

# The

# SPEX

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# Speaker

## THE ELECTRON MICROPROBE\*

ARNO ARRAK

Grumman Aircraft Engineering Corp., Bethpage, L. I., N. Y.

WHEN, within three years after introduction, 60-odd analytical instruments are sold by one manufacturer alone for upward of \$80,000 apiece, everyone takes notice. To those of us who can recall the days when an outlay of \$50 for a pH meter or \$90 for a balance meant dipping into the capital budget and hesitatingly requesting the approval of a skeptical research director, it seems a wondrous phenomenon. As more sophisticated tools were introduced, their value proved, management gradually became accustomed to requests for as much as \$40,000. Notwithstanding this preparation, we can still imagine some startled faces among those 60-odd hardheaded, pioneering board members as they were asked to approve the purchase of an electron microprobe costing as much as a respectable fleet of autos.

That they bet on the right horse is evident, for the microprobe has already become one of the most significant analytical tools ever devised. Until its invention, analysts found that, whatever their ingenuity, they could not determine the composition of a microscopic dot. Often their curiosity had been aroused by a tantalizing glimpse of small areas neatly outlined under a light or electron microscope. The composition of the areas could yield a significant clue to the behavior of the material under study. Were these observed specks inclusions of an unsuspected tramp metal or slag in the alloy specimen or were they an inter-metallic compound of two or more constituents that had precipitated out of the surrounding material? On the spot analysis was unheard of and not even the fanciest micro-manipulator could pry it loose for external examination. Biochemists faced similar, dead-end problems. Questions such as what happens to the iron inside the body's manufacturing plant when a patient develops anemia or its opposite, polycythemia, went begging for answers. Geochemists longed to find out how rare elements are distributed or compounded in their parent materials, but had little more than guesswork, based on indirect methods, to go by. To all researchers alike, only one thing—size—stood in the way of meaningful answers.

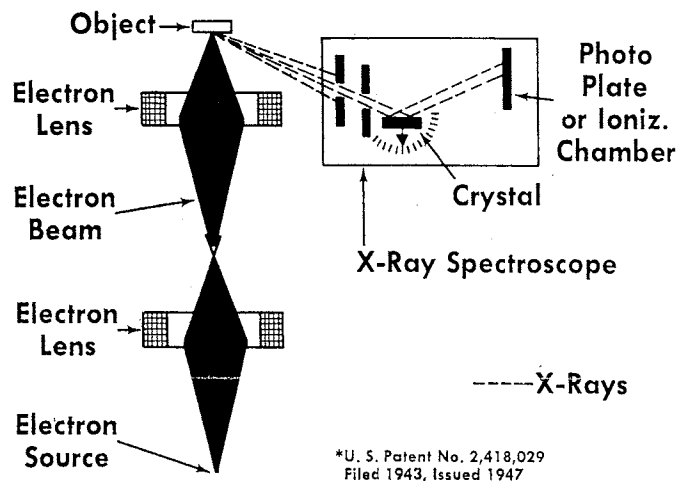
Such questions can now be answered directly rather than inferentially. The electron microprobe is capable of analyzing regions as small as one micron in diameter. It focuses a fine beam of electrons, under a high vacuum, causing characteristic x-rays to be emitted from the surface of the sample at point of impact only. This radiation as well as any electrons scattered by the sample or visible light given off by it are then analyzed by detectors in the instrument to determine the chemistry of the emitting area.

The idea of using magnetic lenses to focus electrons for micro analysis first occurred to J. Hillier, a pioneer in electron microscopy, who patented it in 1943. Apparently he never

\* Expanded from a paper presented to the Society for Applied Spectroscopy, New York Section, February, 1963.

### ELECTRON PROBE MICROANALYSIS

HILLIER PATENT (1943\*)



\*U. S. Patent No. 2,418,029  
Filed 1943, Issued 1947

Fig. 1. The Hillier patent presaged the electron microprobe to be constructed a decade later. A doubly focused beam of electrons impinges on an object. Characteristic x-rays excited by various elements present and related to their concentration are dispersed in an x-ray spectroscope; intensity is recorded photographically or electronically.

built the instrument and his work lay neglected in U. S. Patent Office files. The first working microanalyzer was built at the University of Paris by Raymond Castaing who, independently, came upon the idea and published it in his doctorate thesis in 1951. He had originally worked with a converted electrostatic electron microscope, which he modified to operate as an electron probe. Having proved the practicality of the concept, he then went on to design a model utilizing magnetic focusing, which was to become the prototype of the first commercial instrument, the "Microsonde," marketed by CAMECA in France. In this design, two magnetic lenses focus the electron beam, as it is directed downward from an electron gun, into a spot (which may be one micron or less in diameter) on the sample surface. The x-rays emitted from this spot as a result of electron impacts are then analyzed by two curved-crystal x-ray spectrometers, one using a bent quartz, the other a bent mica crystal. Curved rather than flat crystals are preferred because the source is effectively a point; advantage can be taken of the focusing properties of curved crystals to obtain superior resolution and speed. Having a smaller lattice spacing than mica, quartz is best suited for the short wavelength or "hard" x-rays from high atomic number elements, while mica, with its larger lattice spacing, serves to diffract and focus longer wavelength, "soft" radiations of the lower atomic number ele-

ments. The longest characteristic x-rays measurable with a mica crystal are those of sodium, atomic number 11. Those of elements below sodium have wavelengths too long for most crystals yet too short for most gratings. This very elusive "ultra-soft" x-ray region has only recently been made accessible by combining several techniques to be described later. In addition to these electron and x-ray optical components, Castaing also incorporated into his instrument a reflecting metallurgical microscope, concentric with the electron beam. Pinpointing the beam on the desired sample area was best accomplished when the operator could see the sample and move it around to bring any part of it under the beam. An aid in locating the beam under the microscope is a brownish spot that, after a few minutes of operation, becomes visible on the sample surface. This contamination consists mostly of carbon, formed by decomposition of vacuum pump oil adsorbed on all surfaces in a vacuum of  $10^{-5}$  torr. It does not interfere with the analysis and forms its own convenient record, indicating where the beam was sitting when a particular reading was taken.

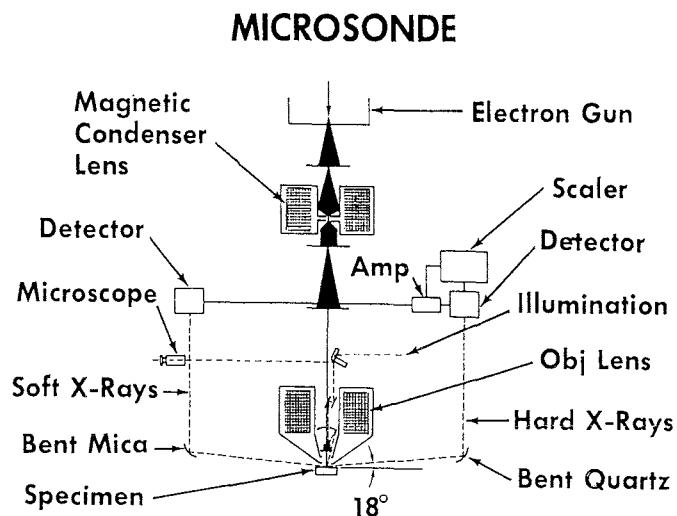


Fig. 2. For convenience, Castaing inverted the concept of Hillier and added a light microscope to view the area as it was irradiated with the electron beam. The original Microsonde provided only point-by-point analysis.

Castaing not only built the first electron probe, he also developed a quantitative theory relating observed x-ray intensity to the chemical composition of the emitting area. Basically, he calculated corrections for absorption and secondary x-ray fluorescence when x-rays are generated below the surface and have to emerge through layers of sample material before entering the spectrometer. The thickness of the sample that the x-rays must penetrate before reaching the spectrometer depends upon the angle between the sample surface and the direction to the spectrometer. The large absorption effect at small take-off angles is due to the longer path-length of x-rays through the sample. Since the largest correction term in Castaing's theory is absorption correction, it can be minimized by designing an instrument with as high a take-off angle as feasible. Castaing used  $18^\circ$  which still provided a system requiring moderately large corrections. To increase the take-off angle farther, the final focus of the beam must be brought further out from the magnetic objective lens. If this is done, however, the spherical aberration of the objective becomes intolerably large, destroying the resolution of the beam. Newer designs circumvent this difficulty either by inverting the lens and taking the x-rays out through the bore of the lens, or else by tilting the specimen so as to present a higher take-off angle toward the spectrometer. Commercial designs now available have take-off angles ranging from  $15^\circ$  to  $52^\circ$ .

Although the choice of take-off angle appears to represent many compromises, all modern commercial instruments offer improved resolution, stability and ease of operation. In addition, the newest probes are capable of television-type scanning to present an overall view of the subject. The detection system, once limited to characteristic x-rays, is now capable of picking up electron backscatter, diffraction lines, cathodoluminescence and target current. These, plus Heinrich's technique known as "concentration mapping," multiply the usefulness of the electron probe many fold.

## ELECTRON PROBE MICROANALYZER TYPICAL ARRANGEMENT

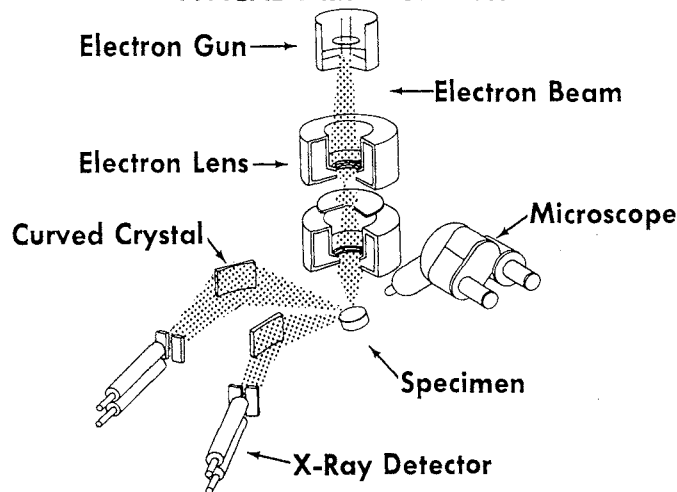


Fig. 3. The basic layout of modern electron probes provides for as many as eight detectors to measure the concentration of that many elements simultaneously. Electronic scanning in two dimensions results in a television-type display, permitting the concentration of a particular element over an area to be correlated with its visual appearance. (Courtesy L. S. Birks and Analytical Chemistry.)

Like x-ray scans, backscattered electron or sample current scans are sensitive to atomic number differences over the area of the sample since the scattering power of the elements varies with the atomic number. Electron scans are often similar enough to the appearance of the sample under a metallurgical microscope to correlate the two. A permanent record of each type of scan can be obtained usually in less than five minutes by recording the oscilloscope image on Polaroid film. Such a set of photographs of scans of a sample for a number of elements is of great value in diagnosing the structure and composition of the sample and in delineating areas for further study.

Where resolution is a prime consideration, x-ray images bow to electron images. This is due to two factors: the electron backscatter can take place from an area of smaller diameter than the area from which x-rays are emitted; secondly, the electron signal is approximately three orders of magnitude stronger than the x-ray signal from a spectrometer. Working with backscattered electrons alone, the researcher can study very small-scale features or steep concentration gradients in the sample. If it happens to be a binary alloy, the study can be made quantitative as well without the troublesome absorption and fluorescence corrections required to interpret x-ray data. Other things being equal, it can be shown that the diameter of the electron beam at best focus varies as the  $3/8$  power of the beam current. If interest is in the electron signal alone, the beam current can be reduced to obtain a back-scattered electron signal from a spot only a tenth of a micron

# ELECTRON PROBE MICROANALYSIS

## TYPES OF SIGNALS AVAILABLE

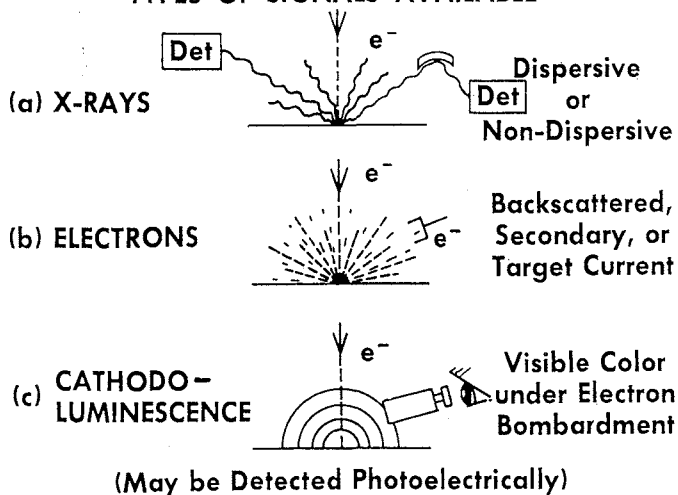


Fig. 4. Where the original instruments were geared to the detection of dispersed x-rays only, modern probes are capable of detecting non-dispersed x-rays (and so extend the element range down to carbon), electrons and cathodoluminescence. Electrons, or current, are displayed with greater resolution than x-rays. The emission of visible light, especially with certain minerals, can be quite useful in identification.

in diameter. This is probably the practical limit of instruments built today, although theoretically, with improved materials and closer tolerances, a beam size of 0.01 micron should give an observable electron signal.

As originally conceived by both Castaing and Hillier, the electron probe was intended to be basically a means of generating the characteristic x-ray spectrum of an extremely small sample volume and utilizing these x-rays for spectrochemical analysis of the emitting sample area. Despite the introduction of other types of signals and modes of operation, analysis of the x-ray spectrum is still the most valuable and informative means of gathering data on a specimen. As previously mentioned, curved-crystal x-ray spectrometers are preferred for this purpose since higher speed, resolution, and line-to-background ratio can be obtained by taking advantage of their focusing properties. The crystal is curved only in one dimension, so that focusing is two-dimensional and a point source will produce a line focus. After the crystal is curved to a radius equal to the diameter of the Rowland circle (known as the Johansson circle to most x-ray workers), its diffracting surface is ground to fit the circumference of the circle. The source and the receiver slit are located on the circle and placed symmetrically with respect to the normal to the diffracting planes. When scanning through the spectrum, both the source and the receiver must maintain their symmetric angular position with respect to the crystal in order to satisfy the diffracting condition for x-rays (Bragg law).

CURRENTLY, the most valued detector of x-rays is the gas proportional counter. As its name implies, this detector generates a pulse with an amplitude proportional to the energy of the x-ray quantum absorbed. This being so, it is possible, by means of appropriate electronic circuits, to distinguish and sort out the pulses coming from high-energy x-rays from those of low-energy x-rays and to count them separately if desired. Since by Planck's law the energy of a quantum is wavelength dependent, and wavelength by Moseley's law is atomic number dependent, we have here a means of x-ray

spectrum analysis independent of dispersion. Separation of adjacent elements by pulse-height analysis is not quite perfect, however; in the middle atomic number range elements two or three atomic numbers apart can be distinguished only above the 10 percent level. What makes pulse-height analysis really valuable is the fact that it can be used to separate higher orders of diffracted x-rays from the desired first-order line. A second-order line appearing in the first-order position will have only half the wavelength of the first-order line and is easily discriminated against. Scattered x-rays of different energy are also discriminated against. The resulting signal from the counter is spectrally "cleaner" and less noisy than a signal from its predecessor, the Geiger tube. The Geiger tube, in addition to being insensitive to photon energy, has a dead time of the order of 200 microseconds, as compared to less than 5 microseconds for the proportional counter. It is also limited to counting rates of less than 10,000 cps vs. 1 million cps. (Recall that in one of the early space probes, Geiger tubes jammed because of the extremely high counting rates in the van Allen belts, and that Dr. van Allen correctly inferred the high radiation density from the failure of these Geiger tubes.)

The wavelength range to which a proportional counter is sensitive depends upon the counter gas and the window material; the counter gas determines the long wavelength limit. The most generally used counter gas is argon (with 10% methane added to quench a continuous discharge following each pulse). When used in a flow-proportional counter, this gas mixture is capable of responding to x-ray wavelengths from 0.3A all the way up to carbon K-alpha at 44A. In the soft and ultra-soft x-ray region, the performance of the counter is limited mainly by the windows. Composed of extremely thin Mylar or collodion, both are semi-permeable and very hard to produce or support. Recently, a combination of a proportional-counter detector and a dispersing system consisting of a multi-layer soap film of barium stearate and barium palmitate has been reported as being capable of detecting carbon K-alpha radiation at concentrations of a few percent. This work was done by R. E. Ogilvie at MIT in Cambridge, Mass., who, reporting a count rate from pure carbon of 1,000 cps, was able to detect carbon in titanium carbide inclusions in titanium sheet. Although previously carbon had been detected non-dispersively with a proportional counter and pulse height analysis, the detection limit was around 10-20%.

At the very short wave end of the x-ray spectrum, the argon flow-proportional counter loses its sensitivity. A sealed xenon proportional counter or a scintillation counter gives better performance. Again, pulse height analysis can be applied with both of these detectors to eliminate undesired spectral orders and background. It is not necessary to push to these very short wavelengths, however, for elements whose K-lines (innermost atomic shell) fall in that spectral region will have L-lines (next shell outwards) in the region where the argon flow-proportional counter can be effectively used. Measurement of L-lines instead of K-lines is sometimes actually more desirable for quantitative work. It is known, for example, that if both K- and L-lines are simultaneously excited, the K-line is always more intense. But the background continuum under the K-line is proportionately higher so that a better line-to-background ratio is obtained with L-lines, even though the absolute intensity is less.

For quantitative analysis, such as in the study of concentration profiles in diffusion couples, point by point analysis supplies the most accurate information because the x-ray counting statistics can be made as precise as desired by taking counts for an extended period of time. In this mode of operation, detection limits for most elements are around 0.1% or even lower, except in the low atomic number region. Ordi-

narily, this extreme precision of statistics is not required; a semi-quantitative picture of the distribution of an element along a line or over an area is much more valuable. Here the scanning microanalyzer really pays for itself. A brilliant piece of medical research by I. Adler at the U. S. Geological Survey, Washington, D. C., and A. J. Tousimis, at George Washington University, illustrates the application of line scanning. They were studying Wilson's disease in which the copper metabolism of the body is upset and, among other symptoms, a change in the eyes takes place. Sections of the eyes taken from patients who had died of the disease were scanned with the detector set for copper radiation. Within the cornea, the copper was found in a thin membrane only about 5 microns wide. The actual concentration was estimated by external standardization, i.e., comparison with the intensity emitted from reference materials of known copper content.

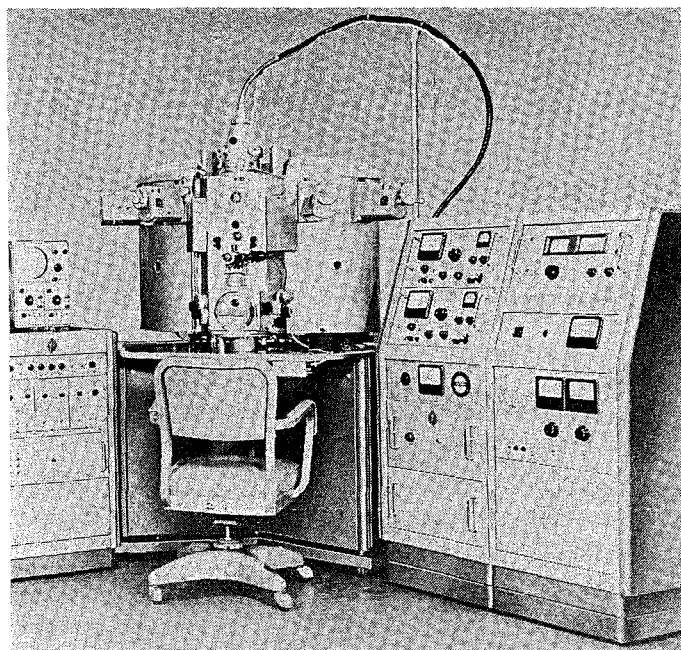


Fig. 5. Applied Research Laboratories' EMX. The basic electron microprobe is flanked by control consoles on the right, an oscilloscope to depict the various displays and a recorder on the left.

THE general approach to analysis today is to employ scanning first and, with this technique, attempt to glean as much information from the sample as possible. The first step is obtaining a back-scattered electron or sample current area scan and comparing it to an optical micrograph to determine how the average atomic number varies over the field of observation. If the principal elements present in the sample are known, area scans are made to determine the distribution of their x-ray emission pattern. Polaroid photos are taken of each scan as it is displayed on the oscilloscope. If the scanning controls are not touched between scans for different elements, the area of the scope corresponds to the same area on the sample so the distributions of the different elements can be fitted together. If there are any boundaries in the sample where the concentration of an element varies, a line scan may be taken across the boundary, recording x-ray intensity as vertical deflection and distance on the sample as horizontal deflection of a spot on the oscilloscope. In order to facilitate interpretation, the researcher takes a double exposure of an x-ray line scan over a backscattered electron area scan. A triple exposure with the x-ray signal disconnected from the oscilloscope, results in a horizontal line marking the locus of line scan on the back-scattered electron picture. If there are two elements involved,

each varying in a different pattern, their line scans can both be recorded over the same underlying scattered electron area scan. In this manner, a lot of microchemical information is compressed into one oscilloscope photo. If the sample is luminescent under the electron beam, a photomultiplier, whose

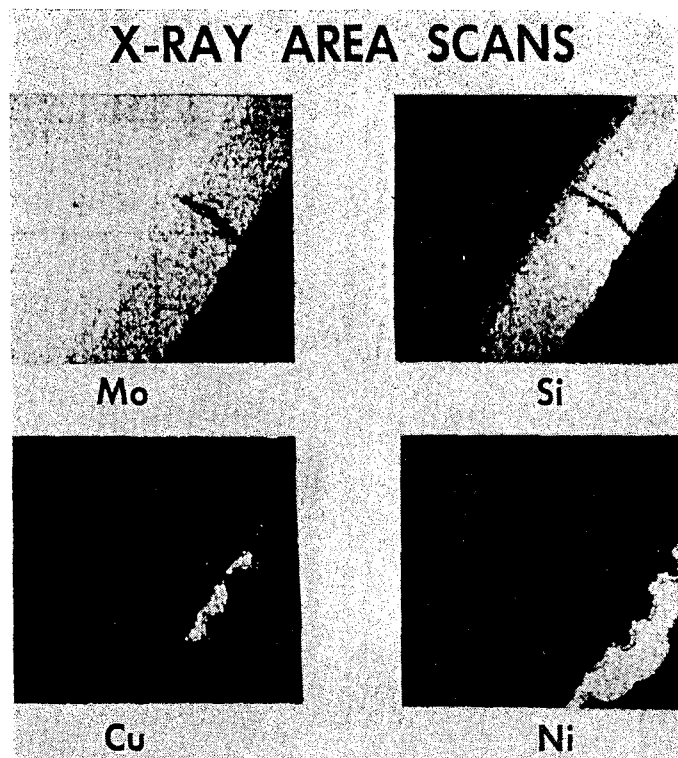


Fig. 6. Successively scanned with the x-ray detector set for the K-alpha lines of four different elements, the distribution of Mo, Si, Cu and Ni in a particular sample is neatly portrayed. Information like this is exceedingly valuable to the research metallurgist engaged in the development of new alloys.

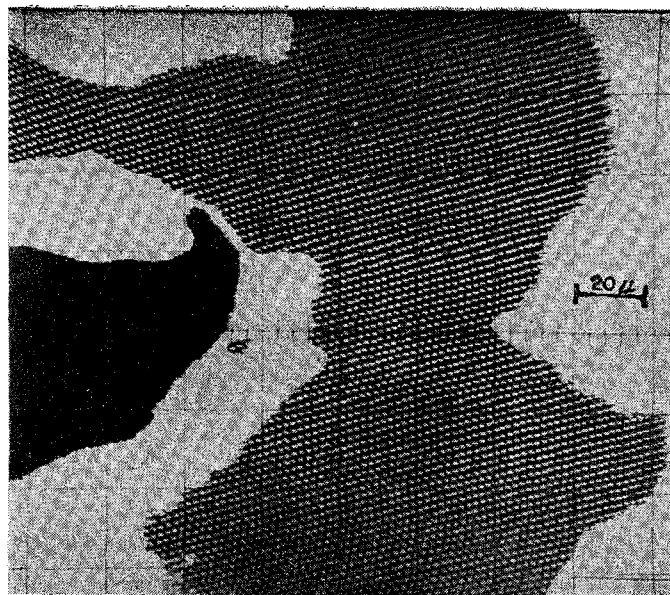


Fig. 7. When copper and nickel are explosively compacted, an interface of the two metals results. Scanned for Cu-K-alpha in the concentration mapping technique the black area indicates no copper, the area containing around 59% is cross-hatched, the area of unalloyed copper is white. The delineation of the iso-concentration areas is much clearer than can be obtained with area scanning. (Courtesy K. F. J. Heinrich and the Review of Scientific Instruments.)

output is fed to the oscilloscope, will produce an area scan on the scope showing what parts of the sample are cathodoluminescent. By inserting different filters in front of the photomultiplier the color of the luminescence can also be determined. Since many minerals, oxides, sulfides, etc. show cathodoluminescence, this provides an additional means of diagnosing the chemical nature of inclusions, phases, etc., that may be present.

Often, however, it is desirable not to know the exact concentration of an element at any one point but to find those areas of the specimen where the concentration is roughly the same. With such information, for instance, intermetallic compounds can quickly be spotted. To portray an iso-concentration scan directly, K. F. J. Heinrich of the duPont Experimental Station in Wilmington, Del., has devised an ingenious scheme. Its essence is a cardboard mask, suitably slotted and placed over the screen of an oscilloscope. A photomultiplier, outside of the mask will, of course, respond only when the electron beam peeps through the cut-outs.

In this so-called concentration mapping, the sample is scanned conventionally, the x-ray signal being fed to a rate-meter and then to the vertical plates of the oscilloscope. With the mask in place, light will pass through the slots only when the counting rate falls between any two preset values. The slot, in effect, acts as a pulse height discriminator. In synchronism with the area scanning, light signals are emitted. Picked up by a photomultiplier, these signals then serve to modulate the gun bias of a second oscilloscope which is set to scan in synchronism with the electron probe. The result, viewed on the second oscilloscope, is a map showing the iso-concentration areas of a chosen element. With a little snipping, the cardboard mask can be made to transmit almost any range of concentration values of the element under study. In fact, several slots can be cut to record as many levels. By suitably shaping the slots on the mask and feeding a saw-tooth signal to the horizontal axis of the first oscilloscope, the regions scanned can be made to appear with distinguishing "cross-hatching."

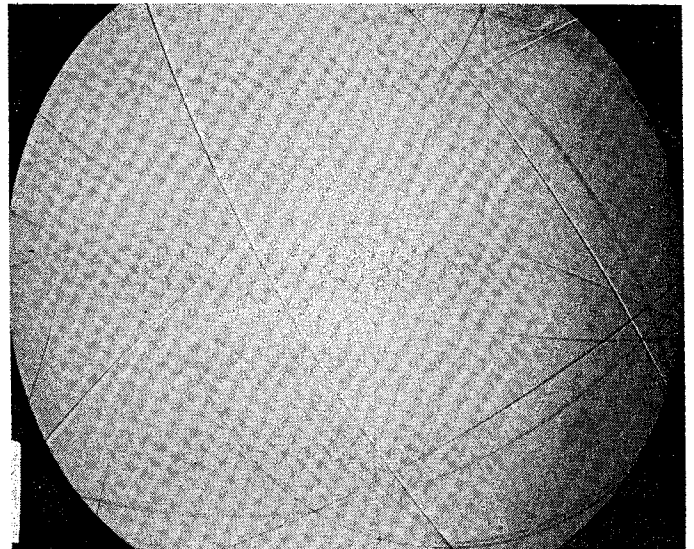
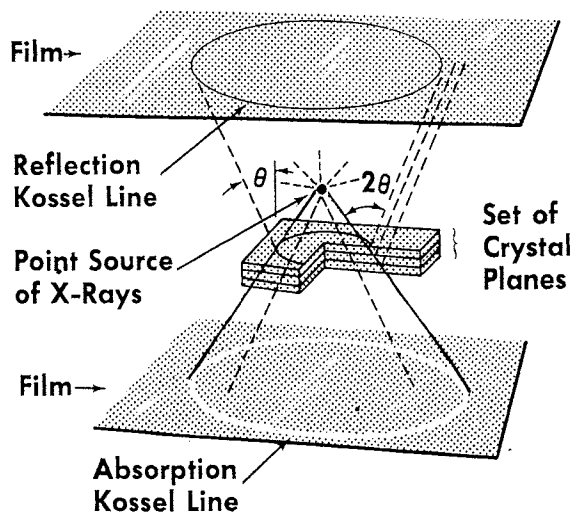
The probe is capable of x-ray diffraction as well as spectrochemical analysis. The effective point source of divergent x-rays produced by the probe's beam focused on a single

crystal produces Kossel line diffraction patterns. Resolution is so good that the K-alpha-1 and K-alpha-2 lines of many elements are separated. The distance between these lines serving as a reference, lattice parameters can be measured with a precision of better than one part in 100,000. Hanneman and Ogilvie have shown that, with this technique, it is possible to detect the change in lattice parameter of single crystals of nickel upon bombardment with neutrons. Spacings show such a small change that the effect had never been detected by other means. In biology where tiny crystals of substances are often isolated, Kossel diffraction studies should prove increasingly important.

Before describing the detailed applications of the probe, some limitations should be noted. Specimens must be electrically conducting to complete the current path. (A non-conductor will very quickly charge up and deflect the beam to a new spot every few seconds.) Non-metals must therefore be coated with a thin evaporated layer of metal or graphite. Fortunately, the thickness of the conducting layer required is thin enough to leave it optically transparent. Secondly, because the instrument operates in a high vacuum, all liquids must be excluded. Biological tissue must be dried and prepared by techniques developed for electron microscopy. Unsuspected changes may occur in this multi-step process.

**S**AMPLE preparation for metals differs little from normal metallographic practice, except that the final finish is with a light diamond polish to remove contamination by other abrasive residues and to guard against the selective removal or redeposition of some component due to chemical etching of the surface. Because diamond polishing may remove any visible distinguishing marks from the surface, it may be necessary to etch the sample first, then mark the surface with a diamond scribe or a micro-hardness tester, take a micrograph, and then apply the final diamond polish. The micro-hardness marks, remaining visible when all other features have been obliterated, serve to position the sample under the beam. In order to provide electrical contact to the sample, the mounting medium can be made conducting by mixing it with a metal powder, or a conducting path can be painted from the sample to the holder with silver paint (used in transistor circuits)

### ORIGIN OF KOSEL LINES



Figs. 8-9. Kossel pattern of nickel foil. The point source of x-rays impinging on a single crystal causes x-ray fluorescence of the element present. Upon passing through the crystal layers, the fluorescing beam is diffracted to form the type of pattern shown. Line doubling, resulting from the K-alpha-1 and K-alpha-2 radiation, is an indication of the excellent resolution attainable. In ordinary x-ray diffraction techniques, the two lines merge. The Kossel camera permits one to obtain lattice parameter measurements with a precision of 1 part in 100,000 and, in combination with the electron probe, is a powerful identification tool. (Courtesy Philips Electronics, Inc., Mount Vernon, N. Y.)

or colloidal graphite, "Aquadag." Sample preparation for minerals is also quite straightforward. The only unconventional step is the necessity of vacuum-depositing a transparent, thin layer (few hundred Angstrom units) of a metal like aluminum or manganese on the polished specimen.

By contrast, a typical procedure for preparing biological tissue for analysis is much more elaborate. Borrowing techniques developed for electron microscopy, the sample, imbedded in a formalin-fixed paraffin block, is sliced as thin as 4 microns in a microtome. After sectioning, it is picked up from distilled water on the end of a flat, polished carbon rod, to which it ultimately bonds. This is followed by dehydration through freeze drying and extraction by organic solvents. Finally, aluminum or carbon is vacuum-deposited on the surface to render the sample electrically and thermally conductive. Despite the care taken in its preparation, the sample is often so fragile that it may be destroyed in a short time if the beam is allowed to stay on at full intensity, which corresponds to a current density of around 100 amp/cm<sup>2</sup> on the analysis spot. For this reason, successful biological analysis frequently depends upon combining high efficiency detectors with low beam currents to reduce the destructive effect of electron bombardment on the tissue.

OF the three principal fields of application of the electron microprobe, metallurgy, geology and biology, the bulk of present literature pertains to metallurgy. And, of the many diverse types of metallurgical problems lending themselves to solution by the probe, the identification of phases and inclusions in polycrystalline substances is probably most significant. As if in anticipation, some of Castaing's earliest work was concerned with phase identifications in ternary Cu-Sn-Sb alloys. Phase identification involves quantitative analysis to characterize intermetallic compounds which often appear on a microscopic scale. The ultimate phase diagram for a particular

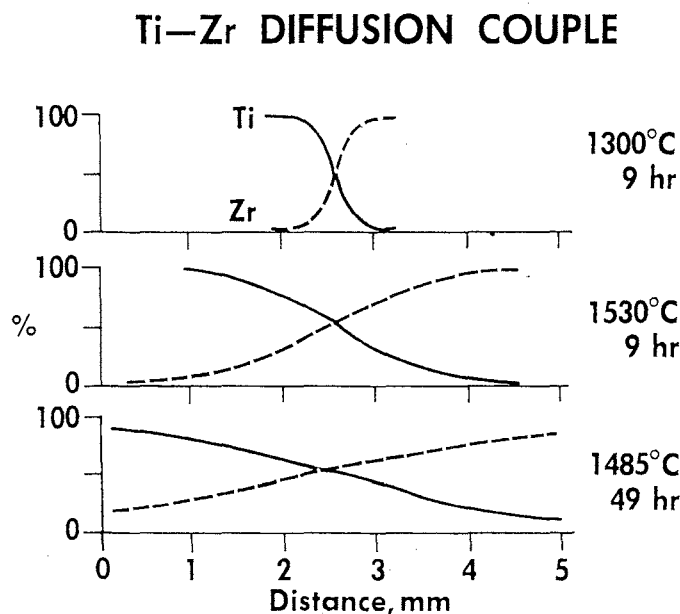


Fig. 10. When two metals are kept in contact at elevated temperatures, they diffuse into each other. At a low temperature and for a short time, the concentration gradient will be very sharp, the composition changing drastically over short distances. The electron probe lends itself beautifully to such measurements. In the example, analysis with the probe was able to map clearly the beginning of the diffusion at 1300°C when the entire diffusion had spread less than 1 mm at the interface. (Courtesy Birks "X-ray Spectrochemical Analysis," Interscience, N. Y., 1960.)

group of elements is a metallurgists's guide to the physical and chemical behavior of the infinite number of alloys that can be prepared by varying the percentage of the elements.

A related metallurgical application of the probe is the study of solid-solid diffusion. When two metals are bonded, what happens at the interface, a region often but a few microns wide? Here the microprobe, with its narrow beam, is capable of measuring very steep concentration gradients. This, in turn, shortens the time necessary to heat the contacting metals and also reduces the number of specimens that have to be prepared to obtain a complete diffusion curve. Often, in studying diffusion couples, two-phase regions may be identified. These are portions of the phase diagram where complete solubility does not exist. The boundaries of such two-phase regions can be mapped from just a single specimen with a composition somewhere in the two-phase field. This is done by varying the heat treatment of portions of the specimen and comparing the composition of the two phases so produced. In this way, the complete phase diagram of a binary system can be very quickly mapped out.

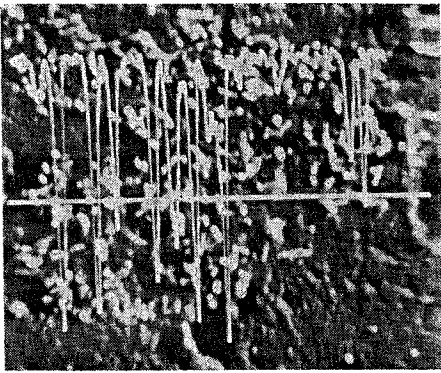
A few other areas particularly suitable to probe studies are: the effect of corrosive media on metal surfaces (liquid lithium has been found to remove chromium selectively from a surface of stainless steel), diffusion along grain boundaries, adhesion of electroplated layers to a metal, phases formed and their effect upon the bonding in different kinds of solders and brazes, the effect of pressure upon the stoichiometry of intermetallics formed by diffusion, measurement of coating thickness of evaporated metal films, the effect of different surface treatments (e.g. "sulfination") of metals.

In the field of mineralogy, phase identification is almost as important as in metallurgy but, owing to the extreme complexity of many mineral species, quantitative analysis is more difficult to carry out. In general, the electron probe is applied to zoning, exsolution precipitation, elemental diffusion, and inclusions or phases present in a polycrystalline mineral. Clues to the origin and development of ore bodies can be found by studying the structure of the ores and minerals on a microchemical scale. Thus, research by Castaing *et al.* of a French oolitic iron ore known as *minette lorraine* was taken into account in planning of a new process of enriching the ore prior to melting it in the furnace. Extensive studies of copper-iron sulfide ores have also been made, and microinclusions of Xero-time (yttrium phosphate) and Zircon (zirconium and hafnium silicate) in the complex silicate ore Thortveitite have been detected and identified. Other mineralogical applications have involved the analysis of dusts of various origins (volcanic, cosmic, sedimentation, or deposited by micro-organisms as in sea plankton).

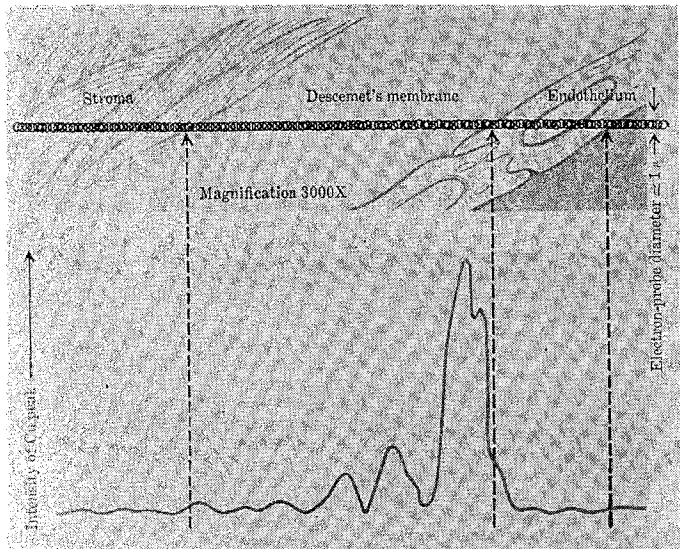
In a brilliant study of the Widmanstatten structure in nickel-iron meteorites, Ogilvie and Goldstein concluded that these meteorites exhibit a non-equilibrium structure with cooling times of the order of 10<sup>8</sup> to 10<sup>9</sup> years. The Widmanstatten structure is a type of double crystal in which the planes of one mesh with that of the other at their junction. To build up to a significant crystallite size requires astronomically long cooling periods, thus affording a means of identifying particles as meteorites.

Applications of the electron probe in biology and medicine have been few up to the present although, potentially, this may turn out to be its most important field. Because of the many metals known to be associated with normal and abnormal functioning of the body, a knowledge of their distribution is virtually certain to advance our understanding of biological systems. The work of Adler and Tousimis already cited shows that under certain specific pathological conditions, metals may concentrate in very small regions of specific organs even if

their total amount in the body is small. In other cases, a specific tissue or layer of cells normally contains a metal whose concentration is low everywhere except in that tissue. Copper in the part of the cornea observed by Adler and Tousimis is pathological. Yet a similar deposit of iron in the front surface layer of tooth enamel in several species of rodents (rats, squirrels), while phenomenologically very similar, is quite normal (it is responsible for the yellow color of their teeth). Observations such as these are being collected now on the role of silicates in silicosis, that of tin in producing pneumoconiosis, beryllium in berylliosis, *etc.* On the assumption that smaller, normal, quantities will behave similarly, massive doses of individual metals are being given experimental animals to determine the tissues in which the metals will ultimately become



**Fig. 12.** Multiple exposure on an original Polaroid film shows the distribution of calcium in the femur of a mouse. The area scan is of backscattered electrons. The line shows the locus of the intensity scan which is depicted in typical strip-chart fashion. (Courtesy of Kenneth Carroll, Sperry Gyroscope Research Center, Sudbury, Mass., R. C. Mellors, Hospital for Special Surgery, N. Y. C., who used a Cambridge Instrument Company probe.)



**Fig. 11.** One symptom of Wilson's disease is a peculiar discoloration of the cornea. Sectioning the eye of a deceased patient, Drs. Adler and Tousimis were able to locate the copper in a film but 5 microns thick between Descemet's membrane and the endothelium. (See *J. Hist. and Cyt.* 11, 40, 1963.)

lodged. In other research, bone and teeth are being examined to learn how calcium is apportioned. Already, it has been determined that calcium distribution varies with age and physical condition. The probe has been found applicable to the study of diffusion and corrosion of metallic implants in the body. Increasingly, such implants are being made in cases of arthritis yet, from a long-term viewpoint, the best metals may not have been chosen. With the electron probe, evidences of diffusion can be found after a short interval and results safely extrapolated.

Despite the sizable number of papers already published (Dr. Heinrich's bibliography lists many hundreds), the surface has not been scratched on the applications of this powerful new analytical tool. Awaiting the inspiration, skill and patience of numerous researchers now at work and those who will work with the probe in the years ahead are exciting problems which have taxed and baffled their predecessors laboring without the probe.

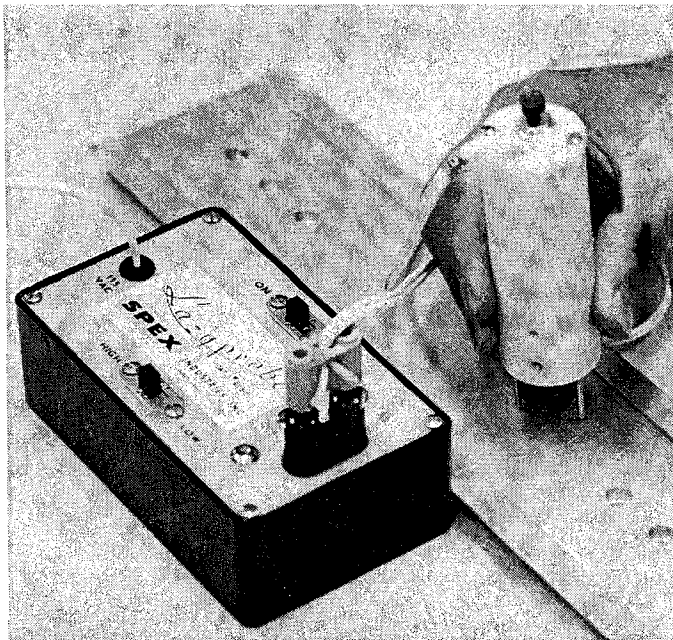
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We do not have any practical ideas about developing mountain-moving equipment but recognize the virtues of a portable, two-pound device that, like Mohammed, can go to the mountain—or your ungainly sample counterpart. We dubbed it the Lazyprobe and visualize it taking on such tasks as helping resolve whether the strut on a jet plane sitting in a hangar is welded with the proper alloy.

By a reasonably convenient procedure, a small amount of material can be transferred from a problem area of a bulky, hard-to-move object to an electrode in a hand-held probe. The power behind the probe is a neatly packaged capacitor circuit with enough energy to discharge a spark from sample to electrode tip. About 20 such sparks deposit sufficient material on



\* Based on a paper given at the Pittsburgh Conference, March, 1964, by Arno Arrak, Grumman Aircraft Eng. Co., Bethpage, N. Y., George Chaplenko, Singer Manufacturing Co., Elizabeth, N. J. and Donald Landon, Spex Industries, Inc., Metuchen, N. J.

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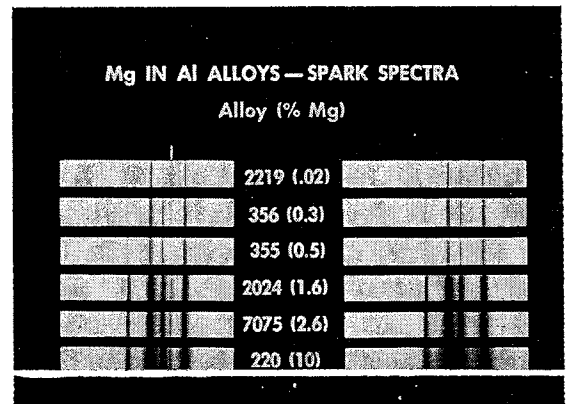
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the electrode for analysis by conventional micro techniques. Essentially non-destructive, the Lazyprobe leaves only an easily sanded-off, shallow sparking scar. As pictured, the electrode is centered inside three spring-loaded legs, which provide a ground connection, and can be positioned so the spark is directed exactly where desired. An alligator clip lead substituted for the tripod completes the ground connection when a sample is small or inaccessible (such as inside a hole).

Spectra taken by Arrak and in our own laboratory indicate excellent agreement between this transfer method and the usual point-to-plane method of alloy identification. Even quantitative results have already proved boastworthy. In steels, acceptable working curves have been obtained for nickel, silicon, vanadium and chromium down to a few tenths of a percent. Because the method is micro rather than trace, the lower limits are not exceptional. Preliminary work has already shown, however, that arcing rather than sparking markedly improves this. Oddly enough, here the periphery of a cupped graphite preform has proved best as the transfer electrode.

The Russians who originated this transfer technique claim that it overcomes matrix and metallurgical history effects. We plan to verify this in further work with many different alloy types and would encourage comments from those of you who might find this line of investigation worth your while. We harbor no notions that the Lazyprobe is a cure-all, capable of analyzing anything anywhere. But it should find major application as a means of sorting stock or finished parts with a minimum of hauling, scarring and machining.



Spectra on the left were taken with the Lazyprobe; those on the right with conventional point-to-plane sparking. Note the ease with which these aluminum alloys can be typed by either method on the basis of the magnesium content. In this work a silver (rather than copper) transfer electrode was used to permit the measurement of copper as well as magnesium. The marked line in the Lazyprobe spectra is of silver.

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