27. B. J. Stallwood, *J. Opt. Soc. Am.* **44**, 171 (1954).
28. A. J. Mitteldorf, *The Spex Speaker* (Spex Industries, Inc.) **2**, No. 3 (1957).
29. D. C. Spindler, *Appl. Spectroscopy* **15**, 20 (1961).
30. L. H. Ahrens, *Spectrochemical Analysis* (Addison-Wesley, Cambridge, Mass., 1950).
31. C. Feldman, *Anal. Chem.* **21**, 1041 (1949).
32. ——— and M. K. Wittels, *Spectrochim. Acta* **9**, 19 (1957).
33. R. L. Mitchell and R. O. Scott, *Appl. Spectroscopy* **11**, 6 (1957); R. L. Mitchell, *Soil Sci.* **83**, 1 (1957).
34. *Spectrographer's News Letter* **2**, No. 9 (1948).
35. A. Paolini, Jr., and R. M. Kennedy, *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy* (1961).
36. C. A. Waggoner, "Some factors influencing excitation in spectrochemical solution analysis," *Pacific Naval Lab. Esquimalt, B.C., Tech. Mem. No. 58-8* (1958).
37. L. C. Flickinger, E. W. Polley, F. A. Galletta, *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy* (1958).
38. T. H. Zink, *Appl. Spectroscopy* **13**, 94 (1959).
39. M. Fred, N. H. Nachtrieb, F. S. Tomkins, *J. Opt. Soc. Am.* **37**, 279 (1947).
40. E. E. Pickett and B. E. Hankins, *Proc. Am. Assoc. Spectrographers, Chicago* (1953).
41. J. M. Morris and F. X. Pink, in "Spectrochemical analysis for trace elements," *ASTM Spec. Tech. Publ. No. 221* (1957), pp. 39–46.
42. C. L. Grant and W. J Hanna, *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy* (1960); C. L. Grant and W. J. Hanna, *Proc. Annual Meeting Assoc. Offic. Agr. Chemists, Washington* (1960); C. L. Grant, *Proc. Soc. Appl. Spectroscopy* (1961); C. L. Grant, *Anal. Chem.* **33**, 401 (1961).
43. J. T. Rozsa and L. E. Zeeb, *Petrol. Processing* **8**, 1708 (1953).
44. W. K. Baer and E. S. Hodge, *Appl. Spectroscopy* **14**, 141 (1960).
45. J. H. Muntz and S. W. Melsted, *Anal. Chem.* **27**, 751 (1955).
46. V. A. Bardocz, *Appl. Spectroscopy* **11**, 167 (1957).
47. C. Feldman, in *Trans. Florida Seminars on Spectroscopy, 1955–1957* (1958), vol. 12, No. 11, pp. 24–35.
48. C. J. Braudo, J. D. Craggs, G. C. Williams, *Spectrochim. Acta* **3**, 546 (1949).
49. S. Mandelstam, *ibid.* **15**, 255 (1959).
50. R. A. Sawyer, *Experimental Spectroscopy* (Prentice-Hall, New York, 1944).
51. R. F. Jarrell, in *The Encyclopedia of Spectroscopy*, G. L. Clark, Ed. (Reinhold, New York, 1960), pp. 243–263.
52. A. J. Mitteldorf, *ibid.*, pp. 308–316.
53. A. L. Kenworthy, in *Proc. Am. Soc. Hort. Sci.* **55**, 41 (1950).
54. G. R. Bradford and R. B. Harding, *ibid.* **70**, 252 (1957).
55. E. E. Pickett and R. H. Dinius, "Trace elements in Missouri soils," *Missouri Agr. Expt. Sta. Research Bull. No. 553* (1954), pp. 1-20; E. E. Pickett, "Mineral composition of Missouri feeds and forages: *Lespedeza*," *ibid.*, *No. 594* (1955), pp. 1-24.
56. H. Hopkins and J. Eisen, *Agr. and Food Chem.* **7**, 633 (1959).
57. *Metal-Binding in Medicine*, M. J. Seven and L. A. Johnson, Eds. (Lippincott, Philadelphia, 1960).
58. H. M. Perry, Jr., and E. F. Perry, *J. Clin. Invest.* **38**, 1452 (1959).

INSTRUMENTS AND TECHNIQUES

New Method for Heart Studies

Continuous electrocardiography of active subjects over long periods is now practical.

Norman J. Holter

Electrocardiography today is an indispensable tool for physiologist and physician. Cardiac electrophysiology began in 1887 when Ludwig and Waller first noted changing chest potentials, and practical electrocardiography began in 1893 with Einthoven's string galvanometer work. Then followed the body of classic work in this field, but the electrocardiograph did not find wide use until the advent of modern direct-writing instruments. Today's clinical instrument is convenient and dependable and will remain an important tool in research and in examinations of established heart conditions. It is still only a hit-or-miss affair for studying long-period heart action or detecting transient heart aberrations.

Until recently, electrocardiography required connecting leads from subject to instrument. This was no handicap in building present-day principles but has been a handicap in studying active subjects. Leads can be detached during exercise and reconnected later, and with special electrodes some exercise is feasible during recording. However, considerably more physical freedom is desirable if one is to learn more about the heart under realistic conditions of daily life.

This article reports a series of concepts and developments concerned with obtaining long-period continuous electrocardiographic records from active subjects in order to obtain data which constitute a statistically valid sample of heart action under conditions that give the subject the greatest possible freedom of activity. This goal automatically generates the problem of handling, in a convenient and practical way, the very voluminous data acquired. No one can adequately examine 100,000 continuous ordinary electrocardiograms (24-hour recording at a pulse rate of 70). A number of early ideas have led to the concept of breaking away from the limitations of orthodox electrocardiography to solve the scientific problem of adequate sampling and the medical problem of obtaining electrocardiograms in situations other than the highly artificial and unrealistic situation of resting quietly on a comfortable pad after a good sleep, with no breakfast, and with calm confidence in one's physician.

In 1939 J. A. Gengerelli and I became interested in remote stimulation of physiological systems as means for minimizing interference with the system. By modifying a classic experiment, we produced contractions of frog muscle by stimulating its nerve supply by means of a changing electric field without electrodes or connecting wires (*1*). This raised the converse question of whether an external field is created by a nerve impulse. From these two basic and converse ideas developed a series of studies leading, on the one hand, to the remote stimulation of the brain of the intact animal and a study of corresponding behavior (*2*, *3*) and, on the other hand, to the use of radio for the accurate transmission of electroencephalograms and electrocardiograms from freely exercising subjects (*4*, *5*). With the electronics of 1942, a nerve impulse field was not detected (*2*), but recently we obtained evidence for the existence of such a field (*6*). Radioelectrocardiography as a practical and convenient technique is now becoming relatively routine; its first clinical application was by MacInnis in 1954 (*7*).

Steps toward Freedom

Up to this point there has been developed only what I would call an initial step toward freedom—the elimination of entangling wires. Moreover, while telemetering per se does provide greater freedom of action, it does not provide practical long-period continuous electrocardiography. It also requires an in-

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dividual to remain within range of radio receiving and electrocardiographic observing equipment and has the disadvantage of being subject to occasional radio interference. W. R. Glasscock and I therefore developed a portable radio-receiver tape-recording unit, to be carried by a subject free to go where he wished as long as he took the "ECG brief case" and left it in his general environment (*8*). Still needed, however, was freedom from such baggage and from radio interference, plus means of rapidly studying the long magnetic tapes obtained. We therefore developed the "electrocardiocorder," which eliminates radio circuits at both ends and, when used with rapid-analysis instruments developed for the purpose, achieves what I call full freedom (*9*). This means freedom from connecting wires, freedom from the restriction of staying in one locality, freedom from the inconvenience of carrying electronic baggage, and freedom to make records of any desired length and still be able to analyze them. Thus the sequence of concepts progressed from remote stimulation of nerves to the hardly anticipated stage of our next efforts—the study of the heart action of swimmers, forest fire fighters, bronco riders, and so on.

Fig. 1. (Top) Laboratory radioelectrocardiograph system; (bottom) portable version in use.

Beginning steps are illustrated in Fig. 1 (top), which shows our current radioelectrocardiograph system; the "electrocardiocaster" is held in the hand, and the radioelectrocardiograph receiver, demodulator, oscilloscope, and clinical electrocardiograph are at the right—a useful system when we need to make observations at the exact moment of the heart beat. The lower part of Fig. 1 shows our ECG brief case in use; a subject is eating in a restaurant while an electrocardiocaster in his upper coat pocket sends data to the unit on the small table by the wall. This system is also one step toward truly long-period continuous electrocardiography, because magnetic tape storage in the unit replaces spot observation on an oscilloscope or on electrocardiograph paper. I define "long-period" as longer than a half hour, the usual limit for one roll of ordinary electrocardiograph paper.

The electrocardiocorder is shown in Fig. 2. It is a small portable unit containing voltage amplifier, power amplifier, oscillator, mixer, temperature compensator, recording heads, motor control, drive mechanism, batteries, tape and reels, case, switches, and connectors. It is oval, measures 19.5 by 9.8 by 4.6 centimeters, weighs 1 kilogram, and is conveniently carried in a man's coat pocket or a woman's strap-type handbag, or is fastened to the chest during unusual physical activity. The power supply is adequate for 80 to 100 hours of operation, and the tape capacity is 10 hours; after 10 hours the tape is changed for longer tests. Our latest model just completed 1000 hours of total operation without failure. The woman shown in Fig. 3 is walking uphill after working 8 hours. The tape, of 10-hour capacity, provides a continuous record of all heartbeats from 1 hour before to 1 hour after her workday. Chest leads, approximately V_4 leads, are used.

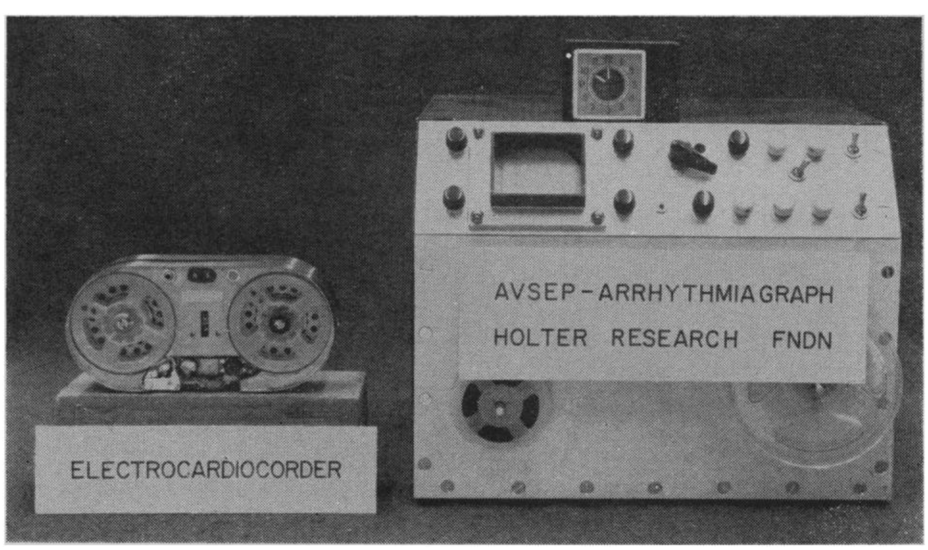


Fig. 2. The recorder-analyzer system for long-period continuous electrocardiography of active subjects and rapid analysis of the resulting voluminous data.

AVSEP-Arrhythmiagraph Analyzer

Long records are useless without means of rapidly locating parts of interest; this is accomplished by the analysis part of the system. Changes in form are detected by "AVSEP" (an abbreviation for "audio visual superimposed electrocardiogram presentation"); the arrhythmia detector is described later. A crude model of the analyzer described in 1957 (*5*), was a floor-rack assembly, but the model shown in Fig. 2 is as portable as an ordinary electrocardiograph. In operation, electrocardiocorder tapes move at relatively high speed and present the signals on an oscilloscope, each electrocardiogram being rapidly superimposed upon its predecessor. Electrocardiograms which are continuous duplicates of each other thus appear as a single, relatively steady electrocardiogram, as shown in Fig. 4 (top). This is a 1-second photograph of the AVSEP screen; during this period, 80 electrocardiograms were displayed. The signals are also presented aurally, as a noisy growl in the low audio region; and the ear notes any change in the nature of this noise, thus adding to the over-all sensitivity of the method. If only one electrocardiogram differs significantly, the change will be seen and heard. During complicated heart attacks the "single" dynamic electrocardiogram pattern of AVSEP appears much like a snake writhing about, showing details of the attack and of its approach and termination.

The tape, run at 60 times the recording speed of 7½ inches per minute, provides two signals from the recording heads, which are mechanically displaced so that AVSEP will begin with the *P* wave rather than the *R* wave used to trigger the sweep. One signal goes through an amplifier stage, through an integrator (to correct reproducing-head distortion), through another amplifier, and to the AVSEP speaker and oscilloscope. The alternate signal goes through an amplifier stage, a clipper-filter stage, and a delay-trigger stage, becoming a sawtooth signal for the horizontal AVSEP sweep; it goes also to a separate oscilloscope (Fig. 5, bottom) to form the arrhythmiagram. A 10-hour record can be examined in 10 minutes; a synchronized clock tells the observer the time of day for any part of the tape, so changes can be correlated with activity. Myographic potentials, when present, rarely interfere because the AVSEP pattern is regular and the unwanted signals are purely random.

Fig. 3. The electrocardiocorder in use, carried in a handbag. The chest leads run down the strap.

The arrhythmiagraph part of the analysis unit presents rapid, quantitative, compact information on pulse irregularities, whereas AVSEP is used to observe changes of form. (Changes in pulse time, the *R-R* interval, are seen on AVSEP only as a rapidly changing tail on the electrocardiogram.) The arrhythmiagraph idea (*10*), which may or may not be new with us, is illustrated schematically in Fig. 6 (top). The diagram shows the conversion of each *R-R* interval to a vertical line whose length is proportional to pulse time; compression of the pattern into a small space; and the resulting prominence of two arrhythmias. (Actually, a premature beat results in a short vertical line, and it is the long line, representing the compensatory pause, that stands out most prominently.) In a test on a certain very long ordinary paper record, 2 hours of a technician's time were required to establish with confidence the existence of 16 premature systoles, whereas the same quantitative result was obtained from the corresponding arrhythmiagram in 6 seconds. Typical arrhythmiagrams are also shown in Fig. 6 (middle and bottom). Premature systoles may be seen; the bottom record is from a subject with an extremely heavy work load, mental and physical fatigue, and inadequate sleep, who had drunk a considerable amount of coffee.

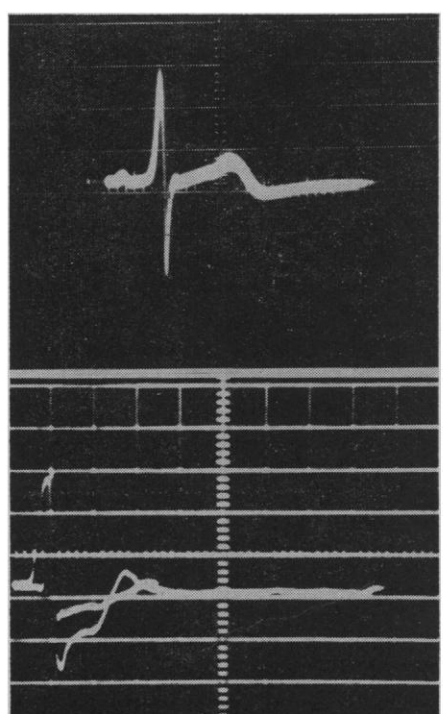


Fig. 4. (Top) Normal AVSEP pattern; (bottom) pattern of a bigeminy attack.

Electrodes

There have been occasional innovations in the design of electrodes for orthodox electrocardiography—innovations in shape, size, and material and in holding devices (elastic straps, suction cups, and so on)—but little attention heretofore has been paid to problems that arise with use over long periods. Such problems are changes in impedance, patient comfort, dermatitis, effects

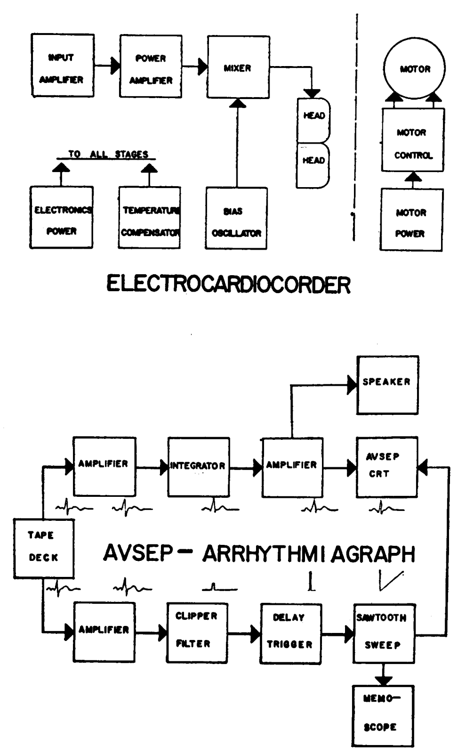


Fig. 5. Block diagram of the recorder-analyzer system.

of moving wires, and so on. With the advent of long-period continuous electrocardiography, various modifications of the usual methods can be introduced, although more work remains to be done. I do not intend to give a comprehensive review, but interested readers can check some references (*11*) and, with a little experience, can readily select something suitable for a particular purpose. Relatively simple methods will suffice in some cases—for example, flat electrodes with the usual paste, held on the chest by small balls of cotton and strips of paper masking tape. An Ace bandage around the chest provides added support. More elaborate methods are needed for recording periods of several hours to several days; it is my present opinion that the best long-period electrodes will be some form of the so-called fluid-type assembly, with electrodes supported some distance from the skin in a manner to seal a suitable electrolyte between electrode and skin. Glasscock proposes carbon electrodes in such assemblies; his preliminary tests show minimal artifacts from motion.

Medical Uses of the System

The electrocardiocorder-AVSEP-arrhythmiagraph system may be used both in clinical research and in routine medical practice. A discussion of medical uses of necessity includes research uses, since routine use of the system at this time often uncovers new facts on heart action. Many individuals come to autopsy without having had either symptoms or treatment of what are found to be heart lesions of a type which would have shown on an electrocardiogram. The problem of asymptomatic heart disease is intriguing and important, both clinically and academically (*12*). As stated in the introduction, orthodox electrocardiography will always have its uses in the measurement of established heart conditions, but it does not provide an accurate sampling of all-day heart activity any more than the analysis of a single rock provides an accurate sample of a mountain of ore. Through AVSEP and arrhythmiagraphic analysis of a long electrocardiocorder record, there is a far better chance of finding heart difficulties at an early stage. According to one authority more than half the individuals who have serious arrhythmias are not aware of them (*13*), and some sudden deaths are deaths from arrhythmia that does not result from coronary occlusion. A thorough modern physical examination takes parts of several days of the patient's time, and I suggest that routine recording with a electrocardiocorder for a suitable interval be included, for the possible detection of any subclinical angina, potentially serious arrhythmias, or other transient heart disorders. A large clinic might have a number of electrocordiocorders in use and one analyzer for examining the results. The effects of drugs or other therapy on electrocardiagraphic form and pulse anomalies can be followed quantitatively.

Figure 7 is an electrocardiographic record (of research and clinical interest) of one of our laboratory subjects at the end of a long attack of paroxysmal tachycardia. The heart had started beating at twice the normal rate 8 hours earlier, and the usual medical measures

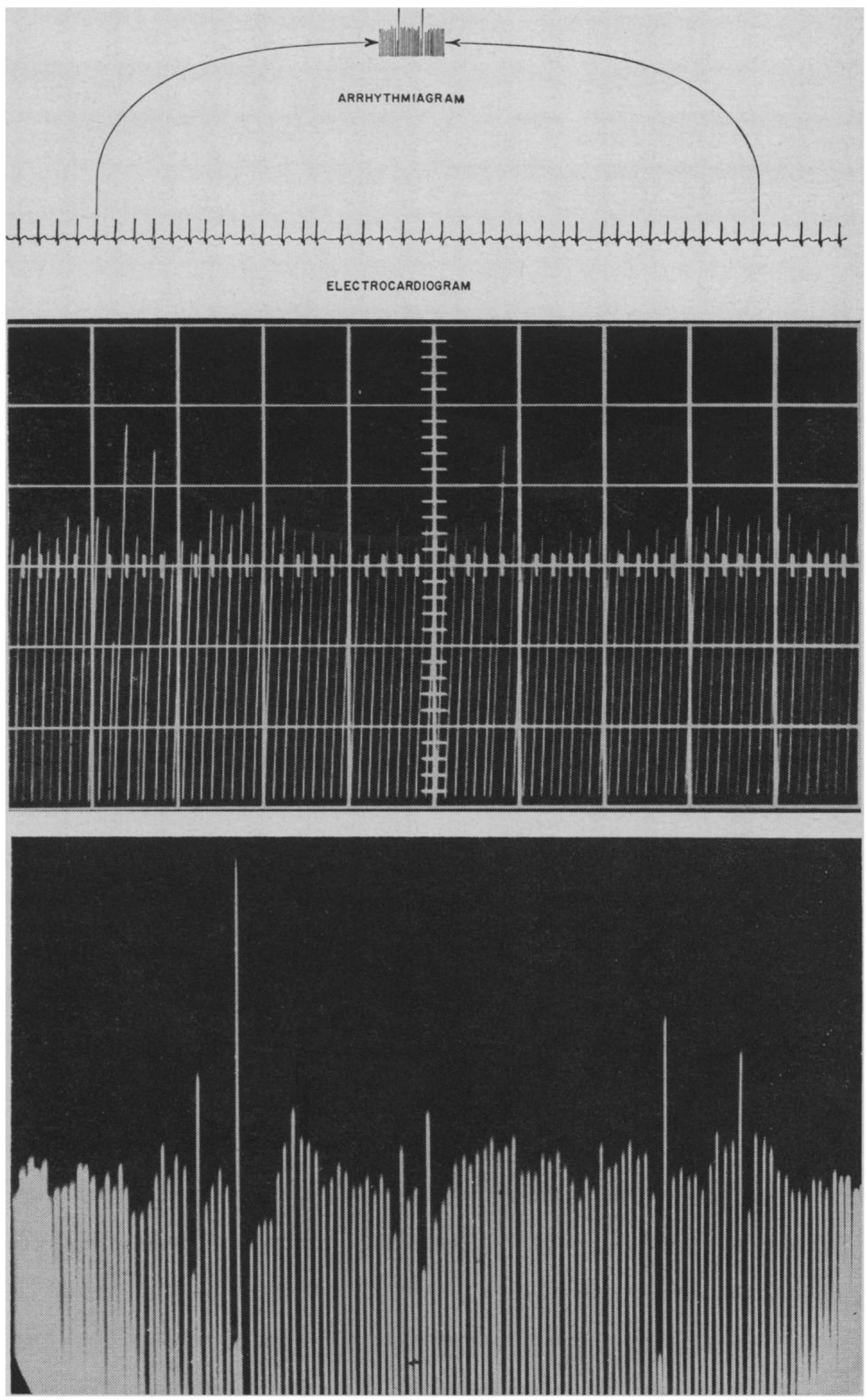
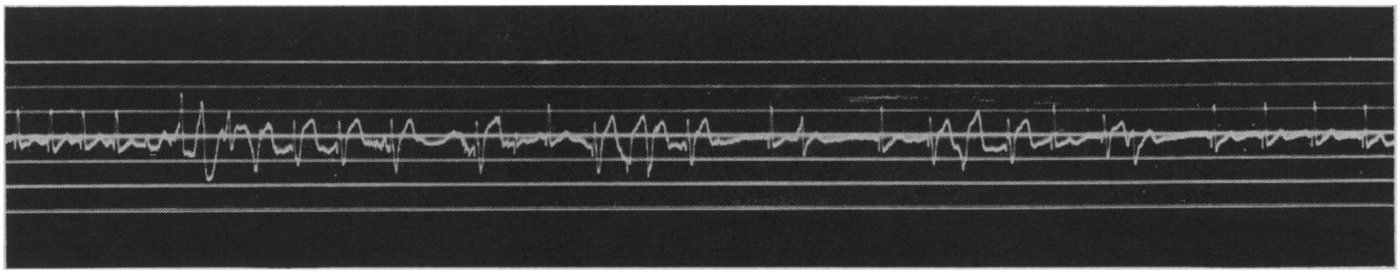
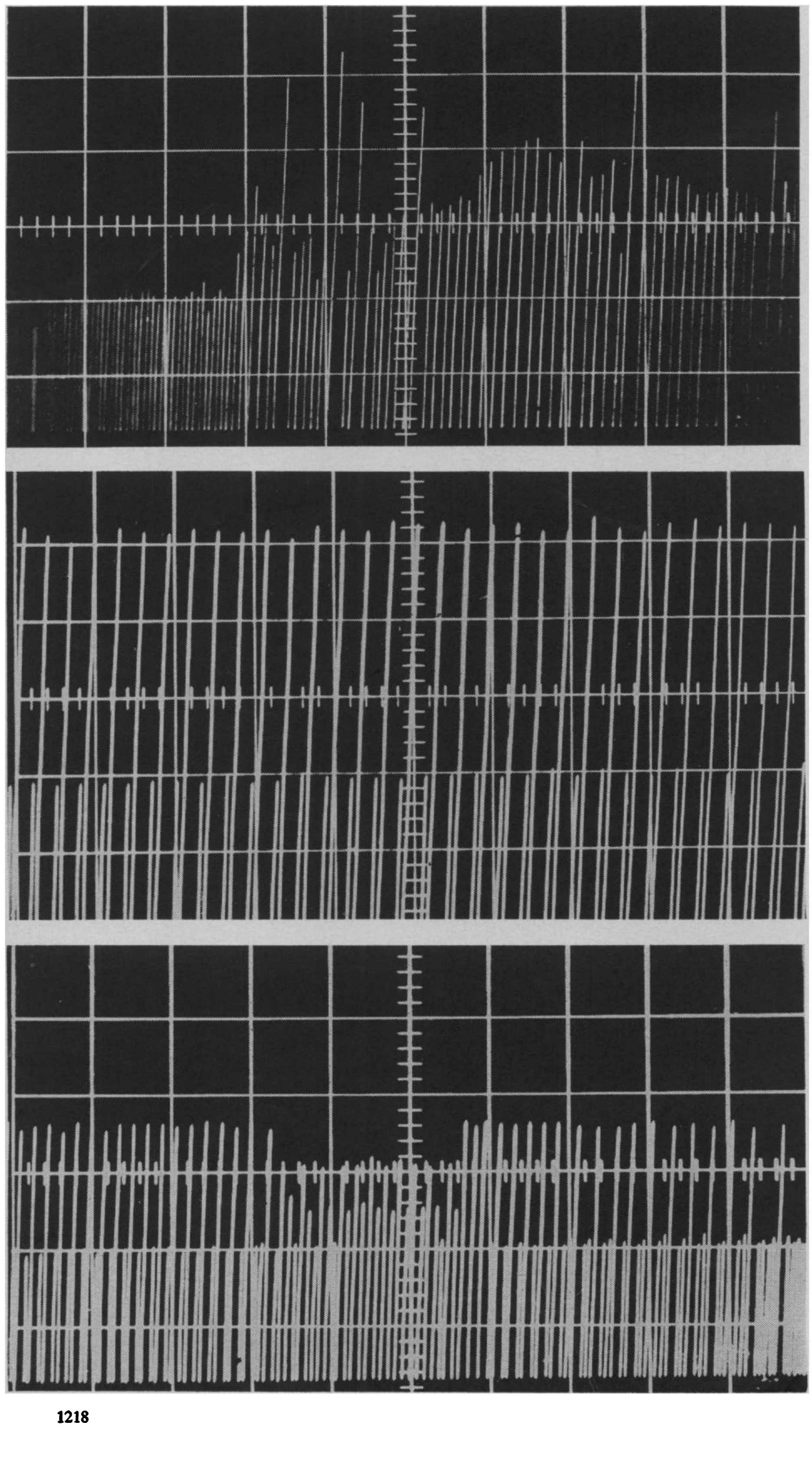


Fig. 6. (Top) Schematic drawing of the arrhythmiagraph; (middle and bottom) typical arrhythmiagrams, showing pulse time variability, including premature systoles.





had not corrected it. The attack later terminated spontaneously, and Fig. 7 shows the complex details of the transition to normal. Figure 8 (top) shows the pulse time details.

I have lent the recorder-analyzer equipment to Dr. John S. Gilson of Great Falls, Montana, who has made records of some 200 clinical cases (*14*). One interesting case is that of a man who, in one occupation, had clinical symptoms of angina pectoris, for which electrocardiographic confirmation could not be obtained. Later, in a different occupation, this individual had no subjective symptoms of angina, but an electrocardiocorder record showed definite anginal changes on AVSEP.

Figure 4 (bottom) reveals a transient attack of bigeminy, a phenomenon in which alternate heart beats differ greatly, both in electrocardiographic form and pulse time. Figure 4 shows two separate electrocardiograms from one heart.

The dynamic nature of the AVSEP pattern is shown in Fig. 9, a series of moving picture frames showing the magnitude of the changes in the AVSEP pattern of a man during an angina attack brought on by lifting heavy boxes in his occupation. On AVSEP this is seen as a single electrocardiogram which begins to "writhe about" as changes occur. Note the great drop in the *S-T* segment of frame No. 7 as compared with frame No. 1. The patient felt pain and took nitroglycerine, and the electrocardiogram returned to what was normal for him. This record enabled Gilson to confirm a questionable diagnosis.

Other arrhythmiagrams of clinical situations are shown in Fig. 8. In the center is the arrhythmiagram of the patient having the bigeminy attack of Fig.

Fig. 7 (above). Detail of an electrocardiogram during termination of paroxysmal tachycardia. Note the high pulse at left and the normal pulse at right. Fig. 8 (left). Arrhythmiagrams of (top) paroxysmal tachycardia at the moment of return to normal and (middle and bottom) of other hearts, showing bigeminy and multiple pulse times.

4. At the bottom, a heart "can't decide" what pulse rate to settle down to; there are several fairly regular pulse times from the same heart. The acoustic effect is interesting in many of these cases; a signal which often sounds like a motor boat suddenly sounds like an entirely different motor boat as anomalies occur.

Two of Gilson's subjects equipped with the unit have been involved in automobile accidents; in each case the patient and equipment survived, but the accident precipitated an angina attack in one subject. One of our subjects, a nervous individual, accidentally violated a traffic law while equipped with the unit and was stopped by the police. The story has an unhappy ending scientifically, for the unit had run out of tape a few minutes earlier. However, this illustrates the kind of real-life situations in which heart studies can be made.

Research Uses

We need to learn more about heartbeat phenomena and the mechanism of production of certain types of electrocardiograms, especially under conditions not measurable by traditional methods. An isolated heart beats very regularly, and all pulse times are equal. Dissected-out parts of suitable hearts beat by themselves at steady rates characteristic of the heart region. However, when the heart is not isolated, outside influences disturb the steadiness seen in the isolated heart. Thus two individuals may each have an average pulse rate of 70 per minute; then why do the two individuals arrive at this average by entirely different routes? Are these variations truly random? What produces them? Is a given variability pattern characteristic of one individual, and does its frequency distribution pattern change and, if so, why? The principle of biological variability is well illustrated when an ounce of alcohol rapidly eliminates a "forest" of premature systoles in the arrhythmiagram of one individual and increases them in another. The quantitative effects of nicotine, caffeine, alcohol, fatigue, tension, and so on, have been easily measured from arrhythmiagrams, hence much new pharmacological research can be conducted with these tools. What I call pulse microstructure needs detailed exploration and statistical analysis, possibly with both our recorder-analysis system and a digital computer. We might profitably use one data-reduction machine to examine the data provided by another data-reduction machine.

In 1957 (*5*) I suggested that significant electrocardiographic changes might occur during the normal active day of a clinically normal individual. We now have good reason to feel that changes of considerable magnitude do occur in normal people, and we propose use of the electrocardiocorder to better understand the correlation of heart activity with eating, exercise, sexual and other emotional activity, fatigue, sleep, and so on.

The recorder-analyzer combination might be adapted for the study of physiological phenomena other than those of the heart. Some physiological tests already provide data which have been "integrated" over a period of time, so that little would be gained by continuous recording. This is illustrated by a single test for sugar in the urine. If such a test is negative, one can say with reasonable assurance that sugar was not produced by the kidney during the several-hour period of filling the bladder. Here one can extrapolate backwards with some safety. On the other hand, the usual electrocardiogram or electroencephalogram is a statistically insignificant sample of what has occurred over a period of several hours. Hence, I suggest that suitable physiological phenomena be recorded at the site of occurrence in such a way as to provide the physical freedom necessary for normal daily activity. The electrocardiocorder can be made into an electroencephalocorder to free a brain-test subject from his radio-receiver environment, and it should be possible to design suitable analyzers.

The Future

When I speak of "full freedom" through the elimination of wires, restricted locations, electronic baggage, and radio interference I mean freedom within the limits of electronic and mechanical performance. Thus, there will always be room for improvement of the equipment, but, basically, "full freedom" means freedom to make long, continuous records of physiological phenomena as close as possible to the geographic site of occurrence. Thus the future—and this development may not be remote, in view of the present increasing interest in medical electronics—will see human beings and other animals of many types "wired for research," with numerous little boxes piling up information about body function. Numerous physiological variables will be recorded in one over-all portable recording system and coded into one record for later study by more sophisticated analyzers than those described here.

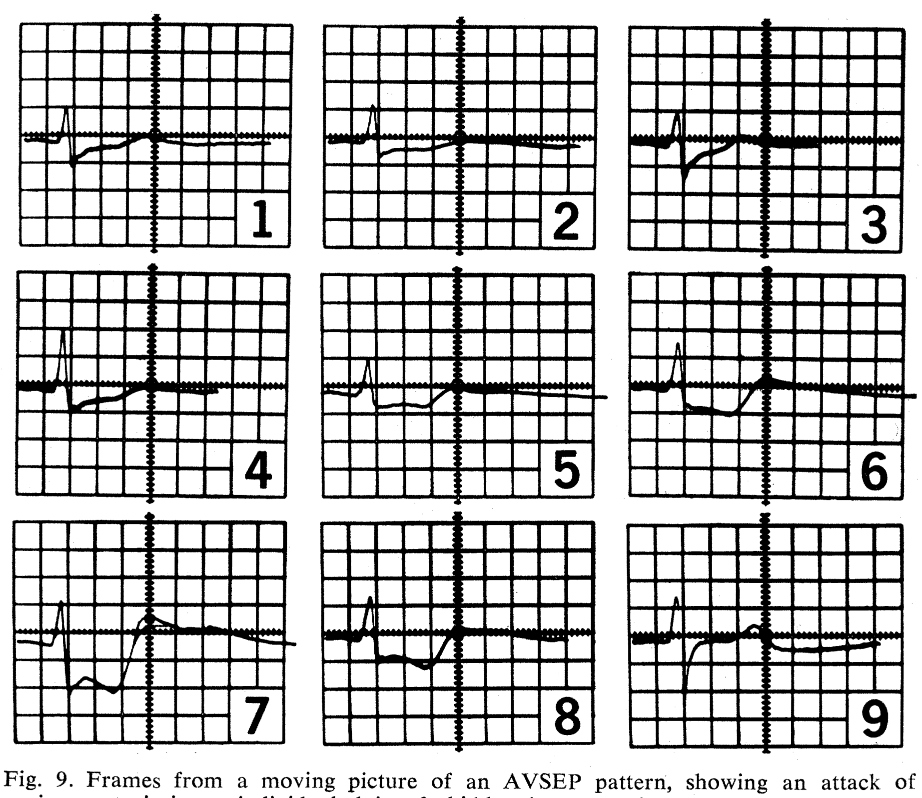


Fig. 9. Frames from a moving picture of an AVSEP pattern, showing an attack of angina pectoris in an individual doing forbidden heavy work.

Summary

I have proposed that orthodox electrocardiography be implemented, both for research and medical purposes, by the use of long-period, continuous recording of heart potentials with a portable, self-contained instrument—the electrocardiocorder together with semiautomatic methods for the rapid analysis of the resulting voluminous data. An electronic system to make this concept practical has been developed in our laboratory and typical results are described in this article.

References and Notes

1. J. A. Gengerelli and N. J. Holter, *Proc. Soc. Exptl. Biol. Med.* **46**, 532 (1941); **49**, 220 (1942).
2. J. A. Gengerelli, *ibid.* **51**, 189 (1942).
3. ———, *ibid.* **52**, 189 (1943); ——— and V. Kallejian, *J. Psychol.* **29**, 263 (195 J. A. Gengerelli, *J. Comp. and Physiol. Psychol.* **44**, 535 (1951 ——— and J. W. Cullen, *ibid.* **47**, 204 (1954).
4. N. J. Holter and J. A. Gengerelli, *Rocky Mt. Med. J.* (Sept. 1949); Proc. AAAS, 117th Annual Meeting, Cleveland (1950); W. R. Glasscock and N. J. Holter, *Electronics* (Aug. 1952).

N. J. Holter, *Ann. N.Y. Acad. Sci.* **65**, 913 (1957).

6. J. A. Gengerelli, N. J. Holter, W. R. Glasscock, *J. Psychol.* **52**, 317 (1961).
7. H. F. MacInnis, *Can. Med. Assoc. J.* **70**, 574 (1954).
8. N. J. Holter, Progr. Rept., Public Health Service research grant No. H-2614(C2) (1959).
9. W. R. Glasscock has made major contributions to the mechanical and electronic design of these instruments. Electronics technician Frank Theobald has given valuable assistance in this study. This work was supported, in part, by Public Health Service grant No. H-2614. The names *Radioelectrocardiograph, Electrocardiocaster, Electrocardiocorder, AVSEP*, and *Arrhythmiagraph* are Holter Research Foundation trademarks.
10. N. J. Holter and W. R. Glasscock, *Proc. Montana Acad. Sci.* **18(1958)**, 35 (1958).
11. R. F. Abarquez *et al.*, *Circulation* **22**, 1060 (1960); C. E. Pruett and J. N. Shellabarger, *Naval Research Revs.* (Feb. 1961); D. A. Rowley *et al.*, *Am. Heart J.* (Aug. 1961); J. S. Gilson and R. B. Griffing, *Am. J. Cardiol.* **8**, 212 (1961).
12. H. A. Lindberg *et al.*, *A.M.A. Arch. Intern. Med.* **106**, 628 (1960).
13. E. Corday, private communication.
14. J. S. Gilson, N. J. Holter, W. R. Glasscock, Proc. American Heart Association, 34th Annual Meeting, Miami Beach (1961).

Mass Spectrographic Analysis of Solids

High sensitivity for bulk and surface impurities is provided by a new analytical method.

N. B. Hannay

In the last few years there has been a great deal of interest in the application of mass spectroscopy to the analysis of solids. This interest has arisen because there clearly exists a need for an analytical instrument with a broad range of capabilities for analyzing very low concentrations of impurities in solids. High-purity materials are rapidly becoming of great technological importance in a number of different fields. For example, concentrations of impurities of 1 part in 10^9 are of great importance in semiconducting materials. The best comprehensive analytical instrument at present is generally considered to be the optical emission spectrograph. This instrument has its limitations, however; impurities at concentrations below 1 part per million cannot generally be detected, and the sensitivity for a considerable number of elements is poorer than this.

In the search for new analytical methods, one of the most promising is mass spectroscopy. Because of the diverse nature of the problems that are of interest in the analysis of solids, several different mass spectroscopic methods of analysis have been developed by workers in this field. Thus, high-sensitivity techniques (*1*) have been developed for the detection of specific impurities in certain cases. For example, the "isotope dilution" method, in conjunction with either a thermal ionization or an electron bombardment source, has been applied to certain kinds of solids analysis and has provided very high sensitivity.

The most useful mass spectroscopic method for general analysis makes use of the vacuum spark source. In this source a high radio-frequency voltage (50 to 150 kv) is applied between two closely spaced electrodes to form a spark; the voltage is pulsed at a repretition rate of some hundreds or thousands of cycles per second, so that the spark is broken and re-formed at this frequency. This method has only very recently been exploited to any appreciable degree. The reason for this undoubtedly lies in the instrumental difficulties associated with the use of the source, although its potential usefulness is great.

The spark source has several advantages for the analysis of solids. It is a source of great generality, in that it has no blind spots for any element and can be used with approximately the same degree of sensitivity for any element. It is quite free from the contamination problems that arise, for example, in connection with the electron bombardment source when a furnace is used to vaporize the solid into the source region. On the other hand, the spark source is erratic in its behavior, and the fluctuating ion current makes recording problems difficult. Ion currents from the spark source are not especially high. The spark source cannot be used with most existing, conventional instruments; a double-focusing instrument, which provides both direction and velocity focusing, is needed because of the large spread in initial energies of the ions. Since double-focusing instruments are relatively rare, the use of the spark source for analytical purposes has been extremely limited despite its potentialities. The very recent introduction of commercial instruments of this type is rapidly altering this situation, however.

Historical Background

The spark source was introduced into mass spectroscopy by A. J. Dempster in 1934 (*2*). At an early date Dempster realized the possibilities of the source for the analysis of solids, and the method was used during World War II by Dempster and his group for

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