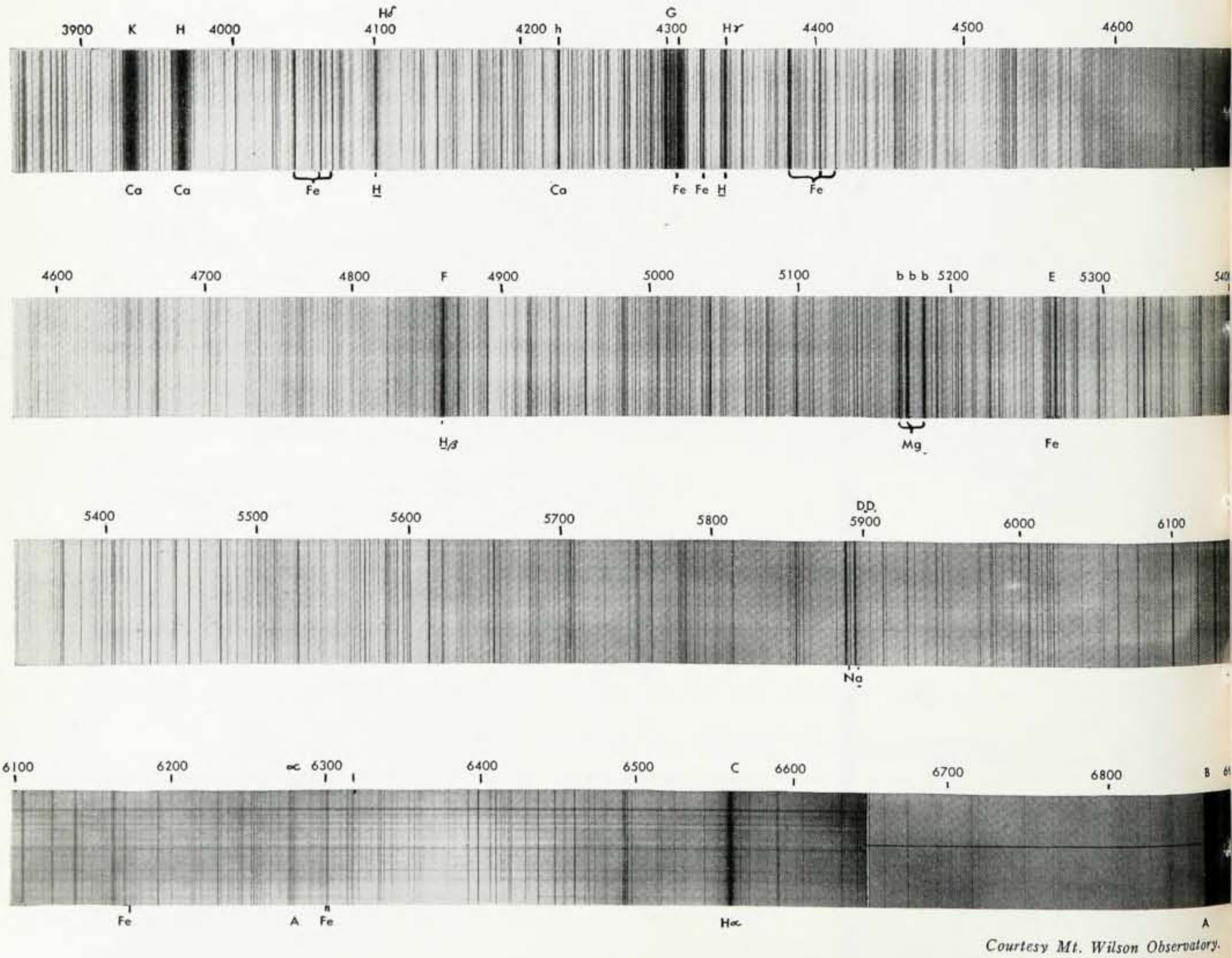
SPECTROSCOPY

Solar spectrum made with thirteen-foot spectroheliograph.



Courtesy Mt. Wilson Observatory.

TOOL FOR SCIENCE AND TECHNOLOGY

by ***Ralph A. Sawyer***

From Newton's curiosity about the "phenomenon of colors" there grew spectroscopy, until recently the physicist's prime tool for exploring atomic structure, and now of ever growing usefulness to industry.

Spectroscopy has provided not only the information but the inspiration for some of the most striking advances in the knowledge of the nature of matter and of the structure of the atom and the molecule. Very early the spectrum stimulated the minds and the imagination of men; and spectroscopic research is one of the keys which has unlocked the secrets of the universe.

The record extends back for three centuries to Newton. In 1666, at the age of 23, Newton bought a glass prism "to try therewith the phenomena of colors." Shining light through a prism, he knew, would disperse it into a rainbow-colored band and this band he called the spectrum. He found that the spectrum is really a series of colored images of the light source and, further, that when once dispersed by a prism, light is not again dispersed, or broken up, by a second prism but is merely further bent or refracted. Newton realized, then, that "light is a heterogenous mixture of rays" and that in the prism they are "parted or sorted from one another." And so Newton's genius solved a riddle of the centuries and wiped out the earlier false notions which had held that colors arose from various mixtures of black and white, and that the colors from a prism

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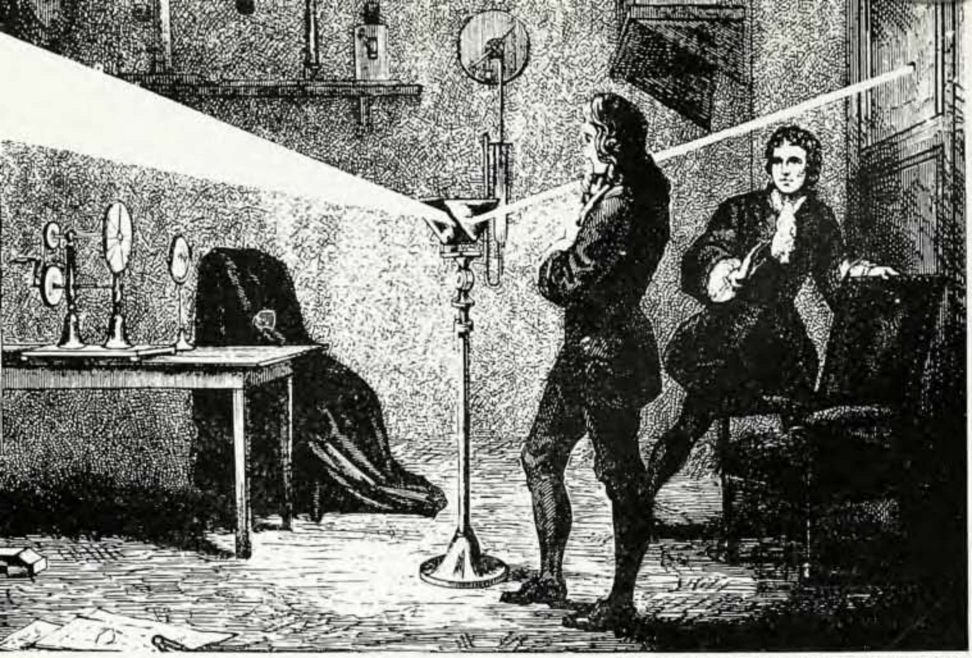
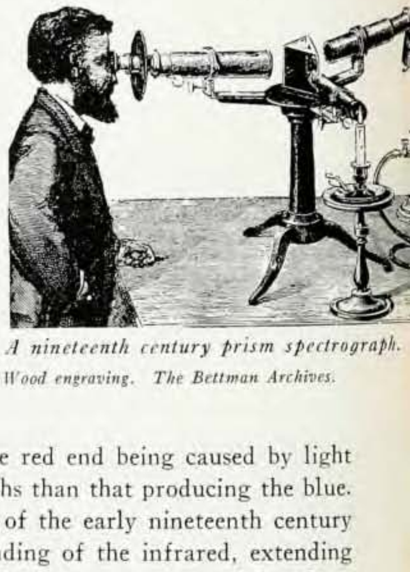


Newton trying the phenomenon of colors.

Woodcut by Guillon. The Bettman Archives



A nineteenth century prism spectrograph.
Wood engraving. The Bettman Archives.

were produced, in some unexplained way, by the prism itself from a homogeneous, white light. Newton's observations were, of course, fundamental to all our present knowledge of light.

Clue to the Sun's Atmosphere

Interest and research in the spectrum was carried on by the succeeding generations of scientists, and the nineteenth century saw, both in Europe and in the United States, considerable study of the spectra emitted by flames, arcs, and sparks. With rather crude equipment, and inaccurate standards and methods of measurement, these early spectroscopists worked at examining and cataloging the brightly colored slit images, or spectral lines, which they saw through the eyepieces of prism spectroscopes, and at classifying their similarities and differences. Fundamentally, their apparatus was a source of light, a prism to disperse the light, and a telescope to observe what had come through and how much it had been bent. A narrow slit placed between the light source and the prism became the effective light source, and thin, sharp line images of this slit were produced in the telescope by the colored light rays which had been separated by the prism. It was possible, then, to measure the angles at which these lines had been bent and on that basis to catalog them.

The lines which they saw, ranging from red through yellow to blue, constitute, of course, the visible spectrum, the red end being caused by light of longer wavelengths than that producing the blue. The spectroscopists of the early nineteenth century had little understanding of the infrared, extending far beyond the visible red spectrum, or of the ultraviolet, extending far beyond the blue end.

Moreover, handicapped as they were by inadequate equipment and impure light sources, they were in doubt on a point that today seems axiomatic, namely, that every different atom or molecule has a spectrum of its own which is characteristic of it. In 1859, however, G. R. Kirchhof, professor of physics at Heidelberg, was able to show that the spectrum emitted by the atoms of any one element is emitted by no other kind of atoms and serves as the surest identification. He went on to explain the dark lines in the sun's spectrum in terms of the absorption

The Balmer series of hydrogen as it appears in one of the hydrogen shell stars.

of light by atomic vapor in the sun's atmosphere. With the aid of his chemist colleague, Bunsen, he identified many elements in the sun's atmosphere and discovered, with aid of the prism spectroscope, two new elements, rubidium and caesium.

These achievements, the first great contribution in this field since Newton, founded modern spectroscopy; but more than that, they electrified the intellectual world of the day no less than did the work of Einstein a half century later. For man had unlocked one of the secrets of the universe: he knew now that the sun was built of the same elements as his earth and he felt, too, that he was a step closer to the mystery of the structure of the atom.

Quantum Theory

With major help from spectroscopy, understanding of the ultimate structure and laws of the atom and the molecule progressed, though slowly. Improvements in equipment and methods led, in 1900, to accurate charts showing the distribution of the light energy, emitted by a "black body," throughout the infrared and visible regions. From these it was clear that the theories of radiation which had developed on the basis of the classical laws of mechanics to explain how atoms in a hot body could give off light of a particular wavelength or energy were inadequate to explain what was actually observed. Max Planck, studying this difficulty, was led to resolve it in 1901 by his quantum theory which has now become the basis for all theories of atomic and molecular action.

To fit the observed facts of spectral radiation, both at high and low temperatures, Planck found it necessary to assume that a radiating or oscillating particle or system cannot have any value of energy from zero upward but only certain discrete values which increase by exact multiples of a minimum value determined by a new universal constant h, and that energy is absorbed or radiated only in transitions or changes from one of these value states to another, again in multiples of this new constant h times the frequency of the radiation.

It was clear that this new and revolutionary theory must have a direct and fundamental application to the emission and absorption of spectral lines by atoms and of bands by molecules. The data which spectroscopists had been accumulating for some years were available, and as early as 1885 Balmer had found that the wavelengths of the nine known lines in the visible and near ultraviolet spectrum of hydrogen could be expressed with great accuracy by a very simple formula which indicated these lines are part of an infinite series of lines approaching a definite limit in the ultraviolet.

In the following years spectroscopists in many countries found similar series, and more complicated ones, in the line spectra of most of the elements. They were able to show similarities between the spectra of the atoms of the same chemical families, such as the alkalis or the alkali earths, or of the same valence, and they furthermore found that the regularities in the spectra of ionized atoms, *i.e.*, atoms which have lost one outermost electron, resembled those of the normal spectra of the element which fits in the preceding column of the periodic table.

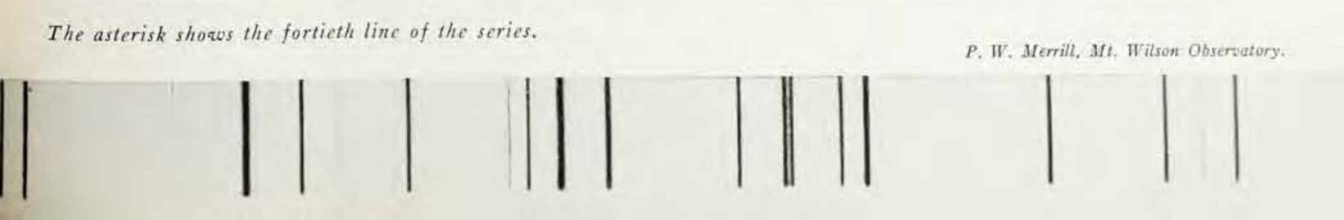
Electricity and the Atom

Another striking spectroscopic achievement of this period that gave a vital clue to the architecture of the atom was the discovery by P. Zeeman in 1896 that the spectral lines emitted by an atom are broadened or split up into several lines when the radiating atoms are subjected to a strong magnetic field. This historic event, which is not so well known as the discovery at about the same time of radioactivity by Becquerel and of x-rays by Roentgen, was nevertheless as important a milestone as those discoveries because of the impetus it gave to our understanding of the structure of the atom and of matter. For, with the aid of the theory developed by Lorentz, it led at once to a calculation of the electrical charge of the particle in the atom whose motions must radiate the light which makes up the spectrum and, indeed, showed that these charges were of the same size as those that J. J. Thomson had just found in his experiments with the charged particles in evacuated tubes. Thomson had discovered the electron; the spectroscope now showed that the electron was responsible for the light emission of the atom and gave another clue to atomic structure.

The stage was set, then, for Bohr's theory of the hydrogen atom. Applying the Planck quantum theory to the atom and assuming that the hydrogen atom consisted of a central heavy and positively

The asterisk shows the fortieth line of the series.

P. W. Merrill, Mt. Wilson Observatory.



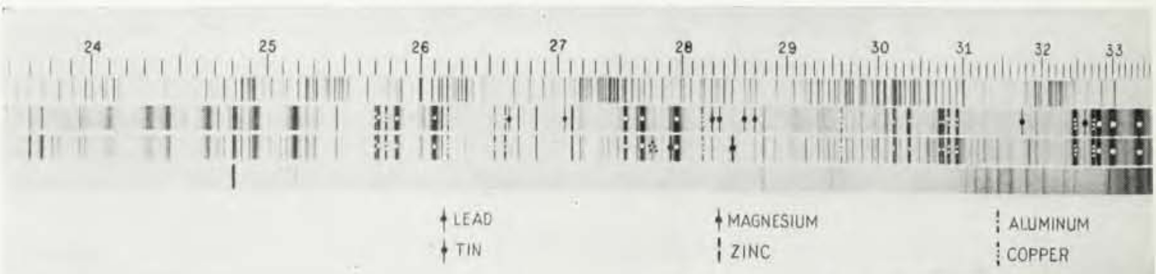
charged nucleus about which a single electron moved in circular orbits and that this electron radiated or absorbed spectral lines in jumps or transitions from one orbit to another, Bohr was able to deduce the Balmer formula and predict precisely where the hydrogen spectral lines should lie. The crowning achievement of this theory was that it made possible the quantitative explanation of the hydrogen spectrum and without the use of arbitrary or adjustable constants.

Bohr's spectacular success with the application of the quantum theory was the stimulus and foundation for the truly remarkable and now familiar and extensive theoretical work on the structure of the atom and the molecule. It became clear that every atom must have as many different and independent spectra as it had electrons—one corresponding to each stage of ionization as one electron after another is stripped from its external structure. Since there are ninety-six elements, and since each element will have as many spectra as the number of its electrons, the number of possible spectra, calculated by beginning with the one of hydrogen and summing up the atomic numbers through the ninety-six of curium, is 4656. It is hardly likely that all of these spectra will ever be analyzed, even partially, for the spectra of increasing stages of ionization move further and further into the ultraviolet and require increasingly violent light sources to excite them and special techniques and skill to separate them from the spectra of higher or lower excitations. The most highly ionized spectrum to date from which any lines have been identified and classified is that of the eighteenth spectrum of copper, *i.e.*, copper from which seventeen outer electrons have been removed. The lines identified in this spectrum all lie in the extreme ultraviolet or vacuum region of spectroscopy, and can be photographed only if light source, spectroscope, and photographic plate are enclosed in a high vacuum, since no known optical materials are transparent to these short wavelengths.

Quick Detection

In the accessible spectral region, which reaches from wavelengths in the far infrared that overlap those of short radio waves to ultraviolet wavelengths as short as those of soft x-rays, literally hundreds of thousands of lines of the ninety-six elements have been measured, and series and other regularities have been found in some four hundred and fifty of the spectra of the various stages of ionization of about eighty of the elements. Yet it is safe to say that no spectrum has ever been completely measured or analyzed, or ever will be, since, as was pointed out above, each spectrum has an infinite number of lines. Nevertheless, from careful measurements of even a few lines much valuable information can be obtained, such as: the energy required to remove the outermost remaining electron in the atom (ionization potential), and magnetic or mechanical data on the atomic nucleus, and the relative abundance of the isotopes of the atom.

Again, since the certain identification of even one spectral line of an element is positive evidence of its presence in the light source, the spectroscope provides a rapid and sensitive means of identifying elements. Thus, not only the elements in the sun, but the elements in any solid or liquid which can be vaporized and excited in an arc or spark discharge, or in a gas or vapor which can be used in a gas discharge tube, can be readily identified. With suitable spectrographic equipment, an experienced



Courtesy of Bausch & Lomb Optical Co.

QUICK DETECTION

Spectra of two die casting alloys bordered with the arc spectra of iron (top) and of graphite electrodes (bottom). The spectrum of the upper alloy, which failed in service, shows excessive amounts of tin and lead were present and magnesium, a beneficial constituent, was absent.

operator, aided by comparison charts showing the location of the important spectral lines of the elements, can rapidly and inexpensively do qualitative analysis of a wide variety of materials. Almost all the ninety-six elements are amenable to spectrographic analysis, although the metals are easier to work with and to excite in discharges than metalloids and nonmetallic elements or gases.

There is a wide range in the sensitivity of response or ease of excitation of the various elements. For the alkali metals, for example, as little as one part in a million can be detected in favorable cases, while for metalloids in minerals or halogen gases in gaseous mixtures, the sensitivity may not be better than one percent. The analysis may be made very rapidly; in some favorable cases observation can be made visually with an eyepiece attachment to a spectroscope, and qualitative analysis—for example of steel samples—can be done almost as rapidly as the samples can be inserted in a spark gap or arc before the spectrograph slit. Even when a photograph of the spectrum must be made and developed, rapid procedures for photographic processing and projectors for viewing the spectrogram alongside an identified and marked comparison chart or spectrum make possible a complete qualitative analysis in fifteen or twenty minutes. Since this type of analysis requires very small amounts of material and need not be destructive of samples, it has great advantages wherever it is applicable.

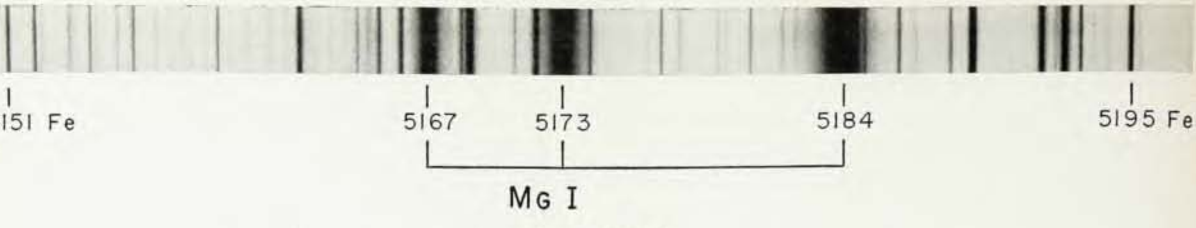
Quantitative analysis by the spectrograph is almost as fast as qualitative analysis and is based on the fact that when an element is present in a body of other materials to the extent of only a few percent, both the number and intensity of its spectral lines are proportional to the amount present. Accordingly, in cases where samples of known and graded content are available, spectra of these samples made under standard conditions with controlled light sources and measured on accurate microphotometers provide standard curves by comparison with which the analysis of unknown samples of similar composition can readily be determined. The concentrations covered may range, under suitable conditions, from a ten-thousandth of a percent to ten percent or more. The accuracy at low concentrations should be better than that of chemical methods and the error ought not to be over five percent in any case. A single analysis can be completed in fifteen to thirty minutes, under favorable conditions once the procedures have been established and the standard samples tested, and a single observer can handle thirty to fifty routine samples a day, determining several minor constituents in each sample.

Hundreds of samples a day may be handled in large industrial installations. For example, the steel laboratory of the Ford Motor Co., operating on a twenty-four hour basis, with three or four operators on a shift, can analyze as many as one thousand samples a day, making determinations of two or three alloying elements in each sample. Equipment is now coming into use by means of which the line intensities are recorded directly by photo-electric cells (rather than on a photographic plate) and can be read instantly from an oscillograph. Such equipment will be able to give an analysis of a routine sample in a minute, or less.

In the metal industries, particularly, the applications of the spectrograph to routine composition and purity analysis have been numerous, and the savings in time and cost are significant. In fact, the great production records of the past war could hardly have been attained without the increased efficiency thus attained in composition control. The applications of spectroscopy to criminal investigations, to medicine, biology, agriculture and to many industrial control problems are numerous and rapidly increasing. Applied spectrographic laboratories throughout the world are numbered in the thousands and it is certain that the spectrographs in such laboratories are now many times more numerous than those in university laboratories.

Molecules, Too

What the line spectrum is to the atom, the band spectrum is to the molecule. The atoms and the electrons in a molecule are moving in such complicated ways in relation to each other that the sharp spectrum lines representing the energy given off as electrons jump from one orbit to another are replaced by dense groups of lines, or bands. The band spectrum of the molecules of any compound, consisting ordinarily of numerous and complicated band systems, is unique and characteristic of that particular molecule and can be used to identify its presence. In some few cases these band spectra may be excited in emission sources similar to those used to excite the line spectra of atoms. More commonly, however, the molecules are rather easily dissociated,

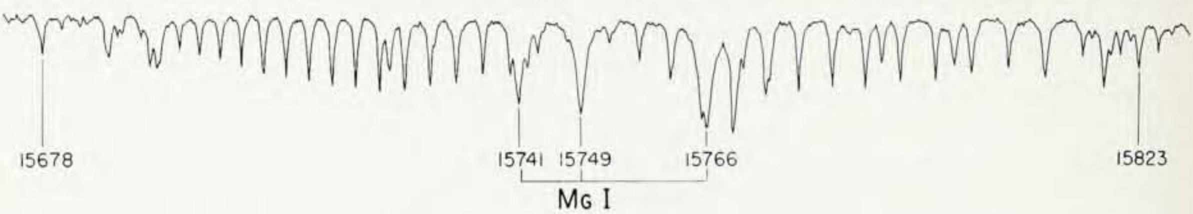


SOLAR SPECTRA

Portion of photographic spectrum, above. The black lines are caused by the absorption by the atoms in the atmosphere of the sun of the light emitted by the hot lower layers. These dark lines were first observed by Fraunhofer in 1813 and explained by Bunsen in 1859. The region shown is in the green part of the spectrum, and a strong triplet of the natural magnesium atom is identified.

Portion of the infrared spectrum made with photo-electric detector, below. The absorption of the magnesium triplet is shown in the center. The symmetrically spaced absorption lines on either side are members of a carbon dioxide band and show the presence of this band in the earth's atmosphere.

Courtesy McMath-Hulbert Observatory, University of Michigan.



or broken up, by such sources, and their band spectra must therefore be observed by passing a beam of white light containing a continuous range of wavelengths through a column of the gas or through a liquid solution of the substance under investigation, and noting the wavelengths removed by absorption.

A very great number of the important molecules or compounds exists as colorless vapors, gases or solutions. This lack of color means, of course, that these substances have little, if any, absorption in the visible part of the spectrum. In this category are most carbohydrates, oils, hydrocarbons, alcohols, ethers and many proteins. These molecules, as well as most other compounds, may have spectra outside the visible region in either the ultraviolet or infrared, or both. However, because significant parts of the band spectra of many important molecules lie in the infrared, the terms molecular and infrared spectroscopy are often used almost interchangeably. In the visible and ultraviolet regions, photographic techniques can be and usually are used, but in the infrared, because photographic-plate sensitivity falls off rapidly there and fails completely as the waves get longer, special observing techniques are needed. The domain is consequently often treated as a separate research field. The detectors of radiation in this region are often those which respond to the absorption of heat energy, such as thermocouples, bolometers, and radiometers, although light-sensitive crystals are also used. Various kinds of automatic recorders are employed and some remarkably effective and rapid systems have been devised which, in a few minutes, can map the energy distribution in an absorption or emission spectrum throughout a wide range of the infrared.

From these infrared data, the molecular structure and dimensions of many of the simpler molecules have been determined, and as the theory of tri-atomic and poly-atomic atoms is developed and extended, the infrared data will provide the indispensable tools and verifications of the theory. Infrared observations of the planets have given much data on their atmospheres—have shown, for example, that methane and ammonia exist in the atmosphere of Jupiter, and that the atmosphere of Venus has at least one hundred times as much carbon dioxide as does our own and that the temperatures are too high to support human life. To cosmogonists and philosophers such information is, of course, challenging and stimulating.

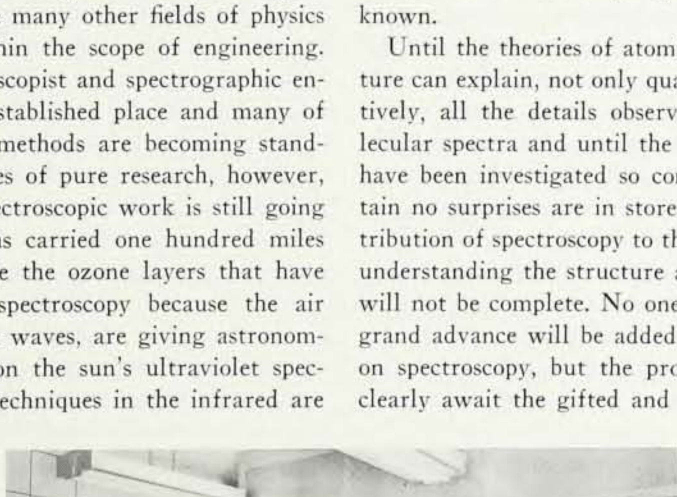
In chemical, biological, and industrial laboratories the molecular spectrum is rapidly assuming the same importance for analytical, purity, and control tests that the line spectrum of the atom holds. Although the band spectrum of a molecule is completely characteristic of the molecule, and the intensity and development of the bands are fixed by the abundance and temperature of the compound, the usefulness of molecular spectra is somewhat limited by the overlapping of the complicated band spectra of different atoms, the similarity of the spectra of related organic compounds, and the difficulty in adequately resolving some of the band structures. Lately microwave spectroscopy, in which very short radio waves are analyzed in the way light waves are for the visible region, is opening up a whole new field in molecular spectroscopy. The infrared spectroscope is rapidly becoming as common as the spectrograph in industrial laboratories. Ten years ago hardly an instrument maker in the world offered for sale an infrared spectroscope or spectrophotometer intended for routine or industrial use. Today several such instruments are on the market and the number of new ones and of new applications indicates their increasing importance. In vitamin production, in the oil industries, in organic chemical work, these instruments are now indispensable.

Applied Physics

Spectroscopy, then, through its analytical applications, has joined the many other fields of physics which have come within the scope of engineering. The industrial spectroscopist and spectrographic engineer now have an established place and many of their procedures and methods are becoming standardized. In laboratories of pure research, however, much fundamental spectroscopic work is still going forward. Spectrographs carried one hundred miles aloft by rockets, above the ozone layers that have limited astronomical spectroscopy because the air absorbs the ultraviolet waves, are giving astronomers new information on the sun's ultraviolet spectrum; and improved techniques in the infrared are similarly extending man's knowledge of the sun's spectrum at the long wavelength end. Recent studies of the hydrogen spectrum by methods of high resolution have shown that the earlier theories of the hydrogen atom are inadequate to explain completely even this simplest atom and will lead to revisions of the theories of atomic structure. The problems of molecular structure, which become tremendously more complicated for poly-atomic molecules than for di-atomic ones, yield slowly to study and advances will be facilitated and inspired by the more extensive and intensive data which are continually being provided.

Some of the spectroscopic equipment now being used bears little resemblance to the prisms and gratings long familiar to spectroscopists. For example, the newly developed ultra-high frequency radio-oscillators and detectors which radiate wavelengths in the conventional infrared regions are being utilized to study the absorption of gases and vapors at resolutions tremendously higher than any previously known.

Until the theories of atomic and molecular structure can explain, not only qualitatively but quantitatively, all the details observed in atomic and molecular spectra and until the details of these spectra have been investigated so completely that it is certain no surprises are in store, the fundamental contribution of spectroscopy to the scientist's problem of understanding the structure and behavior of matter will not be complete. No one can say when another grand advance will be added to those already based on spectroscopy, but the problems and possibilities clearly await the gifted and inquiring mind.



MODERN INDUSTRIAL SPECTROGRAPHIC INSTALLATION USING PHOTOGRAPHIC RECORDING

A powerful arc and spark light source with automatic controls is shown in the center with control panel at right and spectrograph slit at left center. At extreme left is a grinder for shaping metal samples.