

lysis is localized, whereas X-ray fluorescence analysis of the longer established kind, which depends on excitation by hard incident X-rays, averages the composition over several square centimetres. The wheel is, however, coming full circle with the introduction of macroscopic X-ray analysis by electron excitation, which in its latest form allows measurements of elements down to boron (Price, *Metals and Materials*, 7, 140; 1973). The use of greatly improved detectors in conjunction with non-dispersive energy analysis has steadily improved sensitivity as well as light-element detection in both microscopic and macroscopic variants of electron-excited X-ray analysis.

Electron probe microanalysis used to be regarded as a form of surface analysis, but in fact the effective depth over which composition is integrated is of the order of  $1\ \mu\text{m}$ . True surface analysis, by contrast, requires physical methods that explore a single surface monolayer, or  $\sim 1\ \text{nm}$  depth at most. There is now a very varied array of techniques available—the emission of photons, electrons, ions or neutral particles can be stimulated by any of these four, or by heat or an intense electric field for good measure.

More than twenty permutations of stimulation/emission exist, each with its own distinct physical theory, sensitivity, speed, depth of measurement, convenience and limitations. Electron-excited X-ray (that is, photon) emission is merely one among many. The on-looker who is concerned with using these techniques rather than developing them may be forgiven for being bemused. Most survey articles, of which there is no shortage, fasten on one technique to the exclusion of all others. For this reason, a new survey entitled "New Developments in the Surface Analysis of Solids" does special credit to the author, Benninghoven of the University of Cologne (*Appl. Phys.*, 1, 3; 1973). (The journal is a new English-language venture by Springer-Verlag which replaces the excellent German-language *Zeitschrift für angewandte Physik*, which ceased publication at the end of 1971.)

Benninghoven is a specialist in surface studies and his name is especially associated with secondary-ion mass spectrometry (SIMS), of all methods the one best suited to analyse a single surface monolayer. He describes in some detail in his survey the advantages of SIMS (including the ability to follow chemical reactions at the surface as they progress), but devotes attention also to the various forms of secondary-electron spectroscopy (including both Auger electron (AES) and photoelectron spectroscopy, the latter usually known by its originator's designation of ESCA—electron spectroscopy for chemical

analysis), and even to the very novel technique of "soft X-ray appearance potential spectroscopy", which depends on the sudden appearance of characteristic X-ray emission lines as the energy of bombarding electrons is gradually increased. Benninghoven explains the essential physics of each technique without getting side-tracked along fascinating but inessential detours (such as the mechanism of surface-ion emission in the sputtering situation) and shows how emission of different types can be reliably distinguished, how the state of chemical combination can be assessed by some techniques but not by others, how and why the effective depth of analysis varies between techniques, which are best for analysing light elements including hydrogen, and how sensitivity varies. The examination of states of chemical combination is particularly important in many applications, but the very power of this technique (see Siegbahn, *Endeavour*, 32, 51; May 1973) has led to its use predominantly in

"bulk situations" rather than in surface studies hitherto.

Another technique, related to SIMS, is ion-scattering spectrometry (ISS). Here an exploring beam of incident low-energy ions, often He or Ar, is scattered from the surface layer: the energy distribution of the same ions is measured after scattering, and simple calculations based on Rutherford scattering theory permit deductions as to the masses of the atoms in the surface layer. This technique is outlined in a clearly and comprehensively written survey of trace analysis techniques for solids (both for surfaces and for bulk solids) by Kane and Larrabee (*Annl. Rev. Mat. Sci.*, 2, 33; 1972). This review can with benefit be read in association with Benninghoven's.

Overall, Benninghoven's most useful survey leaves the impression that SIMS, a technique not yet widely familiar, has particular promise as a highly sensitive and discriminating method of identifying and analysing surface species.

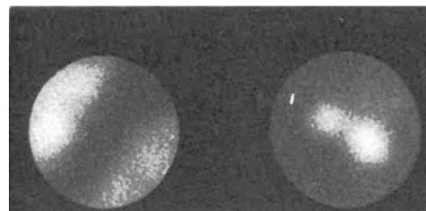
## New Techniques for Ionospheric Research

THE simplest model of the ionosphere is one in which the electron concentration at a given height does not vary with position. It is a good first approximation in most situations, but for many years ionospheric workers have been considering the ways in which it fails to represent the real ionosphere; for example, spatial irregularities of various kinds are often found, and there have been attempts to study their structure and movements, often in the hope of obtaining information about winds or waves in the ionosphere.

Two Australian communications in *Nature Physical Science* next Monday (June 18) each describe a different improvement in technique to study such phenomena. Both use large arrays of aerials which can achieve high angular resolution in the reception of radio waves at frequencies from 2 to 6 MHz, but differ greatly in their method of handling the received signal. Briggs and Holmes use for each aerial a superheterodyne receiver connected to a transducer which forms part of an acoustic array—an analogue of their radio receiving system—under water. If the acoustic sources lie on a plane surface they would simply produce an acoustic field analogous to the original electromagnetic field, and this is not immediately useful. The sources are, however, arranged on a spherical surface in such a way that a plane wave falling on the aerials gives rise to an acoustic wave focused on an image plane. The position of this focused point is a measure of the direction of arrival of the original radio wave. A set of transducers on this image plane

energizes an array of light-emitting diodes to make visible the directions of all incident radio waves.

The figure here shows on the left the distribution of radio wave intensity over the array and on the right the angular distribution obtained from it by the acoustic technique; two modes of propagation can be distinguished. The method can also be used to follow the reflexion points of waves from a fixed transmitter and thus to study irregularities. The transmitter need not be pulsed nor indeed controlled by the experimenter, so uses in radio astronomy and in direction-finding are quite possible.



The method of Brownlie *et al.* is more limited in application. A beam is formed by transmitting pulses from one arm of a cross and receiving them on the arm at right angles, and is steered by phase shifters under computer control. By rapid scanning a display can be produced showing the angular distribution of received radio waves. The technique is clearly very suitable to the study of highly irregular ionospheric structures such as "spread-F". Similar systems have been constructed previously for different purposes, but with receiving beams only (for example, Morris *et al.*, *Proc. Instn. elect. Engrs.*, 110, 1569; 1963).