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ABSTRACT
                This booklet is one of the "Understanding the Atom"
Series. The science of spectroscopy is presented by a number of
topics dealing with (1) the uses of spectroscopy, (2) its origin and
background, (3) the basic optical systems of spectroscopes,
spectrometers, and spectrophotometers, (4) the characteristics of
wave motion, (5) the electromagnetic spectrum, (6) types of spectra,
(7) line spectra, and (8) interpretations of spectra information. In
addition, there is a discussion of the fundamental concepts of
quantum mechanics, the origin of spectra, and of the different kinds
of spectroscopic techniques including x-ray spectrography, mass
spectrometry and infrared, fluerescence, magnetic, Raman, and
electron spin resonance spectroscopy. References to popular books,
technical books, and journal articles are provided. (LC)

SPECTROSCOPY

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**ONE
OF A SERIES ON
UNDERSTANDING
THE ATOM**

Nuclear energy
is playing a vital role
in the life of
every man, woman, and child
in the United States today.
In the years ahead
it will affect increasingly
all the peoples of the earth.
It is essential
that all Americans
gain an understanding
of this vital force if
they are to discharge thoughtfully
their responsibilities as citizens
and if they are to realize fully
the myriad benefits
that nuclear energy
offers them.

The United States
Atomic Energy Commission
provides this booklet
to help you achieve
such understanding.

Edward J. Brunenkant
Director
Division of Technical Information

spectroscopy

by Hal Hellman

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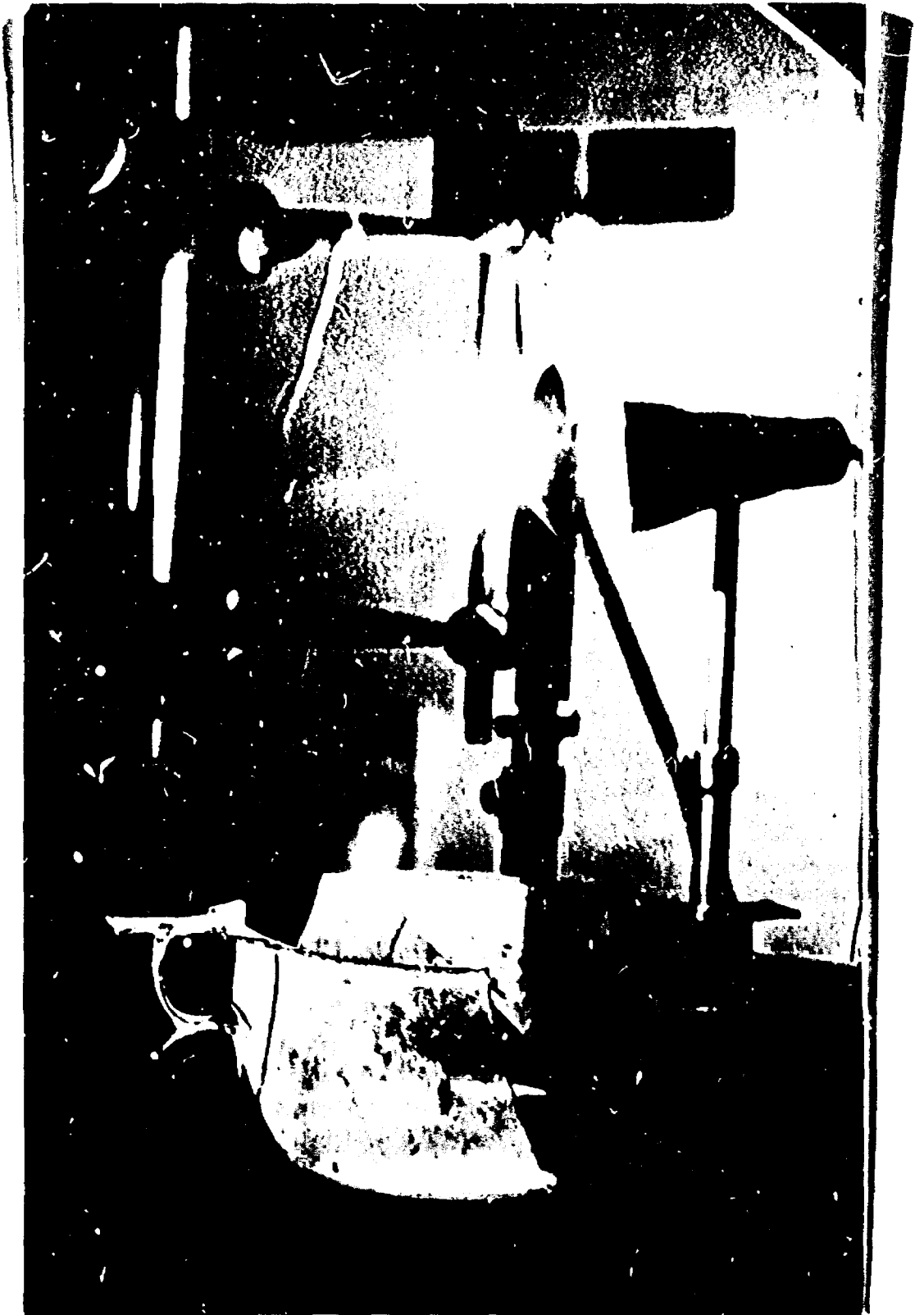# spectroscopy

By HAL HELLMAN

INTRODUCTION

A painting by an old master is a precious, irreplaceable commodity — so precious that highly talented artists sometimes spend months duplicating such paintings. These copies are so perfect that it is virtually impossible to tell them from the real thing. Indeed, some of these craftsmen are so talented that they can create a new painting in the *style* of an old master and are able to fool just about everyone. Obviously such a picture is worth far more than an original painting by the forger.

This is a serious problem in the art world. There are tests that will show whether the paints used are old or new, but most chemical tests require a fair-sized sample. (A complete analysis could require approximately a gram of material. Depending on the thickness of the paint, this might require a square inch or more of pigment surface.) And there are few dealers who would be happy to have you poke around with a knife for even a small bit of paint.

This broken 1st century glass drinking vessel was discovered in London following World War II. Tiny glass dust samples were burned in a carbon-arc flame (shown above the vessel). Spectroscopic analysis of the light from the samples revealed a high antimony content, which was typical of glass produced from the 6th century B.C. to the 4th century A.D. in lands under Greek and Roman rule.

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However, that new wonder, the laser, was recently teamed up with a time-proven instrument, the spectroscope, and they made a good combination. The exquisitely narrow beam of the laser was used to vaporize a hundred thousandth of a square inch of pigment surface. This tiny sample, invisible to the naked eye, was enough for the spectroscope, which can analyze even the vapor from a small specimen. The painting being tested was a portrait of an old woman, which had been attributed to a 15th century Flemish artist, the Maitre de Bruges (see cover).

It was a fake. Certain of its paint ingredients were shown to be materials not discovered or used by artists until the 19th century !

A spectroscope can thus "fingerprint" a material by disclosing what elements the material contains and in what proportions.

In certain cases it is not even necessary to touch the object being studied. Almost anything that emits, absorbs, or reflects light is fair game. Hence spectroscopy (spek-fros co pee) is used widely in astronomy and astrophysics. Studies of the recently found, and profoundly puzzling, quasars* depend largely upon it.

This enormously powerful technique permitted 19th century chemists to analyze and identify thousands of complex substances. In 1868 the element helium was found in the sun by a spectroscope—27 years before it was found here on earth.

Not only can elements be identified (the method is called spectrochemical or elemental analysis), but information can also be obtained on the constituents of the elements—the electrons and atomic nuclei—as well as the atoms and molecules themselves. This aspect is sometimes referred to as atomic or molecular spectroscopy.

Spectroscopy has been the means whereby physicists and chemists have learned most of what they now know about the nature of matter. It was originally limited to visible light, but new ways of generating and detecting other kinds of energy are constantly being developed. These are quickly put to work and have widened the range of spectroscopists

*A quasar is a very distant star-like object.

2
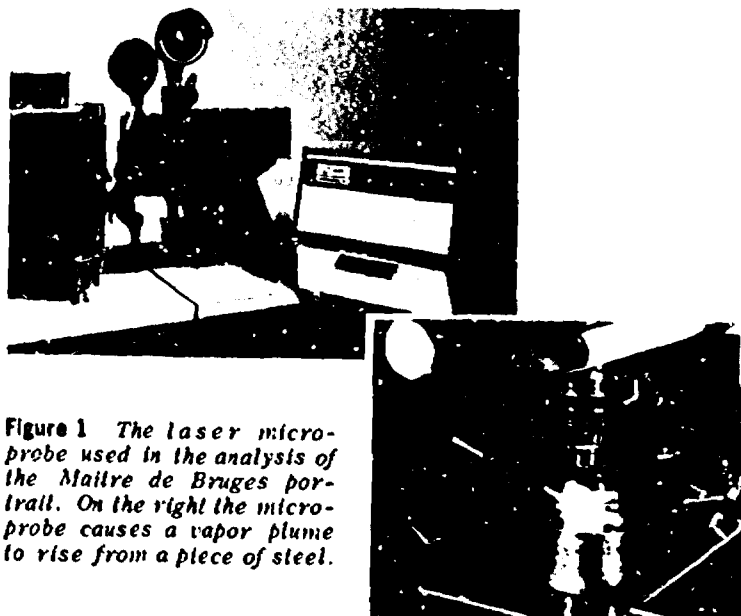
Figure 1 *The laser micro-probe used in the analysis of the Maitre de Bruges portrait. On the right the micro-probe causes a vapor plume to rise from a piece of steel.*

tremendously. We now have X-ray, gamma-ray, microwave and mass spectroscopy, plus many other kinds. We shall consider some of these later in the booklet. However, the basic idea is the same for all.

The importance of the technique was well stated by Robert B. Leighton, Professor of Physics at the California Institute of Technology: "Of all the tools that have been applied to the study of the detailed structure of matter, it can fairly be said that *spectroscopy* has been applied in more ways to more problems, and has produced more fundamental information, than any other." *

For example, of the various independent characteristics of atoms, such as their atomic spectra, chemical properties, and weight, atomic spectra have provided by far the greatest amount of information. Even that mysterious science, quantum mechanics, arose largely as a way of explaining certain irregularities in the spectrographic analysis of atoms.

Principles of Modern Physics, Robert B. Leighton, McGraw-Hill Book Company, Inc., New York, 1959, p 251.

3

ORIGINS AND BACKGROUND

Although Isaac Newton's present fame rests largely on his work with gravitation and on his *Principia Mathematica*, perhaps the greatest scientific masterpiece of all time, it was his work in optics that made his reputation. In spite of many advances in science, light had remained a totally incomprehensible phenomenon.

When he was 23 Newton built his own telescope, but he was troubled by blurred, rainbow-colored outlines around the celestial images. The search for a solution to this problem led him to experiment with light.

In the first experiment, he painted half of a piece of paper blue and the other half red. When he observed the paper through a prism he saw that the blue half appeared to lie in a different plane from the red half. Next he wound black thread around each half. With a convex lens he brought the thread on the red strip into focus, but the thread on the blue half was now blurred and vice versa. He concluded that *light is bent (or refracted) when passing through glass and that the colors in light are refracted by different amounts.* The light from the blue half was refracted more than that from the red half.

He realized that with the simple telescopic lenses he was using, he would always have a blurred image so he invented the first reflecting telescope. In this device, light was concentrated by *reflection* from a mirror instead of by *refraction* through a lens. Light was thus reflected from, rather than absorbed by, the glass, and the blurred edges were eliminated.

In his next experiment, he cut a small hole in a window shade and then held a prism in front of the beam of sunlight coming through the hole. Instead of seeing a white spot of light on the opposite wall, he saw a narrow band of colors (the spectrum) just as one would see in a rainbow (Figure 2). This was probably the most famous scientific experiment ever performed.

Newton was not the first to do this. In the 1st century A.D. Seneca, the Roman statesman and philosopher, observed that if sunlight were shone through an angular piece of glass it would reveal all the colors of the rainbow. But
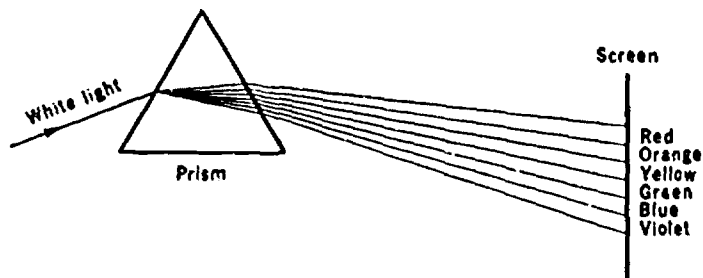
4

Figure 2 *A glass prism disperses (breaks up) white light into its constituent colors.*

Seneca thought the glass had *added* the colors to white light.

By placing a second prism opposite the first and recombining the colors into white light (Figure 3), Newton demonstrated that all the colors of the rainbow are *contained* in white light.

From these experiments came Newton's first scientific paper, "A New Theory About Light and Colours". In his own words this was "the oddest, if not the most considerable detection which hath hitherto been made in the operations of nature".

It is easy to see the significance of dispersion in Newton's experiments. Not so obvious is how this becomes useful in spectroscopy.

Perhaps a musical analogy will help. A person with some musical training can listen to a chord on a piano and tell you without any trouble what notes it consists of. That is, using only his ears, he can analyze the chord.
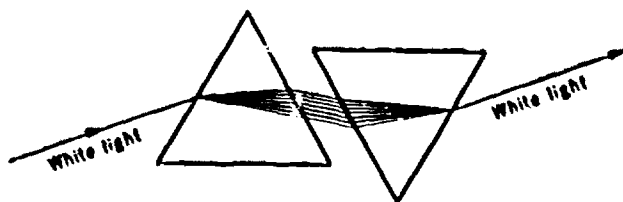

Figure 3 *With the aid of a second prism, turned opposite to the first, Newton showed conclusively that white light is composed of the colors we see in the spectrum.*

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Each note in the chord can be compared with a color. If we mix several colors together we can make another color, which might be called a "color chord". But while the musical version is easily perceived to be a chord or mixture, the color version is not. It simply looks like a new color.

For example, we can mix gray from black and white. On the other hand, we can mix another gray from green and red, which, to the eye, will be absolutely indistinguishable from the first gray. The most experienced color expert won't be able to tell them apart, but a spectroscope can.

The color chords, once spread out, are easily seen to be of different origin. This capability is extremely important in paint and dye industries where two mixed colors may look alike in one kind of light, but quite different in another. Exact matching of colors would be virtually impossible without the aid of the spectroscope and its later developments.

Before we go on to discuss how the technique is used in chemical analysis and in the study of atoms and molecules, let us take a brief look at some of the instruments themselves.

BASIC OPTICAL SPECTROSCOPES

The optical system of a simple spectroscope is shown in Figure 4. Light enters the slit S and is made parallel by the collimating lens C. Prism P disperses the light, which is then focused by the telescope lens T along curve F. It can be seen that red is dispersed least and violet most.
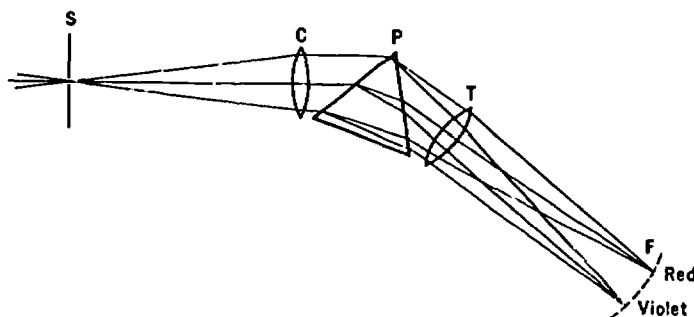

Figure 4 *The optical system of a basic spectroscope: S, slit; C, collimating lens; P, prism; T, telescope lens; F, focus.*

The term *spectroscope* derives from two root words: the Latin word *spectrum*, meaning image, and the Greek word *skopein*, to view, (e.g., *micro*scope, tele*scope*, etc.). So a spectroscope is an instrument that permits visual observation of spectra. Instruments that record a spectral image on a photographic plate (the spectroscope plus the tube plate holder at lower left in Figure 5) are commonly called spectrographs.*

And finally if, instead of an eyepiece or photographic plate, we use a photoelectric cell we can measure how much of each color appears. The instrument is then called a spectrometer (from the Greek *metron*, measure). In this case, however, the prism is rotated so that only a narrow portion of the spectrum is received by the detector at any time (Figure 6). In some cases the whole operation is done

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*Although the word graph and the combining form "graph" derive from the Greek *graphein*, to write, it generally refers to an instrument for making a record of some kind.

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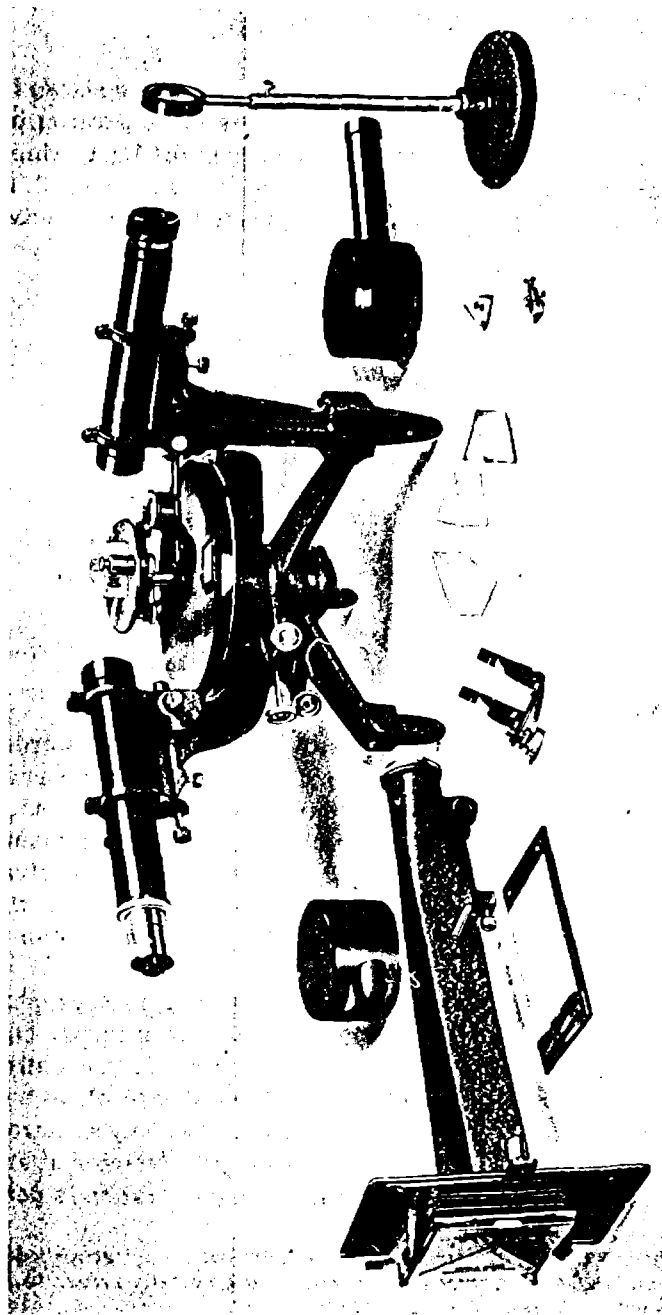
Figure 5 A basic prism spectroscope. Light enters from the right, and is viewed in the telescope at left. At lower left is an accessory photographic plate holder that converts the device into a spectrograph.

8
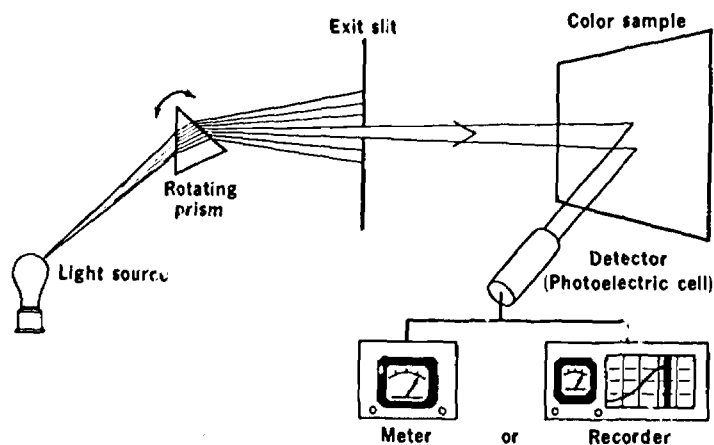
Figure 6 *Principle of spectrometer or recording spectrophotometer.*

automatically and the results are fed to a recorder that inks in a complete record of the spectrum. Since a device for measuring the intensity of radiation is called a photometer, the final combining term for the automatic device (Figure 7) is *spectrophotometer*, or recording spectrophotometer.

Often, as in the instruments illustrated in Figures 5 and 7, the same instrument is adaptable to various methods.
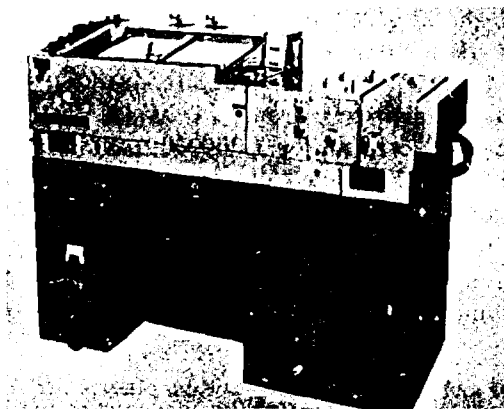
Figure 7 *This modern, multipurpose recording spectrophotometer can perform automatic analyses in ultraviolet, visible, and infrared regions on transparent, translucent, and opaque materials.*

9

WAVE MOTION

Newton believed that light might travel in the form of tiny particles. But since light could not always be explained with this theory, he thought that the particles might have waves traveling with them. Toward the end of the 17th century the Dutch astronomer Christiaan Huygens developed the idea that light is a wave motion.* This concept was validated in 1803 when the British physician Thomas Young ingeniously demonstrated interference effects in waves. He shone light of one color through two narrow openings. Then he put a screen in front of the openings and saw that there was a shadow in the center of the spot where the two rays of light met. They were *interfering* with each other. In this way, it was finally realized that the only difference between the various colors of light was one of wavelength.

As with all kinds of waves, light has both a frequency and a wavelength. Wavelength is the distance from the crest of one wave to the next one. Frequency is the number of waves that pass a given point in a certain length of time. Ocean waves, for example, might be measured in terms of a dozen or so per minute.

Light waves are of course quite a different matter. They can't be seen and their rate of vibration goes up to something like 100 million million (10^{14}) per second. The wavelength of light is also very small — in the range of .00002 inch. This is a very awkward number, and so scientists have used the metric scale, which lends itself much better to small units. The angstrom† (A) is generally used, and is equal to 10^{-8} centimeter (.00000001 cm). Red light has a wavelength in the range of about 6200 to 7600 A, while violet ranges from about 3800 to 4400 A. The visible spectrum is shown in Figure 8.

Although a rate of 10^{14} cps cannot be counted directly, there are methods for measuring small wavelengths. The

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*Particles and waves demonstrate each other's properties under certain conditions. This particle-wave duality is discussed in the chapter called "The Atom" beginning on page 30.

†Named for Anders J. Angstrom, a nineteenth century Swedish physicist.

frequency can then be found by a very simple mathematical relationship:

$$\nu = \frac{c}{\lambda}$$

where ν = frequency in cycles per second,
     c = velocity of light in a vacuum (a constant), and
     λ = wavelength in angstroms.

Clearly, as wavelength goes up, frequency goes down, and vice versa.

3800	4400	5000	5700 5900 6200

| Violet | Blue | Green | Y e l l o w | O r a n g e | Red |

| 4000 | 5000 | 6000 | 7000 |

Wavelength, angstroms
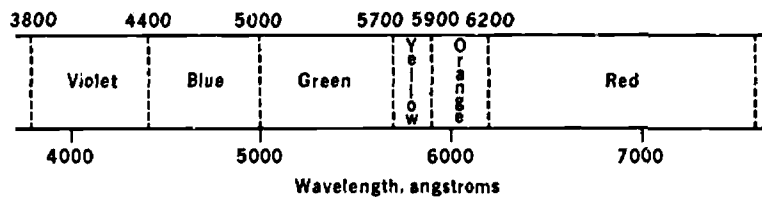
Figure 8 *The spectrum of visible light. Divisions are arbitrary since colors blend gradually into one another.*

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THE ELECTROMAGNETIC SPECTRUM

The obvious question is: What happens at the two ends of the visible spectrum? Does it just end? In the year 1800 the German—British astronomer Sir William Herschel (who was an organist before he became an astronomer) performed a most intriguing experiment. Using very sensitive thermometers, he "took the tem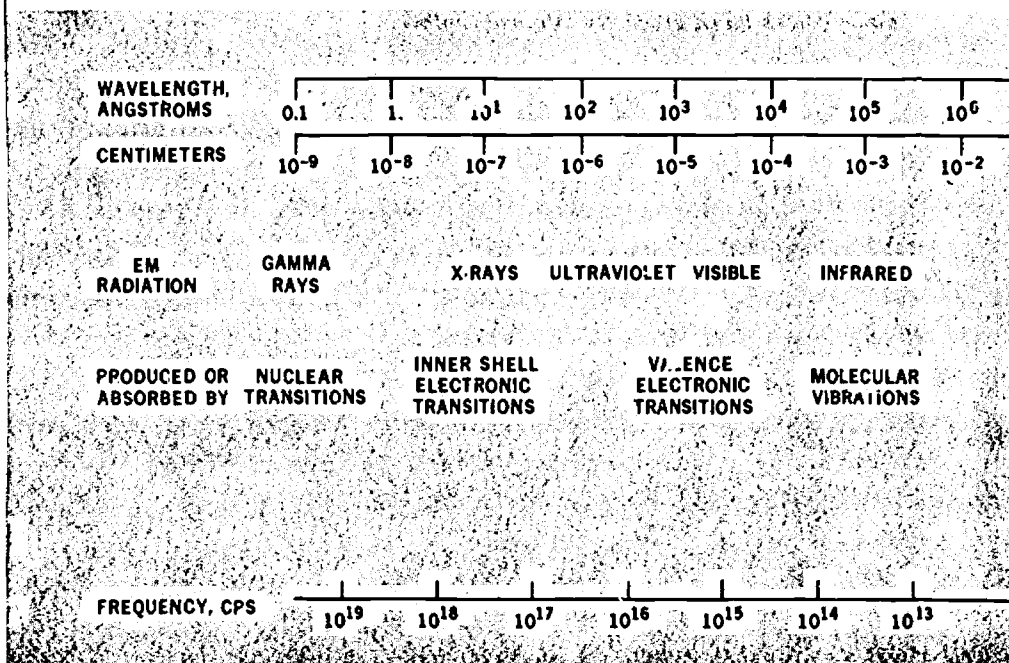perature" of the visible spectrum by placing a thermometer in the colors of light spread out by a prism. He found that the temperature rose as the wavelength grew longer (toward the red). And the temperature continued to rise beyond the red, where no color could be seen!

Although the implications of this experiment were not understood until later, Herschel was the first to find a relationship between light and radiant heat (the kind we get from the sun or an outdoor fire). Both are examples of *electromagnetic radiation*. The name infrared (the Latin

WAVELENGTH, ANGSTROMS	0.1	1.	10^1	10^2	10^3	10^4	10^5	10^6
CENTIMETERS	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}

EM RADIATION	GAMMA RAYS	X-RAYS	ULTRAVIOLET	VISIBLE	INFRARED

PPODUCED OR ABSORBED BY	NUCLEAR TRANSITIONS	INNER SHELL ELECTRONIC TRANSITIONS	VI..ENCE ELECTRONIC TRANSITIONS	MOLECULAR VIBRAIIONS

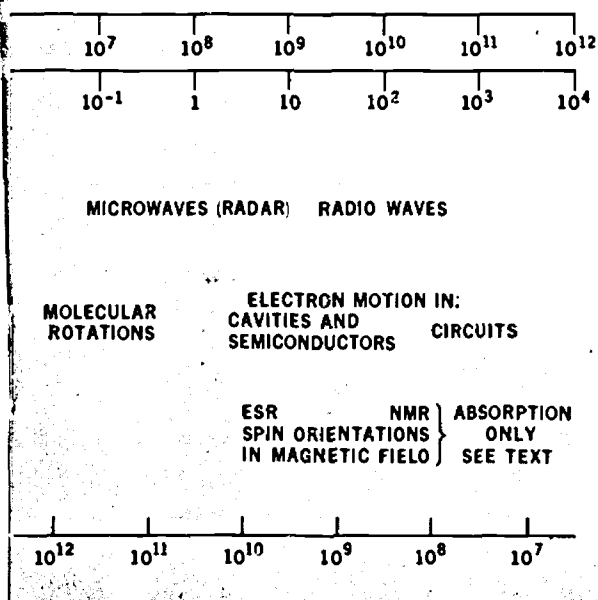| FREQUENCY, CPS	10^{19}	10^{18}	10^{17}	10^{16}	10^{15}	10^{14}	10^{13}

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word for below is *infra*) was given to these rays, the wavelength of which ranges from the red end of the spectrum at about 7600 A all the way up to about 1 millimeter or 10^7 A long.

Only a year later the German physicist Johann W. Ritter found waves that were shorter than visible light. These were named ultraviolet (the Latin word for beyond is *ultra*) and range from the violet end of the visible spectrum down to about 25 A. It should be noted that there are no actual "divisions" between the various kinds of radiation; they blend gradually into one another.

Before the end of the century the Scots mathematician and physicist James Clerk Maxwell showed theoretically, and Heinrich Hertz* proved experimentally, the essential identity of light, heat, and other electromagnetic radiations.

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*The unit of frequency, cycles per second (cps), is sometimes called hertz; 1000 hertz = 1000 cps.

| 10^7 | 10^8 | 10^9 | 10^{10} | 10^{11} | 10^{12} |

| 10^{-1} | 1 | 10 | 10^2 | 10^3 | 10^4 |

MICROWAVES (RADAR)   RADIO WAVES

MOLECULAR
ROTATIONS

ELECTRON MOTION IN:
CAVITIES AND
SEMICONDUCTORS   CIRCUITS

ESR   NMR ⎤ ABSORPTION
SPIN ORIENTATIONS ⎬ ONLY
IN MAGNETIC FIELD ⎦ SEE TEXT

| 10^{12} | 10^{11} | 10^{10} | 10^9 | 10^8 | 10^7 |

Figure 9   *The electromagnetic spectrum and the transitions involved in emission and absorption. Boundaries are not exact.*

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Since then many kinds have been found, ranging from the tiny 1-A high-frequency gamma rays to the extremely long, low-frequency radio waves. A diagram of the more common kinds is presented in Figure 9. The inverse relationship of frequency and wavelength is obvious.

What is important to us is not so much that these various kinds exist, but that they represent different activities in atoms and molecules. Before we discuss this, however, let us see what *kinds* of spectra there are and how information can be obtained from them.

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TYPES OF SPECTRA

Any substance will begin to glow (if it does not evaporate first) when heated to a high enough temperature. You need only think of the heating coils in an electric heater or range. The light emitted contains a range of colors that combine into a reddish glow at temperatures in the range of 1400°F. The tungsten filament of an electric bulb incandesces at about 4200°F and emits an intense yellowish white light. An electric arc, which is hotter still (about 6300°F), is even more intense and is bluish in color.

Both the color and the intensity of the light emitted by a glowing or incandescent body depend on how hot it is, and *not on the substance*. This is one aspect of blackbody radiation.* The color of the light source must also be taken into account when doing spectroscopic work on colors.

The intensity of light that is emitted by an incandescent body increases as its temperature increases, and the prevailing wavelength (its color) shifts from the red toward the blue end of the spectrum.
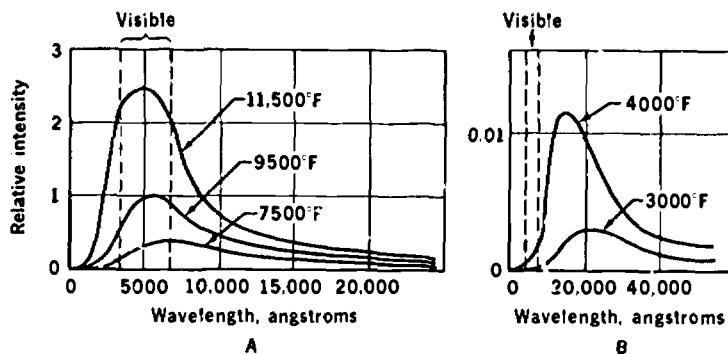
Figure 10, a set of spectrographic plots taken by a spectrophotometer, shows how the intensity of blackbody radiation varies with wavelengths of different temperatures; the color can be seen to be shifting slowly as the temperature decreases. In the bottom curve of part B we see that the radiation is practically all infrared (as in a hot iron or the lowest setting on an electric range).

When the light produced by an incandescent object is passed through a spectroscope, the result is what is called a continuous spectrum. Examples are the continuous plots shown in Figure 10, and in part A of Figure 11 on page 20. This is difficult to show without the use of color, but is equivalent to a vertical slice taken out of the center of a rainbow.

At first glance, a spectrum of the sun's light appears to be a continuous one. However, critical examination with proper instruments shows that this is not so and reveals features that are both interesting and useful.

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*A perfect black body absorbs all radiation falling on it and when heated to incandescence emits all wavelengths of radiation. (Although no such body exists, one can be approximated artificially.)

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Visible

3

Relative intensity

2 — 11,500°F

— 9500°F

1 — 7500°F

0

0   5000 10,000 15,000 20,000

Wavelength, angstroms

A

Visible

0.01 — 4000°F

— 3000°F

0

0   20,000 40,000

Wavelength, angstroms

B

Figure 10 *Spectrographic plot of radiation emitted by incandescent objects at different temperatures. Top curve in A corresponds to surface temperature of the sun (6000°C). It can be seen that a large percentage of the total radiation is in the visible region of the spectrum. The upper curve in B corresponds roughly to an electric light bulb. Note that relatively little of its radiation falls into the visible region. Most of its energy is in the infrared region, which is why a bulb gets hot. A and B are not to same scale.*

In 1802, well over a century after Newton's experiments, the English scientist William H. Wollaston noticed that the apparently continuous spectrum of the sun was crossed with a number of black lines, but he did not know what to make of them. He thought they might be divisions between the colors. (As we know now, this cannot be, since all forms of radiation blend gradually into one another.)

About 12 years later these dark lines were rediscovered by the brilliant German physicist Joseph von Fraunhofer. Using much better equipment than Wollaston's, he found that the spectrum was crossed with "an almost countless number of strong and weak vertical lines". He realized that, contrary to Wollaston's idea, they could not be divisions between colors since some of them clustered near the centers of colors. He still didn't understand their cause, but he put them to work as landmarks or points of reference that could be used to describe precisely any desired part of the spectrum.

One of the things that made this possible was the development, by Fraunhofer, of a different kind of dispersion device, the diffraction grating. This is typically a transparent or opaque plate of material on which have been in-

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In 1818 Joseph von Fraunhofer exhibited his newest spectroscope before his partners in a glass-works and optical establishment.

scribed many thousands of fine lines per inch. The action of these lines is to break up the light as a prism does, but with certain useful differences.

One of the advantages of the grating is that it disperses the light much more evenly; in the prism the dispersion is greater in the blue or short wavelength side than in the red. Further, in a prism the positions of the spectral lines depend upon the properties of the material used. In the grating, however, there is a definite and simple geometrical relation between the position of the spectral line and its corresponding wavelength (e.g., a separation of 10 A per mm on a photographic plate). Hence with a grating spectroscope it is possible to make a direct determination of absolute wavelength. This is not possible with a prism instrument.

And finally, the grating provides a much greater dispersion of light than the prism; that is, the different lines of wavelengths are spread much further apart, particularly in the long end of the scale. This of course greatly facili-

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tates observation, and was perhaps the most important factor in Fraunhofer's work.

In spite of the advantages of the grating, the prism spectroscopes are commonly used in schools and for demonstration purposes because of their simplicity and low cost, and because they throw a bright spectrum.

Fraunhofer charted and identified by letters 576 of the lines seen in the sun's spectrum. He also performed the following important experiment concerning them. He separated the opening of his spectroscope into two halves. One was lighted by the sun and the other with a sodium flame. A dark pair of Fraunhofer's D-lines in the sun matched the brilliant pair of yellow lines in the sodium flame.

For some reason he did not pursue this interesting line of research, and the origin of the lines remained a puzzle.

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LINE SPECTRA

While Fraunhofer's work laid the foundations for an accurate science of spectroscopy, the edifice itself remained to be built. Undiscovered was the fact that *each element has its own characteristic spectrum*, which is as individual to it as fingerprints are to the human race. This step was necessary for an understanding of the lines and was taken by the German physicist Gustav R. Kirchhoff in 1859, in collaboration with the German chemist Robert W. Bunsen (of Bunsen burner fame).

Gustav R. Kirchhoff (left) and Robert W. Bunsen in 1862.

To help us understand what went on, let's look at Fraun-
hofer's experiment again. As we know, a solid, when heated
to a high enough temperature, emits a light that is a mix-
ture of all wavelengths; hence we have a continuous spec-
trum, as in Figure 11A. However gases, when excited by
heat, electricity, or other means, give off light of quite a
different kind. If we introduce into the barely visible flame
of a Bunsen burner a small amount of table salt, for ex-
ample, we find that the flame turns a brilliant yellow.

And if we look at this flame through a spectroscope, we
do not find the usual rainbow-colored band, but a pair of
closely spaced, narrow yellow lines on a generally dark
background (Figure 11B). These bright *emission* lines are
produced by the sodium in the salt. They always appear
when a substance containing sodium is burned, and will not
appear if sodium is lacking. The lines appear at 5889.96
and 5895.93 angstroms, which, as you can see, lie in the
yellow region of the spectrum.

In his landmark experiment Kirchhoff shone sunlight
through a sodium flame and, with his spectroscope, ob-
served two dark lines on a bright background just where
the D-lines of the sun were. When he blocked out the sun-
light the bright background grew dark and the black lines
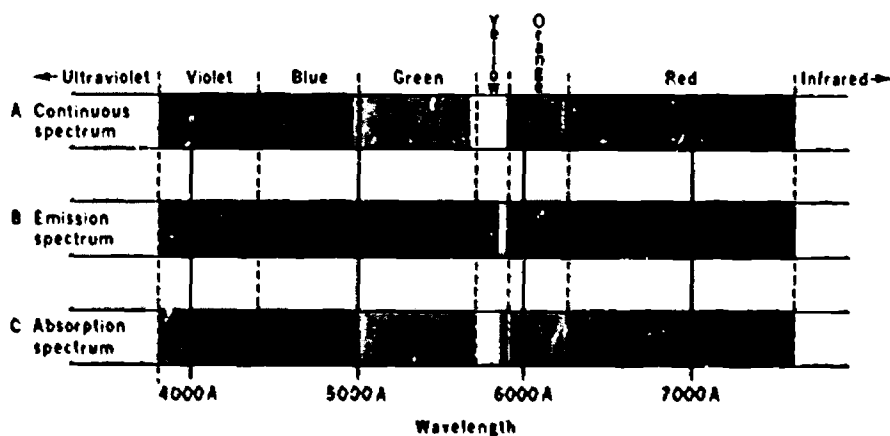became brilliant yellow. He concluded that the gases in the

Figure 11 *Comparison of continuous, emission, and absorption
spectra. Lines in B and C are sodium lines that appear at 5889.96
and 5895.93 A.*

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Bunsen's laboratory in Heidelberg.

sodium flame absorbed the D-line radiation from the sun; the result is an *absorption spectrum* (Figure 11C).

He also realized after further experiments that all the other Fraunhofer lines were also absorption lines; that is, gases in the sun's atmosphere absorbed some of the radiation coming from inside the sun, thus forming these lines or "holes" in the solar spectrum. He observed in this way that sodium and calcium were present in the sun, while lithium appeared to be absent.

By comparing the solar lines with the spectra of known elements, Kirchhoff and Bunsen found a number of elements present in the sun, the most abundant of which is hydrogen.
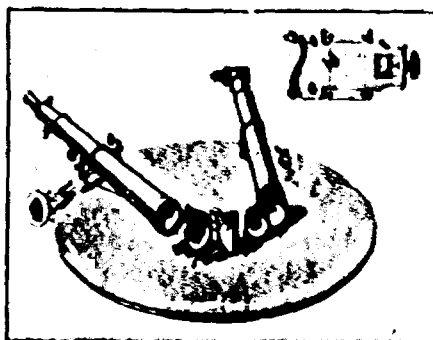
The Kirchhoff—Bunsen spectroscope.

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The two scientists also applied themselves to the application of the spectroscope to chemical analysis. In 1861 they discovered the presence of a fourth alkali metal, cesium (whose spectrum could not be matched with that of any known element). And later in the year they found a fifth one, rubidium. Shortly thereafter they isolated these new elements and described their properties.

A few years later, in 1868, a bright line was discovered in the sun's spectrum that appeared nowhere else. The English astronomer Sir Joseph Norman Lockyer attributed it to an unknown solar element, which he called helium


Sir Joseph Norman Lockyer

(from the Greek *helios*, meaning sun). His fellow scientists dismissed this idea, which is not surprising. After all, spectroscopy was still a new science, and it did seem a little presumptuous to create a new element on the basis of a line in a spectroscope. The majority of astronomers believed the line represented some known element under abnormal circumstances.

It took almost 30 years for the element to be found here on earth. Happily, Lockyer lived long enough to see his position vindicated.

As is generally the case in science, this discovery had other ramifications. The helium line was a prominent one because the sun contains a good deal of helium. In other words, there is a relationship between the amount of a substance and the density of spectral lines. Very accurate instruments, called densitometers, are now available for measuring the density of photographic lines. By comparing

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the results with known information, this relationship has been put to use in *quantitative analysis*, i.e., in finding out *how much* of a substance is present in a material. (See Figure 12.)
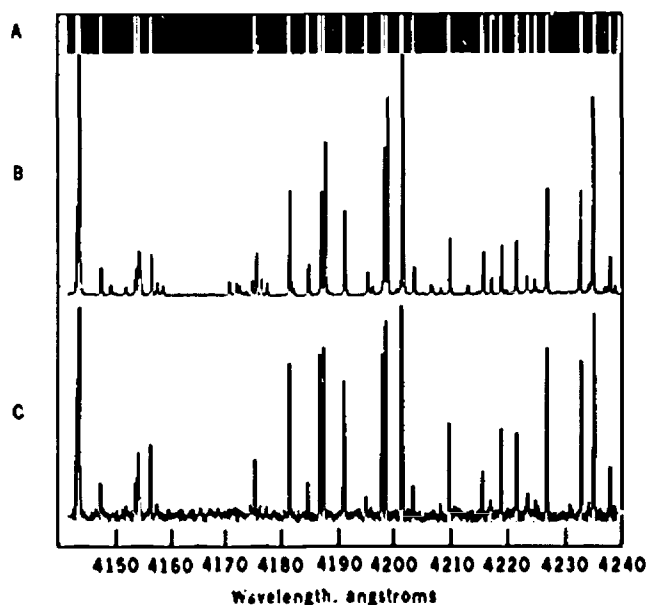
Figure 12 *Photographic, photoelectric, and densitometric records of the same spectrum. A is a photograph of the spectrum of iron in the violet region; B is a photographic plot made on a spectrophotometer; C is a densitometric record of the spectrogram in A.*

The spectroscope was also turned to other uses in astronomy, and provided an incredible amount of information about the heavens. Information can be gleaned on such items as the presence of galactic dust, the velocities, composition, magnetic characteristics, and temperatures of stars, whether a star is single or double, and so on — and all from the little pinpricks of light we see above us! Of great use in these endeavors was the development of photography during the latter part of the 1800s.

Because of Kirchhoff's and Bunsen's research, scientists around the world were stimulated to look into this "new" science, which, in addition, aroused great popular interest.

Indeed it has been stated that the work of these two men was as great a stimulus to popular interest in science as was the relativity theory of Einstein a half century later.

During this early period of spectroscopy, interest was largely concerned with the chemical and physical properties of matter, and with correlating and charting the lines of the various elements.

A second great period, beginning around 1890, concerned the power of spectroscopy to unlock the secrets of the atom itself.

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INTERPRETATIONS OF SPECTRAL INFORMATION

It had been seen very early that the spectrum of a gas was the same regardless of the quantity of that gas. Thus each atom (or molecule) must be emitting all or most of the absorption and emission lines, and only those lines. When molecules are involved, *band* rather than line spectra are produced; but the principle is the same, for under high dispersion the band spectra have been found to have a line structure. That is, they are groups of lines, and th. arrangement always enables them to be distinguished from atomic spectra.

The only effect of increasing or decreasing the amount of the gas is to increase or decrease the intensity of the lines, as we observed in the case of helium.

The implication is clear. If a tiny quantity of each element emits the complete spectrum, a mechanism must exist in each atom or molecule to make this possible. The visible spectrum of hydrogen is relatively simple (see Figure 13), but that of iron is extremely complicated and contains thousands of lines. Hence the atom of hydrogen must be simple while that of iron must be complex.

But this was as far as the study could go for a while. What was necessary was a change in outlook. It was not until attention was turned from the lines themselves to the spaces *between* the lines that progress could be made.
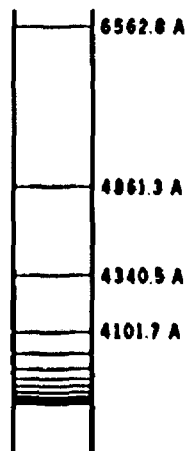
6562.8 A

4861.3 A

4340.5 A

4101.7 A

Figure 13 *Emission spectrum of atomic hydrogen.*

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Look again at the hydrogen spectrum shown in Figure 13.
A regularly decreasing spacing can be seen. This was
noted early, but what did it mean? In 1885 Johann J. Balmer,
a Swiss mathematician, physicist, and schoolteacher, came
up with a simple formula for the regular spacing of the
hydrogen lines. The formula showed that the frequencies
of light emitted by a hydrogen atom are proportional to

$$\frac{1}{2^2} - \frac{1}{n^2}$$

where n is an integer.

Clearly the formula meant something, but what?

A generation was to pass before Niels Bohr, in 1913,
made use of the formula to deduce the first really useful
picture of the atom. While his picture was oversimplified
it was basically correct—and indeed is still the picture
presented to the beginning science student. Bohr saw the
atom as a sort of miniature solar system, consisting of a
central nucleus being circled by electrons that could move
around it in any one of a number of fixed orbits just as
planets revolve about the sun.
Hydrogen, the simplest of the
atoms, has only one electron in
orbit.*

The orbits of the planets can
be changed slightly by a large
enough force. But with the input
of the proper amount of energy
an electron can only jump from
its fixed orbit to one of a num-
ber of higher, though still fixed,
orbits. However, this is an un-
natural position, and the elec-
tron would quickly fall back to
its original orbit.

Niels Bohr

As the electron drops into the lower orbit (see Figure
14), it emits the energy it had gained earlier. This takes

*For more about atomic structure see *Our Atomic World*, a com-
panion booklet in this series.

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the form of radiation, which has the wavelength of visible light. This energy is emitted as a packet, or *quantum*, of electromagnetic energy, and it is called a photon.
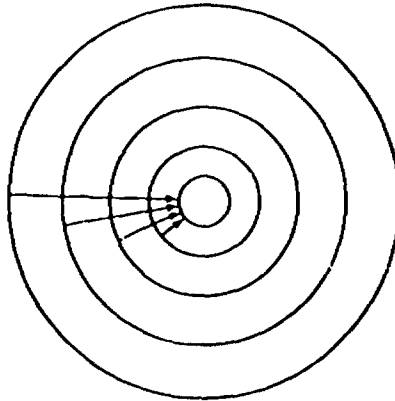
Figure 14 *Energy level diagram shows how electrons can drop from higher to lower energy levels.*

When Kirchhoff passed sunlight through his sodium flame, the sodium atoms absorbed the particular energy they needed to move into a higher orbit. This energy change left the gaps or dark lines. When the sunlight was removed, the sodium electrons fell back into their old orbits by emitting their newly absorbed energy in the form of radiation. This produced the bright yellow glow* of the two lines.

The multitude of dark lines that Fraunhofer observed in the solar spectrum represents the energy changes of the elements in the sun's lower atmosphere as white light from the sun's surface passes through them.

The energy input can be of many kinds, including thermal (heat), electrical, chemical, and electromagnetic. With certain exceptions, which we will discuss on pages 44 and 52, the energy input will match the energy output. But in wave motion, energy has a very particular meaning, and one that is somewhat different from our usual conception of energy (e.g., an object of a certain mass moving at a particular speed).

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*This would only be a momentary effect. The glow is normally produced by the heat of the burner.

All types of electromagnetic radiation, which includes gamma and X rays, travel at the speed of light (186,200 miles per second), and their energy is proportional to the *frequency* of the wave.* The higher the frequency, the higher the energy:

$$E = h\nu$$

where E = energy,
ν = frequency, and
h = Planck's constant.

Two things now become apparent. First, we see why X rays (with high frequency and hence high energy) can penetrate our bodies while light cannot. And second, we can understand why atoms absorb the same light that they produce. Or, in terms of spectroscopy, we see why the absorption lines of an atom are identical with the emission lines.
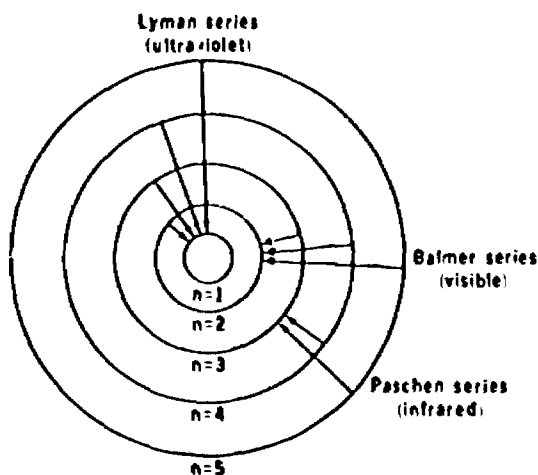
Figure 15 *Higher energy electrons can drop to different inner orbits, thereby producing lines in the ultraviolet and infrared as well as visible regions of the hydrogen spectrum.*

*Remember that frequency is the number of waves that pass a given point in a certain time.

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If we recall that an atom emits an amount of energy that is the difference between two energy states, we can restate the formula given above. If E_2 and E_1 represent the energies of the upper and lower states, the amount of energy gained or lost is given by

$$E = h\nu = E_2 - E_1 = h(\nu_2 - \nu_1)$$

But note how similar this last form is to Balmer's formula. At last we can see the meaning of the formula: It represents the *difference* between two energy states.

Indeed not only did Balmer's formula correspond to existing lines, but it could be used to predict the existence of additional lines by simply changing the 2^2 to 1^2 or to 3^2. This was equivalent to stating that the electrons were falling from higher orbits down, not to the second orbit, but to the first or third orbit in the hydrogen atom. Two new sets of hydrogen lines were later found in the ultraviolet and infrared regions (Figure 15).

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THE ATOM

Bohr's picture, which was added to over the next 10 years, explained many aspects of the spectra of various elements. As a result, he was awarded the coveted Nobel Prize in physics in 1922.

Bohr could not, however, explain why the orbits were fixed. He had simply chosen those orbits that would give the correct results with respect to the *observed* absorption and emission of light.

The first step in solving the problem was taken by the French physicist Louis Victor de Broglie, who drew an analogy between the set of discrete energy levels in an atom and the set of discrete mechanical vibrations that are characteristic of violin strings, organ pipes, and so on. Is it possible, asked de Broglie, that the optical properties of atoms are due to some kind of waves within their tiny bodies? A stretched string, for example, can vibrate as shown in Figure 16A, B, and C—that is, with an integral number of wavelengths. Clearly it cannot vibrate as shown in D, since the right side of the string is not fastened down.
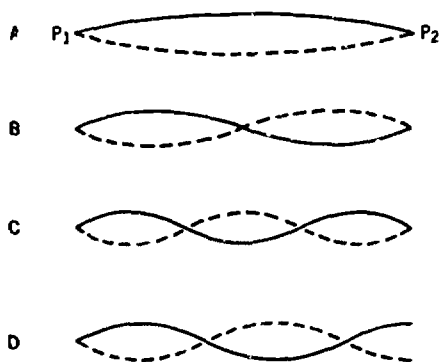
Figure 16 *A string stretched between points P_1 and P_2 can vibrate as shown in A, B, or C, but not D.*

Applying similar reasoning to the atom, de Broglie suggested that the electron did not simply circle the nucleus as a planet circles the sun, but rather was guided by a wave of some sort that existed, so to speak, in all parts of the orbit at once. He was able to show that the first, second, third, etc., of Bohr's orbits in the hydrogen atom have

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Louis Victor de Broglie

circumferences equal to 1, 2, 3, etc., wavelengths of these "pilot" waves. That is, an integral number of wavelengths would fit the Bohr orbits (Figure 17A), while a non-integral number such as $2\frac{1}{2}$ would not (Figure 17B).

Now what are these wavelengths? De Broglie made a startling proposal. Just as electromagnetic radiation has many of the characteristics of particles (for example, photons of light), particles of matter, such as electrons, display the characteristics of waves!* This wave-particle duality made Einstein's belief that matter is only a form of energy and that the two were interchangeable more understandable.

A "particle wave" would have a wavelength λ that is inversely proportional to the momentum of the particle. The formula is:

$$\lambda = \frac{h}{m \times v}$$

where h = Planck's constant,
   m = the mass of the particle, and
   v = its velocity.

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*Particles and waves demonstrate each other's properties under certain conditions. Normally, however, a particle displays particle characteristics and a wave displays wave characteristics, and while each can display the other's characteristics, they cannot display both at the same time. See *Microstructure of Matter*, a companion booklet in this series, for more about wave-particle duality.

De Broglie received the Nobel Prize in Physics in 1929 for his work.

The wavelength associated with electrons moving at moderate speed, de Broglie calculated, would be in the X-ray region, or about 1 angstrom. And indeed X rays can be and generally are produced when high-energy electrons bombard suitable targets (and are thus slowed to moderate speed).


| A Integral number of waves | B Non-integral number of waves |
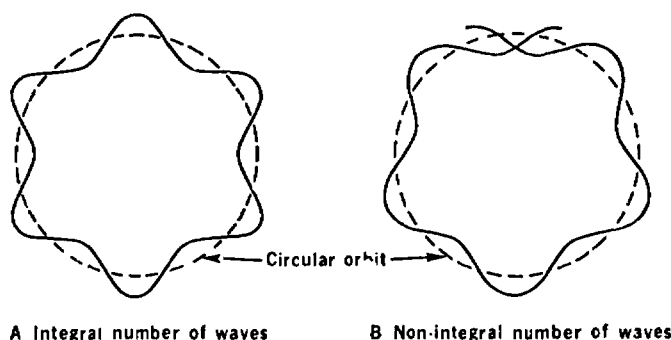
Figure 17   *Only an integral number of waves will fit the Bohr orbits.*

In the Bohr theory, one supposedly knew simultaneously the position and the momentum of an electron. However it is not possible to know both at the same time. To determine the position one could theoretically use radiations of short wavelength and then observe the particle in a microscope (although no such powerful tool exists). However if one did this the radiations would disturb the momentum.

Conversely, a diffraction grating could be used to measure the electron's wavelength and then the momentum could be calculated. But when an electron is diffracted its direction is changed and its position would no longer be known. In other words the means of observing particles of atomic dimensions would disturb the motions of the particles. This is called the Heisenberg Uncertainty Principle after the German physicist Werner Heisenberg, who formul_ted it.

Notice that when we wish to know the position of an electron it is observed as a particle, but when the momentum is desired it is studied as a wave.

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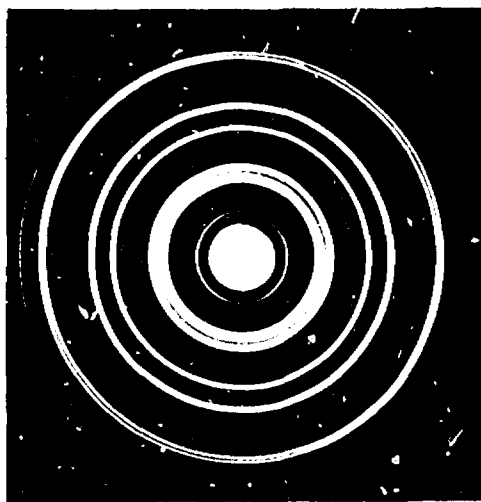
Figure 18 *Wave properties of particles. The interference pattern was produced by electrons shot through a thin foil. No electron, of course, really moved along a wavy path, but the wavelike distribution of electrons is described by mathematics of waves, and the alternate bright and dark lines in the photograph are similar to effects of interference phenomena in water waves or in light.*

While Newton's classical mechanics can be used to calculate the movements of large bodies both on earth and in space, it cannot be used for atomic particles for this reason: While its inaccuracies are unimportant and almost unnoticeable for large bodies, for particles of atomic dimensions, which are so tiny, the inaccuracies of classical mechanics obscure any meaningful results.

Thus a new scheme of calculations was needed. This new mechanics—quantum or wave mechanics—was developed by the Austrian physicist Erwin Schrödinger, who was a Nobel Prize winner in 1933. It was this theory that brought us to our present understanding of the atom. Quantum mechanics concerns the likelihood of discovering the position of a particle by means of an equation similar to one used for wave motion. While a discussion of this would take us beyond the scope of this booklet, we have seen where and how the study of atomic spectra played a fundamental part in the construction of quantum mechanics, one of the great scientific theories of the twentieth century.

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The X-Ray Spectrograph

Since X rays are similar to light, but have shorter wavelengths, their spectra can be studied with the same type of instrument that light can. While it is not possible to rule a transmission diffraction grating sufficiently fine to produce X-ray spectra, nature has provided excellent gratings similar in size to X-ray wavelengths in the structure of certain crystalline materials, where the crystals occur in parallel layers 1 or 2 A thick. X-ray spectra can be produced independently of crystals by using a ruled diffraction grating of the reflection type and directing a narrow beam of X rays upon it so that it only grazes the surface.

With such techniques X-ray spectrographs or spectrometers can be constructed (see Figure 19) that are quite similar to the visual type we have already discussed. However, physical slots (S) are used for collimation of the X-ray beam since optical lenses have little effect on it. And either photographic plates or counting chambers must be used since X rays of course cannot be seen. A modern X-ray spectrometer is shown below.
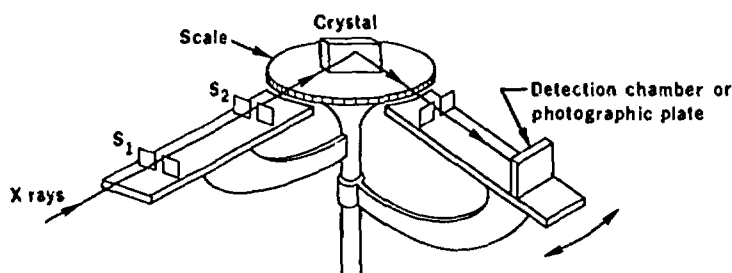
Figure 19 *An X-ray spectrometer is similar to the optical type except that optical prisms and lenses cannot be used. An automatic X-ray spectrometer is on the right. Once the machine is set for detection of a particular element, the operator merely inserts and removes the sample. At the end of the cycle the percent concentrations are visually displayed and/or printed.*

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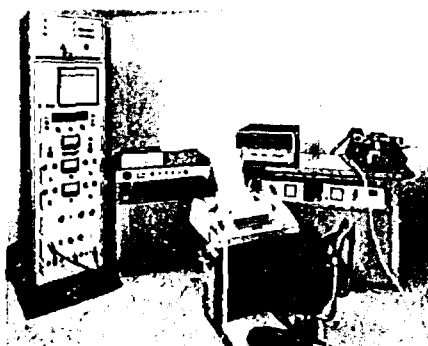
Two Americans, Clinton J. Davisson and L. H. Germer, used a similar technique in 1927 but replaced the X-ray beam with a beam of electrons. They discovered that a beam of electrons focused on a nickel crystal was diffracted (and diffraction is a characteristic of waves rather than particles) as well as being reflected. The wavelength corresponded with the value predicted in the de Broglie theory and thus provided corroboration.

In a variation of the X-ray technique, we have a relatively new development, the electron microprobe. This is basically an X-ray spectroscopic instrument that uses a focused beam of electrons as the exciting source. The focused beam strikes the specimen, which functions as the target of an X-ray tube, and produces X rays characteristic of the materials present in the sample. The ability of the electron microprobe to perform analysis at a selected microscopic area of a sample makes it one of the more valuable analytical tools.

FUNDAMENTAL DIFFERENCES IN THE
ORIGIN OF SPECTRA

Although light waves and X rays are both examples of electromagnetic radiation, and although both are produced by transitions of electrons within atoms, there is nevertheless a basic difference between them. Light rays are produced by transitions of the outer electrons, while X rays result from transitions of the inner electrons (or when moving electrons are slowed by a target).

The other forms of electromagnetic radiation are also produced in different ways, which are generally the basis for distinguishing between them. For example, waves 1 A long can be *either* X rays or gamma rays. If they result from changes in inner electrons they are called X rays; if they arise from transition; within the nucleus itself (as in radioactive decay), then they are called gamma rays.

The common radio wave is produced in quite a different way, namely by the motion or oscillation* of free electrons in a radio antenna. Microwaves, with smaller wavelength, (less than 30 centimeters) are produced as a result of electronic vibrations in a small physical cavity or semiconductor equivalent.

Radio and microwave radiation can also be *absorbed*, though not produced, by rotation of molecules. Thus these forms of radiation can be applied to studies of very low-energy transitions arising from reorientations of nuclear and electron spins† in the presence of a magnetic field. These studies use a different kind of spectroscopy, the so-called resonance techniques, which we shall discuss later.

In both radio and microwave production, the frequency of the radiation emitted is equal to the frequency of oscillation of the charges and is thus subject to rigid control. While such a correspondence cannot be shown when the emitting system is of molecular dimensions, it has proved very helpful to assume that molecules do vibrate and rotate

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*Oscillation is the back-and-forth movement of an object like the pendulum on a clock.

†Each electron has an angular momentum or spin around its axis. See *Microstructure of Matter*, another booklet in this series.

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with frequencies closely related to the frequencies of emitted or absorbed radiation. These generally fall into the infrared range. The near-infrared (7600 A to about 250,000 A) corresponds roughly to the region containing the vibrational frequencies, while the far infrared (up to 10^7 A or 1 millimeter) arises from the rotational frequencies.

In all cases, transitions between different levels of energy give rise to emission or absorption of radiation with a frequency related to the energy change of the atomic or molecular system (equation on page 29). *The objective of the spectroscopist is to measure the relative amounts of energy emitted (emission spectroscopy) or absorbed (absorption spectroscopy) at each frequency.* The difference is shown schematically in Figure 20. Each type has advantages for certain applications.
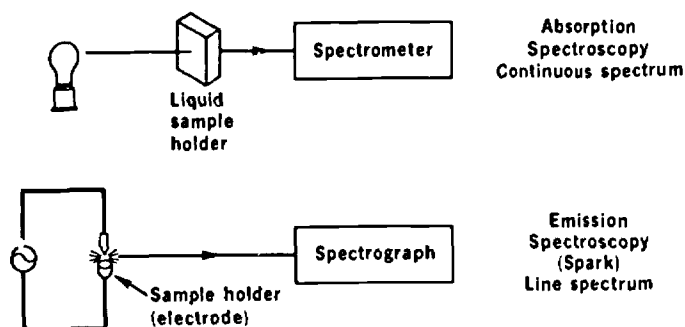

Figure 20 *Comparison of absorption and emission spectroscopy.*

The different types of transitions provide separate tools for the researcher interested in a particular area. If one is interested in the inner electrons he will work with X rays and not with the spectra of visible light, which is caused by movements of the outer electrons.

Infrared Spectrophotometry – A Case History

The following case history, from the files of J. P. Luongo, Bell Telephone Laboratories, shows how infrared absorption spectroscopy is used in qualitative analysis, i.e., to find what materials are present.

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In an attempt to determine why a pole-mounted relay failed while in service in a rural area, a telephone company engineer submitted the contacts for analysis. Initial inspection revealed a gummy substance on the contacts. Previous experience had shown that certain components of the wire insulating varnish, gasket materials, etc., sometimes "evaporate" and redeposit to produce a thin coating on the contact points. When this happens the resistance across them increases and may cause the relay to fail.
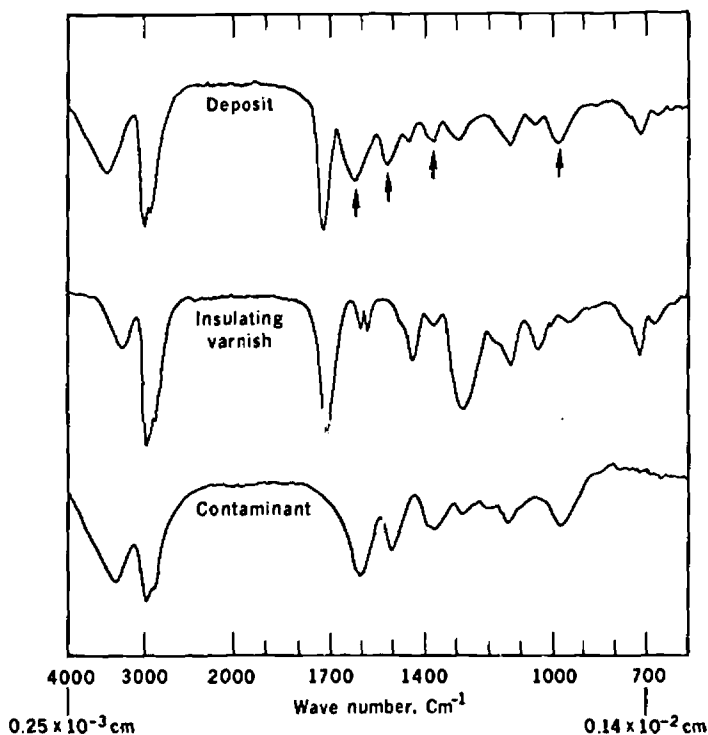
Figure 21   *Infrared spectrometric curves used in analysis of contaminant.*

Nevertheless the deposit was removed from the contacts and analyzed on an infrared spectrometer. The spectrum of the deposit (top curve of Figure 21) had the characteristic absorption bands of an insulating varnish (middle curve). However, there were additional bands (arrows in

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Figure 22 *Burning a paint sample on an FBI emission spectrograph in a Washington, D.C., laboratory. Photographic plate is in rack just above operator's hand. Examples of continuous and line spectra are seen on wall.*

top curve) at 1625, 1525, 1425, and 980 cm^{-1}.* These were indicative of an N—H bond (nitrogen—hydrogen bond) or molecular group such as would be found in nylon. But analysis of materials used in the manufacture of the relay failed to uncover the existence of any material containing an N—H group.

Further discussion with the engineer who submitted the relay revealed that the pole on which the relay had been mounted was located near an ant hill. Feeling rather silly, but not wanting to leave any stones unturned, the engineer gathered up some local ants and sent them to the lab. There they were prepared for analysis and their infrared spectrum recorded. The result is shown in the bottom curve.

It can be seen that the unidentified absorption bands in the spectrum of the deposit on the contacts were identical with those in the spectrum of the ants (proteinaceous material). Thus the deposit was actually a mixture of the volatile components of the wire insulating varnish and an ant that had apparently strayed between the contacts at a bad time. Steps toward better ant-proofing were taken.

It would seem then that spectroscopy is not limited to purely scientific applications (i.e., physics, chemistry, and astronomy). Far from it. Food processors, oil companies, crime detection labs (see Figure 22) medical researchers, color labs, and a host of other users find spectroscopy an extremely potent tool.

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*Note that the horizontal axis is labeled Wave Number. This is the reciprocal of wavelength; in physical terms it is the number of waves per cm. Wave number is often used in infrared work because of the convenient numbers involved. Equivalent wavelengths are given for the two end points of the scale.

MASS SPECTROMETRY—ISOTOPES

In addition to the types of spectroscopy we have dis-
cussed, the term has also been applied to several fields in
which electromagnetic radiation is not involved. The sepa-
ration or dispersion principle remains intact, as in the
separation of a beam of particles according to energy or
other property. Beta-ray (electron) spectroscopy, for ex-
ample, measures the energies of electrons emitted from
nuclei while mass spectrometers sort out charged particles
according to their masses (or weights).

Mass spectrometry played a fundamental part in the
discovery of isotopes, which are used in medicine, industry,
and various other branches of science and technology.*
The basic device was developed in 1919 by F. W. Aston;
the essential parts of his machine are shown schematically
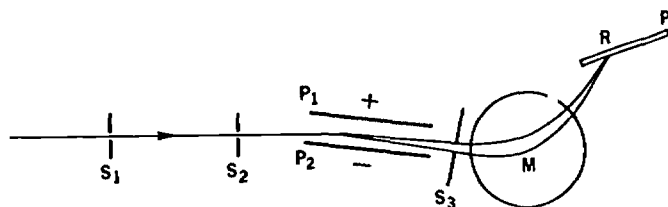in Figure 23. Positively charged ions (atoms stripped of

Figure 23 *Aston's mass spectrograph.*

one or more electrons) are accelerated toward the machine
from the left and are passed through two narrow slits S_1
and S_2 to produce a thin beam. The electrically charged
plates P_1 and P_2 bend the beam downward, at which point
a kind of dispersion takes place. The faster particles of a
given mass and charge are deviated less than the slower
ones. The resulting divergent beam enters the area marked
M, where a magnetic field (perpendicular to the plane of
the diagram) acts to bend the beam upward again.

The application of the two fields in this way causes all
particles having a certain ratio of mass-to-charge to con-

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*See *Radioisotopes in Medicine*, *Radioisotopes in Industry*, and
Power from Radioisotopes, companion booklets in this series.

verge in region R of the photographic plate P, regardless of their velocity. The points of focus for particles having a different value of this ratio would fall along other points of the plate.

If all the atoms of one element, say cadmium, are singly ionized (one electron removed), then the atoms of the element would be separated by mass—assuming there is such a variation. In such case (or if different types of ions are present) several regions are blackened, and the plate resembles an optical spectrum (Figure 24). For this reason, Aston called the instrument a mass spectrograph, and the resulting photographs mass spectra. Thanks to the great precision of the method it has been found that neon, for example, with an atomic weight 20.18, is actually a mixture of three different kinds (or isotopes) of the element. The great majority, 90.5%, is neon of mass 20 (10 protons and 10 neutrons), 0.3% has mass 21 (10 protons and 11 neutrons), and 9.2% has mass 22 (10 protons and 12 neutrons).
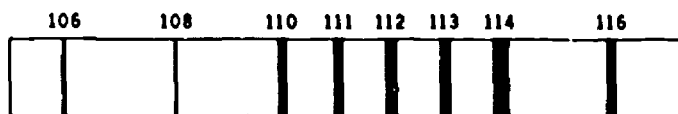
Figure 24 *Mass spectrum of cadmium (atomic weight, 112.41) shows it to consist of a number of isotopes.*

It can be seen that the isotopes of a given element differ from each other in the number of neutrons present in the nucleus. But, except in special cases, the number of neutrons has no effect on the number of electrons or on the chemical properties of the atom; and, by the same token, isotopes cannot be separated by chemical means. Mass spectroscopy is therefore considered a physical method of separation: The lighter isotopes are simply bent more than the heavier ones during their flight through the machine.

Today there are a number of advanced and even more accurate pieces of apparatus for separating isotopes and Aston's device now seems crude by comparison. But at

the time it was a remarkable example of experimental ingenuity.

In the 1940s oil companies began to use mass spectrographs to study the changes produced in the course of refining crude oil. The instrument can also be used for very precise analysis of complex mixtures and organic materials. (The disadvantage of the mass spectrograph is that it is expensive and complicated.) It can also be used to measure small amounts of impurity; a modern instrument can detect amounts as low as one part in 50 million. Hence it can be used as a leak detector of high sensitivity. It is also used in dating rocks for geological purposes, using a method that depends on the relative amounts of certain isotopes of strontium and rubidium.* Indeed the rubidium-strontium method has been very useful to supporters of the controversial continental drift theory in geophysics. It has provided strong evidence that South America and Africa were once a single piece of land that has since split open and drifted apart.

A recent development is the time-of-flight spectrometer. In this type the time for the ions to travel between two electrodes is used to distinguish between the groups. These instruments show promise of producing even greater sensitivity than the magnetic type, and are also simpler to construct. Time-of-flight mass spectrometers have been built into rockets and used to analyze the upper atmosphere continuously as the rocket ascended.

*See *Nuclear Clocks*, another booklet in this series.

OTHER TYPES OF SPECTROSCOPY

Fluorescence

Sometimes, as we mentioned earlier, atoms will reradiate electromagnetic energy of a different type from that which they absorb. Since in physics we cannot get something for nothing, the reradiated energy must be of lower energy and hence longer wavelength. The higher energy X-ray or ultraviolet radiations are generally used as the incident or excitation energy and the emitted radiation is called fluorescence. For example, many of you have undoubtedly seen rocks that glow when irradiated with ultraviolet or "black" light. If the specimen does glow, its type can often be determined by the color of its fluorescence.

Figure 25 *A technician of the Brookhaven National Laboratory adjusts a 4th-century glass bottle for X-ray bombardment. The elements in the glass will fluoresce at different wavelengths and reveal its composition. The bottle was discovered in an Italian tomb a century and a half ago. The engraving depicts the luxurious Roman harbor resort of Puteoli, near Naples.*

Many organic materials fluoresce. Even certain types of bacteria have characteristic fluorescence and different strains of the same type may show different colors. Bacterial growth and molds on meat samples can sometimes be detected and identified in this way. Many types of food products can be tested for quality by fluorescence analysis. Spectroscopy makes this type of analysis more specific than simple visual observation in the same way that it does with visual wavelengths.

Sometimes the atoms do not re-emit the radiation immediately but after delays ranging from fractions of a second to days. In such case the effect is called *phosphorescence*. Again the emission is characteristic of the material and can be used to gain information about it.

Comparative spectra — excitation and emission — taken on a modern instrument (a spectrophotofluorometer!) are shown in Figure 26. It can be seen that the two peaks of the original or exciting radiation are combined into one in the emission spectrum, which is shifted to a longer wavelength.
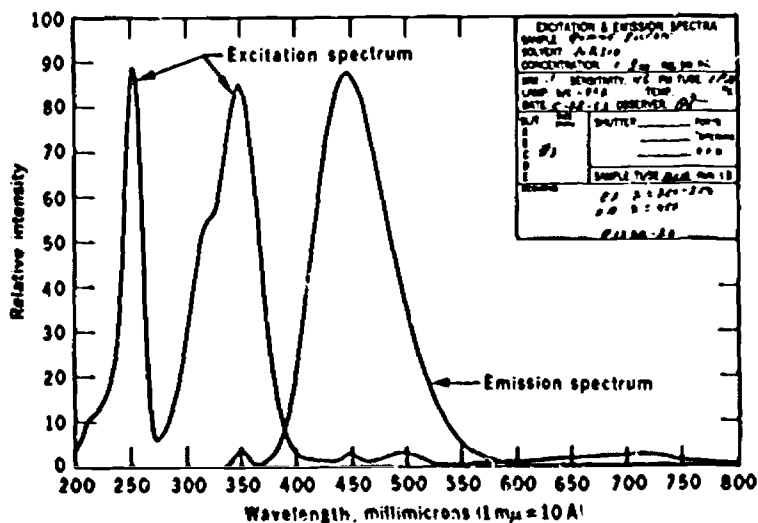

Figure 26 *Fluorescence spectrum of a quinine sulphate sample produced on the Aminco-Bowman SPF (spectrophotofluorometer). Excitation spectrum of the incident ultraviolet light is shown for comparison. (1 millimicron = 10 A)*

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Magnetic

We have seen that we can gain information about materials and atoms by dispersing electromagnetic radiation, and by separating ions according to their mass as well. There is yet another broad class of spectroscopic techniques that depends on separating a beam of particles by their energy, which in this case means momentum (mass times velocity). Again the technique is useful in both theoretical and analytical work.

One of the major types is called magnetic spectroscopy, which, as we shall see, is somewhat similar in principle to mass spectroscopy. However it finds its greatest use in determining momenta of charged particles emitted from radioactive nuclei or from nuclei that have been bombarded in a particle accelerator.
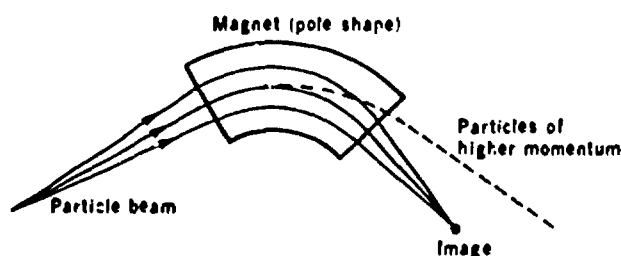
Figure 27 *Principle of magnetic spectroscopy. Particles are sorted by energy or momentum.*

This latter case is similar to looking at an object that is illuminated by light. We are really examining the rays reflected from it. In accelerators particles are scattered when they strike the atoms in a target, and by observing the results of these collisions researchers have learned much about atomic structure. As we saw earlier nuclei are much tinier than a wavelength of light and so cannot be seen. However, these accelerated particles are useful because, as explained by de Broglie's matter wave theory, their wavelengths grow smaller as their speed increases. Hence they can be used to "see" nuclei.

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Studying the particles emitted in radioactivity, on the other hand, is more like working with phosphorescent radiation. In both cases the atom has been energized in some way and is now emitting radiation.

And just to round out the picture, we could compare fluorescence with high-energy physics, where the nuclei are hit with particles of such high energy that they burst apart and emit many other particles—which were not there originally! — in the process.

There are many ways of studying these particles and from these studies we have learned most of what we know about nuclear structure. In high-energy physics, bubble and spark chambers are popular detectors. Both of these instruments use large magnets that cause the particles to curve in characteristic ways. Knowing the strength of the field, we can study the particles by direct measurements of the track curvatures.*

Although these detectors are not called spectrographs their use of the magnetic field is basically the same as in the mass spectrograph and in the magnetic spectrograph as well. The latter type of instrument is very useful in the study of fast-moving electrons, which are much lighter than protons and other "heavy" particles.

Several spectacular examples of magnetic spectrographs have recently been put into service at the Stanford Linear Accelerator Center in California. The usual image conveyed by the word spectrometer is totally inadequate to describe the scale of these devices, the largest of which (background in Figure 28) is 165 feet long and weighs 1700 tons! Yet they are built to move around a central point on rails and can measure angles to a precision of better than 0.01 degree.

In nuclear structure physics, where energies of millions of electron volts are used (as opposed to billions of ev in high-energy physics), the magnetic spectrograph has always faced competition from various other detectors that can be used for energy determination. Examples are the ion-

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*See the booklets *Accelerators* and *Microstructure of Matter* in this series, or *High Energy Physics*, H. Hellman, J. B. Lippincott Company, 1968.
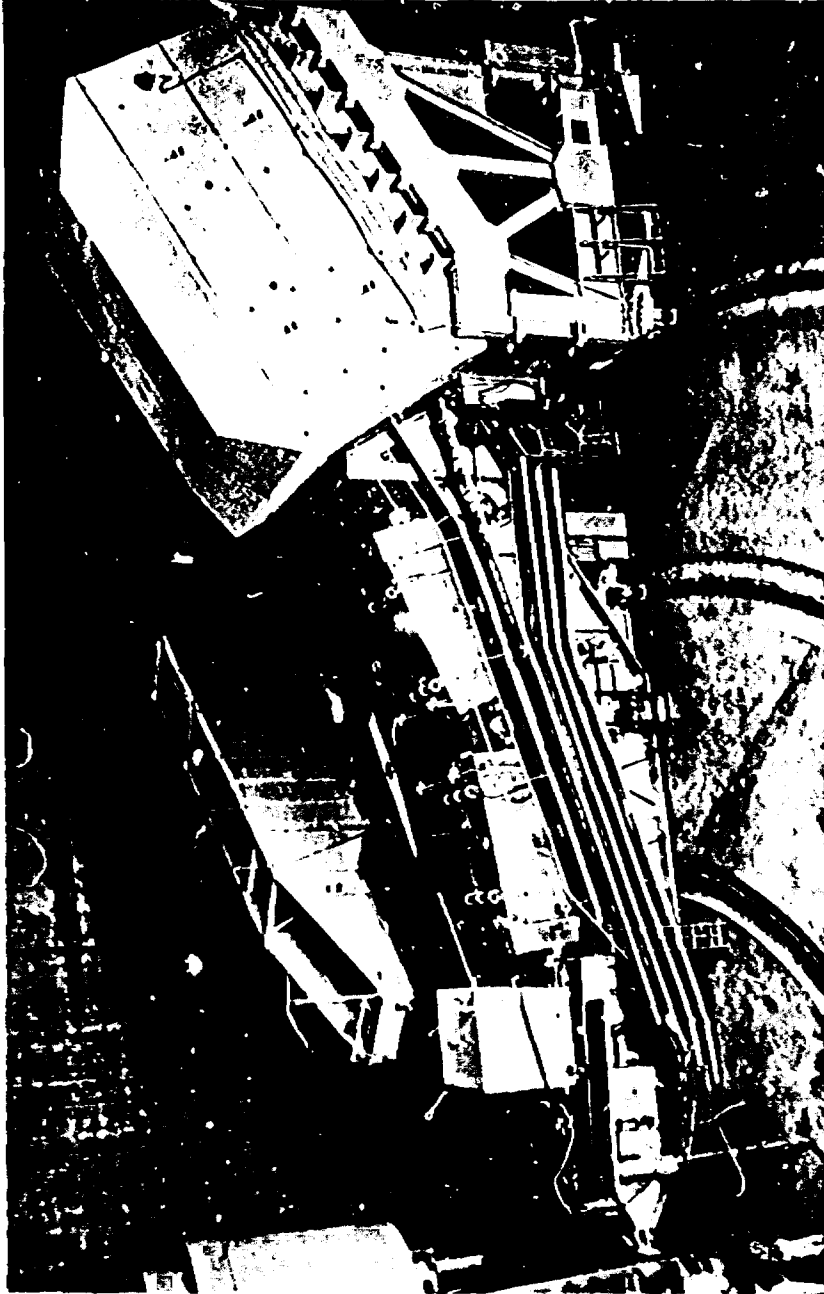
Figure 28 *Giant magnetic spectrometers at Stanford Linear Accelerator Center (SLAC) in Stanford, California. Electron beam strikes target nuclei at left. Emerging particles are separated and analyzed by powerful magnets in spectrometers. Note size of men at far left.*

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ization chamber (for example, a Geiger counter), scintillation counter, and solid-state counter.

The solid-state counter (essentially a semiconductor device whose conductivity changes momentarily when struck) has proved its value. It is simple and inexpensive, but cannot match the resolving power, accuracy, and "signal-to-noise ratio" of the magnetic type.

Among the particles of interest in high-energy physics are neutrons. But neutrons, being uncharged, will not respond to electric or magnetic fields.* Nor can they be ionized as atoms can. Therefore means other than magnetic *must* be used to sort them out. Here the time-of-flight method has proved useful. That is, the transit time of the neutron over a specified flight path is measured. The starting time is fixed by mechanically interrupting a neutron beam, and terminal time is obtained from a neutron detector at the end of the flight path. (Detection must be accomplished by observing the ionization produced by the charged-particle or gamma-ray products of the reaction.) The faster the flight of the particle, the higher its energy. Timing accuracies of a billionth of a second have been achieved with this method.

Alpha Scattering

In a variation of the scattering technique mentioned earlier, one forms a spectrum directly of energy rather than of scattering angle. When a material is bombarded by alpha particles, the particles are scattered by the atoms in the material at various angles and energies. The atomic number (number of protons in the nucleus) controls these angles and energies. The particles scattered by each element have a characteristic energy spectrum that can be detected and counted.

An exciting application of this scattering technique was carried out when Surveyor V landed on the moon. The spacecraft carried a small box that was lowered to the lunar surface on command from the earth. Alpha par-

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*This is not strictly true, for neutrons have been found to have a magnetic moment. Hence, they will respond to magnetic fields, although too weakly to affect our argument.

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ticles from a radioactive source, curium-242, bombarded a $4\frac{1}{2}$ square inch patch of lunar surface. Particles that struck nuclei of atoms in the top thousandth of an inch of lunar material were scattered in ways that depended on the elements involved. In addition some of the struck nuclei emitted protons. Semiconductor detectors measured the number of returning alpha particles or protons, and the exact energy of each particle. This information, which revealed the kinds and numbers of atoms present on the surface of the moon, was telemetered back to earth. The analysis indicates a surface of basalt (a volcanic rock found over wide areas of the earth), leading to the tentative conclusion that the moon is made of essentially the same materials as the earth.

Activation Processes

Information can be gotten on radioactive materials by inspection of the decay products, namely alpha, beta, and gamma rays. But nonradioactive materials can be *made* radioactive by bombarding them with electromagnetic radiation or energetic particles such as neutrons.


Figure 29 *View of a modern research reactor (TRIGA Mark I) used in neutron activation analysis.*

The general class of methods is called activation analysis, and when done with neutrons it is called neutron activation analysis.* This is an exquisitely sensitive method for the detection and quantitative determination ' most elements. In many cases it is 100 to 1000 times more sensitive than its nearest rival.

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*See *Neutron Activation Analysis*, a companion booklet in this series.
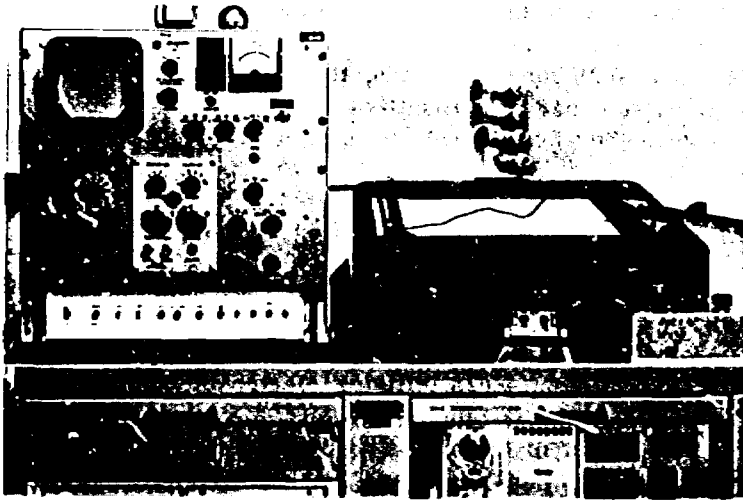
Figure 30 *Multichannel gamma-ray spectrometer used in activation analysis.*

The sample to be tested is inserted into a nuclear reactor (Figure 29), where it is bombarded with neutrons. By studying the resulting radiation spectrum as a function of time after irradiation, it is possible to figure out the quantity of each element present in the sample. An advantage of the method is that greater sensitivity can be achieved by simply subjecting the samples to longer periods of
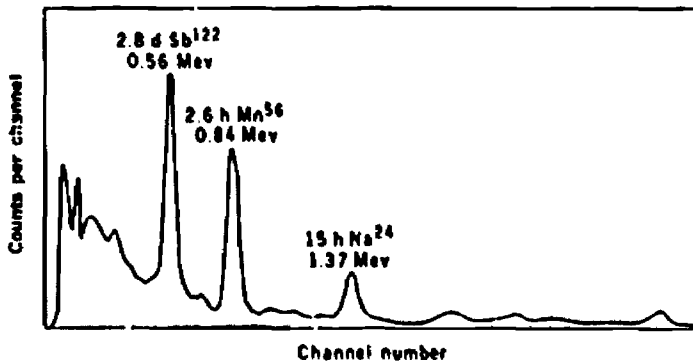
Figure 31 *Gamma-ray spectrum of a neutron-activated sample of paint.*

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bombardment. In the typical case of a 1-hour bombardment an average of a millionth of a gram of an element can be detected. With longer periods, the sensitivity rises to as high as a hundred-millionth of a gram.

The method has already been used as evidence in court on such materials as soil, paint, liquor, tape, and putty.

Raman

Widespread application of spectroscopy to analytical as well as theoretical problems did not occur until the time of World War II. What made it possible was the development of spectrometers utilizing electronic amplification. Further, optical systems were developed that could span the infrared or ultraviolet as well as the visible spectrum. In this sense, one could say that the field of absorption spectroscopy is a new one. And, as a matter of fact certain branches are quite new.

One branch, Raman spectroscopy, is only now overcoming some unique problems in instrumentation, even though the effect was discovered in 1928. Raman spectroscopy is based on an important exception to the rule that incoming photons must possess just the right amount of energy for transitions to occur. Under certain conditions, frequencies in the ultraviolet or visible regions may be partially absorbed and may cause molecules to rotate or vibrate. The photons are then re-emitted with a new frequency, represented by the Raman line, which is lower in frequency than the original photons and equal to the difference between the incident frequency and the rotational or vibrational frequency.

Eve i newer are the resonance techniques, which we discuss in the next section.

Resonance

Since electrons and protons are charged particles they react to a magnetic field. In such a field, the spin axis of each particle will line up with or against the direction of the field. This is true even when these particles are part of an atom or molecule. The two orientations represent two different energy levels !

As a simple example of what is going on, refer to Figure 32. Here we see the results of the capture of an electron by a hydrogen nucleus in space. The electron can fall into position with its spin either parallel to that of the proton (like two magnets lining up) or antiparallel. The former orientation is more stable than the latter, and can be thought of as a lower energy level.

Hydrogen
nucleus   Electron
(proton)

Stable (lower energy level)

Unstable (higher energy level)
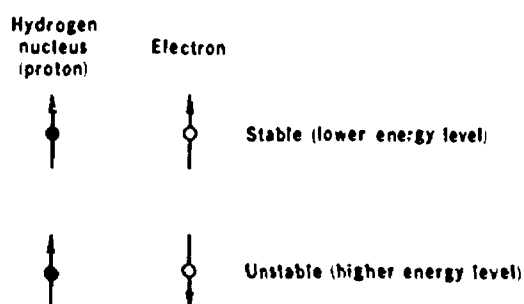
Figure 32 *Electron captured by hydrogen nucleus can fall into position representing higher or lower energy level.*

It can also be shown that the parallel position is three times more likely to occur than the other. Should the electron flip from the antiparallel to the parallel position, it emits a quantum burst of electromagnetic radiation in the radio frequency range. In radio astronomy this has come to be known ε the 21 cm line. By carefully plotting the variation in intensity of this line in different regions of the sky, we can obtain a fairly reliable picture of the distribution of gas and dust in a galactic plane (for example, the Milky Way) and out of it.

Conversely, if the electron is in the parallel position (also known as the stable, or lower energy, position), and is irradiated with 21 cm radiation, it will absorb a characteristic amount of the signal and flip over. Unpaired electrons in other elements will react in the same way to radiation of different, though still characteristic, wavelengths.

What we have then is a kind of absorption spectroscopy, because the amount of radiation absorbed at different wavelengths will be a function of the number of unpaired elec-

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trons present and absorbing at each characteristic frequency. If a known amount of 21 cm radiation is beamed at a sample and none is absorbed, it is immediately known that no hydrogen is present. If absorption takes place, the amount of radiation taken up is an indication of how much hydrogen is present. Other elements will absorb at different frequencies, but only if they contain unpaired electrons.

The method depends on the fact that the radiation and the energy differences are the same, or in "resonance". Hence the term electron spin resonance (ESR) or electron paramagnetic resonance (EPR) is used.

In practice ESR spectrometers supply their own fields, and rather strong ones at that. Typical field strengths range from 3000 to 12,000 gauss. (Earth's field is about 0.5 gauss.) For convenience the shorter microwave radiation is generally used, although some radio work is carried on them.*

Figure 33 *A modern powerful nuclear magnetic resonance (NMR) spectrometer. Sample is placed between poles of large electromagnet seen at rear.*
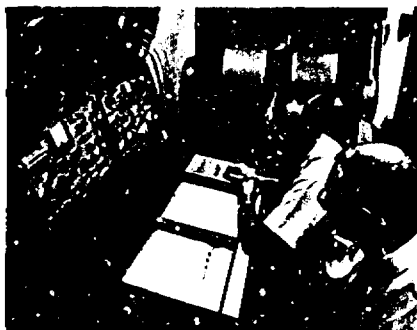
The spectrum of resonances for a sample under analysis can be displayed as a series of blips on a cathode-ray tube; it can also be recorded on various types of graphic output devices.

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*In truth, the method is slightly more complicated than we have pictured here. Actually the electrons precess — a kind of angular rotation — about the field axis at a frequency that is directly proportional to the field strength. If the sample is then irradiated with a microwave field, resonances will occur when the frequency of the microwaves equals the frequency of precession of the electrons.

A somewhat similar technique can be used for unpaired protons in a nucleus. For protons in a magnetic field of 14,000 gauss, the "flip" frequency is in the radio frequency region—at about 60 mc or 60 million cps. This technique is called nuclear magnetic resonance (NMR) and has become a powerful and versatile tool in the study of complex molecules, both organic and inorganic. A modern, powerful NMR spectrometer is shown in Figure 33.

CONCLUSION

Clearly the basic principle of spectroscopy is applied in many ways and to many purposes. Basic scientific investigation has paid off in many ways, particularly for industrial and scientific firms. But how about the workers themselves?

Kirchhoff, one of the early workers in the field, was looking into the question of whether certain lines seen in the spectrum of the sun revealed the presence of gold there. Kirchhoff's banker heard of this and remarked to him, "What do I care for gold in the sun if I cannot fetch it down here?"

Shortly afterwards Kirchhoff received a medal plus a cash prize in gold for his work. As he handed over the prize to the banker he observed, "Here, I have succeeded at last in fetching some gold from the sun."

Figure 34 *This 150-foot spec'rographic absorption tube, the world's largest, is used at the Pennsylvania State University to study the atmospheres of planets.*

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THE COVER

This portrait, owned by the Museum of Fine Arts in Boston, was originally identified as the work of a 15th century Flemish artist. The scientific curator of the museum suspected that the picture was a later work when he examined it with X rays. The rays should have been stopped by the lead carbonate used in contemporary paints, but they went right through the pigment. The Jarrell-Ash Company then examined the portrait using a laser and spectroscope and discovered the presence of zinc in the paint. Zinc paints were not used by artists until 1820.

THE AUTHOR

HAL HELLMAN is a free-lance science writer. Although he writes for both specialists and the non-technical public (including young adults), he prefers to interpret science for the latter, believing that it is both more difficult and more rewarding. The titles of some of his books, published or forthcoming reflect a wide range of interests — *Navigation: Land, Sea and Sky, Light and Electricity in the Atmosphere, The Art and Science of Color, Defense Mechanisms: From Virus to Man, Controlled Guidance Systems. High Energy Physics*, and *Lasers*, another booklet in this series.

Prior to going into full-time writing, Mr. Hellman was with General Precision, Inc. for 10 years. During the second five-year period he was Manager of Information Services, and it was during that time that his interest in science writing began.

Mr. Hellman holds a B.A. in Economics, an M.A. in Industrial Management, and an M.S. in Physics. He is a member of the National Association of Science Writers.

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