TECHNIQUES OF CHEMISTRY

VOLUME I

PHYSICAL METHODS OF CHEMISTRY

Edited by

ARNOLD WEISSBERGER

AND

BRYANT W. ROSSITER

PART IA

Components of Scientific Instruments

TECHNIQUES OF CHEMISTRY

VOLUME I

PHYSICAL METHODS OF CHEMISTRY

INCORPORATING FOURTH COMPLETELY REVISED AND AUGMENTED EDITION OF TECHNIQUE OF ORGANIC CHEMISTRY, VOLUME I, PHYSICAL METHODS OF ORGANIC CHEMISTRY

Edited by

ARNOLD WEISSBERGER

AND

BRYANT W. ROSSITER

Research Laboratories
Eastman Kodak Company
Rochester, New York

PART IA

Components of Scientific Instruments

WILEY-INTERSCIENCE

A DIVISION OF JOHN WILEY & SONS Inc.

New York · London · Sydney · Toronto

Library of Congress Catalog Card Number: 77-114920

ISBN 0 471 92724 4

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

PLAN FOR

PHYSICAL METHODS OF CHEMISTRY

PART I

Components of Scientific Instruments, Automatic Recording and Control, Computers in Chemical Research

PART II

Electrochemical Methods

PART III

Optical, Spectroscopic, and Radioactivity Methods

PART IV

Determination of Mass, Transport, and Electrical-Magnetic Properties

PART V

Determination of Thermodynamic and Surface Properties

AUTHORS OF PART I

LEROY L. BLACKMER

Research Laboratories, Eastman Kodak Company, Kodak Park, Rochester, New York

CURTIS E. BORCHERS

Department of Chemistry, Northwestern University, Evanston, Illinois

JOHN FIGUERAS

Research Laboratories, Eastman Kodak Company, Kodak Park, Rochester, New York

MURRAY C. GODDARD

Research Laboratories, Eastman Kodak Company, Kodak Park, Rochester, New York

ROBERT J. LOYD

Department of Chemistry, Northwestern University, Evanston, Illinois

LEON F. PHILLIPS

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

DAVID R. SIMONSEN

Manufacturing Experiments, Kodak Park, Rochester, New York

DONALD E. SMITH

Department of Chemistry, Northwestern University, Evanston, Illinois

NEW BOOKS AND NEW EDITIONS OF BOOKS OF THE TECHNIQUE OF ORGANIC CHEMISTRY SERIES WILL NOW APPEAR IN TECHNIQUES OF CHEMISTRY. A LIST OF PRESENTLY PUBLISHED VOLUMES IS GIVEN BELOW.

TECHNIQUE OF ORGANIC CHEMISTRY
ARNOLD WEISSBERGER, *Editor*

Volume I: Physical Methods of Organic Chemistry
Third Edition—in Four Parts

Volume II: Catalytic, Photochemical, and Electrolytic Reactions
Second Edition

Volume III: Part I. Separation and Purification
Part II. Laboratory Engineering
Second Edition

Volume IV: Distillation
Second Edition

Volume V: Adsorption and Chromatography

Volume VI: Micro and Semimicro Methods

Volume VII: Organic Solvents
Second Edition

Volume VIII: Investigation of Rates and Mechanisms of Reactions
Second Edition—in Two Parts

Volume IX: Chemical Applications of Spectroscopy
Second Edition—in Two Parts

Volume X: Fundamentals of Chromatography

Volume XI: Elucidation of Structures by Physical and Chemical Methods
In Two Parts

Volume XII: Thin-Layer Chromatography

Volume XIII: Gas Chromatography

Volume XIV: Energy Transfer and Organic Photochemistry

INTRODUCTION TO THE SERIES

Techniques of Chemistry is the successor to the Technique of Organic Chemistry Series and its companion—Technique of Inorganic Chemistry. Because many of the methods are employed in all branches of chemical science, the division into techniques for organic and inorganic chemistry has become increasingly artificial. Accordingly, the new series reflects the wider application of techniques, and the component volumes for the most part provide complete treatments of the methods covered. Volumes in which limited areas of application are discussed can be easily recognized by their titles.

Like its predecessors, the series is devoted to a comprehensive presentation of the respective techniques. The authors give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling. It is hoped that the series will contribute to a better understanding and a more rational and effective application of the respective techniques.

Authors and editors hope that readers will find the volumes in this series useful and will communicate to them any criticisms and suggestions for improvements.

Research Laboratories
Eastman Kodak Company
Rochester, New York

ARNOLD WEISSBERGER

PREFACE

Physical Methods of Chemistry succeeds, and incorporates the material of, three editions of *Physical Methods of Organic Chemistry* (1945, 1949, and 1959). It has been broadened in scope to include physical methods important in the study of all varieties of chemical compounds. Accordingly, it is published as Volume I of the new Techniques of Chemistry Series.

Some of the methods described in *Physical Methods of Chemistry* are relatively simple laboratory procedures, such as weighing and the measurement of temperature, refractive index, and determination of melting and boiling points. Other techniques require very sophisticated apparatus and specialists to make the measurements and to interpret the data; x-ray diffraction, mass spectrometry, and nuclear magnetic resonance are examples of this class. Authors of chapters describing the first class of methods aim to provide all information that is necessary for the successful handling of the respective techniques. Alternatively, the aim of authors treating the more sophisticated methods is to provide the reader with a clear understanding of the basic theory and apparatus involved, together with an appreciation for the value, potential, and limitations of the respective techniques. Representative applications are included to illustrate these points, and liberal references to monographs and other scientific literature providing greater detail are given for readers who want to apply the techniques. Still other methods that are successfully used to solve chemical problems range between these examples in complexity and sophistication and are treated accordingly. All chapters are written by specialists. In many cases authors have acquired a profound knowledge of the respective methods by their own pioneering work in the use of these techniques.

In the earlier editions of *Physical Methods* an attempt was made to arrange the chapters in a logical sequence. In order to make the organization of the treatise lucid and helpful to the reader, a further step has been taken in the new edition—the treatise has been subdivided into technical families:

Part I	Components of Scientific Instruments, Automatic Recording and Control, Computers in Chemical Research
Part II	Electrochemical Methods
Part III	Optical, Spectroscopic, and Radioactivity Methods

Part IV Determination of Mass, Transport, and Electrical-Magnetic Properties

Part V Determination of Thermodynamic and Surface Properties

The changes in subject matter from the Third Edition are too numerous to list in detail. We thank previous authors for their continuing cooperation and welcome the new authors to the series. New authors of Part I are Dr. Leroy L. Blackmer, Dr. Curtis E. Borchers, Dr. John Figueras, Mr. Murray C. Goddard, Mr. Robert J. Loyd, Dr. Leon F. Phillips, and Dr. Donald E. Smith.

We are also grateful to the many colleagues who advised us in the selection of authors and helped in the evaluation of manuscripts. They are for Part I: Mr. D. C. Barton, Dr. E. R. Brown, Mr. M. C. Goddard, Mr. W. K. Grimwood, Mr. H. O. Hoadley, Mrs. A. Kocher, Dr. W. R. Ruby, and Mr. J. G. Streiffert.

The senior editor expresses his gratitude to Bryant W. Rossiter for joining him in the work and taking on the very heavy burden with exceptional devotion and ability.

ARNOLD WEISSBERGER
BRYANT W. ROSSITER

January 1970
Research Laboratories
Eastman Kodak Company
Rochester, New York

CONTENTS

COMPONENTS OF SCIENTIFIC INSTRUMENTS

Chapter I

INTRODUCTION

Leon F. Phillips

1 GENERAL DESIGN CONSIDERATIONS

The Role of Instrumentation in Chemistry

Not very long ago it was possible to do interesting and useful work in most areas of chemistry with little help from instrumentation. The classical sequence of preparation, analysis, and characterization of new substances which formed the basis of chemical research programs would sometimes include the measurement of an ultraviolet spectrum or magnetic moment, but measurements of this nature were usually regarded as incidental to the main objectives of the research. Mass spectrometers and infrared spectrometers, to name two of the most useful modern chemical instruments, were difficult to operate, and were in the province of physicists and a few borderline physical chemists. Even the measurement of an absorption spectrum in the visible region was a tedious operation. Magnetic resonance in its present form had still to be invented. A generation ago organic chemists as a group were just beginning to realize the amount of insight to be gained from purely physical measurements: the change that has occurred since then has been virtually a revolution. An indication of the readiness with which physical instruments and methods are now adopted is provided by a comparison of the time lags between invention and large-scale chemical application of mass spectrometry (about 40 years), nuclear magnetic resonance (about 10 years), and Mössbauer spectroscopy (about three years). It has become appreciated that the first people to work in a new field, or to apply a new instrumental technique in an old field, are those who make the most interesting discoveries, and it is only a slight exaggeration to say that if a new

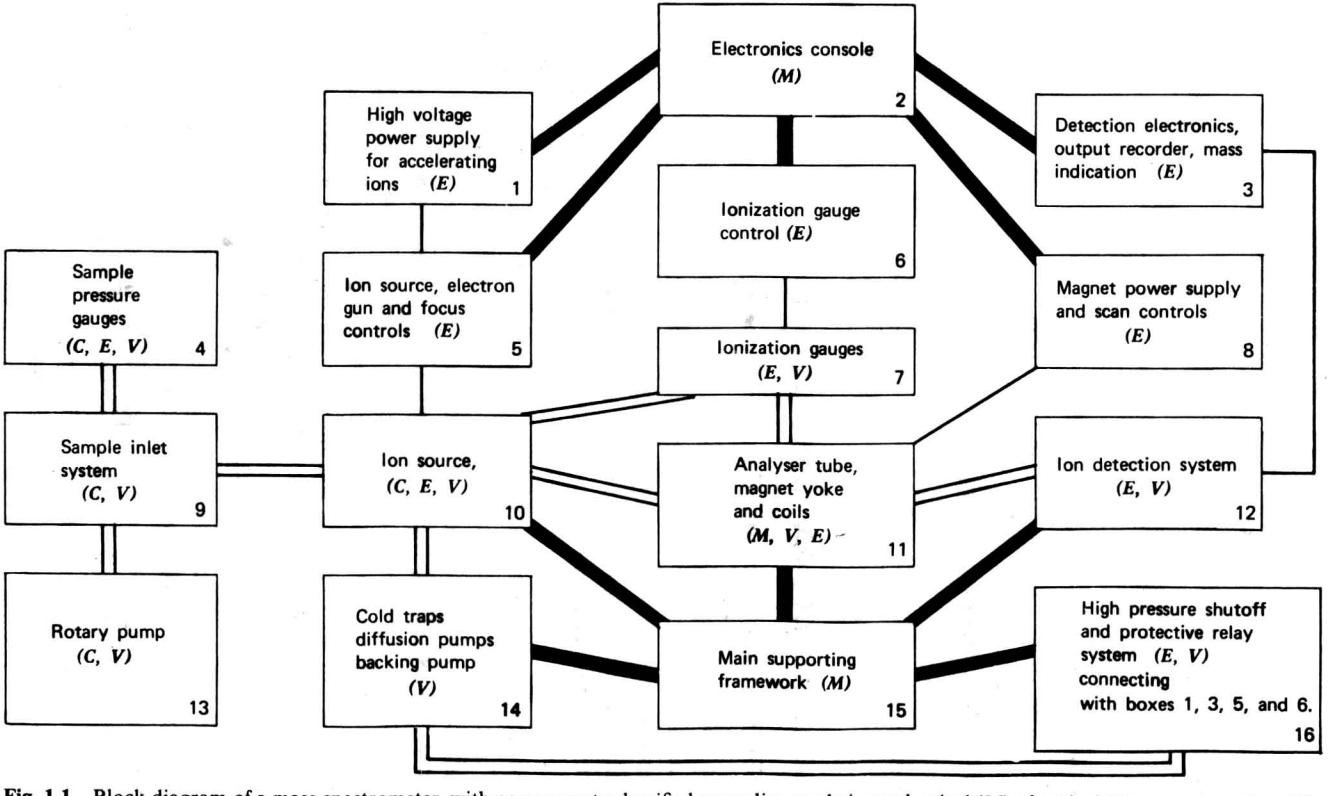

Fig. 1.1 Block diagram of a mass spectrometer, with components classified according to their mechanical (*M*), electrical (*E*), vacuum system (*V*), or chemical handling (*C*) functions. ▬▬ mechanical support; ═══ vacuum connection; ——— electrical connection.

type of spectroscopy were to be announced on a Monday chemists in the vicinity would be running the spectra of their latest compounds by the end of the week and a commercial instrument for the purpose would be advertised during the following month. Even a new way of using an old technique, as in the automation of x-ray structure determination, or of combining two techniques, as in optical rotary dispersion, can yield important dividends. It follows from this discussion that the education of a chemist at the present time is incomplete unless it includes training in instrumentation that is at least sufficient to enable the student to understand the operating principles and to recognize the potentialities and limitations of any instrument that he is likely to encounter. The need for a systematic approach to instrumentation is demonstrated by the observation that a complete catalog of the scientific instruments used in chemistry would contain items ranging in complexity from a thermometer to a cyclotron. It is the main purpose of this introduction to point out the features that are common to all instruments, of whatever degree of complexity, and to consider the general factors that govern the choice of a suitable design for an instrument which is to be built or bought. In the chapters that follow a number of specific topics relating to instrument design and construction are discussed in detail. It is hoped that our account will be of value not only to people whose responsibility it is to acquire or build scientific equipment but also to those who employ equipment that is already available. Uncritical users of "black boxes" generally pay for their lack of understanding by failure to exploit an instrument's full performance or to detect errors that arise from exceeding an instrument's capabilities.

Block Diagrams

Many scientific instruments are simple in form and have an obvious mode of operation; many others, unfortunately, are not in this category. The first step toward understanding any complex entity is to analyse it into its components. One way of doing this with a scientific instrument is to classify the components in terms of their functions. Such a classification, for example, might include categories for mechanical components, optical components, vacuum systems, electrical supplies and connections, electronics, and chemical handling systems. A block diagram of a reasonably complex instrument (a mass spectrometer) based on this type of classification is shown in Fig. 1.1. This kind of diagram is useful in elucidating the gross structure of an instrument, as an aid to devising a suitable physical layout for a large construction, and as the basis of a flow chart to determine the best order of construction and assembly when a new instrument is to be built.

The two basic functions of instruments are measurement and control. Measurement is the more fundamental, since a physical quantity such as

temperature or magnetic field intensity must be measured to determine whether it differs from the required value before it can be controlled. This leads us to a different way of constructing a block diagram in which the emphasis is on the flow of signals (i.e., information) from the system whose properties are being measured to the output of the instrument. The resulting diagrams are more general and correspondingly more abstract in character than Fig. 1.1. A typical block diagram of this type for a chemical instrument is given in Fig. 1.2, in which the chemical system is represented by a circle and the components of the instrument itself are represented by rectangles.

A signal consists of a change in the value of some measurable quantity, such as light intensity, temperature, or electric current, and to detect such a change it is necessary to have a standard of comparison. For this reason the signal paths in Fig. 1.2 are shown as double lines, one line for the varying quantity and one for the standard or reference signal. In electrical instruments the reference signal is usually, though not invariably, provided by a point at earth (zero) potential. The *transducers* are devices for transferring signals, or their information content, from one form or medium to another; for example, a thermocouple is a transducer for converting information in the form of a temperature difference to equivalent information in the form of a voltage difference; a photocell is a transducer for converting a difference in light intensity into a voltage or current difference; a pen recorder is a transducer for converting a voltage or current signal into a change in the position of a line drawn on a chart. In recent years a great variety of extremely powerful signal-handling techniques has been developed in the field of electronics and most instruments are now built to exploit this development as much as possible. Information is most often conveyed from one part of an instrument to another in the form of electrical signals so that a device such as a thermocouple or photocell, which produces an electrical signal, is normally used as an input transducer, whereas a pen recorder, or galvanometer, which gives a visual readout of an electrical signal, is commonly used as an output transducer. In consequence of the predominance of electronic signal-handling methods some basic understanding of electronics on the part of the experimenter is desirable. The *signal modifier* of Fig. 1.2 would in most cases be an amplifier of electrical signals with the function of converting

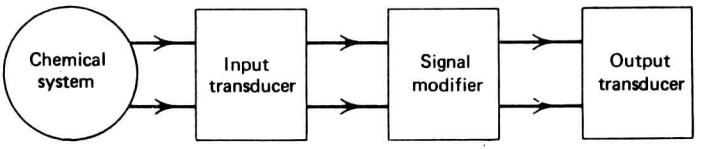

Fig. 1.2 Block diagram of an instrument for measuring some property of a chemical system. Signal paths are shown by arrows.

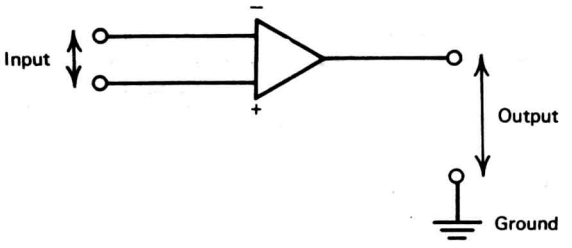

Fig. 1.3 Conventional amplifier symbol. (Often the (+) input lead is directly connected to ground.) A signal applied to the (+) input produces an output signal of the same sign. A signal applied to the (−) input produces an output signal of the opposite sign.

the relatively feeble voltage or current from the input transducer into a signal powerful enough to operate the output transducer. This should be accomplished with no loss of information due to noise or distortion along the way. Other possible functions of a modifier include the averaging of a signal over a period of time, the chopping of a steady voltage or current to produce an alternating signal, the rectification of an alternating signal to produce a steady voltage or current, and pulse shaping and pulse-height discrimination. It is often useful to distinguish an amplifier by using the conventional triangular symbol of Fig. 1.3. Some other modifiers, notably those used in digital logic circuitry, also have their own conventional symbols, which are described in Chapter IV.

Even for an instrument as simple as a thermometer the analysis implied by Fig. 1.2 is possible in principle; here the small mass of mercury is essentially a transducer for converting a temperature change into a volume change, the long capillary is a modifier for converting the volume change to a change of length, and the engraved scale is an output transducer for converting the length change into a readable change of so many degrees. In this case the analysis is hardly more than an academic exercise, but in the design or understanding of a complex piece of equipment it is an essential first step.

As an example of the use of block diagrams in the design of a moderately complicated piece of equipment, let us suppose that we require instrumentation to measure the progress of a chemical reaction as a function of time. The chemical system will consist of the reaction vessel and its contents and a transducer is needed to respond to a change in the nature of the contents. To be more specific, suppose that the reaction is accompanied by a color change (e.g., the reaction of iodine with acetone or of nitric oxide with oxygen) and that the transducer is to respond to the change in optical density at some suitable wavelength. Most commercial spectrophotometers are not designed to allow the optical density at one wavelength to be recorded as a function of time, and so we decide to build an apparatus for the purpose.

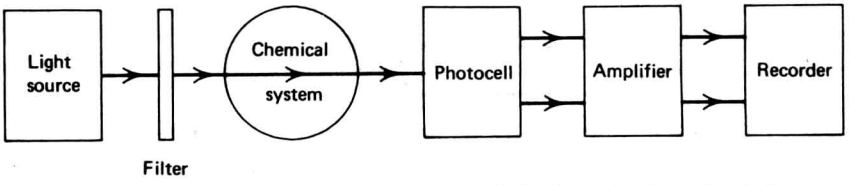

Fig. 1.4 Block diagram of an instrument for observing light absorption by a chemical system.

Our first ideas give rise to the block diagram shown in Fig. 1.4 in which the combination of light source, optical filter (a modifier for light signals), and photocell constitutes the input transducer.

It now becomes apparent from the diagram that no path has been provided for a comparison signal, and in order to measure a change in optical density it would be necessary to remove the reaction vessel periodically and replace it with an identical vessel in which no reaction had occurred. We can improve this arrangement by splitting the light beam into two parts, as in Fig. 1.5, and arranging for a rotating or vibrating shutter—a "light chopper"—to present the two light beams to the photocell alternately. The resulting apparatus should be adequate to measure a change in optical density of a few percent with sufficient accuracy for kinetic studies. To complete the experimental system we should also include a thermostat to fix the temperature of the reaction mixture, power supplies for the amplifier, photocell, and any other electronic units that become involved, a rectifier to convert the alternating signal that results from our use of a light chopper into a steady signal for the chart recorder, and connections to the mains for thermostat, recorder, and power supplies. We might also wish to introduce one or more *feedback loops* to improve the stability of the measuring system; for example, the intensity of the comparison signal received by the photocell could be used

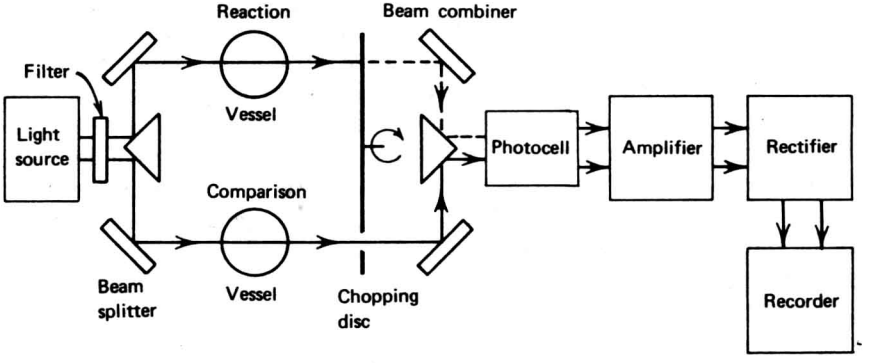

Fig. 1.5 Addition of a comparison light signal to the apparatus of Fig. 1.4.

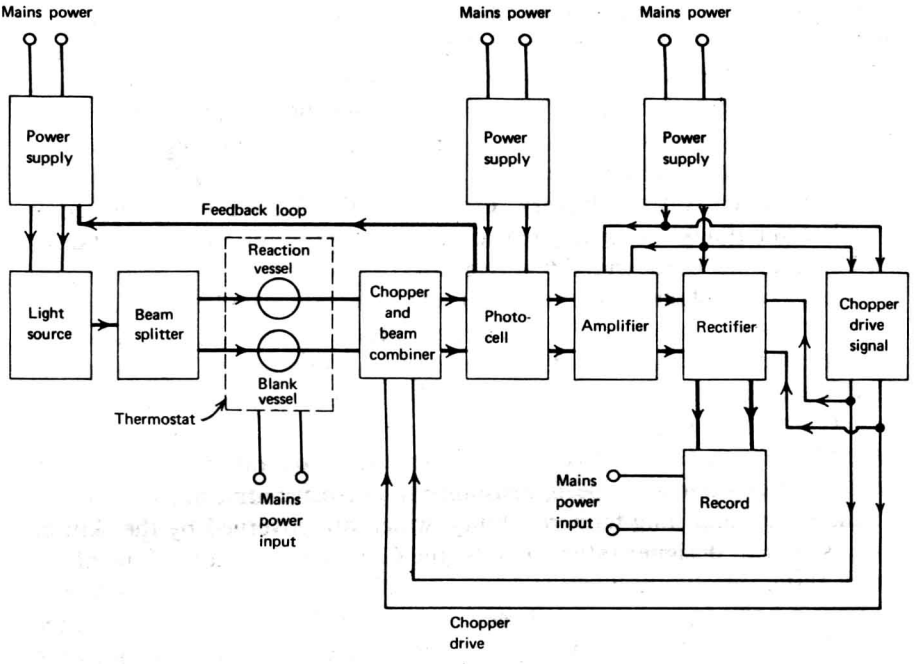

Fig. 1.6 Complete block diagram for the apparatus begun in Fig. 1.4. Main signal paths indicated by heavy lines.

to control the amount of power supplied to the light source in such a way that an increase in intensity would result in a decrease in power and vice versa. The negative feedback would then have the effect of holding the comparison signal at a constant value. The same principle is involved in the operation of the thermostat and in any other automatic control system. A block diagram that includes all of the features mentioned so far is shown in Fig. 1.6.

Specifications and Economics

Once a decision has been made to acquire a new piece of equipment, one of the first questions to follow is whether to build it or whether to buy a commercial instrument. In general it is better to buy a commercial instrument if one can be found to meet the desired specifications. Indeed, with instruments that are in large-volume production the commercial instrument is likely to be less expensive than anything an individual could build to give the same performance, particularly if he includes the value of his time in the calculation. Factors in favor of building rather than buying include the lack of a commercial machine that could give the required performance at a

reasonable price, the possibility that the development of a new instrument would itself constitute a worthwhile advance, the ready availability of components from which the instrument could be assembled, the availability of good workshop facilities and technical assistance, and the possibility of actually saving time by beginning to build immediately rather than going through the sequence of obtaining price quotations, placing the order, waiting through the manufacturer's delivery time, and finally obtaining delivery from a distant factory. Obviously, the answer to the question whether to build or buy in any particular case depends on the circumstances and inclinations of the individual scientist.

When a piece of scientific equipment is to be bought, whether as a complete entity or as a component for something larger, the problem of obtaining the optimum combination of performance and price must be considered. The basic performance characteristics that need to be specified and will largely govern the price to be paid are precision, stability, and accuracy. Other factors, such as compactness, convenience of operation, compatibility with other components, speed, resistance to corrosive atmospheres, ease of maintenance, and long-term reliability, which are governed by the skill of the instrument designer rather than by the fundamental nature of the measuring system itself, are likely to have less effect on the price and will thus provide a basis for choosing between competitive instruments. Of the three main factors precision is a measure of the range of values within which the result of a single measurement can be located, stability (or reproducibility) is a measure of the range over which the result of successive measurements can be expected to wander because of changes within the instrument itself, and accuracy is a measure of the range of values about the true value which is likely to be found when successive measurements are made with different instruments of the same type. Ideally these three quantities should be of similar magnitude, since there is nothing to be gained by having one or two of the ranges specified within very narrow limits if one of the other ranges is relatively large. To give a simple example of such an unbalanced specification, it means very little in practice that the output of a mains-operated power supply, relative to an internal voltage standard, is stable to 0.001% with respect to line-voltage fluctuations, if the standard reference voltage has a temperature coefficient of 0.01% per degree. Again, if an instrument is to serve as a component of a larger apparatus, then there is usually no point in specifying characteristics that are appropriate to a level of precision of the order of, say, 0.01%, if some other factor limits the overall accuracy to $\pm 1\%$. In other words, for optimum performance and price the components of a large apparatus should all be of similar precision, stability, and accuracy. Exceptions to this rule occur when a component is needed for a number of projects in addition to the one immediately at hand or when, as with a