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DEPARTMENT OF MINES AND TECHNICAL SURVEYS

GEOLOGICAL SURVEY OF CANADA
TOPICAL REPORT NO. 70

VISITS TO ORGANIZATIONS CONCERNED WITH ELECTRON
AND X-RAY MICROANALYSIS IN THE UNITED STATES. ATTEND-
ANCE AT ELEVENTH ANNUAL CONFERENCE ON APPLICATIONS
OF X-RAY ANALYSIS, DENVER, COLORADO, AND THIRD INTER-
NATIONAL SYMPOSIUM ON X-RAY OPTICS AND X-RAX MICROAN-
ALYSIS, STANFORD, CALIFORNIA, SUMMER 1962.

BY
R. J. TRAILL



OTTAWA
1963

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Visits to organizations concerned with electron and X-ray microanalysis in the United States. Attendance at Eleventh Annual Conference on Applications of X-ray Analysis, Denver, Colorado, and Third International Symposium on X-Ray Optics and X-Ray Microanalysis, Stanford, California, Summer 1962.

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Introduction

The main purpose of the trip was to learn something of the present state of the art in the rapidly advancing field of electron probe microanalysis. The trip included one-day visits to five laboratories in the United States. Two of the laboratories, at Lemont, Illinois and Ames, Iowa, were equipped with Elion D. E. M. 301 electron microanalyzers similar to the instrument recently delivered to the G. S. C. In two other laboratories, at Los Angeles and La Jolla, California, A. R. L. microanalyzers have been in operation for about two years. The fifth laboratory, at Claremont, California, was of interest because an Al target X-ray tube has been built and used effectively in that laboratory for the analysis of Na and Mg in granitic rocks. Visits to the University of Denver Conference on Applications of X-ray Analysis and Stanford University Symposium on X-ray Optics and Microanalysis were included because they presented an excellent opportunity to meet leading scientists in the field of electron probe microanalysis from many parts of the world.

Argonne National Laboratories, Lemont, Illinois

The visit was confined to an electron probe laboratory in the Metallurgy Division of the Argonne National Laboratories. This laboratory is under the direction of Dr. Raymond K. Hart who obtained his Ph.D. in surface chemistry at Cambridge, England, and has subsequently gained considerable experience in electron microscopy.

The laboratory is equipped with an Elion D.E.M. 301 Electron Micro-analyzer.

The instrument was delivered to Argonne in April 1962. Difficulty was encountered in obtaining a good vacuum and the entire electron optical column had to be dismantled and each component cleaned ultrasonically before a suitable vacuum could be obtained. Minor modifications were made to the high voltage supply and one of the X-ray readout channels was found to be wired incorrectly.

The electron column has so far failed to meet specifications. The intermediate lens appears to hinder rather than help the system and might better be removed, thereby shortening and simplifying operation of the column. Dr. Hart believes that the electron optics might be improved by installing an adjustable aperture before the condenser lens and a fine aperture after the final lens. Alignment of the column has proved to be very difficult and the beam wanders considerably as its size is adjusted. Although no precise measurements of beam size have been attempted, Dr. Hart estimates that the smallest beam diameter they have observed is in the order of several microns. His estimate is based on the resolution obtained on a specimen current image of a 1000-mesh screen, and experiments with a fine aperture and Faraday cage mounted in the specimen position.

Dr. Hart plans to discard the present specimen stage, chamber, and controls, and build a new one. He is considering a revolving stage to hold 8 metallurgical specimens. Mechanical

traversing of the specimen in 3 orthogonal directions will be provided so that the specimen can be positioned within one micron. The present cumbersome system of specimen current leads to each specimen will be replaced by a single brush-type contact. A reflected light viewing system will be incorporated by means of a long working distance objective such as the Leitz UM 32/0.30 with a 18 mm. working distance, and a right angle light path using a 45 degree mirror below the specimen. A hole cut in the mirror will permit passage of the electron beam.

No results have been obtained through use of the vacuum-path X-ray spectrometer. Preliminary runs only have been made and these have shown extremely poor resolution of the X-ray spectra. Part of the trouble is believed due to the method of mounting the variable-bending mica crystal or possibly a poor crystal supplied with the instrument.

The instrument was turned on during the writer's visit and an attempt was made to produce on the cathode ray tube a specimen current image of a 1000-mesh screen. The beam that was obtained was obviously quite large, certainly greater than 5 microns in diameter, and oblong in shape, and the scanning raster proved to be incapable of resolving the 1000-mesh screen.

Dr. Hart was hopeful that the instrument would eventually meet or come close to meeting its specifications and did not appear to be concerned about the poor performance at present.

Iowa State University, Ames, Iowa

An Elion D. E. M. 301 microanalyzer is installed at the Ames Laboratory, Iowa State University. The microprobe laboratory forms part of the Metallurgy Department and is under the direction of Dr. R. H. Heidel. Dr. Heidel's main work has been in the field of X-ray spectroscopy, particularly applications to metallurgical problems.

The Elion instrument was one of the first production models. Installation of the instrument began in October 1961 and is still not complete. The electron optical system shipped with the original unit has apparently proved to be completely unsatisfactory and a new electron column was to be installed in August. Dr. Heidel has made no attempt to modify the instrument and has left development work on the unit entirely in the hands of Elion Instruments Inc. Work on the instrument by Elion technicians and engineers has been devoted entirely to attempts to produce a usable electron beam. No results have been obtained from the X-ray readout system. Dr. Heidel was satisfied that the Elion group were doing everything possible to make the unit operational, that good progress was being made, and that it was only a matter of time until the instrument would meet its specifications.

The writer accompanied Dr. Heidel on a brief tour of the Metallurgy and Metals Process Development buildings which are part of the Ames Laboratory (Institute for Atomic Research). Much of the research at this Institute is devoted to the rare-earth elements; extraction from ores, purification, and uses.

Brief discussions were held with Dr. V.A. Fassel the chief spectrographer at Ames.

Professor Donald Biggs kindly showed the writer around the Geology Department. Biggs is studying dolomite-ankerite relationships in recrystallized brecciated limestones. Some remarkable zonal growths are developed in these rocks and Biggs hoped to carry-out some electron probe studies to determine compositional variations.

Eleventh Annual Conference on Applications
of X-Ray Analysis, Denver, Colorado

The eleventh annual conference, sponsored by the University of Denver was held at the Albany Hotel on the 8-9-10 August. The writer attended the first two days of the conference and spent most of that time in informal discussions on matters concerning electron probe microanalysis. Titles and abstracts of all papers presented at the technical sessions are given below.

1. A High Temperature X-ray Diffractometer Furnace Utilizing High Frequency Heating by E.W. Franklin and S.M. Lang, Owens-Illinois Glass Company, Toledo, Ohio.

The adaptation of high frequency heating techniques to a vertical diffractometer is discussed. The heating system functions as a portion of an integrated system that provides a wide range of atmospheric and temperature control. Some of

the design problems and operating characteristics of the system are described. The useful temperature range is from less than 200°C to more than 1600°C, depending upon the furnace atmosphere and susceptors used. Gaseous pressures may be from vacuo of about 10^{-6} to about 30 psia; and the sample may be heated in oxidizing, neutral, or reducing atmospheres.

2. An X-Ray Diffractometer Cryostat Providing Temperature Control in the Range 4 to 300°K. by F. A. Mauer and L. H. Bolz, National Bureau of Standards, Washington, D. C.

The diffractometer cryostat described at the Tenth Annual Conference (1961) has been modified to provide a means for controlling temperature and for confining the vapor in equilibrium with volatile samples. Materials with vapor pressures as great as 1 atmosphere can be handled without loss of insulating vacuum, and temperatures can be controlled with an accuracy of $\pm 0.1^\circ\text{K}$ in the range 4 to 20°K, decreasing to $\pm 1.0^\circ\text{K}$ at 300°K. Data on the lattice constants and thermal expansion of the noble gases, neon, argon, krypton and xenon are given to demonstrate the suitability of the apparatus for maintaining a desired temperature while working with a volatile material.

3. Low Temperature Transitions of Some Ammonium Salts by M. Stammer, D. Orcutt and P. C. Colodny, Aerojet-General Corporation, Sacramento, California.

X-ray diffraction studies were performed on the fluoroborate, perchlorate, chloride and phosphate of ammonium within a temperature range of ambient to -185°C . A specimen holder has been designed to effect rapid cooling of the sample. Ammonium chloride shows a transition at about -30°C . The fluoroborate and perchlorate salts undergo a polymorphic transition at -185°C ; decreasing intensities of the (011) and (112) reflections of the orthorhombic modification indicates a first order reaction. Ammonium phosphate, which is tetragonal at ambient temperature, undergoes a transition when cooled to -185°C . The kinetics of the latter reaction are discussed.

4. X-ray Diffraction Analysis of Aerosols from Exploding Wires

by J. J. Stoffels, F. G. Karioris and A. G. Barkow, Marquette University, Milwaukee, Wisconsin.

Metallic wires are exploded by the current surge from a 4000 joule capacitor bank. The resulting aerosols are collected on molecular filters and analyzed with a recording X-ray diffractometer. Aerosols consisting of metallic particles result from the explosion of noble metals in air or from common metals exploded in argon. Base metal wires exploded in air produce aerosols consisting of mixtures of oxides. Studies were made on copper oxide aerosols prepared with various initial voltages on a 20 uf capacitor bank. Cupric oxide predominates in the

aerosol from explosion above 6 Kv. The cuprous oxide content is about 50 per cent at 1 Kv; 5 per cent at 6 Kv and remains fairly constant between 6 and 18 Kv. Approximately 5 per cent metallic copper is observed in all samples.

5. Recent Developments in the Measurement of Orientation in Polymers by X-Ray Diffraction by Z. W. Wilchinsky, Esso Research and Engineering Company, Linden, New Jersey.

From pole figure data, the orientation of a crystallographic direction R in any reference direction Q in a sample can be quantitatively expressed by the average $\langle \cos^2 \sigma \rangle$ where σ is the angle between Q and R in a crystal. In general, $\langle \cos^2 \sigma \rangle$ can be evaluated in terms of the experimental averages $\langle \cos^2 \phi_{hkl} \rangle$ where ϕ_{hkl} is the angle between Q and the normal to the (hkl) planes. The number of independent $\langle \cos^2 \phi_{hkl} \rangle$ measurements needed varies from one to five depending on the crystal system, hkl indices and other factors discussed. Experimental techniques found useful for measuring $\langle \cos^2 \phi \rangle$ are described.

6. Applicability of Routine Methods of Crystallite Size Analysis by R. C. Rau, General Electric Company, Cincinnati, Ohio.

A series of six beryllium oxide powder specimens whose average crystallite sizes range from about 35\AA to nearly 3000\AA were used to test a number of X-ray diffractometers. By using a predetermined diffraction geometry for each instrument tested,

measured crystallite sizes were found to be quite reproducible and well within the limits of experimental error.

7. The Zirconium-Iron System by F.N. Rhines and R.W. Gould, University of Florida, Gainesville, Florida.

A recent study conducted in this laboratory on the constitution of Zircaloy has revealed that the Zr-Fe system is not as simple as is indicated by the present phase diagram presented in the literature. This diagram indicates only a single f. c. c. intermetallic phase of the composition $ZrFe_2$. Based upon X-ray diffraction and metallographic evidence a new diagram is presented which proposes two additional intermetallic compounds of compositions Zr_3Fe and Zr_2Fe . Verification of these findings has been made by Dr. David Levinson of Armour Research Foundation utilizing electron microprobe analysis.

8. X-Ray Diffraction Studies on the Ti-Ni System by J.V. Gilfrich, U. S. Naval Ordnance Laboratory, Silver Spring, Maryland.

X-ray diffraction studies were made on the Ti-Ni system around the stoichiometric intermetallic compound Ti Ni in an attempt to clarify some confusion that exists about the phase diagram in this region, and to explain some anomalies in the physical properties of this material. Wrought and cast samples were examined at room temperature both before and

after heat treatment and at temperatures both above and below ambient. The compound Ti Ni does exist at room temperature. The phase purity of the particular sample was found to be greatly affected by such factors as minor variations in composition, heat treatment and method of sample preparation. Some confirming metallographic and physical property data will also be presented.

9. The Crystal Structure of ThPd₄, by J. R. Thomson, Imperial College of Science and Technology, London, England.

The structure of ThPd₄ has been determined by X-ray powder methods. It has the simple cubic Cu₃Au structure with $a = 4.110 \pm 0.002 \text{ \AA}$ at 80 at. per cent Pd. Interatomic distances and the range of stability of this compound and of ThPd₃ are discussed briefly.

10. The Effect of Cold-Work on the X-Ray Diffraction Pattern of a Copper-Silicon-Manganese Alloy by D. O. Welch and H. M. Otte, RIAS, Baltimore, Maryland.

Data are presented for a Cu-Si-Mn alloy deformed at room temperature by various amounts of uniaxial tension, wire drawing and filing. The observed changes in the diffraction pattern are explained in terms of the numbers of various types of imperfections introduced into the metal during cold-working.

11. Lattice Spacings in Some Transition Metal Terminal Solid Solutions

by Henry Chessin, D. S. Miller and Sigurds Araj's, United States Steel Corporation, Monroeville, Pennsylvania.

The lattice parameters of binary transition metal alloys have been determined in their terminal solid solution ranges as a function of the concentration of solute atoms and at various temperatures. A simple, reasonable theoretical calculation leads to an understanding of the relationships between initial lattice distortion and atomic size of the constituent elements when provision is made for the partial compressibility of the atom. Under these assumptions it appears, in several cases, that Vegard's Law is satisfied in terms of the partial atomic volumes. This investigation is part of a larger program to study the magnetic and crystalline lattice properties of binary transition metal alloys in terminal solid solutions.

12. X-Ray Determination of "Plastic" Changes in Copper in the Elastic Region of the Stress Application by C. M. Glass and M. K. Gainer, Aberdeen Proving Ground, Maryland.

During deformation of annealed copper, linear stress-strain relations are obtained at low values of load. However, if X-ray techniques are used to study the changes in crystallographic orientation within polycrystalline specimens, it is observed that cyclic changes in preferred orientation occur. These changes show

that in the range of load application generally considered as being below the elastic limit, large plastic deformations are occurring in microscopic regions in the metal. Analysis of the results shows that a smooth stress-strain relation may be obtained if the absolute values of orientation changes are summed, but that a cyclic relation is obtained if the quantitative changes are considered with respect to the stress axis. Theoretical justification of these results is found in application of the Erickson analysis of liquid plastics, as applied to metals. A strain orientation vector is obtained that indicates a cyclic change in the orientation vector should be formed with changes in stress. The reported X-ray studies are the first experimental proof obtained showing this change.

13. Helium Path Diffractometry and Its Application to Determination of Retained Austenite and Macrostress in Steel by R. A. McCune, University of Denver, Denver, Colorado.

The helium X-ray Path has long been used in spectrography to increase the intensity of the long wavelength X-rays. The same principle has been applied to diffractometry. Up to three-fold intensity increase is observed with chromium $K\alpha$ radiation with very little increase in background. The peak to background ratio, therefore, is improved by almost the same factor as the increase in intensity. Application of the technique is illustrated by analysis of gauge block steel for retained austenite and macrostress.

14. Some Aspects of Nondestructive X-Ray Spectrochemical Analysis of Alloys by J. R. Rickenbach Jr., The Carpenter Steel Company, Reading, Pennsylvania.

A review is presented of three basic methods of X-ray spectro-chemical analysis: the internal standard method, the absolute intensity method, and the ratio method. The ratio method is discussed at length. Included are methods of acquiring standards, sample preparation, curve plotting and a discussion of the factors contributing to the precision of the analysis. Various analytical curves are presented and discussed and the sensitivity for minor constituents is shown.

15. Design Considerations for On-Stream X-Ray Analysis by R. W. Deichert and W. R. Kiley, Philips Electronics Instruments, Mount Vernon, New York.

The sample is presented to the X-ray spectrograph through a vertical cell having a mylar window and a device to measure variations in sample density. The X-ray Spectrograph is of fixed channel, modular design, with a capacity of up to six channels. The complete Spectrograph can be translated in a horizontal plane to position itself and determine the elemental composition in a series of sample cells. The data handling uses digital circuitry to permit normal use of analog readouts or digital data logging systems.

16. Continuous Determination of Zinc Coating Weights on Steel by X-Ray Fluorescence by J. A. Dunne, Philips Electronic Instruments, Mount Vernon, New York.

The measurement of the area density of zinc coatings on steel by X-ray fluorescence is considered from an instrument design point of view. Two general approaches, measurement of the attenuation of the iron emission by the zinc coating and measurement of the zinc emission, are discussed. Calculations indicate that contrast requirements are best satisfied by the iron attenuation technique in the coating weight interval 0.2-1.2 oz/ft²/side. Experimental data collected on zinc foil samples support this contention. Advantages in the application of the zinc emission method to very thin zinc coatings are pointed out.

17. The Use of X-Ray Emission Spectrography for Petroleum Product Quality and Process Control by J. L. Caley, Standard Oil Company of California, Richmond, California.

A Norelco Autrometer is being used for process control and product quality control by a petroleum refinery. As many as one hundred analyses covering thirteen elements are run per day. Concentrations range from a few parts per million to 25 per cent.

18. Specifications and Performance Data for the A. R. L. Electron Microprobe X-Ray Analyzer by L. P. O'Brien, Applied Research Laboratories Inc., Detroit, Michigan.

Detailed E. M. X. specifications are presented.

Performance data obtained on several production instruments are discussed and some future applications of microprobe analysis are suggested.

19. Oscilloscope Readout of Electron Microprobe Data by K. F. J.

Heinrich, E. I. DuPont de Nemours and Company, Inc.,
Wilmington, Delaware.

In view of the amount of data per time unit the electron probe is capable of producing, time economy in data representation is of great practical importance. The characteristics and advantages of various previously known techniques of data representation are described, and some novel procedures are proposed.

Note: This paper by Dr. Heinrich was one of the highlights of the technical sessions. Three of the techniques described are particularly worthy of mention.

(1) Accurate quantitative analyses on binary systems can be made using specimen current measurements. The specimen current varies inversely with the atomic number of the target element, and the current can be displayed on a C. R. T. or chart recorder. Specimen current measurements have the advantage over X-ray readout that they are less dependent on the electron beam focus and are independent of X-ray optics alignment.

- (2) C. R. T. pictures of cathode luminescence effects on non-metallic specimens (and oxidized metals) are easily obtained with the A. R. L. instrument by replacing the illuminator in the light optics system with a photomultiplier tube and feeding the output to the C. R. T. scanning in synchronism with the electron beam. Such pictures often show better resolution than either X-ray or back-scattered electron images.
- (3) A concentration mapping technique was described in which areas of the sample where the concentration of a certain element falls within pre-established limits are portrayed on a C. R. T. picture of the sample. The amplified X-ray signal (or electron signal) is fed into a high-speed ratemeter and the ratemeter output is displayed on the vertical axis of an oscilloscope. A photomultiplier receives the light of the oscilloscope beam, and a mask in front of the oscilloscope screen limits this light reception to a predetermined range of the ratemeter output, and hence a predetermined range of concentration of the element in question. The amplified photomultiplier output modulates the gun bias of a second oscilloscope scanning in synchronism with the beam of the electron probe. This second scope will thus mark those areas of the sample on which the concentration of the unknown element falls between the pre-established limits. The horizontal deflection of the first oscilloscope is normally inactive, but it can be used for changing programs by shifting the beam to another set of slits. Also, by applying a horizontal sawtooth

deflection to the beam and making part of the slit so narrow that the light spot vanishes periodically, a dotted region can be applied, in addition to black and white. Multiple slits may also be used in order to create several isoconcentration contours in one operation.

20. Some X-Ray Generator Characteristics to Consider in order to Realize the Optimum Stability and Reproducibility of Intensity Measurements by R. Torkildsen, General Electric Company, Milwaukee, Wisconsin.

This paper presents some of the physical considerations which must be considered in operating an X-ray generator to obtain maximum stability and reproducibility of intensity measurements. A typical X-ray generator is discussed from the standpoint of enabling the user to realize all of the stability and reproducibility capabilities which were designed into the equipment.

21. The X-Ray Investigation of Pre-Precipitation in Supersaturated Solid Solutions by A. Lutts, Centre National de Recherches Metallurgiques, Liege, Belgium.

The study of the pre-precipitation or cold-ageing stage of the decomposition of supersaturated solutions is of considerable practical as well as theoretical interest because it is during pre-precipitation that changes in many physical and mechanical properties take place without the formation of a precipitate phase. Examples are given to show the types of zones encountered during

this stage in various age-hardening alloys. These will attempt to illustrate the contribution which the study of diffuse scattering of X-rays, guided by concepts of crystal imperfections, has made towards a better understanding of the precipitation process in alloys.

22. An X-Ray Determination of Debye-Waller Factors for Cu_2O and UO_2 and Atomic Scattering Factor for Cu in Cu_2O by C. J. Sparks Jr., and B. S. Borie, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The characteristic temperature of a material, which may be determined from the Debye-Waller factor, is an important physical property for a variety of applications. By a method developed by Borie, the Debye-Waller factor for Cu_2O and the atomic scattering factor for Cu were determined independently of each other. The scattering factor agreed well with that computed from theory. The characteristic temperature for Cu_2O at 300°K was found to be 182°K , at 88°K , its value is 162°K . Similar measurements of the Bragg maxima with a powder sample of UO_2 were not useful because of preferred orientation. However, the diffuse intensity is not so sensitive to preferred orientation and may be used to determine the characteristic temperature. Its value for UO_2 was found to be 188°K at room temperature.

23. Absorption Effects in X-Ray Fluorescence Measurement of Elements in Oil by E. L. Gunn, Humble Oil and Refining Company, Baytown, Texas.

The influence of absorption of fluorescent intensity under specific conditions of interest has been studied from three viewpoints: varying the depth through oil of a solid elemental specimen, varying the depth of a solution containing the element dissolved in oil, and varying the amount of the dissolved element in oil over a broad range in concentration. The experimental results are compared between elements as well as with theory.

24. Sodium and Magnesium Fluorescence Analysis, Part I, Method
by Burton L. Henke, Department of Physics, Pomona College,
Claremont, California.

It is well known that sensitive sodium and magnesium analysis is extremely difficult if not impossible with conventional X-ray spectrographs. It is demonstrated, however that analysis for sodium and magnesium can be accomplished with sensitivity comparable to that conventionally obtained for elements such as aluminum, silicon and phosphorus providing that the conditions for excitation and measurement of the associated soft X-rays are optimized. A high intensity demountable tube using an aluminum anode has been developed which can be used interchangeably with the conventional spectrographic X-ray source. This provides a large amount of incident radiation, aluminum foil filtered, optimumly close in wavelength to that of the line radiation being excited. A gypsum analyzing crystal is used along with greatly

reduced beam collimation. The standard flow proportional counter and pulse height discrimination is employed. An appropriate filter, such as aluminum foil is used as a window for the counter to provide further discrimination and enhanced signal-to-background ratio.

Note: Dr. Henke's main work at present is on methods of analyzing for the light elements carbon, oxygen, nitrogen and fluorine.

Preliminary studies on the use of photo and auger electron measurements for analysis in the light element range looks very encouraging and an analytical apparatus is now under construction. It is anticipated that results of this study will be made known at the next annual conference in Denver (1963). The aluminum anode X-ray tube is interchangeable with the Norelco X-ray tube in the Norelco Vacuum X-ray spectrograph. The tube is operated at 10-15 Kv and 150 Ma. Fluorine in teflon has been detected with a peak intensity of 46 c.p.s. and a background of 4 c.p.s. Analyses can be performed on milligram amounts of material; for example, analyses have been made for P, Na and Mg in a single drop of blood.

25. Sodium and Magnesium Fluorescence Analysis, Part II - Application Silicates by A.K. Baird, D.B. McIntyre and E.E. Welday, Pomona College, Clarmont, California.

Counting rates in excess of 400 c.p.s. at a peak to background ratio of 18 on 3.5 per cent Na_2O in rocks permit high precision quantitative analysis for light elements in silicates.

Special advantages of fluorescence analysis in the 10\AA region include an ease of discrimination by excitation potential and by high dispersion using crystals having large $2d$ spacings. Minor modifications to the X-ray optic path combined with electronic discrimination make the method ideal for Na and Mg. Routine runs over periods of several days have been made possible by a new technique of calibration involving computer corrections for systematic drift from any source. Repeated tests show that the total analytical error, including specimen preparation, closely approaches that of the counting statistics used, and that the drift corrections are complete. In granitic rock analyses the resulting precisions (standard deviation/mean) are one per cent for the determination of two to five per cent Na_2O , and two per cent for 0.25 to 1.0% MgO.

26. Determination of Catalyst Residues in Polyolefins by X-Ray

Emission Spectroscopy by G. D. Smith and R. L. Maute, Monsanto Chemical Company, Texas City, Texas.

Methods have been developed for the direct determination of aluminum, chlorine, titanium and iron in polyolefins.

27. Experiences of X-Ray Analysis in Steel and Ferroalloy Production

by J. Baecklund, Avesta Jernverks Aktiebolag, Sweden.

Avesta steel works manufacture stainless steel, low alloy steel, alloys for precision casting, welding electrodes and

ferrealloys. A spectrographic laboratory for production control has been in operation for two years. Carbon, phosphorus and sulphur are determined optically, while silicon, titanium and heavier elements are determined on X-ray equipment.

28. Precision X-Ray Diffractometry by L. F. Vassamillet, Mellon Institute, Pittsburg, Pennsylvania, and H. W. King, Imperial College of Science and Technology, London, England.

Errors arising from imperfections in the instrument and misalignment of the X-ray source with respect to the diffractometer have been studied experimentally. The results are presented and discussed in terms of the resultant error in the determination of the lattice parameter of a cubic crystal. Errors determined both analytically and empirically are discussed in relation to the extrapolation procedures commonly used for diffractometers. It is shown that, depending on the construction of the instrument, the effect of imperfections in the gears may almost double the error in the final extrapolated value of a lattice parameter.

29. Recent Advances in Electron-Probe Analysis by J. V. P. Long, University of Cambridge, Cambridge, England.

The electron-probe analyzer has been developed to the point where analyses can be made on volumes of about one cubic micron at the surface of a specimen for elements above sodium in

the periodic table with a concentration sensitivity of the order of 0.1 to 0.01 per cent. Progress in the analysis of the light elements centres at present mainly on the use of non-dispersive detectors and computer techniques for the resolution of overlapping pulse-height distributions. With such methods qualitative detection of elements down to beryllium has been achieved in the presence of their near neighbours. Efforts to increase the spatial resolution of the probe have led to the use of thin specimens which are partly transparent to electrons. As a consequence of this approach, apparatus has been developed in which an electron microscope with facilities for selected area diffraction has been combined with an electron-probe analyzer. The widening range of application of the electron-probe technique has disclosed problems in the interpretation of quantitative data, and it is clear that more information on the process of X-ray production by electrons is required before semi-empirical methods can be entirely eliminated. Examples of the use of the method in metallurgical and mineralogical studies illustrate some of the current trends in the refinement of measurement technique and interpretation of experimental data.

30. Factors Governing the Structure of Intermetallic Phases by

F. Laves, Institut für Kristallographie und Petrographie, Zurich, Switzerland.

A review of the crystal structures of the elements shows some prevailing tendencies of atomic arrangement. These are

discussed as packing, symmetry and connection principles. Counteracting temperature and bond factors can be recognized. The same principles and factors are responsible for the formation of alloy structures, taking into account additional factors due to the components' similarities and dissimilarity in size and electronegativity. Similarity favours solid solution and dissimilarity favours compound formation. A discussion of 1 and 2 component structures will be given in some detail to show (1) the competition of geometrical principles and physico-chemical factors in determining atomic arrangements of alloys, and (2) the value of rules for making guesses on the probable occurrence of compounds and their chemical composition of poly-component systems yet unknown.

31. Indexing of Powder Diffraction Data by P. M. de Wolff, Technisch Physische Dienst T. N. O. en T. H., Delft, Netherlands.

Despite the advances of the electron micro-diffraction technique, the determination of unit cells of microcrystalline compounds still depends in many cases on the interpretation of the X-ray powder pattern. The interpretation depends strongly on the precision of the data which can be improved by application of monochromators in diffractometry. Some possible methods are discussed. Some of the existing methods of interpretation are suitable for computers, at least in the initial phase of the procedure. This is illustrated by application of a zone-finding program for the complete solution of a given pattern.

32. Iron Oxide Determination by X-ray Fluorescence for In-Process Control of Solid Propellant and Premixes by R. E. Lamborn and

F. J. Sorenson, Thiokol Chemical Corporation, Brigham City, Utah.

Finely divided iron oxide is used as a burning rate catalyst in several solid rocket propellants. The concentration is critical and must be accurately determined as a quality control point before the propellant is cast in the motor case and cured. The use of X-ray fluorescence has been investigated as a means of satisfying the analysis time requirements while meeting the prescribed accuracy of ± 1 per cent of the amount present. When ten specimens from each of three premixes were analyzed for iron content, the observed within-mix mean relative standard deviation was 0.28%; for propellant analyzed under the same conditions, the mean relative standard deviation was 0.35%.

33. Determination of Aluminum in Iron-Aluminum Alloys by Means of Vacuum Fluorescence by J. C. Wagner and F. R. Bryan, Ford Motor Company, Dearborn, Michigan.

Aluminum is determined within the range 2-13% in an iron matrix. A calibration curve is based on chemically analyzed samples. Repeatability of X-ray determinations is within a standard deviation of $\pm 0.25\%$ Al. Chemical and X-ray agreement is reached within a standard deviation of 0.3% Al. X-ray analytical time is approximately one-tenth the time required for chemical analysis.

34. The Daily Use of a Basic Norelco X-Ray Spectrograph in an Aluminum Reduction Laboratory by W. B. Eastman, Kaiser Aluminum and Chemical Corporation, Ravenswood, West Virginia.

The X-ray spectrograph is used for (1) the determination of calcium in reduction cell electrolyte, (2) the analysis of cast iron for Si, P, Mn and S, (3) the analysis of carbon materials for S, K, Ca, V, Mn, Fe and Ni.

35. Practical Applications of Filters in X-Ray Spectrography by M. L. Salmon, Fluo-X-Spec. Laboratory, Denver, Colorado.

Applications of filters are routine and useful techniques in X-ray diffraction and can also be useful in X-ray spectrography to improve analytical results with very simple procedures. Filters over the window of the X-ray tube may be used to minimize background from the target element and/or elements in other components of the X-ray tube. Placement of filters in the X-ray beam path between the sample and the analyzing crystal or between the analyzing crystal and the detector is also a useful procedure to reduce interferences by elements exhibiting lines at closely adjacent wavelengths.

36. X-Ray Spectrographic Analysis of Rare Earths in YFe Garnet Powders by J. C. Lloyd, and J. D. Kuptsis, I. B. M. Thomas J. Watson Research Center, Yorktown Heights, New York.

Analysis schemes for eleven rare earths (Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb) are presented. Straight line calibrations result in all cases, usually over a range from below 0.5% to better than 6.0%. Errors were held to $\pm 5-10\%$ even using simple sample preparation techniques.

37. Particle Size and Mineralogical Effects in Mining Applications by F. Bernstein, General Electric Company, Milwaukee, Wisconsin.

Data are presented relating to particle size effects. Problems arising from differences in mineralogy in samples are discussed.

38. X-ray Analysis of Mining and Mineral Processing Material by H. T. Dryer, Applied Research Laboratories Incorporated, Dearborn, Michigan.

39. The Preparation of Pole Figures for Polymers by Computer Techniques by J. W. Jones, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware.

The diffraction data are collected on punch tape under the control of a programmer for the orienter which permits stepwise or continuous scanning. A computer is programmed to prepare the data for an off-line automatic curve plotter.

40. Diffraction Effects from Irradiated Aluminum Single Crystals by H. E. Kissinger, General Electric Company, Richland, Washington.

Large single crystals with extensive substructure and crystals essentially free of substructure, all with faces cut parallel to crystal planes, were subjected to neutron irradiation. Subsequent examination by X-ray diffraction revealed pronounced changes in integrated intensity and Debye-Waller temperature factor for the crystals free of substructure; these effects disappeared upon re-etching the surface. Laue photographs showed that the normal single-crystal pattern was partially obscured by a polycrystalline effect which also disappeared upon etching. Crystals with extensive substructure showed no such effects. The diffraction evidence supports the view that irradiation-induced defects in aluminum migrate to and collect at the crystal surface if no internal trapping sites exist.

41. Oriented Single Crystals of Aluminum for X-Ray Diffraction

Analysis by J. Dhosi, C.P. Gazzara and R. Middleton, Watertown Arsenal Laboratories, Watertown, Massachusetts.

A simple gradient heating apparatus has been developed and used successfully in reproducibly growing oriented aluminum single crystals of 99.995% purity suitable for X-ray diffraction analysis. The crystals are grown from 3/16 inch diameter rods and the shape of the crystals eliminates the necessity of a cutting operation. The crystalline perfection is approximately ten times greater than those obtained by the Czochralski technique.

42. The Characterization of Large Single Crystals by High Voltage X-Ray Laue Photographs by H. S. Peiser, National Bureau of Standards, Washington, D. C.

Large single crystals can be examined by conventional X-ray diffraction procedures only at their surface or by destructive sectioning. With the limitations inherent in polychromatic X-ray photography, high voltage Laue pictures are found to give some information on the internal quality of large crystals. Observed asterism is similar to that seen in conventional Laue photographs and gives information on crystal perfection. A primary extinction effect can be used as striking proof of good crystals being capable of scattering coherently over large distances.

43. An X-Ray Study of the Structure of the Oxide Cathode by P. Lublin, General Telephone and Electronics Laboratories, Inc., Bayside, New York.

An X-ray diffraction study has been conducted on the emissive coating (Ba, Sr, CaO) of experimental diodes from which thermionic emission data were taken before X-ray analysis.

44. X-Ray Measurement of the Static Lattice Distortion in the Solid Solution of Oxygen in Titanium by F. R. L. Schoening and F. Witt, The Franklin Institute Laboratories, Philadelphia, Pennsylvania.

Oxygen was introduced into single crystals of titanium in successive stages up to the limiting concentration of 33 atomic

per cent. The intensities of selected Bragg reflections were measured with a single crystal diffractometer. The variation of the intensities with oxygen concentration is attributed to three factors: (1) the additional scattering from the oxygen atoms, (2) a change in the Debye-Waller factor and (3) an exponential factor originating from the distortion around the oxygen atom.

It was confirmed that the oxygen atoms occupy the octahedral, interstitial sites in the hexagonal titanium lattice. The Debye-Waller factor, for the $h00$ reflections which are not influenced by the lattice distortions, increased with increasing oxygen concentration indicating an increase in the characteristic temperature. For the $00l$ reflections, which are affected by lattice distortions as well as thermal vibrations, the combined Debye-Waller and static distortion factor decreases with oxygen concentration. The exponential strain factor was obtained from these data by assuming that the Debye-Waller factor was anisotropic but varied uniformly with oxygen concentration. The experimental strain factor was then compared to a theoretical estimate.

Using published data on the variation of the lattice parameter with oxygen concentration, it is possible to predict the intensity reduction due to lattice strains. The need to introduce simplifying assumptions and lack of detailed values of the elastic

constants for titanium limited the calculations to finding upper and lower limits of the effects to be expected. Nevertheless, a quantitative agreement between the predicted and measured intensity reduction within a factor between two and three was found. It was therefore concluded that the interpretation of the observations in terms of strains around the interstitial atoms was justified.

45. On the Use of a Modified Radial Distribution Analysis for Indexing Powder Patterns by A. F. Berndt, Argonne National Laboratory, Argonne, Illinois.

A modification of the theory of X-ray radial distribution analysis is presented. This modification can serve as a guide to the unit cell dimensions and may be useful in indexing powder patterns of unknown structures, although the use of trial and error methods is not eliminated. This technique is shown to give consistent results with known structures and is applied to the indexing of powder patterns of Pu_3Ru and Pu_5Ru_3 . The powder pattern of Pu_3Ru can be indexed on the basis of an orthorhombic unit cell with $a = 6.216$, $b = 6.924$, $c = 8.093\text{\AA}$; and Pu_5Ru_3 on the basis of a tetragonal unit cell with $a = 8.092$, $c = 10.023\text{\AA}$.

Pomona College, Claremont, California

The interesting papers presented at the Denver meeting by Henke and Baird on analysis for Mg and Na in rocks by the X-ray spectrographic method prompted the writer to visit Dr. Baird's

laboratory in the Geology Department at Pomona College. Pomona is a small and apparently well-endowed college with a maximum enrollment of about 2000 undergraduate students. Dr. Baird is currently engaged in a chemical study of a Cretaceous granite body in California. The chemical analyses of the rock samples are being made by the X-ray spectrography method.

Samples are prepared for analysis by simply grinding the rock to a particle size of about 2 microns and pressing the powder into a bakelite jacket, with no addition of binder, using a hydraulic press. Although Claisse and others have shown that particle size effects can cause serious analytical errors, no such effects have been noted in the analyses at Pomona.

A Norelco Vacuum X-ray Spectrometer is used for the analyses. Sensitivities have been improved greatly in the range Al to K by modifying the number of plates in the parallel plate collimator to give best over-all response in this region. A special X-ray tube used to excite the Mg and Na spectra has been designed so as to be readily interchangeable with the standard W or Mo tube of the Norelco instrument. Modifications to the Norelco unit involve only removal of the specimen rotation shaft and addition of a mounting plate to the cover panel. The X-ray tube is a demountable water-cooled tube which is evacuated by means of a small vac ion pump attached to the tube assembly. A specially shaped anode coated with Aluminum provides a large amount

of incident radiation. The collimator is removed and a gypsum analyzing crystal used for the determination of Na and Mg.

Samples are run in batches of between 50 and 150. A standard sample is read before and after the complete run and the elapsed time since starting the analyses is recorded for each intensity measurement. Instrumental drift has been found to vary linearly with time and a drift correction computed from the elapsed time is applied to each measurement.

Dr. Baird plans to build a simplified two-position spectrometer around the Al anode tube to do the analyses for Na and Mg in rocks; he will use the standard Norelco unit for determination of the heavier elements. He informed the writer that the Norelco company are now developing a commercial version of the Al anode tube which will be sold as an accessory item for use on the vacuum spectrometer.

University of Southern California, Los Angeles

A visit was made to the Microprobe Laboratory in the School of Engineering at U.S.C. The laboratory is under the direction of Dr. D.B. Wittry, designer of the electron probe microanalyzer that is manufactured and sold by Applied Research Laboratories Inc. The visit coincided with a special two-week summer course on methods and applications of electron analysis being given by Dr. Wittry and guest lecturers. Although little time was available for discussion with

Dr. Wittry the writer was able to meet several of the participants in the course and guest lecturers, all of whom are presently or will soon be working in the field of electron microanalysis.

Mr. Ray W. Fitzgerald from the University of California at La Jolla was in charge of the laboratory work on the summer course and kindly showed the writer the A. R. L. instrument and discussed its capabilities. Breakdown of the recorder, however, prevented an actual demonstration and forced cancellation of the laboratory program for that date. Some of the features of the instrument are as follows:

(1) The electron gun uses a 0.004" tungsten hairpin filament operated at saturation.

(2) The HV supply is variable from 3 to 50 KV. Line and load regulation is 0.005%; ripple tolerance on 60 cycle is 0.005% and long term stability is rated within 0.02%.

(3) Positioning of the specimen can be made to less than one micron, and the specimen can be step-scanned automatically in increments of from 1 to 10 microns.

(4) The diameter of the electron beam is variable within useful limits of between 0.3 microns and 300 microns. The maximum beam current obtainable in a beam of about 0.3 microns diameter is 0.02 microamps.

(5) Electrostatic deflection plates are used for beam scanning. The standard scanning area is 45 x 45 microns and this area is reproduced on a C. R. T. screen at magnifications of 22, 444, 888 and 1776X. The

scanning area may be modified to 4.5×4.5 microns resulting in a possible magnification of 17,760X.

(6) The X-ray optic system is capable of both high resolution and high sensitivity. The $\text{Ni K}\alpha_1$ and $\text{Ni K}\alpha_2$ lines are resolved using an 11 inch LiF crystal. Pure Mg excited at 30 KV with a beam of diameter 0.3 microns and a beam current of 0.03 microamperes gives a measured peak intensity of 11,500 c.p.s. and a peak/background ratio of 370:1. The half-width of the Mg peak under these conditions is 0.007\AA .

University of California at La Jolla, California

The writer spent a profitable day with Drs. G. Arrhenius and K. Fredriksson at the microprobe laboratory at the Scripps Institute of Oceanography. The laboratory is equipped with an A.R.L. micro-analyzer and studies are undertaken on materials of geological interest. Fredriksson is conducting an extensive study of stony meteorites, using the electron probe to determine the chemical compositions of large numbers of grains of olivine, orthorhombic pyroxene, nickel-iron phases and troilite in each meteorite.

The following techniques of sample preparation are in general use: (1) The samples are polished using standard metallographic and petrographic techniques. The final stage of polishing is accomplished using a Syntron Vibratory Polisher loaded with microcloth and one micron diamond powder dispersed in a thin oil. (2) Before coating with a conductive layer, the samples are cleaned ultrasonically and are dipped

in distilled acetone. (3) A carbon coating is used almost entirely and is applied by means of a standard Edwards High Vacuum coating unit. Tests have shown that the thickness of the carbon layer can vary by a factor of two or three without affecting the results of quantitative analyses. Film thickness is not measured but is kept reasonably constant by using the same coating conditions each time. (4) The carbon coating is applied to metals samples as well as non-conducting materials. This has been found effective in reducing beam wander on some of the smaller metal samples surrounded by plastic. (5) Standards are mounted in hollow brass screws about 1/8" in diameter which are polished and adjusted as to height of surface by screwing them into a brass disc. A dozen or more standards are mounted on a single brass disc which occupies one of the sample holder positions in the instrument.

Third International Symposium on X-Ray Optics and X-Ray Microanalysis,
Stanford University, Stanford, California

The symposium was attended by about 180 scientists from many countries. With the exception of Russian institutions, nearly all of the main laboratories where electron probe studies are undertaken were represented. The writer was thus able to meet and enter stimulating discussions with many leading scientists in this relatively new field of analysis.

It was apparent from the tone of the symposium that in most of the laboratories that have been in operation for several years

instrumental problems have been largely solved, and considerable effort is now being put forward towards perfecting the quantitative analytical aspects of this method of analysis. Problems that have been outlined and are under active investigation include: grain boundary effects; secondary fluorescence; atomic number corrections; and absorption corrections. Development of new types of instrumentation is continuing and preliminary reports have been made on the following: an instrument having a 90 degree X-ray take-off angle; a combined electron microscope and microanalyzer; and an all-purpose interchangeable electron column.

One full day of the symposium was devoted to technical sessions on electron probe microanalysis. Abstracts of some of the more interesting papers follow.

1. Electron Probe Measurements Near Grain Boundaries by S. J. B. Reed and J. V. P. Long, Department of Mineralogy and Petrology, Cambridge, England.

Electron probe measurements close to grain boundaries require correction for the effects of fluorescence and finite probe diameter.

Measurements of fluorescence excitation across artificial boundaries between pure elements provide data which can be used to determine the fluorescence correction near grain boundaries in natural specimens. The observed concentrations of calcium in narrow exsolution lamellae in pyroxenes have been corrected in this way. The same information has been used to check a modified

form of Castaing's formula for fluorescence correction in homogeneous specimens, covering a wider range of accelerating potentials and atomic numbers.

When there are concentration changes within the probe diameter it should be possible to improve the effective resolution, given a knowledge of the distribution of X-ray intensity in the source. This can be obtained by scanning the probe across an artificial boundary over a distance of a few probe diameters. Such a technique has been used to determine the nickel concentration in taenite at the boundary with kamacite in iron meteorites.

2. Calculation of Fluorescence Excited by Characteristic Radiation in the X-Ray Microanalyzer by P. Duncumb and P.K. Shields, Tube Investments Research Laboratories, Cambridge, England.

Four expressions are available from the work of Castaing, Wittry, and Birks, for calculating the intensity of K fluorescent radiation excited by K characteristic radiation of another material. These relate the intensity of fluorescence to that of the primary radiation, so that the contribution due to fluorescence in the total intensity measured in the spectrometer can be evaluated. Birks' formula is simple but approximate; the expressions of Castaing and Wittry become successively more accurate but more complicated as the form assumed for the distribution of primary emission with depth is made to approach that obtained in practice.

It is thus of some interest to compare the expressions in some detail for a number of practical cases, in order to see whether the extra complexity is justified. A method is also suggested for extending the theory to cover the case of K emission excited by characteristic L lines and vice versa.

3. A Suggested Correction for Secondary Fluorescence in Electron Probe Analysis in a Region of a Steep Concentration Gradient by R. Dils and L. Zeitz, Department of Materials Sciences and Biophysics Laboratory, Stanford University, Stanford, California.

When concentrations are determined by means of the electron probe near a steep concentration gradient, a correction must be made for the secondary fluorescence contribution from the higher concentration matrix. In measurements on the diffusion of a relatively heavy element in a light matrix, e.g., Zn in Mg, it can be shown that the required correction is so great as to make the uncorrected profile grossly in error. With the position of the electron beam as far away as 150 microns from the boundary of the Zn/Mg couple, it can be shown that the correction required as a result of secondary fluorescence from the pure Zn is still large.

There are several factors which make it impractical to develop a general analytical expression for the correction: (a) anisotropy of emission from the primary source; (b) lack of an adequate expression for the energy distribution of primary X-rays

for a sample of varying composition; (c) complexity involved in determining the volume distribution of the intensity of emitted secondary fluorescence radiation which is detected.

A correction based on the measurement of secondary fluorescence obtained from a mechanical couple of the pure elements is proposed. A Zn/Mg couple with the diffusion profile accurately determined by tracer techniques is used to determine the error involved in the proposed correction.

4. The Target Absorption Correction in X-Ray Microanalysis by
M. Green, Cavendish Laboratory, Cambridge, England.

When a solid target is bombarded by an electron beam, characteristic X-rays are generated below the surface. The intensity of the radiation reaching a detector set at an angle, θ , to the surface is reduced to a fraction $f(\chi)$ of its original value by absorption in the target. The amount of absorption depends on the take-off angle θ , and on the spatial distribution of X-ray production within the target. These factors are in turn related to the parameter $\chi = (4/e) \text{ cosec } \theta$, and E_0 , the incident electron energy. The results of X-ray microanalysis may require correction and in this process values of $f(\chi)$ can play an important part.

Experimental measurements of $f(\chi)$ have been made for 13 elements with E_0 in the range 1-50 keV. For elements where

characteristic radiation is produced mainly by direct electron impact, the experimental results are well represented by a universal set of curves, when plotted in terms of $(E_0 - E_k)$. This quantity is the difference between the incident beam energy and the K shell ionization energy. In heavy elements, where fluorescence produced by the continuous X-ray spectrum is important, the experimental values of $f(\chi)$ do not fit the universal curves. Agreement is achieved when a suitable correction is made for the fraction of the characteristic radiation produced by the photoelectric absorption of the continuous spectrum.

5. A Method to Calculate the Absorption Correction in Electron Probe Microanalysis by J. Philibert, Institut de Recherches de la Sidérurgie, Saint-Germain-en-Laye, France.

The principles of the absorption correction to be applied to intensities measured with an electron probe microanalyzer have been given by Castaing. If k_A is the ratio of the intensities of a given line as emitted by the specimen and by the corresponding standard (pure A), and if C_A is the true concentration (weight per cent):

$$C_A = k_A \cdot F_A(\chi^A) / F_{sp}(\chi^{sp}).$$

This relation holds as far as the first approximation is valid (α coefficients equal unity). The $F(\chi)$ function depends on two parameters, namely, the accelerating voltage and the atomic

number. Since only a limited number of experimental $F(\chi)$ curves are available, a theoretical formula has been derived, the simplified form of which permits a rapid calculation of the correction:

$$1/F(\chi) = (1 + \frac{\chi}{\sigma}) \left[1 + h (1 + \frac{\chi}{\sigma}) \right]$$

where $\chi = \frac{u}{\rho} \operatorname{cosec} \theta$

θ = take-off angle

σ = Lenard's coefficient

$h = K \cdot A/Z^2$

The parameter σ depends only on the accelerating voltage, and the parameter h only on the atomic number and the atomic mass. Therefore the latter will be different for standard and specimen. The σ and k values have been adjusted to fit the experimental curves of Castaing and Descamps.

6. The Effect of Atomic Number in Quantitative X-Ray Microanalysis by G.D. Archard and T. Mulvey, Research Laboratory, Associated Electrical Industries, Limited, Aldermaston, Berkshire, England.

In the early stages of X-ray microanalysis it was assumed that there would be an approximately linear relation between the intensity of characteristic X-radiation generated within a specimen and the concentration of the element under consideration. The extension of the range of elements that can be analyzed and the desire for accurate quantitative analysis of multi-component

specimens have made it desirable to re-examine the fundamental basis of the electron probe method of X-ray microanalysis from first principles. Such an investigation involves an accurate calculation both of the penetration of the electrons into the specimen and the back scattering of electrons from the specimen. A suitable method of calculation has been developed and applied in the first place to binary alloys such as Cu-Zn and Cu-Al. For close neighbours in the periodic table a linear relation between intensity and concentration in general applies, but for elements of considerable difference of atomic number a correction amounting to as much as 40 per cent may have to be applied in extreme cases. This correction has to be made in addition to any correction of the measured intensities to allow for absorption and fluorescence effects in the specimen.

7. Correction for Atomic Number Effects in Microprobe Analysis by D.M. Poole and P.M. Thomas, U.K.A.E.A. Atomic Energy Research Establishment, Harwell, Berkshire, England.

Consideration is given to the necessity for carrying-out a correction to take account of the so-called atomic number effects when alloy samples are analyzed by direct reference to pure metal samples; i.e., a correction of the type given by Castaing's second approximation. A procedure for estimating the parameters involved in the correction has been suggested by Poole and Thomas (J. Inst. Metals, 1961-62, Vol. 90, p. 228); the success of this

method is assessed in the further case of a series of copper-gold alloys examined at various probe voltages and for which accurate chemical analyses are available. Details are also given for the lattice parameter curve at 25°C for the copper-gold system determined from samples taken from the alloys examined in the microprobe.

8. Scattering of Electrons from a Microanalyzer Target by G. Shinoda and R. Shimizu, Osaka University, Osaka, Japan.

A simple theoretical expression of backscatter ratio from film target at given incident angle, based on the assumption that simple large-angle scattering is dominant and energy loss is given by Thomson-Whiddington law, is derived and its validity discussed from the experimental point of view. The backscatter ratio of electrons from Al film is measured using electrostatic retarding potential technique for 4 - 20 kev. incident electron. Above 10 kev theoretical curves come to better quantitative agreement with experiments while quantitative correspondence, unlike the qualitative one, becomes poorer with the decrease of incident energy.

If Whiddington's experimental value is taken up as the constant "a" in the Thomson-Whiddington law, the theoretical curve in case of Al-film of twice the thickness corresponds well to the experimental one. The results show that if we apply this

simple model to the backscattering phenomenon of electron, the electron behaves as if its travelling pathlength in the target were about two times longer than that assumed in the experiment, and Everhardt's theory is quite applicable to the film targets of light elements.

9. X-Ray Microanalysis of Elements in the Range $Z = 4-92$, Combined with Electron Microscopy and Electron Diffraction by P. Duncumb, Tube Investments Research Laboratories, Cambridge, England.

New methods of X-ray spectroscopy offer the hope that X-ray microanalysis can be extended to cover elements down to atomic number 4, though some loss of quantitative accuracy is to be expected. At the same time it should be possible to improve the resolving power by a factor of 10 or so, ie. to 0.1 micron. For the study of thin specimens such as extraction replicas of carbide particles, there is considerable advantage in combining X-ray microanalysis with electron microscopy and diffraction in the one instrument. Selected particles can then be studied by their morphology and crystal structure as well as by their composition. The combined techniques could also be profitably applied to the study of metal film specimens prepared from bulk material.

An instrument to fulfill these various functions is at present under development. In addition to a normal crystal spectrometer it makes use of a thin-window proportional counter

for detection of wavelengths greater than 10\AA . The effective wavelength discrimination of the counter is improved by a technique of spectrum synthesis, in which the unknown spectrum, recorded on magnetic tape, is matched by mixing spectra from the pure elements recorded in synchronism.

10. Electron Microscopy and X-ray Microanalysis by W. C. Nixon and R. Buchanan, Engineering Laboratory, Cambridge University, England.

Several methods have been suggested for improved resolution in X-ray microanalysis when using thin specimens. One method of combining electron microscopy and X-ray microanalysis in the same instrument is to employ two electron guns. One gun is used to illuminate the specimen and the following lenses form a magnified image for location of a selected area. The other gun is used to form a reduced probe of electrons for X-ray production from this small area. A horizontal electron optical bench has been constructed to test this configuration.

11. The Use of Specimen Current in Electron Probe Microanalysis by J. Philibert and E. Weinryb, Institut de Recherches de la Siderurgie, Saint-Germain-en-Laye, France.

If the specimen in a electron probe microanalyzer is isolated from the ground, a current I_{sp} may be measured through a galvanometer. The relation between the ratio of the specimen and

probe currents I_{sp}/I_{probe} and back scattering coefficient is derived. The experimental conditions for the measurement of the true back-scattering coefficient are given; in particular the introduction of a negatively biased grid just above the specimen surface is required. The possibilities of such measurements for the purpose of quantitative microanalysis are discussed. Images of the specimen surface may be obtained with the help of a scanning device. Applications of this technique to the study of multiphase alloys, non-metallic inclusions in steels, and fracture surfaces are briefly described.

12. The "Intercol" Electron Beam System by W. C. Nixon, R. V. Ely, and C. R. E. Legg, Engineering Laboratory, Cambridge University, England, and Electron-Physical Instruments Ltd., New Malden, London, England.

An interchangeable electron beam column has been designed and constructed for use in a variety of electron optical applications. When the components are assembled to produce a point source of electrons this unit may be used as the electron source for X-ray microscopy and X-ray microanalysis. Interchangeability of the electron lenses, work chambers, etc., permits a variety of applications, both X-ray and electron, with the same basic instrument.

13. On a New Electron Probe X-ray Microanalyzer Having a 90 Degree Take-Off Angle by S. Shirai and A. Onoguchi, Akashi Seisakusho Ltd., Tokyo, Japan.

In the electron probe microanalyzer the best way to take off the X-rays is along the normal to the sample surface to the crystal goniometer, while the electron beam illuminates the sample perpendicularly. We have examined several basic characters of 90 degree take-off angle by using a simple experiment equipment in which the electron beam is bent almost 90 degrees between the electron lens system and the sample. The advantages of this system are as follows: (1) the intensity of continuous X-rays becomes minimum in the normal direction, thus the background level of the X-ray spectrum is diminished. (2) Absorption of X-rays in the sample itself can be reduced, thus the accuracy of quantitative microanalysis is much increased and moreover the sensitivity of detection of light elements contained among heavy elements can be increased. (3) Error in quantitative microanalysis caused by the topography or microstructure of sample surface is eliminated completely.

14. An X-ray Microanalyzer for Elements of Low Atomic Number by R. M. Dolby, Cavendish Laboratory, University of Cambridge, England.

A microanalyzer system has been developed especially for coping with the long wavelength X-rays emitted by the light

elements, notably carbon, nitrogen and oxygen. From the outset it was considered important to be able to produce scanning pictures at a usefully high rate. For this reason low collection efficiency spectrometers such as diffraction gratings could not be used. The proportional counter was therefore chosen as the detector and disperser, compensation for low energy resolution being achieved by a special pulse analysis scheme in which the outputs of several pulse height analyzers and ratemeters are treated as a set of simultaneous equations which can be solved in a simple computer network, thereby recovering the intensities of the individual lines. The apparatus is described and its use is demonstrated in several scanning picture examples which show the surface concentration of elements as light as beryllium with a resolution of 4-5 microns.

15. Analysis of Heavy Elements (Z>80) with the Castaing Microprobe:

Application to the Analysis of Binary Systems Containing Uranium

by A. Kirianenko, F. Maurice, D. Calais, and Y. Adda, Centre d'Etudes Nucleaires de Saclay, Gif sur Yvette S. et O., France.

The essential point for quantitative microanalysis by the Guinier and Castaing method is its absoluteness. R. Castaing has given all the physical basis necessary to calculate the different corrections which must be applied to the experimental results for the analysis of elements lying between magnesium ($Z = 12$) and gold ($Z = 79$). In the case of heavier elements the experimental results

had shown the importance of some correcting factors and this has led us to determine some physical data in order to apply the Castaing theory to high Z elements..

The analysis of uranium in the binary systems U-M, where M is any element of the periodic table, is taken as an example; ten different systems have been studied experimentally. The obtained results allow us to perform analysis without any calibration alloys or standards except pure elements.

16. The Application of X-Ray Microanalysis to the Study of Micro-segregation in Steel by D.A. Melford, Tube Investments Research Laboratories, Cambridge, England.

A study of diffusion in a complex material - mild steel - is at present in progress. Diffusion of copper and nickel in steel in the temperature range 850-900°C is predominantly via grain boundaries at which marked microsegregation of these elements can occur. The aim of this investigation is to determine what factors, apart from temperature, affect diffusion rates under these conditions.

The X-ray microanalyzer is being used extensively in several roles in this investigation in an experimental attack on the problem which would not be possible by any other method. In addition to point-by-point quantitative analysis, semi-quantitative imaging techniques have been found helpful. The addition of a hot-stage so that dynamic observations can be made is also of great assistance.

17. The Use of the Electron Microprobe Analyzer in the Study of Binary Metal Alloy Systems by P. Pietrokowsky and J.R. Maticich, Autonetics Research Center, Division of North American Aviation, Inc., Anaheim, California.

The electron microprobe analyzer has been used to investigate phase relationships in the copper-titanium binary alloys system. The literature concerning these alloys indicates that there is lack of agreement as to the number and composition of intermediate phases in that portion of the phase diagram between copper and the intermediate phase TiCu. We have investigated as-cast and homogenized alloys in this region of the phase diagram by means of the electron microprobe analyzer. The results of the optical metallography are compared with results obtained from observing back-scattered electrons.

18. Electron Probe Analysis of Minerals in the System FeS_2 - CoS_2 - NiS_2 by G. Springer and J. V. P. Long, Department of Mineralogy and Petrology, University of Cambridge, England.

In the system FeS_2 - CoS_2 - NiS_2 , four naturally occurring minerals, pyrite (FeS_2), cattierite (CoS_2), vaesite (NiS_2), and bravoite ($(\text{Fe}, \text{Ni}, \text{Co})\text{S}_2$) are involved. Earlier experimental studies on this system, using dry melts, suggested a large area of immiscibility. Chemical analyses have shown, however, that most natural bravoites lie exactly in this immiscibility range. More

detailed chemical information became desirable when microscopical observations revealed that the analyzed bravoites were mostly inhomogeneous, exhibiting in many cases a zonal structure of variously coloured shells several microns apart.

In the present work, zoned bravoites have been analyzed with the electron probe. Analyses have also been made on synthetic bravoites, prepared under hydrothermal rather than dry melt conditions. The synthetic products had grain sizes less than 50 microns and showed complex zonal structures, some of which have been resolved by the electron probe.

It has been found that the compositional range of the hydrothermally synthesized bravoites coincides with that of the natural minerals. Results are presented in the form of scanning pictures, and graphs showing quantitative distribution of elements.