Computers in Chemistry & Instrumentation. Vol. 5

LABORATORY SYSTEMS AND SPECTROSCOPY

EDITED BY

James S. Mattson Harry B. Mark, Jr.

Hubert C. MacDonald, Jr.

LABORATORY SYSTEMS AND SPECTROSCOPY

EDITED BY

James S. Mattson
National Oceanic and Atmospheric Administration
Environmental Data Service
Center for Experiment Design and Data Analysis
Washington, D.C.

Harry B. Mark, Jr.
Department of Chemistry
University of Cincinnati
Cincinnati, Ohio

Hubert C. MacDonald, Jr.
Koppers Company, Inc.
Research Department
Monroeville, Pennsylvania

MARCEL DEKKER, INC. New York and Basel

Library of Congress Cataloging in Publication Data

Main entry under title:

Laboratory systems and spectroscopy.

(Computers in chemistry and instrumentation ; v. 5)
Includes bibliographical references and indexes.
1. Chemistry, Analytic--Data processing.
2. Spectrum analysis--Data processing. I. Mattson, James S. II. Mark, Harry B. III. MacDonald, Hubert C.
QD75.4.E4L3 543'.028'5 75-32388
ISBN 0-8247-6207-X

COPYRIGHT © 1977 by MARCEL DEKKER, INC.
ALL RIGHTS RESERVED.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

INTRODUCTION TO THE SERIES

In the past decade, computer technology and design (both analog and digital) and the development of low cost linear and digital "integrated circuitry" have advanced at an almost unbelievable rate. Thus, computers and quantitative electronic circuitry are now readily available to chemists, physicists, and other scientific groups interested in instrument design. To quote a recent statement of a colleague, "the computer and integrated circuitry are revolutionizing measurement and instrumentation in science." In general, the chemist is just beginning to realize and understand the potential of computer applications to chemical research and quantitative measurement. The basic applications are in the areas of data acquisition and reduction, simulation, and instrumentation (on-line data processing and experimental control in and/or optimization in real time).

At present, a serious time lag exists between the development of electronic computer technology and the practice or application in the physical sciences. Thus, this series aims to bridge this communication gap by presenting comprehensive and instructive chapters on various aspects of the field written by outstanding researchers. By this means, the experience and expertise of these scientists are made available for study and discussion.

It is intended that these volumes will contain articles covering a wide variety of topics written for the nonspecialist but still retaining a scholarly level of treatment. As the series was conceived it was hoped that each volume (with the exception of Volume 1 which is an introductory discussion of basic principles and applications) would be devoted to one subject; for example, electrochemistry, spectroscopy, on-line analytical service systems. This format will be followed wherever possible. It soon became evident, however, that to delay publication of completed manuscripts while waiting to obtain a volume dealing with a single subject would be unfair to not only the authors but, more important, the intended audience. Thus, priority has been given to speed of publication lest the material become dated while awaiting publication. Therefore, some volumes will contain mixed topics.

The editors have also decided that submitted as well as the usual invited contributions will be published in the series. Thus, scientists who have recent developments and advances of potential interest should submit detailed outlines of their proposed contribution to one of the editors for consideration concerning suitability for publication. The articles should be imaginative, critical, and comprehensive, survey topics in the field and/or other fields, and which are written on a high level, that is, satisfying to specialists and nonspecialists alike. Parts of programs can be used in the text to illustrate special procedures and concepts, but, in general, we do not plan to reproduce complete programs themselves, as much of this material is either routine or represents the particular personality of either the author or his computer.

The Editors

此为试读,需要完整PDF请访问: www.ertongbook.com

PREFACE

This volume contains sections on the application of computers to instrumentation, laboratory data acquisition and reduction problems, and various applications in spectroscopy.

As mentioned in the preface to Volume 3, entitled "Spectroscopy and Kinetics," the various applications of computers to the numerous types of spectroscopic or optical methods for the study of atomic and molecular structure, chemical reactions, chemical analysis, etc., are so large that both complete volumes and parts of volumes will be devoted to this subject. Thus the second part of this volume, concerned with various applications in spectroscopy, represents only a part of the material which will be discussed in this series.

Chapter 1 is concerned with the design of real time control and digital data acquisition, both with and without a dedicated computer. Thus, this chapter presents alternative approaches to digital data systems, and discusses the applicability and limitations of the different approaches. This information will be particularly useful to research groups with either very specialized problems and/or limited financial or hardware resources.

Chapter 2 is a comprehensive discussion of computer-controlled single-crystal x-ray diffractometers. Although this is a highly specialized instrumental topic, the system illustrated and discussed in this chapter will be of significant use to those interested in applying on-line computer control to other instrumental systems.

Chapter 3 discussed methods of using the computer in the resolution of x-ray powder patterns.

Chapter 4 discusses the applications in spectroelectrochemical analysis.

Chapter 5 is on the application of digital computers to color matching. The applicability of this technique and its extension to other areas of spectroscopy and chemical analysis could be quite important in the future.

Chapter 6 represents a very comprehensive and extensive presentation on pattern analysis and recognition systems which are becoming more and more important in the chemical analysis of complex systems such as are found in environmental, biological, and toxicological studies.

Cincinnati, Ohio

James S. Mattson
Harry B. Mark, Jr.
Hubert C. MacDonald, Jr.

CONTRIBUTORS TO THIS VOLUME

DALE H. CHIDESTER, Department of Chemistry, Wayne State University, Detroit, Michigan

GERALD G. JOHNSON, JR., Material Research Laboratory, Computer Science Department, The Pennsylvania State University, University Park, Pennsylvania

MARVIN MARGOSHES, Technicon Instruments Corporation, Tarrytown, New York

JAMES S. MATTSON,* Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida

RONALD R. SCHROEDER, Department of Chemistry, Wayne State University, Detroit, Michigan

C. E. SCHUTT, Division of Applied Mathematics, Harvard University, Cambridge, Massachusetts

ROBERT A. SPARKS, Syntex Analytical Instruments, Cupertino, California

WILLIAM G. WEE, Department of Electrical Engineering, University of Cincinnati, Cincinnati, Ohio

---

*Current affiliation: National Oceanic and Atmospheric Administration, Environmental Data Service, Center for Experiment Design and Data Analysis, Washington, D. C.

LABORATORY SYSTEMS AND SPECTROSCOPY

CONTENTS

此为试读,需要完整PDF请访问: www.ertongbook.com

Chapter 1

REAL TIME CONTROL AND DIGITAL DATA ACQUISITION WITH AND WITHOUT A DEDICATED COMPUTER

Ronald R. Schroeder

Dale H. Chidester

Department of Chemistry
Wayne State University
Detroit, Michigan

I. INTRODUCTION

In recent years, progress in instrumentation has been tied to digital data acquisition especially to minicomputer-based systems. The terms "digital data acquisition systems" and "computer-based laboratory systems". are almost synonymous. Yet, a fair number of noncomputerized devices from which digital data acquisition systems can be constructed have been developed concurrently with the minicomputer. The utility of these devices has been frequently overlooked, perhaps because of the decreasing cost and increasing versatility of the minicomputer now available. Nevertheless, non-computer-based digital data acquisition does offer an alternate approach to computer-based systems. To be sure, such devices do not and cannot possess the wide applicability and versatility of minicomputer-based systems. However, in individual cases, especially where a single type of experiment is to be performed repeatedly, less intelligent devices may suffice and offer a reduction in cost.

If one adopts as the goal of his instrumentation the gathering of data in digital form and if the inconveniences of handling intermediate storage media are not of major concern, then digital acquisition systems design can be quite flexible.

A. Control and Data Acquisition

Real time control and digital data acquisition normally bring to mind a dedicated computer with associated peripherals including a real time clock, AD converter, etc., with software programs controlling the start of the experiment, the rate of data acquisition, and the amount of data to be taken. Immediately following or perhaps during the data acquisition, the computer can be calculating and perhaps reducing data into a more useful format. The limit to the data reduction lies in the programmer's ability to anticipate the form and trends in the data taken. Obviously, such a system provides almost the maximum of flexibility in experiment design requiring only different programs and perhaps a few different peripherals for any new experiment.

Of course, there are alternatives to this approach. These can be deduced by considering the real goals of the system design and experiment itself together with an examination of the essential role played by the computer.

First, consider the role of the computer and the possibility that certain of its functions can be performed by other and perhaps less intelligent devices. Since timing and analog to digital conversion are performed by external devices, the principal functions of the computer are sequencing of operations, storage of data, manipulation of the stored data, control of I/O devices, and in some cases, decision making (i.e., changing the experiment via programmed decisions).

Of these operations, sequencing and data storage can be performed by other types of digital devices. Manipulation of data can be done in any computer, not necessarily in the immediate locale, provided an intermediate storage medium is provided and access to a computer is available. This leaves decision making and I/O device control as the functions unique to the computer. Obviously, in experiments involving straight data acquisition on a single channel where data strings of consistent character and length will be obtained, the computer is not a necessity.

II. THE EXPERIMENT

The following discussion provides an example of how real time control and digital data acquisition were implemented in this laboratory with and without a dedicated computer. The experiments involved staircase voltammetry [1, 2, 3] with a varied current sampling time (SV) and stationary electrode polarography (SEP).

The SV experiment is in many ways similar to ordinary linear ramp SEP. In SV, the applied voltage is a stepwise increasing "staircase" waveform characterized by a step time τ, a step amplitude ΔE, and a number of steps N. The current during each of the N steps is sampled at a present

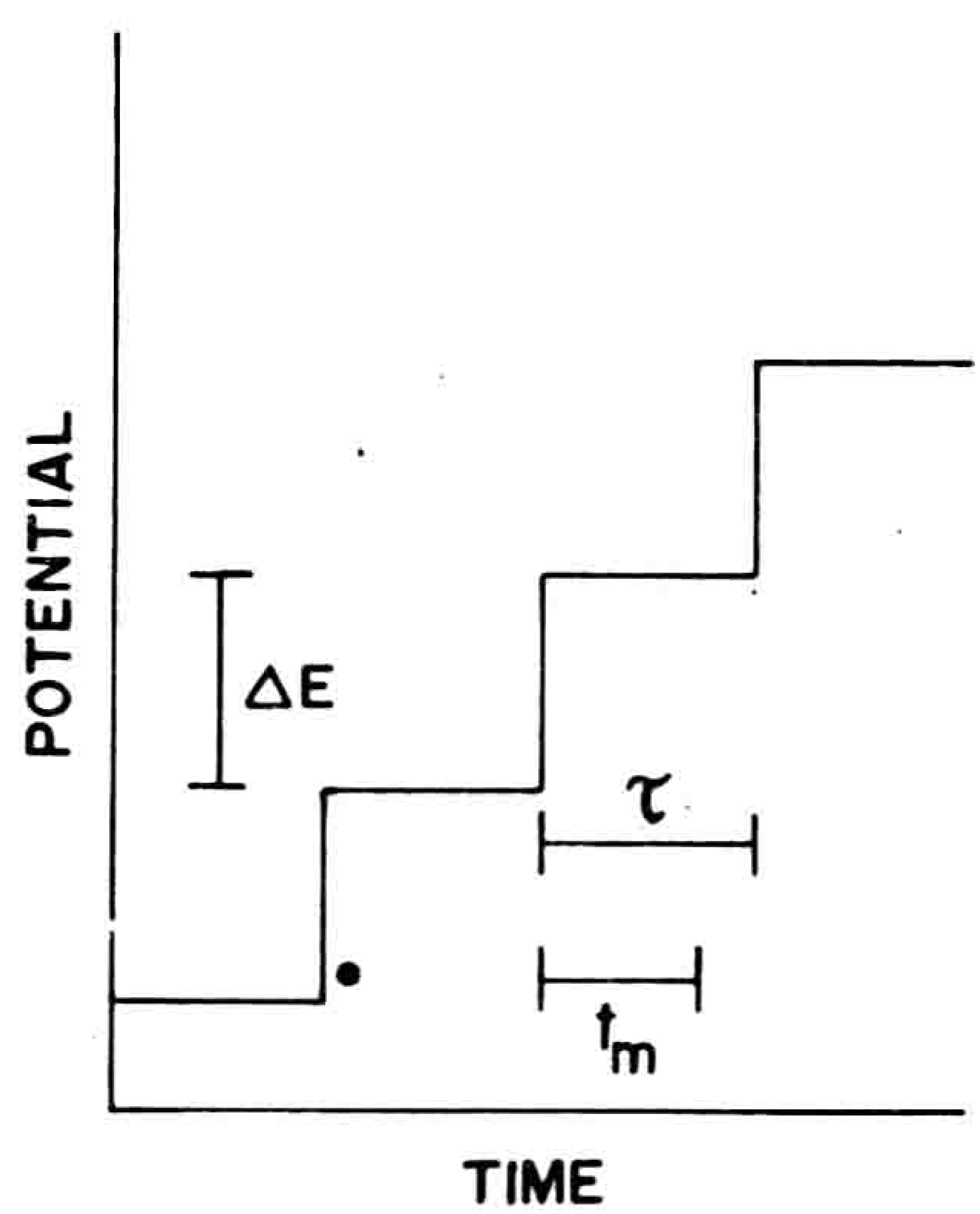

Fig. 1. A portion of the staircase waveform: ΔE, voltage step amplitude; τ, the step time; t_m, the current sampling time.

time t_m following the potential rise (Fig. 1). Unique voltammograms are obtained for each set of ΔE, τ, and t_m values. The ratio τ/t_m serves as a convenient means of defining t_m and of organizing the data. Ordinarily, ΔE and τ are maintained constant for a series of experiments while t_m (τ/t_m) is changed from one experiment to the next. The parameters of the voltammogram are the peak potential E_p and the peak current i_p.

Prior to the construction of the digital systems, SV experiments were run using a hybrid analog digital system from which the data were taken as photographs of an oscilloscope display.

To overcome the limitations of previous staircase instrumentation, to reduce the tedium and error associated with manually digitizing analog data, and thereby increase the confidence associated with experimental SV measurements, it was decided that digital control of the staircase signal and current sampling time would be used [2, 3]. One goal of the system design was that digital data should be rendered in a format compatible with the Wayne State University time-shared computer system (WSU MTS) so that the full resources of that system could be used to process it.

Two SV systems have been assembled which satisfy the objectives set forth for this project [3]. Digital techniques are used for the generation of the applied staircase signal with an accuracy of better than 0.1% in both step size and step time. Both systems use intermediate data storage on perforated paper tape because of the low cost for implementation and its compatibility with a WSU MTS teletype terminal.

III. SYSTEM FOR CONTROL AND DIGITAL DATA ACQUISITION WITHOUT A DEDICATED COMPUTER

A. Control Philosophy

The first digital data acquisition system for staircase voltammetry utilized a transient recorder (TR) (Model 610, Biomation, Inc., Cupertino, California). A somewhat unusual means of controlling the staircase signal had to be used because the TR allows control only of the rate of data acquisition, not the instant at which a datum is acquired. The most straightforward method of control would be to apply a step and wait for a period of time (t_m) before acquiring data (see Fig. 1). Such an approach could not work with a free-running data recorder such as the TR. With a periodic signal, however, it makes no difference after the first event if the data acquisition controls the step or the step controls the data acquisition. Reversing the logic of control, one can just as easily acquire data and wait for a period of time ($\tau - t_m$) before applying the next step. After the first step: step, sample, step, sample, etc., is identical to: sample, step, sample, step, etc.

B. The Transient Recorder

To assist in understanding the Biõmation System, the following brief description of the Biomation itself is included (Fig. 2). A comprehensive description of its operation is available elsewhere. The TR acquires and stores 128 6-bit binary words of data. Data are gathered in time at rates from 50 msec to 100 msec per word as selected by a 1, 2, 5 time base. Provisions are included for remote arming and triggering of the TR and a record signal is turned on during the time data are actually being acquired. Internally, a crystal-controlled 20 MHz master clock sequences the TRs operation and generates the time base. Derived from the time base is a signal called the Memory Buffer Clock which makes a logical 0→1 transition to trigger the acquisition of data. The TR was modified to bring this Memory Buffer Clock and a 1 MHz submultiple of the master clock to connectors on the back panel for use in controlling experiments.

Data gathered by the TR are available in either digital or analog form. In analog form (automatic display mode), the data are presented recurrently at 2 μsec/word for display on an oscilloscope or at a slow rate (0.1 sec/word) for plotting on a conventional x-t recorder. Digital data are available in negative logic 6-bit parallel binary form at DTL-TTL compatible levels and can be read in a synchronous manner at 2 μsec/word or asynchronously at a rate determined by a signal applied to the Word Command. For asynchronous operation, the Word Command is held at a logical 0 until the next word is desired. A logical 0→1 transition of the Word Command signals the TR to present the next word at its output. As the TR begins looking for the next word, the Flag makes a logical 1→0 transition at which time the Word Command must again become 0 to prevent the TR from going into the synchronous output mode. The Flag then returns to a logical 1 level within 256 μsec indicating that the next word is available. Data are available for asynchronous output only immediately after acquisition. Once the automatic display mode has been entered, it is impossible to return to the asynchronous mode. While in the asynchronous mode, analog data for display are not available. The last (128th) Flag is at a logical 1 for only about 100 nsec, and the last word is available for only 2 μsec at the digital output. After the last word has been presented asynchronously, the TR internally holds the Flag at a logical 0 level, and the Word Command has no further control over the data since the TR has entered the automatic display mode.

C. Staircase Signal Generator

1. Delay Timer

To achieve digital control of the signal generation, two signals are used to synchronise and control the delay between data acquisition and signal application. The 1 MHz clock from the TR is first conditioned by the Divider

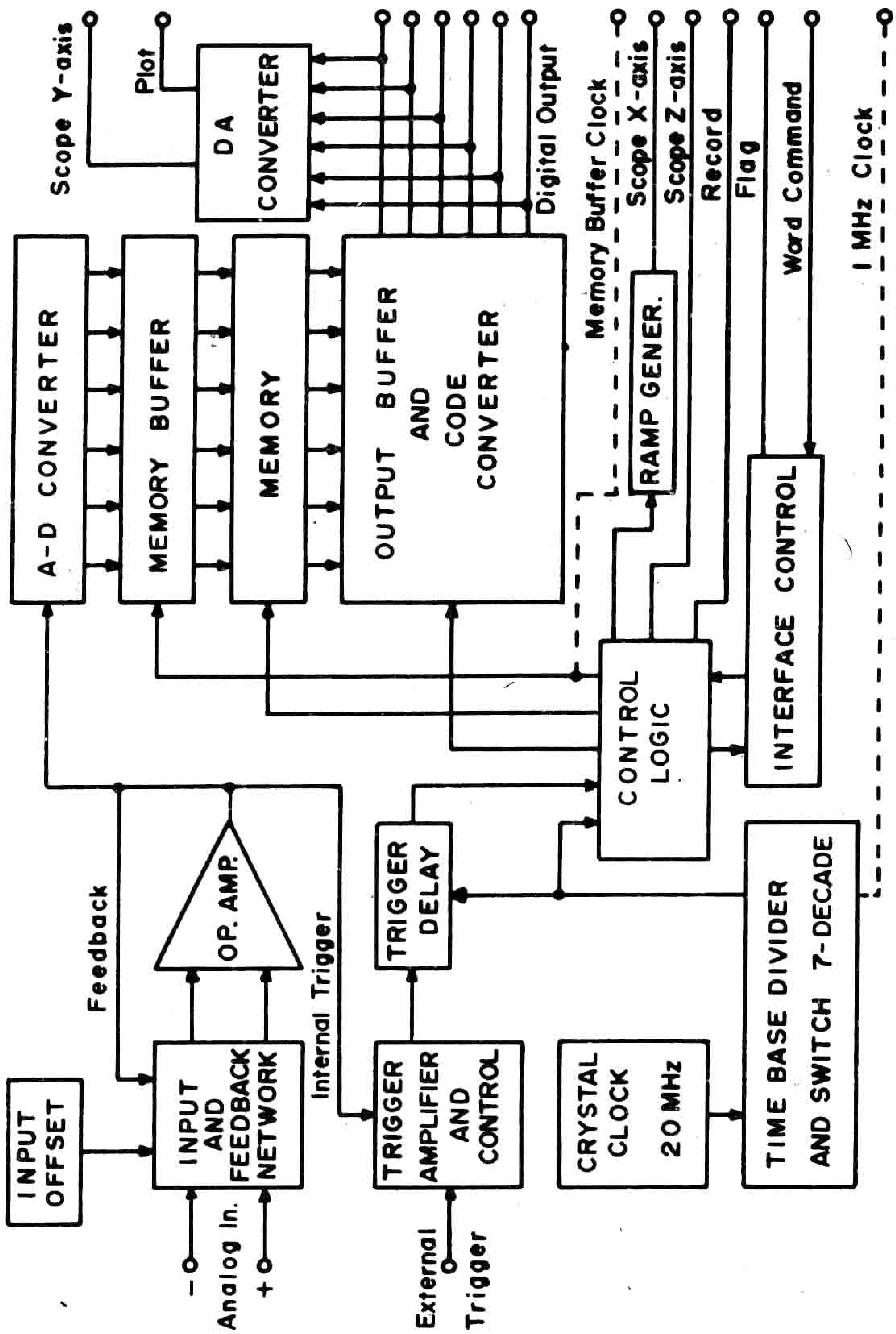

FIG. 2. Block diagram of the Biomation 610 Transient Recorder, with modifications.