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 (1950); 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).
5. 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, AV-SEP,* 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 repetition 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

---

Dr. Hannay is chemical director, Bell Telephone Laboratories, Murray Hill, N. J.

analytical purposes. One brief report of this work has been published (*3*), which points out some of the advantages of the method. Dempster's work showed that the sensitivity of the mass spectrographic method was at least as high as 1 part per million, and it clearly indicated the possible usefulness of the spark source for general analytical work, but it was not sufficiently broad to establish firmly the sensitivity limit or the wide scope of the method.

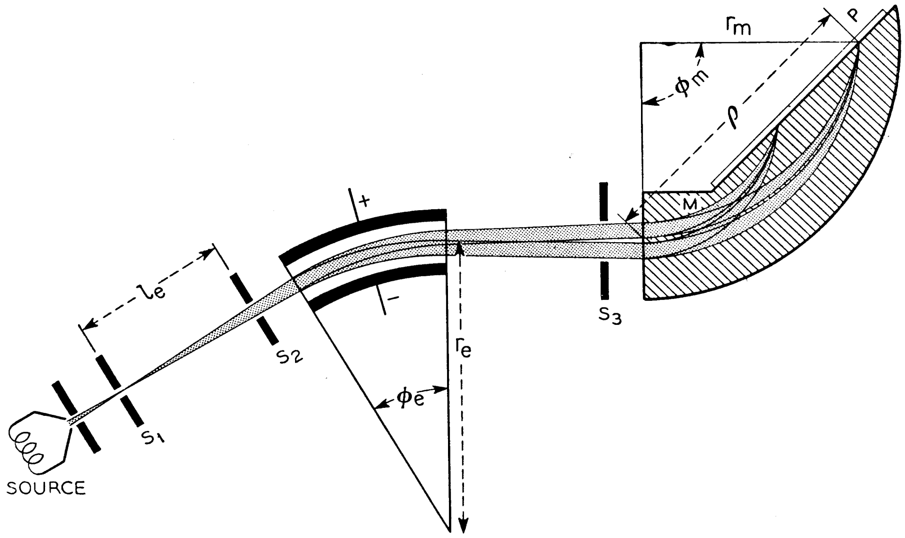

Fig. 1. Double focusing in a Mattauch-type mass spectrograph.

The next application of the method was that of Gorman, Jones, and Hipple (*4*). In this work, a Dempster double-focusing mass spectrograph was adapted for analytical purposes, the principal modification being the introduction of electrical recording. This was accomplished by measuring the ratio of the mass-analyzed ion current emerging from the exit slit to a monitoring current representative of the total current from the source. Difficulties due to the fluctuating nature of the spark source were thus circumvented, and electrical detection was made not only feasible but quantitative. These authors applied the method to the analysis of a series of stainless steel samples and determined chromium and nickel concentrations ranging from 0.25 to 25 percent with a high degree of accuracy and precision. The construction of an instrument designed for analytical purposes was described by Shaw and Rall (*5*), but no results were reported.

Instrumentation

A mass spectrograph for the analysis of solids was described in 1954 (*6*), and analytical results were also given (*7*). The commercial instruments that have more recently become available are similar in general design. In each case double-focusing mass spectrographs of the Mattauch type have been used. For photographic recording the Mattauch geometry offers great advantages over other double-focusing designs because of its property of being simultaneously double-focusing for all masses. This permits simultaneous photographic recording of a large range of masses. Figure 1 shows schematically how the focusing works; the electrostatic analyzer selects for transmission ions of a certain energy range, with no mass separation, and focuses the ions of a given energy at infinity. Two such beams of parallel ions are shown in Fig. 1, representing two typical initial ion energies, with two different masses present. The magnetic field refocuses the parallel beam and compensates for the divergence of the beam resulting from the spread in initial energies, providing mass analysis at the same time.

The large voltage in the spark results in a wide range in initial energies. A slit between the electric and magnetic fields determines the fraction of these which is used. Usually ions with a spread in initial energy of well over 100 electron volts are admitted. It turns out that ions with a spread in initial energy of more than 5000 electron volts originate from the source.

Figure 2 shows schematically one such instrument (*6*). At the left is the source region, showing two electrodes made from the material being analyzed, together with the mechanism for adjusting their position. The removable source plate is shown in Fig. 3. The electrodes, which are about 1 millimeter in diameter and 5 to 10 millimeters long, are held in stainless steel pin chucks. The operation of the spark is observed through the three windows provided in the all-metal system. After acceleration of the ions into the slit system, the ions are deflected electrostatically through an angle of 31°50′ into the cylindrical electrostatic analyzer. Upon emerging from this analyzer, the ions are deflected through an angle of 90° in the magnetic analyzer. The final focusing of the ions occurs at the exit plane of the magnetic analyzer, the ions emerging at an angle of 45° to this plane.

The ions may be recorded either photographically or electrically, the former method being generally preferred. For electrical recording a metal plate carrying an exit slit is inserted in place of a photographic plate, and the ion beam emerging through this exit slit is collected in a Faraday cage. With photographic recording, it is desirable to put more than one exposure on a single plate, and a rack and pinion mechanism is used to move the plate across the exit of the magnetic analyzer, thereby allowing several exposures to be made on one plate without breaking the vacuum.

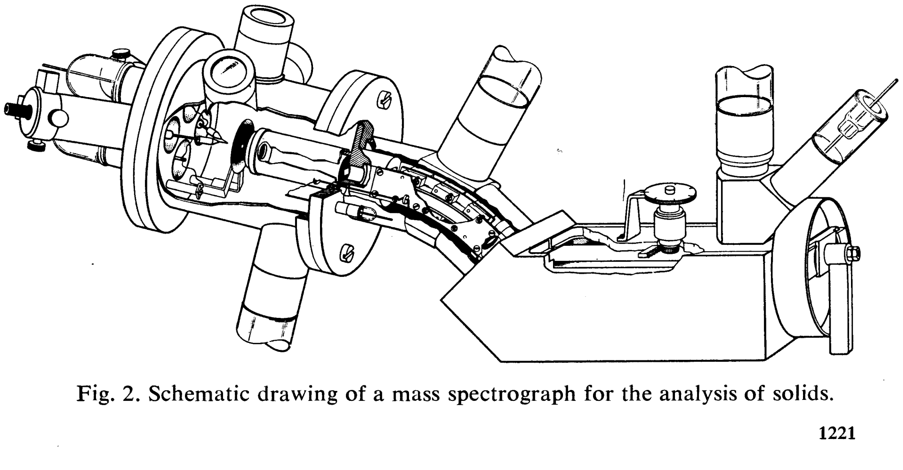

Fig. 2. Schematic drawing of a mass spectrograph for the analysis of solids.

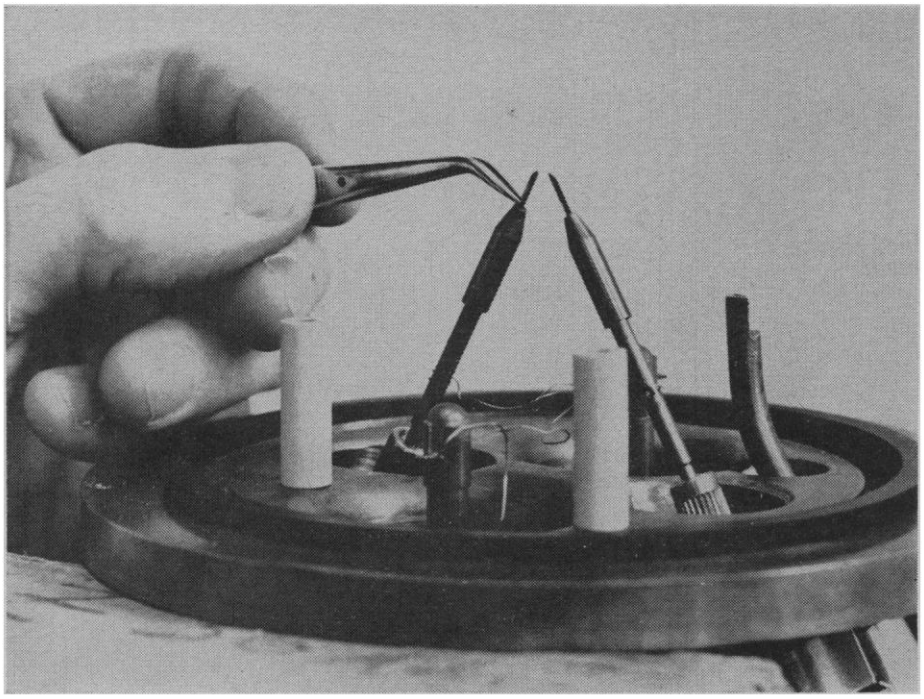

Fig. 3. Source plate, showing electrode system.

The advantages of photographic recording are that all masses are simultaneously recorded and that the sensitivity is very high.

Two separate vacuum systems are provided, one for the source chamber and one for the analyzer region. The only connection between these is through the entrance slit, which may be of the order of 0.002 inch wide, so that gases generated in the source during the operation of the spark do not give as large a pressure rise in the analyzer region as in the source region. Cut-offs are provided on the vacuum lines to facilitate the changing of samples; the procedure requires the venting only of the instrument itself, while the pumps and traps are kept in operation. A preferable arrangement is to provide a cut-off valve between the source and the analyzer regions, and this is done in the commercial instruments. The source plate can be removed for changing samples, and a lock on the magnetic analyzer gives access to the photographic plate region. A chamber for pre-pumping the photographic plates is provided on commercial instruments.

The spark source is operated on a pulsed basis, as it is desirable to keep the voltage in the spark high to avoid selectivity effects for different elements in the sample. In the newer commercial instruments the pulse length and repetition rate are easily varied, and this provides a convenient means of selecting a wide range of exposures. A series of graded exposures for a given sample is recorded on a single photographic plate. By comparing impurity and major-component mass spectral lines that fall within the measurable range of optical densities, impurity concentrations covering several orders of magnitude can be determined on a semiquantitative basis.

Typical plates are shown in Fig. 4. The line widths and positions increase with the square root of the mass. About a 15-to-1 mass range can be covered in a single exposure, and the range may be selected by an appropriate choice of the magnetic field; a convenient range has been found to be from mass 8 to mass 120. In Fig. 4 are reproductions of mass spectra representing, respectively, a high-purity lead sample, a high-purity germanium sample containing added antimony (6 parts per million), an antimony sample containing arsenic (100 parts per million), a steatite sample, a copper sample with one monolayer of gold deposited on its surface, and a germanium sample with one monolayer of indium deposited on the surface. In the case of the last two exposures the impurity lines appear only on the first exposure and disappear in subsequent exposures. In all other cases all of the lines remain constant during successive exposures.

Table 1. Determination of concentrations of impurities in aluminum (in parts per million).

Element	Known composition	Av. for five analyses	Standard deviation
	Sample AA1		
Silicon	476	480	110
Titanium	12	7	1
Manganese	10	8	2
Nickel	5	8	2
Copper	11	11	3
Zinc	6	4	1
	Sample AA3		
Silicon	1975	1370	120
Titanium	34	36	7
Manganese	110	93	7
Nickel	46	49	7
Copper	83	90	20
Zinc	33	30	4

Bulk Impurities

In order to discuss the analytical uses of the instrument, let us first consider what kinds of questions we may reasonably hope to answer with the method. One kind of problem in the determination of bulk impurities is that of obtaining purely qualitative information as to the impurities that may be present in the solid sample. When this kind of information is obtained, one usually finds that it is also desirable to make at least a rough estimate of the concentration. It is frequently of interest to obtain fairly accurate data in comparing two samples—that is, to determine with considerable precision what the relative amounts of an impurity may be in two samples. Finally, there is the problem of determining with a high degree of accuracy the exact concentration of an impurity in a solid sample. Except for the last of these problems, the photographic plate is preferable in many respects to electrical detection. For a general survey of an unknown sample, where one does not know what impurities to expect, the fact that the plate records simultaneously all masses is an enormous advantage. For comparison of samples, and for rough estimation of the impurity concentration, the photographic plate can give results accurate to within a factor of 2 or 3, and this is usually adequate.

Where a high degree of accuracy is needed, one must resort to electrical detection. The nature of the problem of sensitivity in electrical detection and recording may be seen from the fact that the total ion current emerging from the magnetic analyzer is approximately 10^{-10} ampere. An impurity at a concentration of 1×10^{-7}, therefore, corresponds to a current of the order of 10^{-17} amperes. This is beyond the range of direct-current amplifiers and vibrating-reed electrometers, although it is within the capabilities of electron multipliers. The still lower impurity concentration (10^{-9}) detectable photographically is beyond the range where even electron multipliers can be used conveniently. The photographic plate is an extremely sensitive detector of positive ions. A current of 10^{-17} ampere can be easily detected on a photographic plate if it strikes an area of approximately 1 square millimeter over a period of 2 minutes. Thus, an easily detectable image is seen on the photographic plate when it is struck by 10^4 ions per square millimeter at an energy of 20 kev. When the ions are focused on a smaller area, still lower currents may be detected. This sensitivity for ion detection is considerably higher than has been previously reported for positive ions.

If time is used as a measure of exposure, inaccuracies appear because the fluctuating nature of the spark makes it difficult to maintain a constant ion current through the instrument while the spark is running. The fluctuating nature of the spark has no effect on the accuracy of the results, however, when the monitor electrode, between the electric and magnetic fields, is used to measure the total exposure. This measurement is conveniently made by simply measuring the total charge collected by this electrode during the run. The exposure is chosen through suitable selection of the spark operation time and pulse conditions, as mentioned earlier.

The photographic line density is proportional to the exposure over a range of approximately two orders of magnitude when Ilford Q-2 plates are used. A comparison of line density and total exposure provides a number which is representative of the mass spectrographic determination of the impurity concentration. Concentrations determined in this way for a series of standard samples of boron in silicon are shown as a function of the known concentration of boron in Fig.

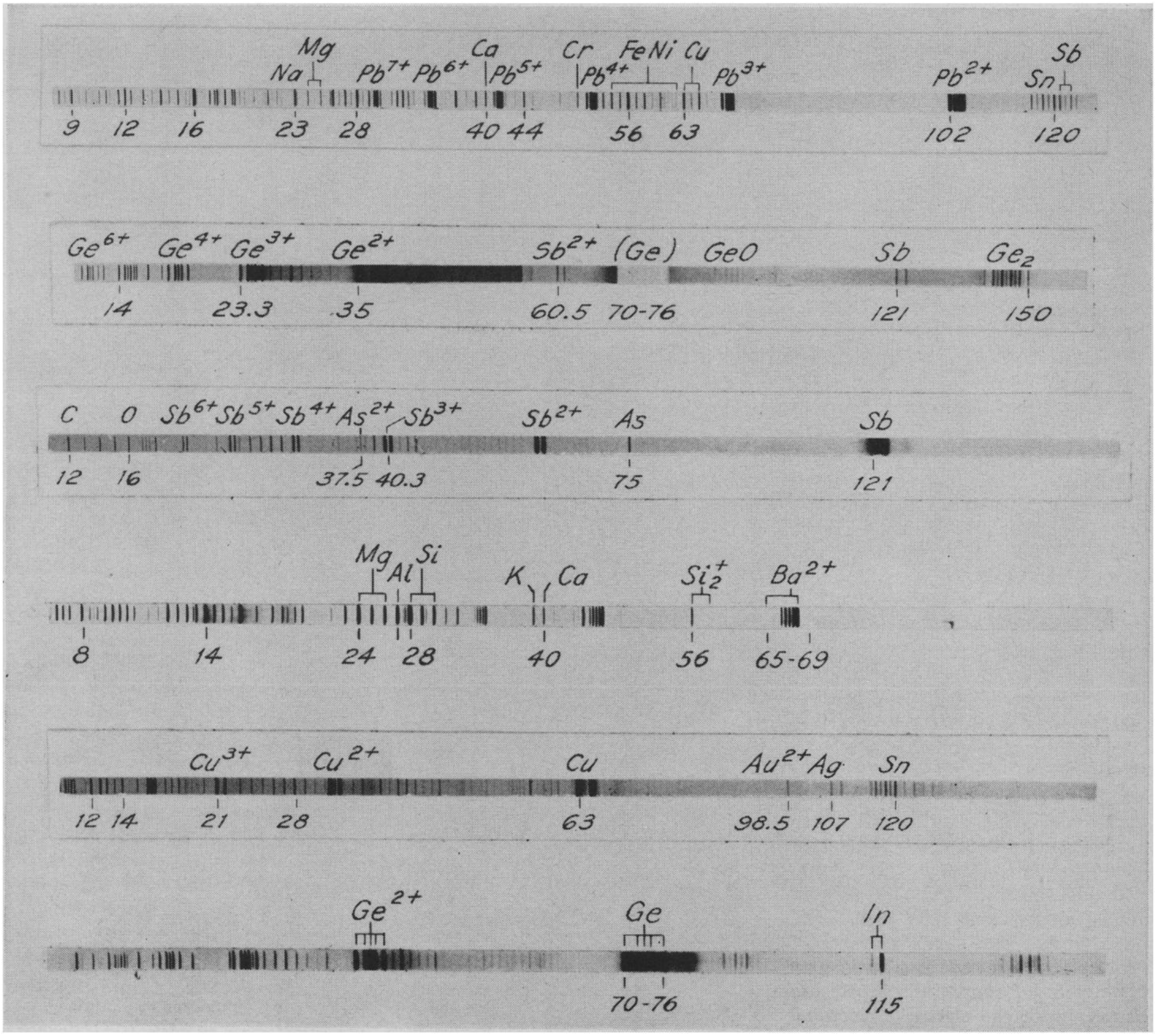

Fig. 4. Typical mass spectra. (From top) "High-purity" lead; germanium with added antimony (6 parts per million); antimony with arsenic (100 parts per million); steatite, with high-purity silicon reference electrodes; copper, with one monolayer of gold deposited on its surface; germanium with one monolayer of indium on its surface.

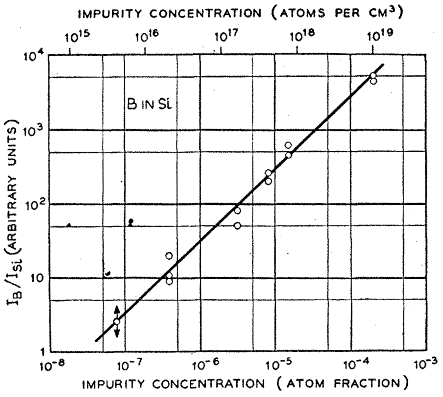

Fig. 5. Mass spectrographic determination of standard samples of boron in silicon.

5. The concentrations for these standard samples were accurately known from measurements of the electrical conductivity. It may be seen from Fig. 5 that with the mass spectrographic method the boron concentration can be determined to within a factor of 2, and that the impurity concentration as determined by the mass spectrograph is directly proportional to the actual impurity concentration over several orders of magnitude. The same kind of information has been obtained for other systems where standard samples were available.

The problem of preparing standard samples is severe, as only a relatively few samples are available for which one has reliable information for very low concentrations of impurities. The kind of standard sample series discussed above, boron in silicon, is available only in the relatively rare case of a semiconducting material such as silicon or germanium. Unfortunately, the preparation of a standard sample involves far more than merely adding a weighed amount of impurity to a melt. The most general and useful method is to add this impurity as a radioactive tracer; by counting the tracer in the given solid sample, one can obtain reliable samples. However, the number of impurities and matrices that are of interest is so great that the preparation of standard samples, even with radioactive tracers, is a formidable undertaking.

Results obtained by the photographic plate method have been found to be reproducible within a factor of 2 in all cases we have examined. One may expect, of course, an even higher accuracy with the electrical recording method. In our own work we have found that a higher accuracy is only rarely required, and that the photographic plate method, when used for comparing samples and for semiquantitative determinations, has been entirely satisfactory. In making comparisons between samples it has been found helpful to mount two pairs of sample electrodes in the source at the same time and to make two groups of exposures on the photographic plate, one group being used to record each of the unknown samples. By this means variations attributable to the photographic plate, to vacuum conditions, and so on are minimized.

The reproducibility of the method is well illustrated by the analytical results obtained for impurities in two samples of aluminum by Craig, Errock, and Waldron (*8*), shown in Table 1. It may be seen from these results that, for all the impurities examined, the mass spectrographic analysis was in good agreement with the independent analysis.

The method may be used for any inorganic solid. Solids containing organic materials are usually excluded to avoid the possibility of contaminating the inside of the instrument with material that would appear thereafter as background. In the case of metals the material is cut into rods and mounted in pin chucks, as shown in Fig. 3. Less than 0.1 milligram of material is actually consumed in several minutes' operation of the spark. Nonconducting materials such as ceramics or quartz are sawed into thin plates, one of which is mounted on the face of one of a pair of conducting

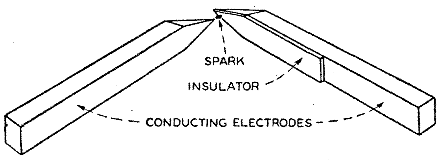

Fig. 6. Electrode system for analysis of a nonconducting solid.

electrodes such as high-purity silicon, as shown in Fig. 6. When the radio-frequency voltage appears between this pair of electrodes, the voltage is high enough across the gap so that, even with the insulator present, a spark is formed. The operation of the spark in this case proceeds very much as though the insulator were not present. One obtains, of course, not only the mass spectrum of the insulator but also that of the reference conducting electrode. By recording the spectrum of the conducting electrodes alone on the same photographic plate, their contribution to the composite spectrum can be readily determined. A similar system has been used by James and Williams (*9*). It is possible to handle powdered samples by packing them into metal tubes of small diameter. In this case, also, a blank run can be made on the metal tube to determine its contribution to the mass spectrum.

The sensitivity of the mass spectrographic method is extremely high. Estimated detection limits for a number of elements in a representative material, gallium phosphide, are shown in Table 2 (*10*). It may be seen from these results that most elements can

Table 2. Estimated concentration detection limits for impurities in gallium phosphide (in parts per million, atomic).

Element	Detection limit	Element	Detection limit	Element	Detection limit
Uranium	0.001	Neodymium	0.008	Arsenic	0.01
Thorium	0.001	Praseodymium	0.001	Germanium	0.03
Bismuth	0.001	Cerium	0.01	Zinc	0.006
Lead	0.002	Lanthanum	0.003	Copper	0.005
Thallium	0.005	Barium	0.2	Nickel	0.005
Mercury	0.003	Cessium	0.01	Cobalt	0.003
Gold	0.001	Iodine	0.01	Iron	0.003
Platinum	0.003	Tellurium	0.03	Manganese	0.003
Iridium	0.002	Antimony	0.002	Chromium	0.01
Osmium	0.002	Tin	0.003	Vanadium	0.01
Rhenium	0.002	Indium	0.001	Titanium	0.01
Tungsten	0.003	Cadmium	0.003	Scandium	0.01
Tantalum	0.001	Silver	0.002	Calcium	0.01
Hafnium	0.003	Palladium	0.004	Potassium	0.01
Lutecium	0.001	Rhodium	0.001	Chlorine	0.01
Ytterbium	0.003	Ruthenium	0.005	Sulfur	0.03
Thulium	0.001	Molybdenum	0.004	Silicon	0.03
Erbium	0.003	Niobium	0.3	Aluminum	0.003
Holmium	0.001	Zirconium	0.006	Magnesium	0.003
Dysprosium	0.004	Yttrium	0.001	Sodium	3
Terbium	0.001	Strontium	0.001	Fluorine	0.003
Gadolinium	0.004	Rubidium	0.05	Boron	0.001
Europium	0.002	Bromine	0.02	Beryllium	0.001
Samarium	0.004	Selenium	0.02	Lithium	0.003

be detected at concentrations in the 10^{-8} to 10^{-9} (atom-fraction) range. Similar sensitivities have been found for another instrument (*11*). A summary of detection limits in four different types of materials, as given by Craig *et al.* (see *8*), is shown in Table 3.

Table 3. A summary of detection limits for impurities in four different types of materials.

Detection range [concentration (atom-fraction)]	Number of elements detected in			
	Aluminum	Graphite	Gallium arsenide	Silicon
$\leq 10^{-9}$	16	41	4	9
2×10^{-9}–10^{-8}	38	27	50	45
2×10^{-8}–10^{-7}	12	3	14	14
2×10^{-7}–10^{-6}	5	0	3	5
$> 10^{-6}$	0	0	0	0

Limitations on the sensitivity of the instrument fall into two categories. There are always present a small number of background lines due to residual gas in the instrument, and these lines may appear at several places in the low mass region. Improved vacuum conditions, of course, result in a reduction in the number of these lines. Because some of them are always present, however, it is not possible to make a determination for carbon, nitrogen, oxygen, and hydrogen at very low concentrations. The second limitation, and a more important one, results from a diffuse background that appears on the photographic plate as a result of scattering of the ions by residual gas. This scattering is frequently accompanied by a change of charge or mass of the ion. According to what change of charge or mass occurs, and where it occurs, one can easily calculate the region of the photographic plate over which the diffuse background should appear. This effect can be greatly reduced by improving the vacuum conditions. One effective way to do this is to bake the instrument.

Surface Impurities

Although the instrument was not primarily constructed for the determination of surface contaminants, this has developed into an application of considerable importance. One can determine surface impurities because the spark initially samples the surface, then, as the operation proceeds, chews into the interior of the material and attacks little in the way of new surface area. Thus, the spectrum that one obtains when the spark is first operated includes not only bulk impurities but surface contaminants, while the spectra obtained subsequently reflect bulk impurities almost exclusively. As indicated earlier, the sensitivity of the instrument in which the electrode arrangement shown in Fig. 3 was used was such that 0.1 monolayer of a surface impurity could be detected. An obvious way to increase the sensitivity for surface contaminants is to change the geometry of the electrode system so that a larger area of surface can be scanned. By using a point against a wedged-shaped surface, approximately 0.1 square centimeter of area can be conveniently scanned, and it has been determined that a surface impurity of less than 0.01 monolayer can be easily detected. In Fig. 4, mass spectra are shown for a monolayer of gold on copper and for a monolayer of indium on a germanium sample. The indium-113 line is clearly visible on the original plate, and this corresponds to a surface coverage of 0.04 layer (corresponding to the 4-percent isotopic abundance of indium-113). Surface impurities on insulating materials, such as ceramics, have also been successfully investigated in this way.

Conclusions

The mass spectrograph is not considered to be an instrument that will replace the emission spectrograph, because it is inherently more complicated. On the other hand, it is an extremely useful instrument and can handle problems of a semiquantitative nature that the emission spectrograph and other methods cannot handle, and thus it complements these methods. As has been shown, these problems include both the determination of low concentrations of bulk impurities and the determination of surface impurities which cannot be handled conveniently by any other known method. Bulk impurities down to a level of 10^{-9} (atom-fraction) and surface impurities of less than 0.01 monolayer can be detected (*12*).

References and Notes

1. For references to the literature see G. P. Barnard, *Modern Mass Spectrometry* (Institute of Physics, London, 1953) and H. E. Duckworth, *Mass Spectroscopy* (Cambridge Univ. Press, Cambridge, England, 1958).

→ A. J. Dempster, *Proc. Am. Phil. Soc.* **75**, 755 (1935).

3. ———, "The mass spectograph in chemical analysis," *U.S. Atomic Energy Comm. Paper No. MDDC-370* (1946).

→ J. G. Gorman, E. J. Jones, J. A. Hipple, *Anal. Chem.* **23**, 438 (1951); J. A. Hipple and J. G. Gorman, "Mass spectrometric analysis of solids with the high-frequency spark," *ASTM Spec. Tech. Publ. No. 149* (1943).

→ A. E. Shaw and W. Rall, *Rev. Sci. Instr.* **18**, 278 (1947).

→ N. B. Hannay, *ibid.* **25**, 644 (1954).

→ ——— and A. J. Ahearn, *Anal. Chem.* **26**, 1056 (1954).

8. R. D. Craig, G. A. Errock, J. D. Waldron, in *Advances in Mass Spectrometry* (Pergamon, London, 1959).
9. J. A. James and J. L. Williams, *ibid.*
10. R. Brown, R. D. Craig, J. A. James, C. M. Wilson, Proceedings, Conference on Ultrapurification of Semiconductor Materials, Boston, Apr. 1961.
11. G. D. Perkins, C. F. Robinson, R. K. Willardson, private communication; C. F. Robinson, G. D. Perkins, N. W. Bell, Proceedings 5th International Instruments and Measurements Conference, Stockholm, Sept. 1960.
12. A number of the techniques described were developed by A. J. Ahearn, to whom I am indebted also for comments on the manuscript.