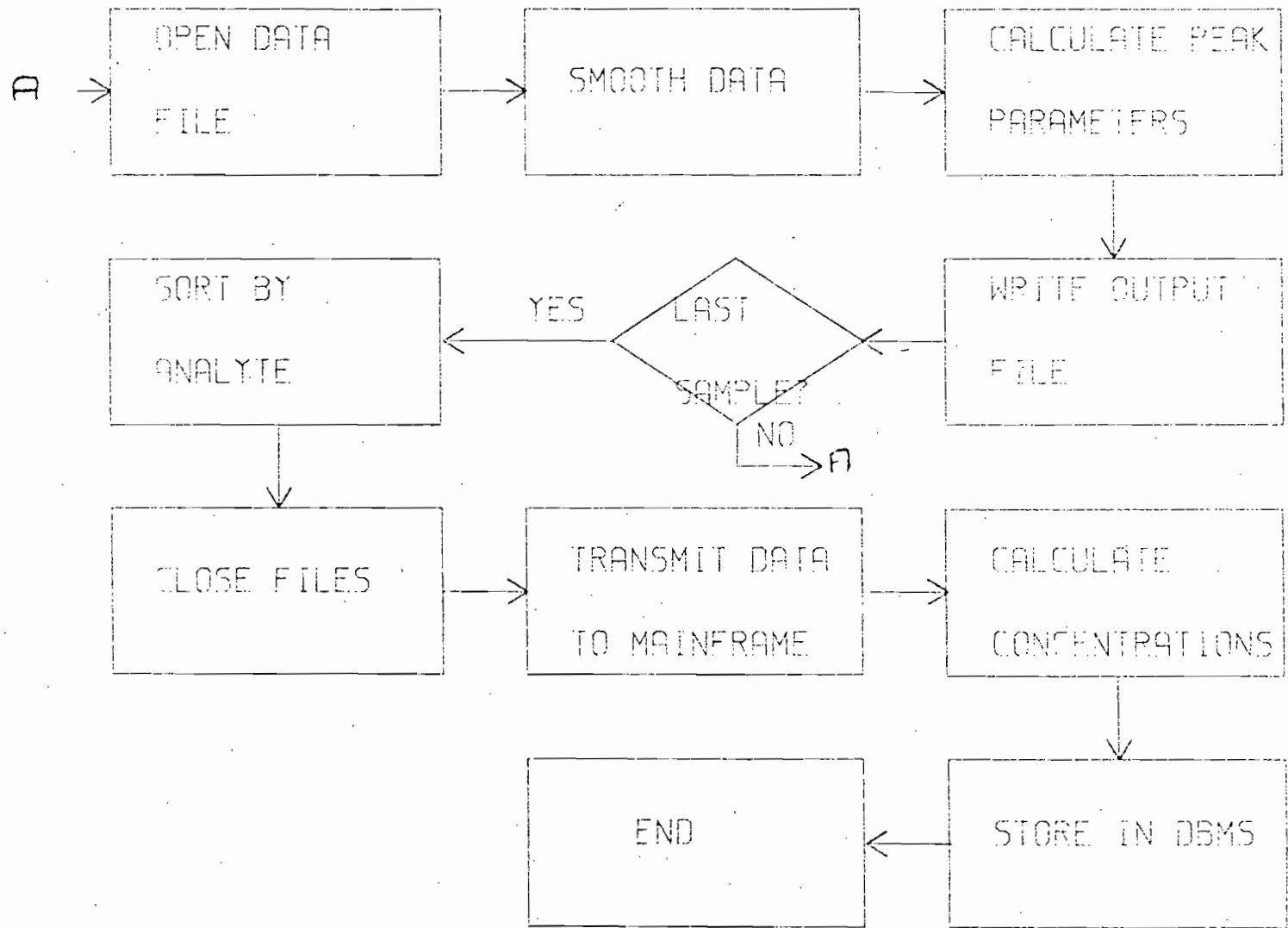
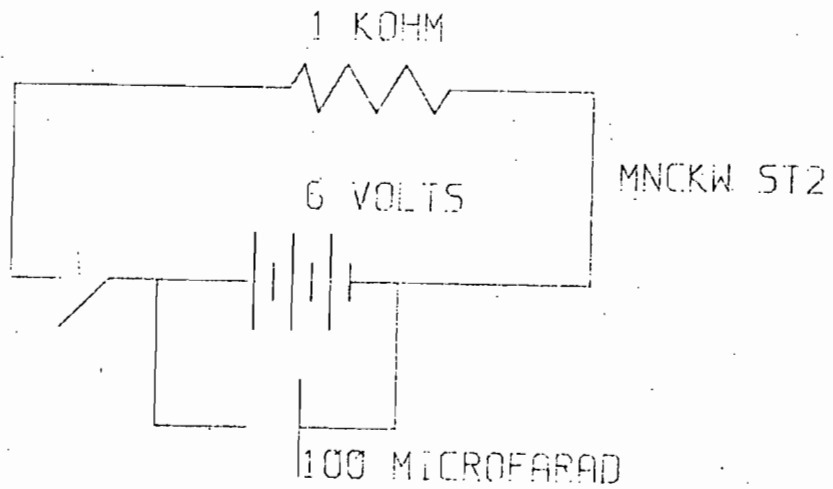


FIGURE 3 FLOW CHART FOR DATA PROCESSING

autosampler had to be completely understood. The timing of actions in the program had to be closely linked to the sequencing of events occurring in the autosampler and to the signals from the ion chromatograph. The autosampler is placed in operation by depressing the multiple/single run button. As the rack rotates under the injection needle, the program delays for several seconds. When the needle has pierced the septum, the rack and vial number information is available as 5 bit binary coded decimal (BCD) output on the interface cable. This information is read by a parallel digital board on the microcomputer and is immediately used to dynamically name and open a data file for the chromatographic data. Since the inject cycle on the autosampler allows for flushing of the tubing carrying sample to the injection loops, the program waits for a signal from the autosampler that the Valco valve has turned to the inject position (See Figure 1).

The signal is quite weak and required that an amplifier circuit be built (Figure 4) which could be detected by the Schmitt Trigger on the Minc. The 0-1 volt signal from the DIONEX is fed via 22 gauge copper wire to the preamplifier on the MINC which allows programmable "autogaining" of the preamplifier. The signal is then fed through the internal bus structure of the MINC to the analog to digital converter. The Schmitt Trigger on the MINC initiates the acquisition and conversion of the analog signal to digital form. Simultaneously a realtime clock is triggered to maintain the time of a run and also to control the timed acquisition of data. The clock module generates interrupts to the processor to signal that an Analog-Digital conversion must be made. Data acquisition requires that buffers be initialized and subsequently filled with the converted data. Data acquisition continues until





the run time as specified by the operator is exceeded. The data as acquired is in integer form, and must, therefore, be converted to floating point. All of the buffer management and integer to floating point conversion is handled by system subroutines. The preceding is continued until the rack and vial number that are read indicate that a stop pin has been encountered, at which time data acquisition ceases and data processing begins.

### Data Storage

After the data is acquired from the DIONEX and is resident in the memory of the microcomputer, the data is transferred to either a floppy disc or the hard disc of the microcomputer system. The files as explained earlier are named and opened as the rack and vial number of the sample are read from the autosampler.

### Data Processing

Data is smoothed using a modified Savitzky-Golay smoothing technique (5,6). The particular technique is a seven point moving box car average. Hacker, et. al. (7) and Walraven (8) indicate that significant shift in the position of a peak may be caused by a single pass of such a smoothing routine. They also showed that insignificant loss of peak height and no resultant peak shift would occur if the algorithm smoothing the peaks were to include four passes--the first and third from time equal zero to end of run, and two and four from time equal to the end of run to zero.

The expression for the filter function is:

$$y(n+3) = \frac{(x(n-3) + x(n-2) + \dots + x(n+2) + x(n+3))}{7} \quad (1)$$

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where  $y(n+3)$  is the value of the filtered data point and the  $x(n-3)$ , etc. are the values of the unfiltered data points.

The transfer function,  $H(f)$ , of this filter formula exhibits unity gain for low frequency output. Higher frequencies are greatly attenuated so that almost no high frequency "noise" appears in the output data. For the moving average filter, the transfer function is:

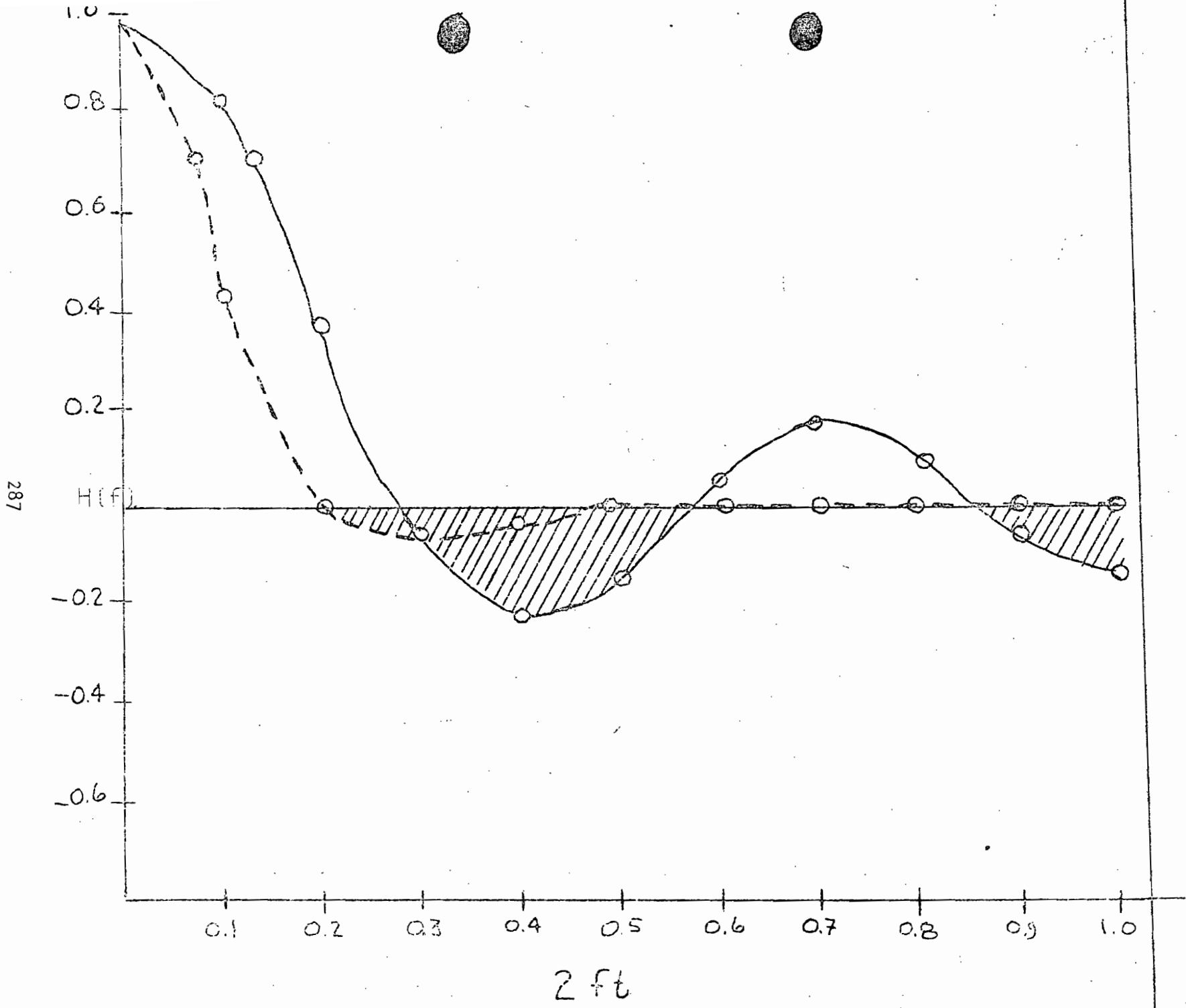
$$H(f) = \frac{1 + 2 \sum_{K=1}^M A \cos 2 K ft}{7} \quad (2)$$

where  $f$  = the frequency of the input data and  $t$  = the sampling rate. For a seven point filter,  $K=3$  and  $M=2$ . This gives the transfer function:

$$H(f) = \frac{1 + 2 \cos 2 ft + 2 \cos 4 ft + 2 \cos 6 ft}{7} \quad (3)$$

7

A graph of  $H(f)$  versus  $2 ft$  enables visualization of the filtering action



The dashed graph represents the transfer function of the smoothing filter employed in the program. It represents the effect of four passes of the moving average formula on the data. The solid graph represents the effect of one pass. As can be seen, the effect of four successive applications of the filter is that noise above a frequency component (2 ft) of 0.20 is for all practical purposes eliminated.

Whereas for the single pass, only those frequency components of 2 ft equal to 0.28, 0.56 and 0.85 are eliminated. In the region between these values, the frequency components are passed and for the region  $0.28 < 2 \text{ ft} < 0.56$ , the amplitude is reversed, thus subtracting from the net signal.

The peak height, peak width, retention time, and several other parameters were determined using chromatography peak processing routines on the MINC. After all of the peaks have been identified and the peak areas tabulated, the data is transferred via a Network communications package to a larger mainframe system for conversion of the peak heights to concentrations using a linear least squares fit of peak height vs. concentration calibration curve. The resulting concentrations and other sample identification data are stored on the mainframe using the RIM-5 data base system. Data retrieval and subsequent statistical analysis of data are accomplished on the mainframe.

#### Future work

In the future, we plan to streamline the working of the program to allow more efficient use of the computer resources and to allow for simultaneous processing and acquisition of data. Several other routines for the sorting and merging of data are currently being written.

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