TECHNIQUES OF CHEMISTRY

VOLUME I

PHYSICAL METHODS OF CHEMISTRY

Edited by

ARNOLD WEISSBERGER
AND
BRYANT W. ROSSITER

PART IB

Automatic Recording and Control, Computers in Chemical Research

TECHNIQUES OF CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

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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

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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
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Second Edition

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Part II. Laboratory Engineering
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Volume IV: Distillation
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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.

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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

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AUTOMOTIVE RECORDING AND CONTROL, COMPUTERS IN CHEMICAL RESEARCH

Chapter **VI**

DETECTION (TRANSDUCERS)

Leon F. Phillips

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1 THE NATURE OF THE DETECTION PROCESS

Electrical Detection

The term detection has two fundamentally different meanings in relation to the components of scientific instruments. In the commoner sense detection is simply the process of observing a change in some physical property of a system and converting this change into an electrical signal. The device that responds to the change in the physical property by producing an electrical signal is called a transducer, and most of this chapter is, in fact, concerned with the nature and characteristics of transducers for measuring changes in different physical properties. In a more technical and strictly electronic sense detection is the process of extracting the information that is present in a modulated ac signal and expressing this information as a dc analog signal. It is not uncommon for both forms of detection to occur in the same instrument, for whenever a transducer is used to respond to a chopped signal—a chopped light beam, for example—it is necessary at some stage to convert the resulting ac signal back to dc. Detection in the electrical sense is seen to be essentially the same as rectification but with the difference that a rectifier is designed with a view to obtaining the most efficient conversion of ac power to dc, whereas a detector is more likely to be designed with the emphasis on linearity and fidelity, that is, faithful conversion of the information content of the signal from ac to dc.

In many applications of electrical detection it is sufficient to employ a simple diode detector, as in Fig. 6.1*a*, with a capacitor filter to provide peak-rectifier action. In the old-fashioned crystal radio the combination of "cat's whisker" and germanium crystal formed a point-contact diode that served to rectify the rf signal received from the antenna; essentially the same system is now used in most microwave spectrometers. More recently it has been common for radio receivers to incorporate a grid-leak (or "leaky-grid") detector for the same purpose. This form of detector, illustrated

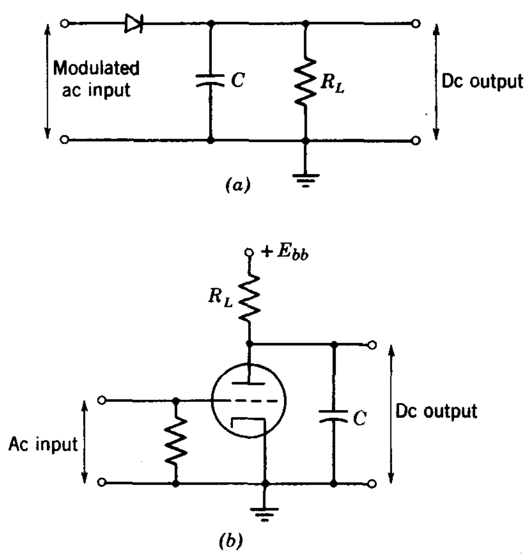

Fig. 6.1 Simple detector circuits: (*a*) diode detector; (*b*) grid-leak detector.

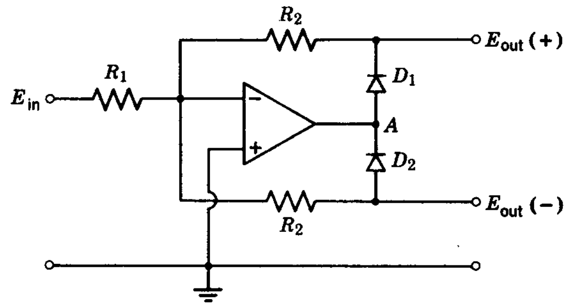

Fig. 6.2 Ultralinear rectifier based on an operational amplifier.

in Fig. 6.1*b*, uses a vacuum tube with the grid biased at the same potential as the cathode so that only the negative-going part of the input signal is amplified by the tube. When the grid attempts to swing positive with respect to the cathode, the grid-cathode diode is forward-biased, grid current flows, and the positive-going part of the input signal is lost.

The nonlinearity of the rectifying elements in the circuits of Fig. 6.1 would be tolerable in many scientific instruments. Extremely linear rectifier action for critical applications is provided by the operational amplifier circuit of Fig. 6.2. This circuit is basically an inverting amplifier in which the voltage gain measured at point A is always $(R_2 + r)/R_1$, where r is the forward resistance of one of the diodes. If the input signal is positive, the output signal is negative, diode D_1 is reverse-biased, and the gain at A is fixed by the feedback loop containing D_2. When the input signal is negative, D_2 is reverse-biased and the gain at A is then fixed by the feedback loop containing D_1. With a positive input signal the diode D_2 is forward-biased and a fraction $R_2/(R_2 + r)$ of the signal at A appears at the negative output terminal, the over-all gain between the input and this terminal therefore being just $-R_2/R_1$, which is independent of r. At the same time the diode D_1 is reverse-biased, its reverse resistance being R, and a fraction $R_2/(R_2 + R)$ of the negative output signal appears at the positive output terminal; the over-all gain between the input and this terminal is $-R_2(R_2 + r)/R_1(R_2 + R)$. Suppose D_1 and D_2 are both type 1N456 general-purpose silicon diodes, with $R > 1000$ M at room temperature and $r < 25\ \Omega$ (at a forward voltage > 0.7 V); let us set $R_1 = 10$ K and $R_2 = 100$ K. Then, with a positive input signal, the voltage gain at the negative output terminal is -10.0 and the maximum voltage gain between the input and the positive output terminal is -1×10^{-3}. With a negative input signal these figures would be reversed, the positive output terminal having the gain of -10.0.

For linearity at high frequencies it would be preferable to set $R_1 = R_2 =$ 10 K, thereby optimizing the loop gain. We may note that the nonlinearity of the diode forward resistance r and, in particular, the requirement of a forward voltage drop before any current will flow, have almost no effect on the output of this circuit. Suppose that the open-loop voltage gain of the amplifier at the signal frequency is 10^4; it can be seen that an input error signal of 50 μV will be sufficient to provide a forward voltage of 0.5 V across one of the diodes at the output of the amplifier. To ensure stability of the circuit at high frequencies it is possible to insert small capacitors in parallel with the resistors R_2, but this will not usually be necessary because the same purpose is served by any smoothing capacitors introduced between the output terminals and ground.

It often happens that the most interesting measurements to be made with a scientific instrument are those that are near the limits of detection and therefore most affected by noise. In Chapter IV we noted that the signal-to-noise ratio in an ac signal can be improved by decreasing the bandwidth of the signal-handling system, and that with very small signals it is helpful to add some of the chopping waveform to the input to ensure that the phase of the signal passed by the narrow-band system is governed by the phase of the input signal rather than by the phase of any random noise that may be present. A further improvement in the final signal-to-noise ratio can usually be obtained by employing a *phase-sensitive detector* to convert the ac signal back to direct current.

A simple form of phase-sensitive detector circuit is shown in Fig. 6.3. A phase-sensitive detector is basically a switch operated in time with the chopper of the input signal. In Fig. 6.3 the FET has a drain-source resistance that is at most 60 Ω when the gate signal is at 0 V and at least 10^{10} Ω (at room temperature) when the gate is at −4 V. Therefore, when the gate is at 0 V (i.e., the switch is closed), the input signal is attenuated by a factor of 10^3, whereas with the gate at −4 V the input signal appears almost unchanged at the output. Since the input and the gate signal in this example

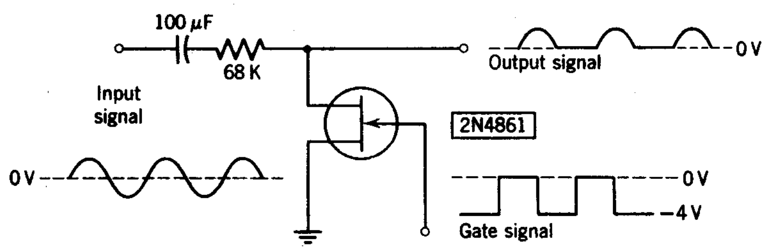

Fig. 6.3 Basic phase-sensitive detector using an FET.

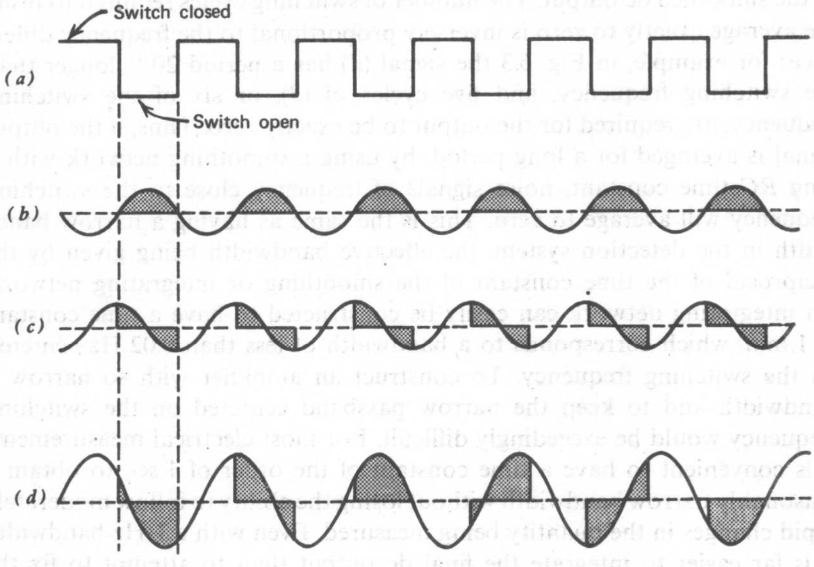

Fig. 6.4 Waveforms in a phase-sensitive detector: (*a*) switching waveform; (*b*) signal of correct frequency and phase; (*c*) signal 90° out of phase; (*d*) signal of wrong frequency.

are 180° out of phase, it follows that only the positive-going portion of the input waveform appears in the output. To see how the use of a phase-sensitive detector can improve the signal-to-noise ratio we consider the waveforms of Fig. 6.4. The switching waveform is shown at (*a*), and a waveform for an input signal exactly in phase with the switching waveform is shown at (*b*). The portion of the input signal that appears in the output is shaded. In practice the output of the detector would be taken to a smoothing, that is, integrating, network and the result would be a positive dc signal. If the relative phase of the switching waveform and the input signal were gradually varied from zero, some of the negative-going portion of the input would begin to appear at the output, and the size of the positive dc output after smoothing would gradually decrease. With a 90° phase difference between the input and the switching waveform, as in (*c*), the smoothed output would be zero, while with a 180° phase difference a maximum negative dc signal would be obtained. Since noise signals are of random phase, it follows that signals due to noise of exactly the same frequency as the input must give a zero contribution to the integrated dc output, provided only that a reasonably long averaging period is used. A signal of different frequency from the switching waveform, as shown at (*d*), also gives a zero average contribution to the smoothed dc output. The number of switching cycles required to bring the average exactly to zero is inversely proportional to the frequency difference; for example, in Fig. 6.3 the signal (*d*) has a period 20% longer than the switching frequency, and five cycles of (*d*), or six of the switching frequency, are required for the output to be exactly zero. Thus, if the output signal is averaged for a long period, by using a smoothing network with a long *RC* time constant, noise signals of frequency close to the switching frequency will average to zero. This is the same as having a narrow bandwidth in the detection system, the effective bandwidth being given by the reciprocal of the time constant of the smoothing or integrating network. An integrating network can easily be constructed to have a time constant of 1 min, which corresponds to a bandwidth of less than 0.02 Hz centered on the switching frequency. To construct an amplifier with so narrow a bandwidth and to keep the narrow passband centered on the switching frequency would be exceedingly difficult. For most electrical measurements it is convenient to have a time constant of the order of 1 sec to obtain a reasonably narrow bandwidth without losing the ability to follow moderately rapid changes in the quantity being measured. Even with a 1-Hz bandwidth it is far easier to integrate the final dc output than to attempt to fix the position of the passband of a sharply tuned amplifier.

Almost any electrical switching device can be used as the basis of a phase-sensitive detector; for example, one of the transistor choppers of Fig. 4.60, an electromagnetic relay, a ring modulator (Fig. 4.77), or a tube with more than one control grid. An interesting development of the method* is shown in principle in the block diagram of Fig. 6.5. At very low light levels a photomultiplier tube is capable of giving an output in the form of discrete pulses, each pulse in excess of the random pulses due to dark current being the result of the arrival of a single photon at the photocathode. In Fig. 6.5 the light beam is chopped at a low frequency (typically 1.0 Hz) and the output pulses are taken to a reversible decade scaler, or "up-down" counter. During the time that the beam is interrupted the pulses are fed into the negative input of the counter so that they subtract from the total count, and then while the beam is not interrupted the pulses are fed into the positive input where they add to the total count. The accumulated count therefore contains a contribution from pulses due to photons, which averages to a finite value, and a contribution from pulses due to the dark current of the multiplier, which averages to zero. The effective bandwidth of the system is the reciprocal of the time in seconds during which counts are accumulated.

In its more usual sense, the term detection covers a large variety of physical operations, with a similarly wide range of associated problems. An extreme

* E. D. Morris, Jr., and H. S. Johnston, *Review of Scientific Instruments*, **39**, 620 (1968).

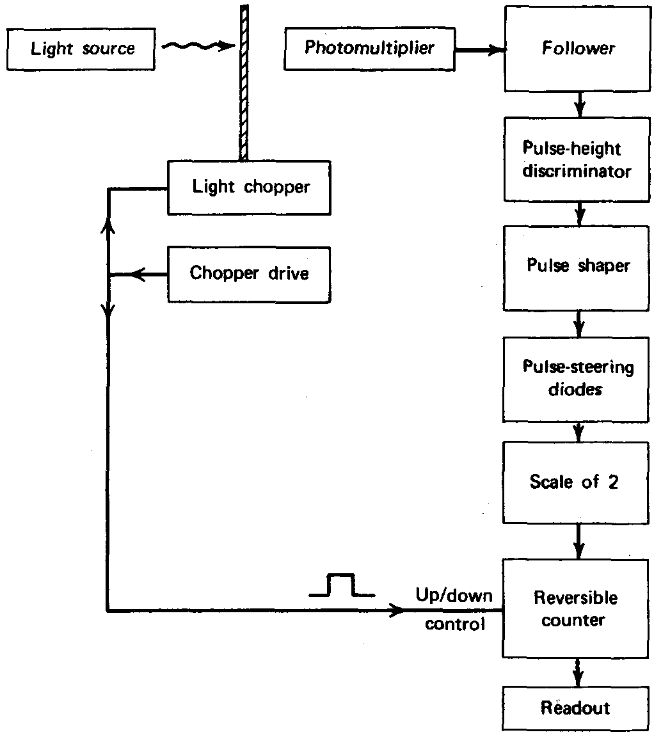

Fig. 6.5 Block diagram of a digital phase-sensitive detection system for handling pulses from a photomultiplier. The circuit described in the reference (footnote 1) includes a second counter for measuring the signal that is 90° out of phase with the chopper-drive waveform and an analog-digital converter for use when the photocurrent is too large to be treated as a series of discrete pulses.

example would be the estimation of 1 part in 10^9 of a hydrocarbon in a stream of argon or the detection of 10^{-11} W of infrared radiation from an exothermic reaction. Obviously not all of the methods of detection that are used in scientific instruments can be discussed here because of space limitations, but many are described in other chapters and volumes in this series. We shall therefore be content to describe and consider the limitations of several of the more important kinds of transducer under the headings (*a*) detectors of electromagnetic radiation, (*b*) nuclear detectors, (*c*) pressure, composition, and field transducers. The devices considered here are almost all input transducers; output transducers, including meters, oscilloscopes, and recorders, are discussed in Chapters III and VII.

2 DETECTORS OF ELECTROMAGNETIC RADIATION

Radiofrequency and Microwave Detectors

The primary element of a detection system for radiofrequency or microwave radiation in free space is the *antenna*, which can be defined as a network that serves to transfer energy from circuits to space or vice-versa. In chemical instrumentation it is most often necessary to detect energy due to microwave radiation within a waveguide or a resonant cavity rather than in free space; we shall return to this point shortly. The effectiveness of energy transfer between an antenna and the adjacent circuitry is governed by the input and output impedances in the usual way; the effectiveness of transfer between an antenna and space, on the other hand, is governed by more complex factors, which include the polarization of the radiation and the antenna gain. For a radiating or receiving antenna the gain is the ratio of the measured radiative intensity in a particular direction to the intensity that would be observed if the radiation were distributed equally in all directions. The gain of an antenna is governed mainly by its size, an antenna that is large in comparison with the wavelength of the radiation normally having a high gain. An extreme example of a large, high-gain antenna is provided by the 1000-ft-diameter radio telescope at Arecibo in Puerto Rico. Two elementary forms of antenna, the monopole over ground, and the dipole, are shown in Fig. 6.6, and a group of high-gain antennas, including the familiar Yagi television antenna, are shown in Fig. 6.7. The first element of a receiver circuit is invariably a tuned *LC* network, the tuning being adjusted to select signals of a particular frequency from the complex sea of radiation that washes against the antenna. A degree of selectivity may also be provided by the polarization of the antenna; for example, AM radio

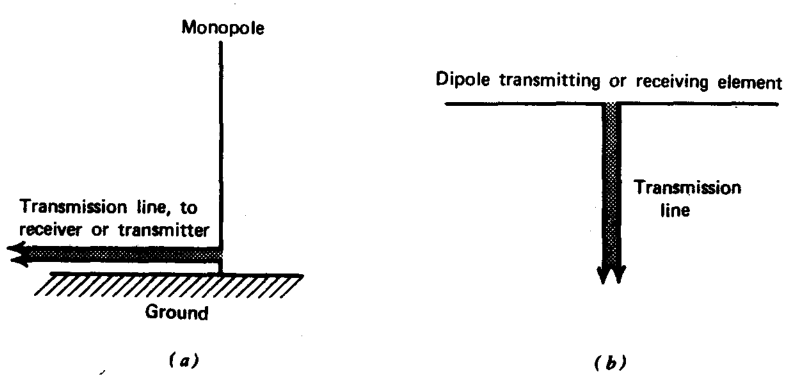

Fig. 6.6 Elementary forms of antenna for radiofrequency radiation: (*a*) monopole over ground; (*b*) dipole.