FRAUNHOFER LINES

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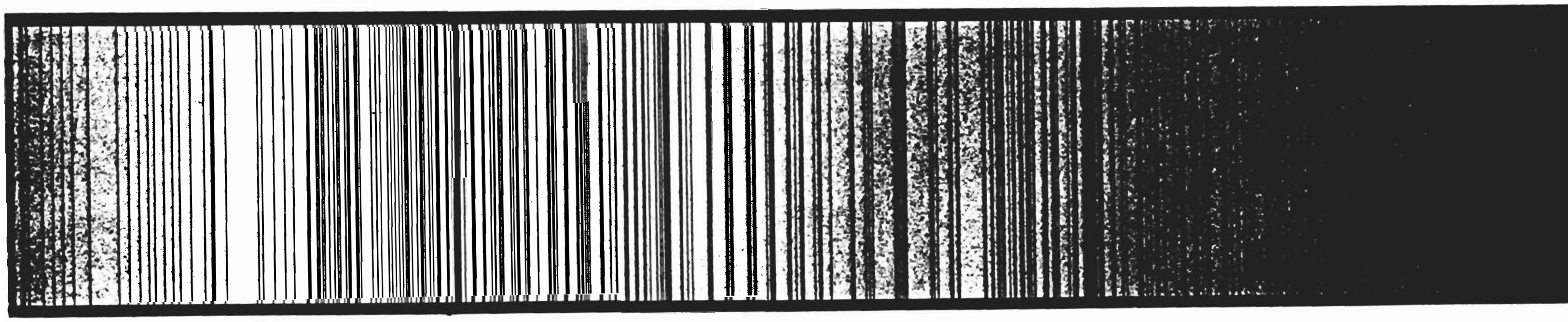

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HISTORY OF SCIENCE CASES

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Joseph von Fraunhofer was born in Straubing, Bavaria, on 6 March 1787, the tenth child of a poor glassmaker. Orphaned at an early age, he was apprenticed to a mirror maker and glass polisher in Munich. Two years later his master's house collapsed and young Fraunhofer was buried. Miraculously, he escaped injury. The ruling prince, Maximilian Joseph, was present at the excavation and presented the frail boy with a handsome sum of money. Fraunhofer used part of it to buy his freedom from his master and the rest of it to buy a glass-grinding machine. He then employed himself making optical glasses, studying mathematics and optics in his spare time. In 1806 Fraunhofer went to the Mathematical Institute in Munich as an optician. His efforts there led him to the discovery of the lines named after him and the means to produce larger refracting telescopes. Other scientists you will meet in this case are:

ISAAC NEWTON, English physicist and mathematician
Born Woolsthorpe, England, 1642; died Kensington, England, 1705.

WILLIAM HYDE WOLLASTON, English physician, chemist, and physicist
Born Dereham, England, 1766; died London, England, 1828.

ROBERT WILHELM BUNSEN, German chemist
Born Göttingen, Germany, 1811; died Heidelberg, Germany, 1899.

GUSTAV ROBERT KIRCHHOFF, German physicist
Born Königsberg, Prussia, 1824; died Berlin, Germany, 1887.

INTRODUCTION

In this HISTORY OF SCIENCE CASE, we shall make a critical study of a part of the development of a major scientific idea. Although we want to learn something about this idea, our chief interest in this case will be to find out as much as we can about

- the methods used by scientists
- the means by which science advances and the conditions under which it flourishes
- the role of scientists as people and the personal characteristics of scientists
- the interplay of social, economic, technological, and psychological factors in the progress of science
- the importance of accurate and accessible records, constantly improved instruments, and free communication

Proper study of this case consists of more than simply reading this little booklet. In the margin of the left-hand pages, next to the narrative, you will find numerous comments and questions. These marginal notes are intended to guide discussion on the points illustrated by the case. On the right-hand pages, the questions are repeated in expanded form and space is provided for you to write your answers. A most important part of the study of this case is the series of experiments suggested on the right-hand pages. You should complete as many of these as possible, so that you can get a real feel for the situations faced by scientists in creating science. Additional related activities and exercises are given at the end of the narrative, and your teacher may suggest others. On the last page you will find a list of suggested books and articles relating to the story of this particular case.

Some students may think that this case is out of date because the story is set in the scientific past. Nothing could be further from the truth. The points about science and scientists that are featured in this case are just as cogent in the present as they were in the past. The methods of scientific investigation are much the same today as they were several hundred years ago; similar nonscientific factors still interact with the progress of science; the character and personalities of scientists are still paramount factors in the development of scientific thought; adequate recording, free communication, and improved instrumentation continue as vital needs. These aspects of science held true yesterday, hold true today, and will hold true tomorrow.

As you study this case and work through the exercises, you will learn a great deal about scientists and about what goes on in science.

L.E.K.

FRAUNHOFER LINES

How can scientists get such information? (1)

Astronomers today can tell us that there is only a small amount of water present on the planet Mars, that there is none on the moon, and that there is very little water present in the atmosphere of the planet Venus. Reaching farther into space, they are quite confident about the chemical elements that exist in the sun and in many of the stars. How do they know these facts about the far-distant heavenly bodies? How is it possible for scientists to get information about the materials making up the moon, planets, sun, and stars when practically the only source of this information is the light by which we see these objects in the sky?

Where investigations in science may lead cannot be predicted in advance.

In this case we shall explore a series of fascinating observations on natural and artificially produced light. We shall see that, through their efforts to explain new observations, scientists of several countries contributed to a better understanding of the characteristics and behavior of light. We shall also see that the developments we will be following in this case led to the opening of a vast new field of scientific investigation—the study of spectra. Active pursuit of investigations in this new science eventually yielded not only new knowledge about the materials in the heavenly bodies, but also new insights into the structure and properties of matter itself. The first high point in the development of the new science of spectroscopy was the careful study by Joseph von Fraunhofer of the thousands of dark bands—now known as Fraunhofer lines—running across the bright, rainbow-colored spectrum of sunlight. Our story, however, begins almost a hundred and fifty years before the work of Fraunhofer. Our story begins with Sir Isaac Newton.

Why is Newton called one of the great scientists of all time? (2)

Almost everyone has heard of Newton, who is hailed as one of the great scientists of all time. Some of Newton's most important scientific work was done in connection with his study of light. Long before Newton many persons had observed that the white light of the sun can produce the brilliant colors of the rainbow. (Some ways of producing these colors from sunlight are suggested in Activity 1, page 28.) However, Newton was the first to make an experimental study of this phenomenon. He describes the beginning of his experiments in this way:

What is the difference between an everyday observation and an experimental study? (3)

Scientific work demands careful observation.

> "In the year 1666 . . . I procured me a Triangular Glass-Prism, to try therewith the celebrated Phaenomena of Colours. And in order thereto having darkened my Chamber, and made a small Hole in my Windowshuts, to let in a convenient Quantity of the Sun's Light, I placed my Prism at its Entrance, that it might thereby be refracted to the opposite Wall. It was at first a very pleasing Divertissement, to view the vivid and intense Colours produced thereby; but after applying myself to consider them more circumspectly, I became surprised to see them in an oblong Form; which . . . I expected should have been circular. They were terminated at the Sides with straight lines, but at the Ends the Decay of Light was so gradual, that it was difficult to determine justly what was their Figure, yet they seemed Semi-circular."

Why do we carry out experiments in science? (4)

This unexpected appearance of the image of the light coming through the circular hole in the window shutter was apparently enough to set Newton off on a series of experiments to learn more about the "Phaenomena of Colours." Newton carried out these experiments in his characteristically thorough way. (You can easily perform some of Newton's experiments yourself. See Experiment 1.) After Newton had completed his experiments, he reported:

> "Concerning Light, I have discovered that its Rays, in respect to the Quantity of Refraction, differ from one another. Of those that have all the same Angle of Incidence, some will have their Angle of Refraction somewhat

[Use these right-hand pages for writing your answers to the questions brought out by the story of the case and for making notes on the experiments.]

1. Like all human beings, scientists get information about the world through their five senses. Yet they also obtain information about nature that does not come directly to their sense of sight, hearing, smell, taste, or touch (such as the amount of water on Mars). How is this possible?

2. Why is Newton called one of the great scientists of all time? What is there about a certain scientist that makes him great?

3. What is the difference between an everyday observation and an experimental study? How are everyday observations and scientific experiments similar? How are they different?

4. Why do we carry out experiments in science?

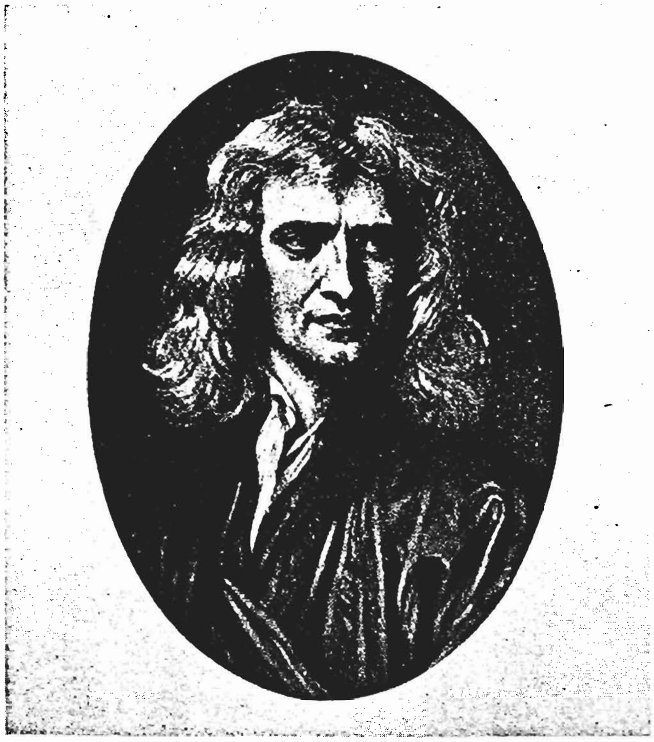
EXPERIMENT 1. Newton's Experiments

You can readily repeat Newton's experiment using a 60° glass prism in a darkened room. Simply darken a room into which the sun is shining. Punch a small hole in the window shade to admit a thin beam of sunlight. Hold the prism in the beam of light and observe the band of colors on the opposite wall or ceiling. What is the shape of the spectrum produced?

Hold a second prism or a convex lens (reading glass) in the beam of light from the first prism. How must you hold the second prism to recombine the colored spectrum into white light? Why does the convex lens produce a similar effect?

Since a darkened room may be hard to come by, you may wish to use a laboratory source of white light, such as a carbon-arc lamp. Mount a narrow slit in front of the carbon arc to produce a beam of light. Let the beam pass through a 60° prism at an angle and then to a white cardboard screen about 10 feet from the prism. (A convex lens between the slit and the prism can be used to focus the beam on the screen.) Try various slits in front of the arc lamp. How do the size and shape of the slit affect the spectrum produced?

By cutting a narrow slit in the cardboard screen, you can let different parts of the spectrum pass through for study. Turn the prism on its long axis so that light of only one color passes through the slit at a time. By using a second prism placed behind this slit in the screen, Newton established that the different colors of light were bent (refracted) in different amounts. Can you verify this by experiment? Which color is refracted most? Which color is refracted least?



Although he plays only a minor role in *Fraunhofer Lines,* Isaac Newton is by far the greatest scientist who appears in the case. In the two years following his graduation from Cambridge, Newton developed the binomial theorem, worked out the elements of differential and integral calculus, developed the concept of universal gravitation, and performed his experiments with the refraction of light. All this at the age of 23–24. Newton's publications invariably provoked great controversy. Although he was vigorous in his defense of his scientific beliefs, he possessed a great modesty that was critical to his intellectual processes. Shortly before his death he said, "I do not know what I may appear to the world, but to myself I seem to have been only like a boy playing on the seashore, and directing myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me." *Picture reproduced by courtesy of Culver Pictures, Inc.*

Do you know what Newton means by "refraction"? by "angle of incidence"? You'd better review if you don't.

greater, others will have it somewhat less . . . I moreover find that the Rays refracted the most produce purple Colours and those the least refracted produce red Colours . . . and so the Rays . . . do generate these Colours in order; red, yellow, green, blue and purple, together with all the intermediate ones that may be seen in the rainbow."

Even the greatest scientists, being human, sometimes fail to see everything. Can you account for the long lapse of time? (5)

Newton gave the name *spectrum* to the band of rainbow colors that he studied so carefully. In spite of his diligent work, however, there was one important observation in the spectrum that Newton missed. This observation, although not a particularly difficult one to make, was not reported until 1802, more than a hundred and thirty years after Newton's work on the spectrum.

An English chemist and natural philosopher, William Hyde Wollaston (see Activity 2, page 28), was the first to see in the spectrum of the sun something that, by strange chance, no one had ever seen before. In a paper entitled "A Method of Examining Refractive and Dispersive Powers by Prismatic Reflection," which he read before the Royal Society of London on 24 June 1802 Wollaston said:

What is the Royal Society? What is its purpose? (6)

"I cannot conclude these observations on dispersion without remarking that the colours into which a beam of white light is separable by refraction, appear to me to be neither *seven* as they usually are seen in the rainbow, nor reducible by any means (that I can find) to *three,* as some persons have conceived; but, that by employing a very narrow pencil of light, *four* primary divisions of the prismatic spectrum may be seen, with a degree of distinctness that, I believe, has not been described nor observed before."

Do scientists always agree on their observations? (7)

Wollaston goes on to tell us how he made this new observation and how he interpreted it:

New observations are always of interest to scientists. Why? (8)

"If a beam of day-light [sunlight] be admitted into a dark room by a crevice

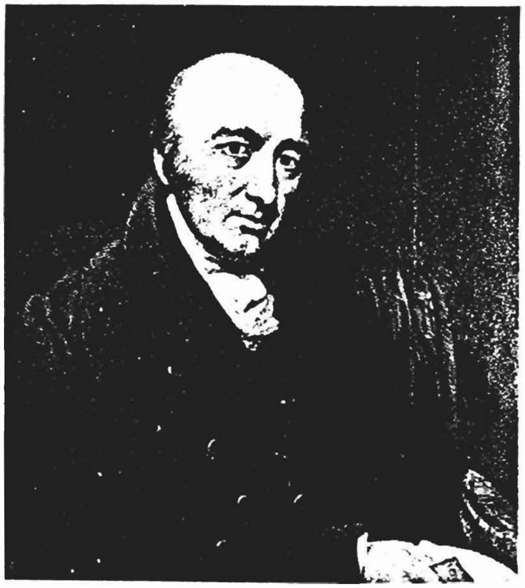
5. Can you account for the long lapse of time between Newton's work on the spectrum and Wollaston's observations? What might be some of the reasons why no further work was reported on the spectrum during these hundred and thirty years?

6. What is the Royal Society of London? What is its purpose?

7. Do scientists always agree on their observations? (We'll be sporting and give you the answer to this question, but we have a more interesting question for you right after.) No, scientists do not always agree on their observations. In fact, important ideas have often developed out of such disagreements.

Now try this one: Two scientists may observe the same phenomenon and then report different observations. What reasons can you give for such a disagreement?

8. Why are new observations always of interest to scientists?



Wollaston's range of interests was extraordinarily wide. He was a lecturer of Greek and Hebrew at Cambridge, studied astronomy under the astronomer royal of Ireland, and practiced medicine from 1788 to 1800. He gave up his medical practice because of his hypersensitivity to the afflictions of his patients. At that time he began his scientific investigations, which he continued to conduct until his death in 1828. Although his research was intended to be limited to chemistry, it soon expanded to a very wide range of projects. He discovered palladium and rhodium and did brilliant work on the physiology of sight, and his electrical experiments brought him to the point of perceiving the magnetic field produced by a current-carrying conductor. All in all, Wollaston published fifty-six papers in his twenty-eight-year career as an experimental scientist. *Picture reproduced by courtesy of Historical Pictures Service, Chicago.*

Why is it important that the glass be free from veins? (9)

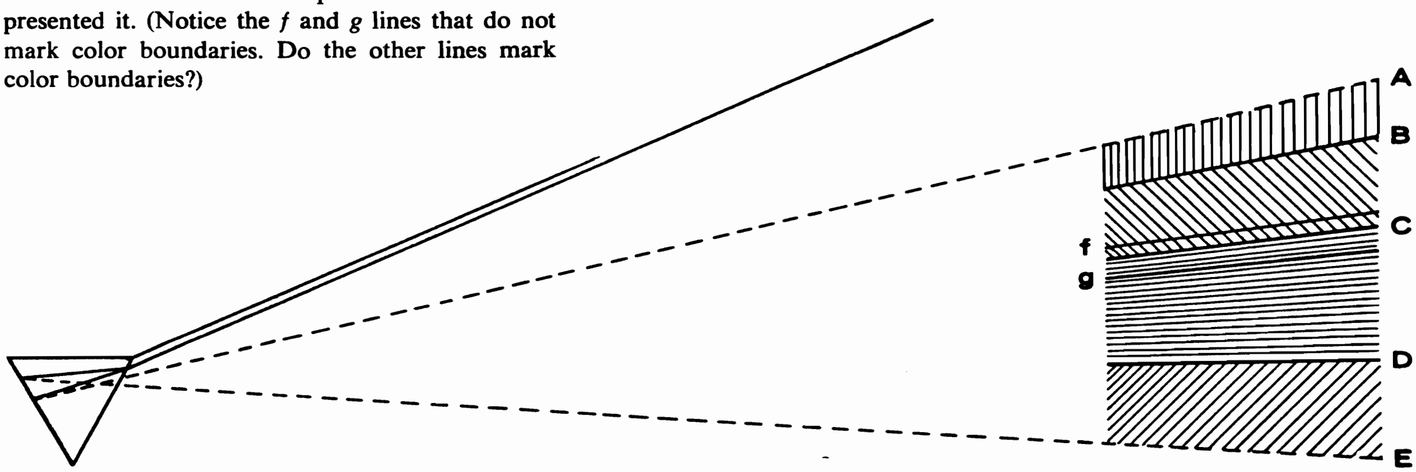
1/20 of an inch broad, and received by the eye at a distance of 10 or 12 feet, through a prism of flint-glass, *free from veins,* held near the eye, the beam is seen to be separated into the four following colours only—red, yellowish-green, blue, and violet, in the proportions represented in [the figure below]. [To see what Wollaston saw, try the observations in Experiment 2.]

Note that Wollaston disregards certain lines.

"The line *A* that bounds the red side of the spectrum is somewhat confused, which seems in part owing to the want of power in the eye to converge red light. The line *B* between red and green, in a certain position of the prism is perfectly distinct; so also are *D* and *E,* the two limits of violet. But *C,* the limit of green and blue, is not so clearly marked as the rest; and there are also on each side of this limit other distinct dark lines *f* and *g,* either of which in an imperfect experiment might be mistaken for the boundary of these colours.

"The position of the prism in which the colours are most clearly divided is

The formation of the solar spectrum as Wollaston presented it. (Notice the *f* and *g* lines that do not mark color boundaries. Do the other lines mark color boundaries?)



EXPERIMENT 2. Wollaston's Experiment

The description of Wollaston's experiment, as given on page 8, is clear enough for you to repeat the experiment for yourself. The physical setup is essentially the same as for Experiment 1. However, you must give careful attention to the size of the slit through which the sunlight is admitted. Can you see some of the dark Fraunhofer lines in the sun's spectrum? How good an observer was Wollaston?

Another means of observing some of the Fraunhofer lines with simple apparatus is given by Henry C. Crew in *The Rise of Modern Physics,* page 156. Lay a strip of white paper 1/16 inch wide on a piece of black velvet in the sunlight. Look at this strip through a 60° glass prism, turning the prism until you see the solar spectrum reflected from the white paper. Do you see any Fraunhofer lines in the spectrum?

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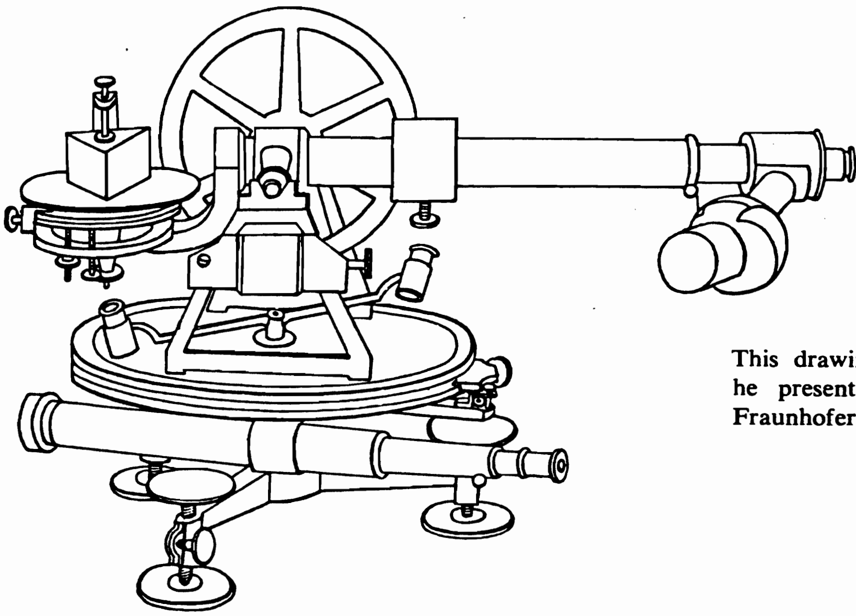
9. Why is it important that the glass be free from veins?



This drawing shows some of Fraunhofer's apparatus as he presented it in his original papers. Picture from Fraunhofer's *Collected Works*.

Of what value are these numbers? (10)

when the incident light makes about equal angles with two of its sides. I then found that the spaces *AB, BC, CD, DE,* occupied by them were nearly as the numbers 16, 23, 36, 25."

What was at fault in Wollaston's work—his observation or his interpretation? (11)

Now it happens that Wollaston was mistaken in believing that the solar spectrum is broken up into four primary color divisions by dark boundary lines. The spectrum is in fact a continuous band of changing colors, and the names we give to different sections of it have no physical divisions. However, Wollaston did report that he saw seven dark lines crossing the prismatic spectrum of the sun. Although he did not interpret this observation correctly and did not follow it up, Wollaston must be given credit for being the first man to observe a few of the dark Fraunhofer lines.

One man cannot do everything. A scientist must choose what he will study.

The man responsible for the first thorough study of these lines, in whose honor they were later named, was a young German optician, Joseph von Fraunhofer. As a maker of fine optical instruments, Fraunhofer was interested in investigating the properties of glass. In the early 1800s he was working on the problem of getting rid of the disturbing colored fringes that always appeared around objects seen through the lenses of telescopes and field glasses. He was trying to perfect an achromatic telescope, that is, a telescope with lenses so arranged that the objects would not be surrounded by the annoying colored fringes. Fraunhofer reported on his trials to the Bavarian Academy of Sciences at Munich in 1814 in an epoch-making paper that included a full account of his careful and skillful observations of the solar spectrum by means of a new instrument that he had devised.

Special instruments are needed in scientific work.

Was this "Academy" a German school? (12)

Of what value are new instruments in science? (13)

What is a theodolite? How is it used? (14)

"In the window-shutter of a darkened room I made a narrow opening—about 15 seconds broad and 36 minutes high—and through this I allowed sunlight to fall on a prism of flint-glass which stood upon the theodolite described before [in an earlier section of the paper]. The theodolite was 24 feet from the window, and the angle of the prism about 60°. The prism was so placed

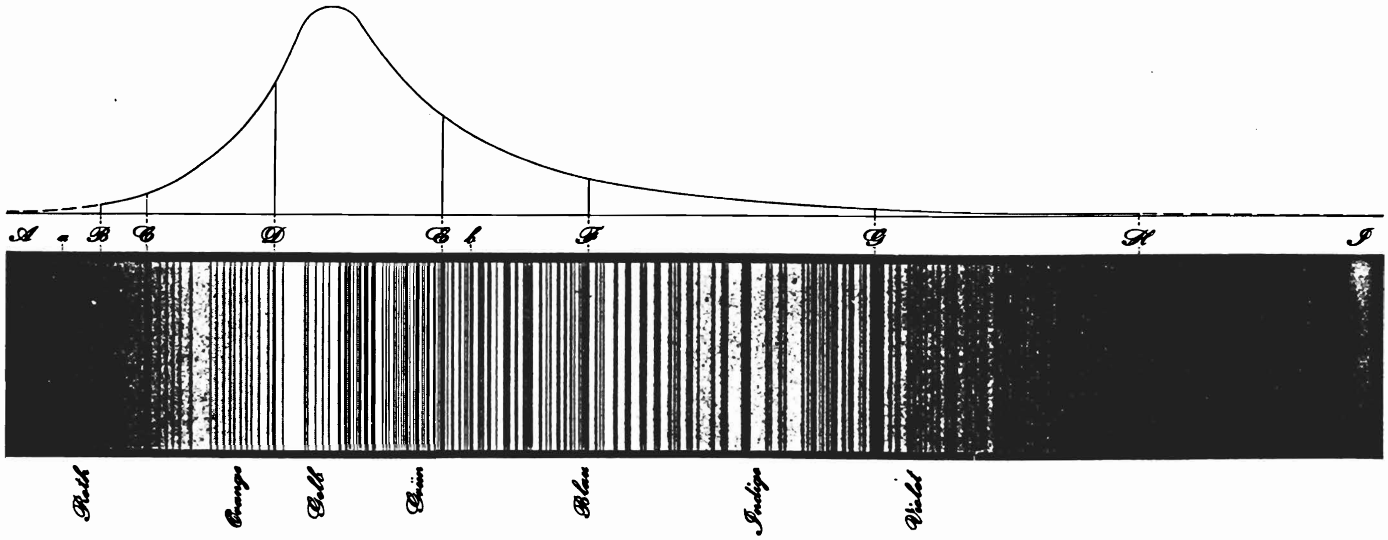
10. Of what value are these numbers? In general, how is science aided by the use of numbers and mathematics?

11. What was at fault in Wollaston's work—his observation or his interpretation?

12. Was this "Academy" a German school? If not, what was it?

13. Of what value are new instruments in science?

14. What is a theodolite? How is it used?



Fraunhofer's drawing of the solar spectrum as he presented it in his original paper. (Why was Fraunhofer able to see so many more lines than Wollaston saw? Do these lines mark color boundaries? How was he able to map them?)

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in front of the objective of the theodolite-telescope that the angle of incidence of the light was equal to the angle at which the beam emerged . . . I saw with the telescope an almost countless number of strong and weak vertical lines, which are, however, darker than the rest of the color-image; some appeared to be almost perfectly black."

Changing the conditions is a useful technique when scientists investigate a new phenomenon.

When Fraunhofer changed the conditions of his experimental setup to discover how the appearances of the dark lines might be affected, he found:

"The distance apart of the lines, and all their relations to each other, remained unchanged, both when the width of the opening in the window-shutter was altered and when the distance of the theodolite from the opening was changed. The prism could be of any kind of refractive material, and its angle might be large or small; yet the lines remained always visible, and only in proportion to the size of the color-image did they become stronger or weaker, and therefore were observed more easily or with more difficulty.

Why was Fraunhofer able to observe more accurately than Wollaston? (15)

"The relations of these lines and streaks among themselves appeared to be the same with every refracting substance; so that, for instance, one particular band is found in every case only in the blue; another is found only in the red; and one can, therefore, at once recognize which lines he is observing. . . . The strongest lines do not in any way mark the limits of the various colors; there is almost always the same color on both sides of a line, and the passage from one color to another cannot be noted. . . .

Fraunhofer rejects any facile explanation for the lines.

"I have convinced myself by many experiments and by varying the methods that these lines and bands are due to the nature of sunlight, and do not arise from diffraction, illusion, etc."

Scientists are continually asking questions of nature.

But Fraunhofer did not stop his investigation at this point. He knew from other experiments that the spectra of light from various flames did not show the dark lines he had seen in the spectrum of the sun. Would the light from other heavenly bodies show the lines?

"I applied this form of apparatus at night-time to observe Venus directly, *without making the light pass through a small opening;* and I discovered in

15. Why was Fraunhofer able to observe more accurately than Wollaston? (This is a double-barreled question, since there are at least two good reasons that you might suggest. One of the reasons is pretty obvious, but others will take a little thought. Incidentally, we assume that the two men had equally good eyesight. The fact that one was English and the other German is irrelevant.)

EXPERIMENT 3. Fraunhofer's Observations

You may wish to verify Fraunhofer's observations of the dark lines in the sun's spectrum. For this purpose it is better to use a modern prism spectroscope rather than Fraunhofer's original arrangement of prism and theodolite. Why? (Your teacher will give you instructions on the use of the particular instrument that is available to you.) You will soon find that you must work quite carefully to obtain a good view of the Fraunhofer lines. Here are some of the precautions given by Fraunhofer in his paper of 1814:

"Since the lines and bands in the color-image have only a very small width, it is evident that the apparatus must be most perfect in order to avoid all aberrations which could make the lines indistinct or entirely scatter them. The faces of the prism must therefore be perfectly plane. The glass to be used in such prisms should be entirely free from waves and streaks; . . . the faces should make an angle of 90°, or nearly so, with the base; this must be placed horizontal, in front of the telescope, if the axis of the latter is horizontal. The narrow opening through which the light enters must be exactly vertical . . .

"If the prism was turned so as to increase the angle of incidence, these lines vanished; they disappear also if the angle of incidence is made smaller . . . If the opening through which the light entered was made broader, the fine lines ceased to be clearly seen, and vanished entirely if the opening was 40 seconds wide. If the opening was 1 minute wide, even the broad lines could not be seen plainly."

On the opposite page is a copy of the drawing that Fraunhofer made to illustrate his observations. He describes his observations more fully in the report. Can you observe as well as Fraunhofer?

"With reference to these lines the color-image is as shown in [the drawing]. It is, however, impossible to show on this scale all the lines and their intensities (the red end of the color-image is in the neighborhood of *A*; the violet end is near *I*.) . . . Direct sunlight, or sunlight reflected by a mirror, seems to have its limits, on the one hand, somewhere between *F* and *H;* on the other, at *B;* yet with sunlight of greater intensity the color-image becomes half again as long. . . . At *A* there is easily recognized a sharply-defined line; yet this is not the limit of the red color, for it proceeds much beyond. At *a* there are heaped together many lines which form a band; *B* is sharply defined and is of noticeable thickness. In the space between *B* and *C* there can be counted 9 very fine, sharply-defined lines. The line *C* is of considerable strength, and, like *B*, is very black. In the space between *C* and *D* there can be counted 30 very fine lines; but these (with two exceptions), like those between *B* and *C*, can be plainly seen only with strong magnification or with prisms which have great dispersion . . . *D* consists of two strong lines which are separated by a bright line. Between *D* and *E* there can be counted some 84 lines of varying intensities. *E* itself consists of several lines, of which the one in the middle is somewhat stronger than the rest. Between *E* and *b* are about 24 lines. At *b* there

EXPERIMENT 3 continued on page 15

the spectrum of this light the same lines as those which appear in sunlight. . . . I have seen the lines *D, E, b, F* perfectly defined. . . . I have convinced myself by an appropriate measurement of the arcs *DE* and *EF* that the light from Venus is in this respect of the same nature as sunlight.

Is this a result that we might have expected? Why, or why not? (16)

"With this same apparatus I made observations also on the light of some fixed stars of the first magnitude. . . . I have seen with certainty in the spectrum of Sirius three broad bands which appear to have no connection with those of sunlight; one of these bands is in the green, two are in the blue. In the spectra of other fixed stars of the first magnitude one can recognize bands; yet these stars, with respect to these bands, seem to differ among themselves."

What hypotheses can you suggest to account for these observations on the stars? (17)

It is often easier to observe a new phenomenon than to explain it.

Fraunhofer himself did not provide any suggestions about what the cause of the dark spectral lines might be. Ironically, in describing his experiments he frequently made an observation which, unknown to him, was an important clue to the explanation.

"If lamplight is allowed to pass through a very narrow opening of 15 to 30 seconds' width and then fall upon a strongly dispersive prism placed in front of a telescope, it is seen that the reddish-yellow bright line of this spectrum consists of two very fine bright lines which in intensity and distance apart are like the two dark lines *D* [in the drawing on page 10]."

Why might he have felt this way? (18)

Perhaps Fraunhofer felt that an explanation of his discovery was outside his area of competence, for at the end of his paper he remarked:

"In all my experiments I could, owing to lack of time, pay attention to only those matters which appeared to have a bearing upon practical optics. I could either not touch other questions, or at most not follow them very far. Since the path thus traced in optical experiments seems to promise to lead to interesting results, it is greatly to be desired that skilled investigators should devote attention to it."

An investigator must select his line of study and put others aside. Is this a good thing? (19)

New instruments can make new experiments possible.

In some of his later work Fraunhofer fashioned diffraction gratings from fine metal wires and ruled several closely spaced gratings on glass. He was the first investigator to study the spectra formed by diffraction gratings, and with his newly devised gratings Fraunhofer made the earliest measurements of the wavelengths of light. (See Activity 3, page 28.)

Now despite the fact that Fraunhofer published reports of his investigations to inform other scientists about the dark spectral lines, an adequate explanation of the Fraunhofer lines was not offered for more than forty years. The explanation was then made possible largely because of new investigations in an area of study which, at first sight, seems far removed from the appearance of dark lines in the spectra of the sun and other stars. The new investigations were made on the colored light of flames.

To what extent can the direction that science will take be predicted? (20)

It had long been known that when certain chemicals are put in a fire, the flame of each burns with a characteristic bright color. As the science of chemistry developed, a number of chemists began to use these characteristic colors as a quick means of testing for the presence of certain chemical elements. Such flame tests are still used today, as you probably know. (See Experiment 4.) However, except for a few elements the flame tests are not very reliable because the phenomena are difficult to observe accurately, and chemists sought a more dependable means of rapid qualitative analysis.

Why are chemists interested in such tests? What is meant by "reliable"? (21)

It had occurred to a number of investigators to examine the colored flames are 3 very strong lines, two of which are separated by only a narrow bright line; they are among the strongest lines in the spectrum. In the space between *b* and *F* there can be counted about 52 lines; *F* is fairly strong. Between *F* and *G* there are about 185 lines of different strengths. At *G* there are massed together many lines, among which several are distinguished by their intensity. In the space between *G* and *H* there are about 190 lines, whose intensities differ greatly. The two bands at *H* are most remarkable; they are almost exactly equal, and each consists of many lines; in the middle of each there is a strong line which is very black. From *H* to *I* the lines are equally numerous.

"In the space between *B* and *H* there can be counted, therefore, about 574 lines, of which only the strong ones appear on the drawing . . ."

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16. Might we have expected that the light from Venus would show the same kind of lines as the light from the sun? Why, or why not?

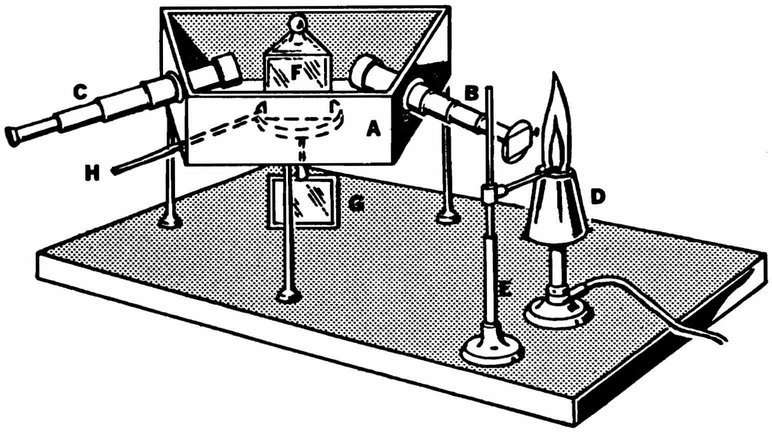
17. What hypotheses can you suggest to account for these observations on the stars?

18. Why might Fraunhofer have felt that an explanation of the dark spectral lines was outside his area of competence? (By the way, what is meant by "area of competence"?)

19. Is it a good thing for an investigator to specialize in one rather narrow line of study?

20. To what extent can the direction that science will take be predicted?

21. Why are chemists interested in reliable tests for chemical elements? What is meant by "reliable"? Why is reliability important?



BUNSEN'S FIRST SPECTROSCOPE

A. supporting box
B. collimator
C. viewing telescope
D. Bunsen burner
E. support rod for sample
F. hollow prism (filled with CS_2)
G. mirror to measure angles through which prism is turned
H. handle to turn prism

How do scientists obtain pure chemicals? (22)

Many observations are often needed to develop a single idea.

New instruments are important in science.

by means of a prism. Again the results were confusing. Three factors were chiefly responsible for the confusion: the chemicals available for experiment were not sufficiently pure; in the burners then in use the burning oil or alcohol produced a spectrum that was superimposed on the spectrum of the chemical put into the flame; and there were no satisfactory instruments with which to view the spectra. Nevertheless a fact of major importance began to emerge from this work. Unlike the spectrum of the sun, which is a continuous rainbow-colored band, the spectra of the chemicals put into a flame appeared to be made up of discontinuous vertical lines of color. Such bright-line spectra were observed by investigators in England, Scotland, France, Germany, and America (see Activity 4, page 30), but it was not until after the introduction of two new pieces of apparatus by Robert Bunsen that they were understood and put to use.

At the age of seventeen Bunsen entered the University of Göttingen, where his father was head librarian and professor of philology. Eight years later he began his teaching career in chemistry at the Polytechnic Institute at Kassel. As a teacher of chemistry Bunsen was almost without rival. He was one of the first to recognize the importance of practical laboratory work for students and was constantly present with his students, giving them personal direction and assistance. In 1834 Bunsen discovered that precipitated, hydrated, ferric oxide is an antidote for arsenic poisoning. During his six years as an active experimental scientist he lost the sight of one eye from a gas explosion and almost died of arsenic poisoning. His most far-reaching achievements, however, result from his investigation of spectra with Kirchhoff. *Picture reproduced by courtesy of The Bettmann Archive.*

22. How do scientists obtain pure chemicals? (What does this tell you about the dependence of science upon advances in manufacturing processes?)

EXPERIMENT 4. Flame Tests

Several metallic chemical elements produce a distinctive color when the element or one of its salts is placed in a Bunsen flame. Several techniques for making flame tests are commonly used. Here is a simple one (A. R. Clark, *Journal of Chemical Education,* 12:242 [1935]):

Prepare separate beakers of solutions of various metallic salts, say sodium chloride, potassium chloride, calcium chloride, barium chloride, strontium nitrate, copper (II) nitrate, lead nitrate. Take a Pyrex test tube three-quarters full of cold water and heat the tube in a Bunsen flame to dry the outside. Dip the tube into one of the prepared solutions and again heat it in the flame. What is the color of the flame? Dip the tube into the same solution again and reheat to confirm your observation.

SODIUM	POTASSIUM	CALCIUM	BARIUM
STRONTIUM	COPPER	LEAD	(OTHER)

After you have tested one solution and before going to another, dip your test tube into a beaker of dilute hydrochloric acid and reheat the tube in the flame. This will remove any residue remaining on your test tube and clean it for the next test.

The name of Bunsen has become a common word in science laboratories, where the highly efficient gas burner he devised in 1856 is standard equipment. Since the Bunsen burner burns with a nonluminous flame, it became possible for the first time to view, without confusion, the spectrum of a chemical placed in a flame. For this purpose Bunsen designed another new instrument, the spectroscope, which was a vast improvement over the apparatus used by Fraunhofer. Bunsen mounted a prism inside a blackened box, on one side of which he fixed a viewing telescope (replacing Fraunhofer's theodolite). At the other side of the box he fitted a collimator, a tube with a narrow slit at one end to admit the light and a lens at the other end to make the light rays parallel. The invention of the Bunsen burner and the spectroscope made possible an entirely new field of investigation.

Why didn't anyone design a good gas burner before this time? (23)

Who made the first spectroscope? (24)

At this time Bunsen was the professor of chemistry at the University of Heidelberg. The professor of physics there was young Gustav Kirchhoff, with whom Bunsen joined in a research that has become memorable. Kirchhoff first reported their work to the Berlin Academy of Sciences on 20 October 1859:

Do all scientists work in universities? (25)

Is it usual for chemists and physicists to work together today? (26)

> "While engaged in a research carried out by Bunsen and myself in common on the spectra of colored flames . . . I made some observations which give an unexpected explanation of the Fraunhofer lines . . .
>
> "Fraunhofer had noticed that in the spectrum of a candle flame two bright lines occur, which coincide with the two dark lines *D* of the solar spectrum. We obtain the same bright lines in greater intensity from a flame in which common salt is introduced. [You can make this interesting observation for yourself. See Experiment 5.]"

Kirchhoff next tried to determine the effects of superimposing the lines of the solar spectrum on those produced by the sodium flame.

Scientists seek answers to their questions by means of experiments.

> "I arranged a solar spectrum and allowed the sun's rays, before they fell on the slit [of the spectroscope], to pass through a flame heavily charged with salt. When the sunlight was sufficiently weakened there appeared, in place of the two dark *D* lines, two bright lines; if its intensity, however, exceeded a certain limit the two dark *D* lines showed much more plainly than when the flame charged with salt was not present. [To repeat this observation, see the second part of Experiment 5.]"

Up to this point in their investigation, Bunsen and Kirchhoff had discovered nothing new, for similar observations had been made previously by other investigators of spectra, notably by Léon Foucault in France (see Activity 4, page 30). However, no one had yet been able to explain how the dark Fraunhofer lines, corresponding to the bright lines of the sodium spectrum, might have been formed. To account for this phenomenon, Kirchhoff suggested that glowing sodium vapor has the capacity to absorb light of certain wavelengths. He said:

Mightn't Kirchhoff's idea have occurred to almost anyone? (27)

> "The phenomenon in question is easily explained upon the supposition that the sodium flame absorbs rays of the same [wavelengths as the light it emits]. It has long been known that certain gases, as for instance nitrous acid and iodine vapour, possess at low temperatures the property of such a selective absorption."

A scientist must be familiar with the work of other investigators. How does he find out? (28)

You may be familiar with an interesting experiment in the study of sound, where vibrations of a certain wavelength are selectively absorbed. This behavior of sounding bodies would be an analogy to the selective absorption of sodium vapor that Kirchhoff is proposing here. Nevertheless, it is not at all obvious that sodium vapor can absorb light, and Kirchhoff therefore described several experiments where this absorption can be observed:

What is this analogy? (29)

23. Why didn't anyone design a good gas burner before this time? (The design of the Bunsen burner is not very complex, so complexity is not the reason why it wasn't invented until 1856. What reasons can you suggest?)

24. Who made the first spectroscope? (The text on the opposite page seems to imply that Bunsen made it, but do you think he did the actual work? Do scientists generally make their own instruments?)

25. Do all scientists work in universities? If not, where do they work?

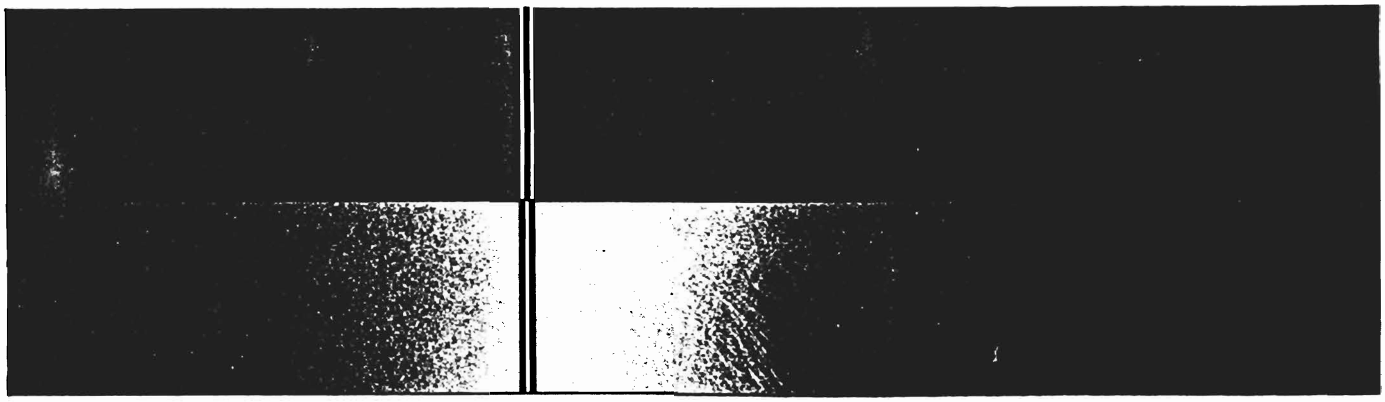
26. Is it usual for chemists and physicists to work together today?

27. Mightn't Kirchhoff's idea have occurred to almost anyone? Or did Kirchhoff have some special imaginative powers? Are scientists generally imaginative?

28. How does a scientist find out about the work of other investigators? List at least five different ways.

29. What behavior of sounding bodies is analogous to the selective absorption Kirchhoff proposes?

D



This picture shows bright and dark sodium lines. (Are their positions coincidental? What led Bunsen and Kirchhoff to produce and compare them?)

"The absorptive power of sodium vapour becomes most apparent when its luminosity is smallest, or when its temperature is lowest. . . . The following experiment . . . very clearly shews this influence of temperature. If a piece of sodium is burnt in a room, and the air thus filled with the vapour of sodium compounds, every flame is seen to burn with characteristic yellow light. If a small flame in which a bead of soda salt is placed be now fired in front of a large one, so that the former is seen projected on the latter as a background, the small flame appears to be surrounded with a black smoky mantle. This dark mantle is produced by the absorptive action of the sodium vapours in the outer part of the flame, which are cooler than those in the flame itself. . . .

An observation is no longer puzzling when a reason for it has been given.

"The same phenomenon is observed in a much more striking manner if a glass tube is used containing some small pieces of sodium, first filled with hydrogen, and then rendered vacuous and sealed. The lower end of the tube can be heated so as to vapourize the sodium. By means of this arrangement, which was proposed by Roscoe, the heated vapour of the sodium, when viewed by the sodium-light, is seen as a dark black smoke which throws a deep shadow, but is perfectly invisible when observed by the ordinary gaslight. [For similar demonstrations, see Experiment 6.]"

Scientists often contribute ideas to one another.

What is a hypothesis? (30)

Kirchhoff next proposed the hypothesis that when the white light from the interior of the sun passes through its cooler outer atmosphere containing sodium vapor, the particular wavelengths of the bright-line sodium spectrum are selectively absorbed. This hypothesis called for further experimental tests. Accordingly, Kirchhoff set up a laboratory source of white light, which he knew gave a continuous spectrum without dark lines, and allowed this light to pass through an alcohol flame charged with sodium chloride to the slit of his spectroscope. He found that

"... in place of the bright lines two dark lines appear, remarkably sharp and fine, which in every respect correspond with the *D* lines of the solar spectrum. Thus the *D* lines of the solar spectrum have been artificially produced in a spectrum in which they do not naturally occur."

Does this result fit in with Kirchhoff's hypothesis? (31)

To explain this appearance of the artificially produced dark *D* lines, Kirchhoff referred to his supposition that sodium vapor selectively absorbs light of the same wavelengths as the light it emits. This was his reasoning:

EXPERIMENT 5. Spectra of Sodium

In this experiment you can observe the bright-line spectrum of sodium and the corresponding dark Fraunhofer lines. You can also match up the bright and the dark lines. They can be matched in two different ways: first, as Fraunhofer suggested, by determining the wavelengths of the characteristic bright sodium lines and then the wavelengths of the dark *D* lines; second, as Kirchhoff demonstrated with Bunsen's spectroscope, by superimposing the bright sodium lines on the solar spectrum.

To find the wavelengths of the bright sodium lines, simply set up a sodium flame in front of the collimator slit of a laboratory spectroscope. You can produce the sodium flame by the technique described in Experiment 4 or by any other convenient means. (You can produce a long-lasting sodium flame by soaking a strip of asbestos in sodium chloride solution and wrapping it around the top of a Bunsen burner, fastening it in place with a wire so that it projects about one inch above the tube of the burner.) From the scale inside the spectroscope or on its base (depending on the model of spectroscope or spectrometer being used), you can read the wavelengths of the bright lines you observe. What is the color of the characteristic sodium lines? What are their respective wavelengths?

Now find the wavelengths of the dark *D* lines in the solar spectrum by using the same spectroscope or spectrometer as above. (Why is it desirable to use the same instrument?) The arrangement of the apparatus will be the same as in Experiment 3. However, you should *be sure to provide some means of regulating the intensity of the sunlight* that falls on the collimator slit of the spectroscope. What are the measured wavelengths of the dark *D* lines?

Kirchhoff allowed sunlight to fall on the slit of a spectroscope and matched up the two dark *D* lines with the corresponding bright lines from a sodium flame. He found different effects when he varied the intensity of the sunlight. To observe these effects, you can use the same apparatus that was used for observing the solar spectrum, except that a sodium flame is added through which the sunlight must pass before reaching the slit of the spectroscope. Look through the spectroscope, first with the sunlight cut off and then with the intensity of the sunlight gradually being increased. Do the bright sodium lines coincide with the dark *D* lines? What do you see as the intensity of the sunlight varies?

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30. What is a hypothesis in science? How is it different from a scientific law?

31. Does this result fit in with Kirchhoff's hypothesis? Explain.

Gustav Kirchhoff was appointed professor of physics at the University of Breslau in 1850. There he met Robert Bunsen, who was instrumental in securing his appointment to the University of Heidelberg. Kirchhoff's contributions to mathematical physics are numerous and important. His strength lay in his ability to state new physical problems in general mathematical terms. A number of his papers were concerned with electrical conduction through thin plates and networks of conductors. His name is best known, however, because of his researches, experimental and mathematical, in electromagnetic radiation. *Picture reproduced by courtesy of The Bettmann Archive.*

Careful reasoning is often needed in scientific work.

"If a sodium flame be held before an incandescent platinum wire whose spectrum is being examined, the brightness of the light in the neighbourhood of the sodium lines would, according to the above supposition, *not* be altered; in the position of the sodium lines themselves, however, the brightness *is* altered, for two reasons: in the first place, the intensity of light emitted by the platinum wire is reduced to a certain fraction of its original amount by absorption in the flame, and secondly, the light of the flame itself is added to that from the wire. It is plain that, if the platinum wire emits a sufficient amount of light, the loss of light occasioned by absorption in the flame must be greater than the gain of light from the luminosity of the flame. The sodium lines must then appear darker than the surrounding parts, and *by contrast with the neighbouring parts* they may seem to be quite black, although their degree of luminosity is necessarily greater than that which the sodium flame alone would have produced. [You can confirm these observations yourself in Experiment 6.]"

Note that the sodium lines appear dark only by contrast with their brighter surroundings.

This experiment showed that the spectral lines from one chemical element, sodium, were responsible for two of the Fraunhofer lines in the solar spectrum. What about the spectral lines of other chemical elements?

Scientists must always check and verify.

"If we introduce lithium chloride into the flame of a Bunsen burner, its spectrum shows a very bright, sharply defined line which lies between the Fraunhofer lines *B* and *C*. If we allow the sun's rays of moderate intensity to pass through the flame and fall on the slit, we shall see in the place indicated the line bright on a darker ground; when the sunlight is stronger there appears at that place a dark line which has exactly the same character as the Fraunhofer lines. If we remove the flame the line disappears completely, so far as I can see."

Is this experiment similar to one that Kirchhoff performed before? (32)

On the basis of these and other experiments, Kirchhoff states his conclusions:

EXPERIMENT 6. Bunsen and Kirchhoff's Experiment

Bunsen and Kirchhoff made the crucial test of the hypothesis that the Fraunhofer lines are produced by the selective absorption of light of certain wavelengths by producing the dark lines due to sodium in a continuous spectrum where they do not naturally appear. A convenient way of reproducing this experiment is suggested by W. C. Badcock in *The Science Masters' Book,* Series II, page 162. The apparatus consists of a laboratory source of white light, a convex lens, a sodium flame, and another convex lens, all mounted in front of the collimator slit of a spectroscope or spectrometer. (By the way, what is the difference between a spectroscope and a spectrometer?)

The continuous spectrum is produced by a projection lamp (250-watt or stronger is recommended) with a rheostat or other form of dimmer in series. A 10cm-focus convex lens forms a real image of the filament of the projection lamp in such a position that a sodium flame can be made to coincide with it. A similar lens focuses the combined light on the slit of the spectrometer. When the lamp is just glowing, the sodium lines will appear in the spectrometer on a faint continuous background. (How does this compare with your observation in Experiment 5 of sunlight of low intensity passing through a sodium flame?) As the brightness of the lamp is increased, this background varies, and the lines show up less and less, becoming indistinguishable at one point. Finally the dark sodium lines are seen on a bright continuous spectrum. Can you see these effects?

Kirchhoff's hypothesis, as we have seen (page 20), was suggested by observing the selective absorption of relatively cool sodium vapor. To demonstrate this, first sprinkle sodium chloride on the wick of an alcohol lamp (which will give a cooler flame than a Bunsen burner). Fit a Bunsen burner with a wing tip and a strip of asbestos soaked in sodium chloride solution to make a wide, hot sodium flame. In a darkened room, place the alcohol lamp on a level with the wing tip of the burner, and light them both. Stand back and view from several directions. What do you see?

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32. Is this experiment with lithium chloride similar to one that Kirchhoff did before? How is it different? What does it show? How does Kirchhoff's hypothesis stand now?

On what does Kirchhoff base his two conclusions? Is his last statement really a conclusion from his experiments? (33)

"I conclude . . . that a colored flame in whose spectrum bright sharp lines occur so weakens rays of the color of these lines, if they pass through it, that dark lines appear in place of the bright ones, whenever a source of light of sufficient intensity, in whose spectrum these lines are otherwise absent, is brought behind the flame. I conclude further that the dark lines of the solar spectrum, which are not produced by the earth's atmosphere, occur because of the presence of those elements in the glowing atmosphere of the sun which would produce in the spectrum of a flame bright lines in the same position."

Kirchhoff finally explains the full meaning of the Fraunhofer lines:

Is this a justifiable assumption? (34)

"We may assume that the bright lines corresponding with the *D* lines in the spectrum of a flame always arise from the presence of sodium; the dark *D* lines in the solar spectrum permit us to conclude that sodium is present in the sun's atmosphere.

A scientist must know about the work of other scientists.

"Brewster has found in the spectrum of a flame charged with saltpeter [potassium nitrate] bright lines in the position of the Fraunhofer lines *A, a, B;* these lines indicate that potassium is present in the sun's atmosphere.

Why is Kirchhoff so cautious on this point? (35)

"From my own observations, according to which there is no dark line in the solar spectrum coinciding with the red line of lithium [between the Fraunhofer lines *B* and *C*], it seems probable that lithium either is not present in the sun's atmosphere or is there in relatively small quantity.

"The investigation of the spectra of colored flames has thus acquired a new and greater importance; together with Bunsen, I will carry it on as far as our means permit. . . ."

Is it usual for scientists to write letters to each other? (36)

And, indeed, Kirchhoff and Bunsen did pursue the investigation further. Alerted by their success in using Bunsen's spectroscope to match up the dark Fraunhofer lines with bright lines in the spectra of several chemical elements, the two collaborators quickly realized that they now had a powerful new research tool. They worked diligently and rapidly. Within a month after Kirchhoff had given the first account of their work to the Berlin Academy, they had learned how to make very accurate spectral analyses. On 15 November 1859 Bunsen wrote a letter to Henry E. Roscoe, an English chemist and a colleague in earlier work, and reported:

Why does Bunsen call this discovery unexpected? (37)

"At the moment I am engaged in a research with Kirchhoff which gives us sleepless nights. Kirchhoff has made a most beautiful and most unexpected discovery; he has found out the cause of the dark lines in the solar spectrum, and has been able both to strengthen these lines artificially in the solar spectrum and to cause their appearance in a continuous spectrum of a flame, their positions being identical with those of the Fraunhofer lines. Thus the way is pointed out by which the material composition of the sun and fixed stars can be ascertained with the same degree of certainty as we can ascertain by means of our reagents the presence of SO_4 and Cl."

As Bunsen says, the puzzle of the Fraunhofer lines was now solved. But, as frequently happens in science, there was also another, more far-searching outcome of the investigation. Bunsen continues:

"By this method, too, the composition of terrestrial matter can be ascertained and the component parts distinguished, with as great ease and delicacy as is the case with the matter contained in the sun . . . For the detection

33. On what does Kirchhoff base his two conclusions? Is his last statement really a conclusion from his experiments, or is it only a reasonable guess? What other factors, besides his experiments, might have led Kirchhoff to make this statement?

34. Is Kirchhoff making a justifiable assumption? (Note the word "always.") Do assumptions have any place in science, or should scientists stick only to experimental data?

35. Why is Kirchhoff so cautious in concluding that lithium is not present in the sun's atmosphere? Is this conclusion, in fact, correct?

36. Is it usual for scientists to write letters to each other? Give two or more reasons why a scientist might want to write a letter to another scientist.

37. Why does Bunsen call this discovery unexpected? Is any new scientific discovery ever expected?

of many substances, this method is to be preferred to any of our previously known processes. Thus, if you have a mixture of Li, K, Na, Ba, Sr, Ca, all you need to do is to bring a milligram of the mixture in our apparatus in order to be able to ascertain the presence of all the above substances by mere observation. Some of these reactions are wonderfully delicate. Thus it is possible to detect 5/1000 of a milligram of lithium with the greatest ease and certainty. [See Activity 5, page 31.]"

What other elements were discovered with the spectroscope? (38)

Clearly, Bunsen was excited by the new possibilities that his spectroscope opened up in the field of chemistry. In fact, Bunsen soon discovered two new elements, cesium and rubidium (named for the colors of their brightest spectral lines), by means of the spectroscope, and other workers found many more elements with this instrument. But Bunsen could have had little more idea of how many applications the study of spectra would have than Fraunhofer could have had when he discovered the dark lines on the rainbow-colored spectrum of the sun.

They couldn't foresee the applications. Why? (39)

In the following years astronomers, chemists, and physicists eagerly took up the study of spectra. Astronomers soon learned that they could use the spectroscope and the Fraunhofer lines not only to study the chemistry of the planets and distant stars, but also to determine the motions of the stars and galaxies, distinguish between galaxies and nebulae, and unravel many other complexities of the vast universe. For the chemists, interested in the analysis of matter here on earth, spectroscopy made possible a tremendous advance in exactness and speed. Besides being able to identify the chemical elements in a compound or mixture, chemists also learned how to make quantitative analyses—to tell *how much* of an element is present—by studying spectra.

How? (40)

How? (40)

For the physicists, the finding that each element has a characteristic spectrum raised difficult problems. We saw (page 24) that Kirchhoff was able to give an explanation for the *dark* spectral lines, but there was still no explanation for the *bright* lines in an element's spectrum. Why does every element have a distinct pattern of bright spectral lines, each with a definite wavelength? The search for an answer to this problem eventually led physicists to revolutionary new ideas about the atom itself. In fact, our present ideas about the composition of atoms and the arrangement of atoms in molecules rest heavily on countless spectroscopic observations and their interpretations. The story of spectra, which we've briefly followed in this case, is only the preface to a long tale that is not yet finished even today.

How is this possible? (40)

38. Do you know what other chemical elements were discovered or identified by means of the spectroscope? (There are at least a dozen.)

39. Why couldn't Bunsen and Fraunhofer foresee the applications that the study of spectra would have? Is this a common situation in science?

40. The closing paragraphs on the opposite page attribute a great variety of important discoveries to observations with spectroscopes (and spectrometers). Perhaps you know how spectroscopy is used in making these discoveries. (Some of the books listed in the Reading Suggestions on the inside back cover can help you find out.) Still, isn't it remarkable that all this can be learned by peering at some colored lines in a spectroscope or by looking at streaks on a photographic film? We return to the question first asked at the beginning of this case: How is this possible?

ADDITIONAL ACTIVITIES

ACTIVITY 1. Spectra

A spectrum can be produced in many ways. Here are two ways, which use a water prism. (Can materials other than glass or water be used in a prism?)

Place a glass completely full of water on a window ledge in bright sunlight. Where does the spectrum appear? What shape is it? (This experiment works best in either midmorning or midafternoon, but does not work around midday. Why?)

Place a tray of water in bright sunlight in a window. Lean a rectangular mirror against the edge of the tray away from the window. Adjust the mirror so that the spectrum appears on the ceiling. What is the shape of the spectrum? Can you trace the path of the light?

ACTIVITY 2. The Natural Philosopher

On page 6 William Hyde Wollaston is called a natural philosopher. What does this mean? Are scientists also philosophers?

In a short visit to the library you can find out about some of Wollaston's numerous discoveries. Did Wollaston specialize in one scientific area, or did he have broad interests? Is this true of scientists today? What discoveries did he make?

Would you call Wollaston a great scientist? Why, or why not?

ACTIVITY 3. Diffraction Gratings

In this activity you will have a chance to see further examples of the way Fraunhofer pursued a scientific problem. You should look for these examples as you read. (To what extent are Fraunhofer's conclusions based on his observations? To what extent are the conclusions based on speculation? What hypotheses might have led him to conduct this experiment?) Also, from Fraunhofer's experimental data, you will be able to derive an empirical law and to find the wavelength of light.

In addition to studying prismatic spectra, Fraunhofer investigated the even more fascinating multiple spectra formed by diffraction gratings. He first reported his findings to the Bavarian Academy of Sciences in Munich on 14 July 1821. On 14 June 1823 Fraunhofer presented to the Academy a second paper on diffraction spectra, "Kurzer Bericht von den Resultaten neuerer Versuche über die Gesetze des Lichtes" (Short Account of the Results of Recent Experiments on the Laws of Light), which was later published in *Gilberts Annalen der Physik,* Vol. 74, pp. 337–378. The following quotations are based on this second paper, Fraunhofer's "Short Account."

"I published a year ago, in a memoir which is printed in the eighth volume of the *Denkschriften* of the Royal Bavarian Academy of Sciences, an account of some new experiments concerning *diffraction* of light and those phenomena which occur owing to the mutual action of diffracted beams of light . . . I have continued these experiments since then; and what follows is an account which is suitable for communication in a brief description.

"In this memoir, I shall designate by *C, D, . . . H* *colored rays* of different kinds: *C* is a ray which lies in the deep red near the end of the spectrum; *D* is orange-colored; *E,* green; *F,* blue; *G,* indigo; *H,* violet. In every spectrum of sunlight which consists of *perfectly homogeneous* light there are found at the places named fixed lines or streaks which are distinguished from the other countless lines of the spectrum either by their intensity or by their position.

"The angles from the axis through which the rays *C, D,* etc., are deflected by the grating I designate by C^{I}, D^{I}, etc., in the *first* spectrum, which is nearest the axis; by C^{II}, D^{II}, etc., in the *second;* by C^{III}, D^{III}, etc., in the *third* from the axis, etc. From the experiments which are described in detail in my previous memoir, I found that, with all gratings, if g denotes the width of a single grating space, and w the width of a single wire, expressed in fractions of a Paris inch, the arcs of these angles are as follows, the radius being taken as 1:

$$C^{I} = \frac{0.00002425}{g + w} \qquad D^{I} = \frac{0.00002175}{g + w}$$

$$E^{I} = \frac{0.00001943}{g + w} \qquad F^{I} = \frac{0.00001789}{g + w}$$

$$G^{I} = \frac{0.00001585}{g + w} \qquad H^{I} = \frac{0.00001451}{g + w}$$

Further, that

$$C^{II} = 2C^{I}, \quad D^{II} = 2D^{I}, \quad E^{II} = 2E^{I}, \text{ etc.}$$

$$C^{III} = 3C^{I}, \quad D^{III} = 3D^{I}, \quad E^{III} = 3E^{I}, \text{ etc.}$$

"The numerator in these general expressions is a number which is absolutely constant for each definite colored ray, but different for different rays, however varied the cases are. If for each colored ray this number is designated by L, and if the angle of deflection of one and the same ray in the first spectrum is designated by r^{I}, in the second by r^{II}, in the third by r^{III}, etc., then,

$$r^{I} = \frac{L}{g + w}; \quad r^{II} = \frac{2L}{g + w}; \quad r^{III} = \frac{3L}{g + w}; \text{ etc.}$$

And if, further, n denotes the number which gives the order of the spectrum (for the axis $n = 0$; for the first spectrum $n = 1$; for the second, $n = 2$, etc; and it can never be a fraction); and if, for the sake of brevity, we call the sum of the width of one grating opening and of one line of the grating, or $g + w$, equal to d, we have as a general equation

$$\text{(I)} \qquad r_n = \frac{nL}{d}$$

"According to the results of the previous experiments (and as is shown by the general equation I, which is derived from them), the angles of deflection of the same colored beams in the series of spectra formed by the grating are in the ratio of the numbers 0, 1, 2, 3, etc. The experiments from which these results are deduced gave, however, such small angles that for them the sine, tangent, and arc do not sensibly differ. With my finest grating, where $d = 0.001952$ inch, D^{I} was equal to 38′ 19.3″. If the angles were larger, that is, if the gratings were many times finer, one might think it probable, from certain considerations, that the arcs themselves *do not* have the relations given above, but that some trigonometric function of them does. . . . Partly in order to verify this directly by experiment, partly because the laws of this modification of light can be deduced with more accuracy from larger spectra, it was greatly to be desired, it seemed to me, that gratings should be made much finer than those which I used in my earlier experiments. . . .

"It was only by means of a diamond that I succeeded in producing sufficiently fine gratings. A machine specially made for the purpose enabled me, by using a diamond-point, to rule lines in the surface of a piece of plane glass which were almost perfectly parallel. . . . By means of my machine I have obtained a grating in which $d = 0.0001223$ inch, and whose lines are so evenly spaced that the fixed lines of the first and second spectra obtained with it can be plainly seen.

"By means of this grating, spectra are obtained which are as long as those obtained from large prisms; . . . And since with this grating D^{I}, for instance, equals 10° 14′, the law of modification of the light produced by it can be deduced with great accuracy.

"When the light fell normally upon the grating in which $d = 0.0001223$, I obtained

C^{I} = 11°25′20″	E^{I} = 9°9′0″	G^{I} = 7°27′19″
C^{II} = 23°19′42″	E^{II} = 18°32′34″	G^{II} = 15°3′9″
D^{I} = 10°14′31″	F^{I} = 8°26′6″	H^{I} = 6°52′36″
D^{II} = 20°49′44″	F^{II} = 17°3′34″	

"The angles are so large that the arcs, sines, and tangents are sensibly different. Since the instrument with which the angles are measured gives, without repeating the observation, readings accurate to 4″, one can easily decide how trustworthy the readings are. . . .

"Using another grating, where d was equal to 0.0005919 inch, I obtained, with light at normal incidence,

C^{I} = 2°20′57″	E^{I} = 1°53′7″	F^{III} = 5°13′23″
D^{I} = 2°6′30″	E^{II} = 3°46′17″	F^{IV} = 6°58′18″
D^{II} = 4°13′7″	E^{III} = 5°39′50″	G^{I} = 1°32′22″
D^{III} = 6°20′7″	E^{IV} = 7°33′41″	G^{II} = 3°4′57″
D^{IV} = 8°27′43″	E^{V} = 9°28′3″	G^{III} = 4°37′30″
D^{V} = 10°35′53″	F^{I} = 1°44′19″	H^{I} = 1°25′0″
	F^{II} = 3°28′45″	H^{II} = 2°50′11″

All the observations, with both glass gratings, can be expressed very closely by the equation:

(II)

"If the light is incident normally, therefore, the ____________ of the distances of a colored ray from the axis in the different consecutive spectra are in the ratio of the numbers 0, 1, 2, 3, 4, etc."

PROBLEM: What word (*arcs, sines,* or *tangents*) belongs in the blank in the last sentence. Secondly, what is Equation II? In other words, what is the relation between the angular deflection of a colored ray and nL/d?

Fraunhofer was able to tease out this relation from the data he obtained for the gratings $d = 0.0001223$ and $d = 0.0005919$, as given above. You can do the same with a little persistence. First compare the observed values of the arcs of the angles in successive spectra with the calculated values of the arcs obtained by multiplying the arc of the first spectrum by 2, by multiplying the arc of the first spectrum by 3, and so on. (This calculation assumes that the desired relation is given by Equation I, which Fraunhofer suggested near the beginning of his paper.) Do the observed values and the calculated values for the arcs agree exactly? If the agreement is not sufficiently exact, make the same calculations for the sines of the angles and for the tangents of the angles. (For these calculations, a table of trigonometric functions that gives sines and tangents for 10″ intervals will be handy. If you don't have such a table, a table of functions for 1′ intervals can be used with interpolation.) Compare the calculated values of the sines of the angles in successive spectra with the values of the sines of the observed angles; compare the calculated values of the tangents with the values of the tangents of the observed angles. Now, what is the relation expressed by Equation II?

In this way Fraunhofer (and you) derived from experiments the law of the grating for light at normal incidence. Using this law, Fraunhofer was able to calculate the first exact values for the wavelength of visible light. His paper continues:

"In the above formula, from the principles of *Interference* which were proposed in 1802 by Dr. Thomas Young and afterwards fully justified by the painstaking labors of Arago and Fresnel, L denotes the *length of a light-wave.* Although this quantity is extremely small, we can deduce it with a high degree of accuracy from the experiments which are described in my memoir. . . . From the experiments with glass gratings we learn this quantity so exactly that, for the bright colors, hardly one-thousandth portion of L can be uncertain. From the experiments with the finer gratings we obtain, by means of the appropriate values for the first spectrum with normal incidence of the light, if L_C denotes the length of a light-wave for the ray C, L_D for the ray D, etc.

	From Grating $d = 0.0001233$	From Grating $d = 0.0005919$	Mean Value of Wavelength
L_C			
L_D			
L_E			
L_F			
L_G			
L_H			

PROBLEM: Calculate the values for the several wavelengths in the above table. To do this, make use of the empirical law that you found before and stated as Equation II. Use data derived from the first spectrum for each colored ray.

The wavelengths you calculate will be expressed in fractions of a Paris inch. Why? What is the wavelength of each colored ray in centimeters? (One Paris inch is equal to 2.707 cm.)

Compare the wavelengths that you (and Fraunhofer) calculated for the above five Fraunhofer lines with the values accepted today for these same lines. (You can find the presently accepted values in the *Handbook of Chemistry and Physics* and in other references.) How good is the agreement? Was Fraunhofer right in saying that "for the brighter colors, hardly one-thousandth portion of L can be uncertain"?

ACTIVITY 4. Men and Nations

Science is an international activity. We can best recognize this when we see that many men in different countries frequently contribute to the growth of a single idea. Listed below are the names and nationalities of men who made some contribution to the understanding of spectra between the work of Fraunhofer and the work of Bunsen and Kirchhoff. Who were these men? What did they contribute to our knowledge of spectra? What else did they achieve or discover? The answers to these questions will provide some good reports for your class. A visit to the library will help you.

England—John Hall Gladstone, John Frederick William Herschel, William Allen Miller, George Gabriel Stokes, William Henry Fox Talbot, Charles Wheatstone

France—Alexandre Edmond Becquerel, Jean Baptiste Biot, Léon Foucault, A. P. Masson

Germany—Johann Müller, Julius Plücker

Italy—Macedonio Melloni, Angelo Secchi

Scotland—David Brewster, William Swan

Sweden—Anders Jonas Ångström

United States—David Alter, John William Draper

While you're at the library, you may also wish to learn some more about the lives and other achievements of the principal participants in the case whose names and countries are listed on the back of the title page.

Incidentally, isn't there something peculiar about the above list? Although there are representatives from seven countries in the list, there were certainly many more countries than seven in the world in the first half of the nineteenth century. Yet there are no scientists from these many other countries on the list (which is a reasonably complete one). Why not? Can you suggest some reasons why one country may produce a considerable number of scientists at a given time while another does not? What does this mean for us today?

ACTIVITY 5. Bright-Line Spectra

Bright-line spectra can be easily seen by using a simple hand spectroscope with a plastic replica grating. To view the bright-line spectra effectively, it is best to work in a dark or dimly lit room. Set up the colored flames of various metallic salts, as in Experiment 4, and look at the flames through the hand spectroscope. What colored lines are characteristic of sodium, potassium, calcium, barium, copper, lithium, etc.?

Other interesting objects to view with the spectroscope are the glowing gases in electric discharge tubes and lamps. For example, look at a neon glow lamp through the spectroscope. What are the bright lines characteristic of neon?

Next turn the spectroscope at night on some "neon" advertising signs. Is neon gas present in the tubes of these signs of various colors?

Look at a mercury vapor lamp through the spectroscope. (BE CAREFUL not to look too long at this kind of light, which can damage your eyes.) Mercury vapor lamps are sometimes called germicidal lamps. What are the bright lines characteristic of mercury vapor?

Look at a fluorescent light tube through the spectroscope. What chemical element is present inside this tube? (Note that this is the kind of test Bunsen speaks of on page 24.)

ACTIVITY 6. Make Your Own Spectroscope

You can make a simple but effective spectroscope of your own out of a shoe box, a razor blade, some masking tape, and a piece of plastic replica grating. This project is suggested by Professor Fletcher G. Watson of Harvard University.

At one end of the shoe box, near an edge, cut a narrow slot perpendicular to the floor of the box. Break the razor blade in half lengthwise. With masking tape, mount the halves of the razor blade, edges together, over the slot on the inside of the box. Arrange them so that they form a narrow vertical slit. At the other end of the box, punch a small eyehole in line with the slit. Inside the eyehole mount with tape a piece of the plastic replica grating. Turn the grating so that the rulings are parallel to the slit. Adjust by thumb pressure the width of the slit until a dark line appears down the middle of the slit. Put the top on the box, and begin your observations.

Aim the spectroscope toward a source of white light. You will see "virtual images" of the continuous rainbow-colored spectrum on either side of the slit. Do you know why there are two images? With a prism there is only one image.

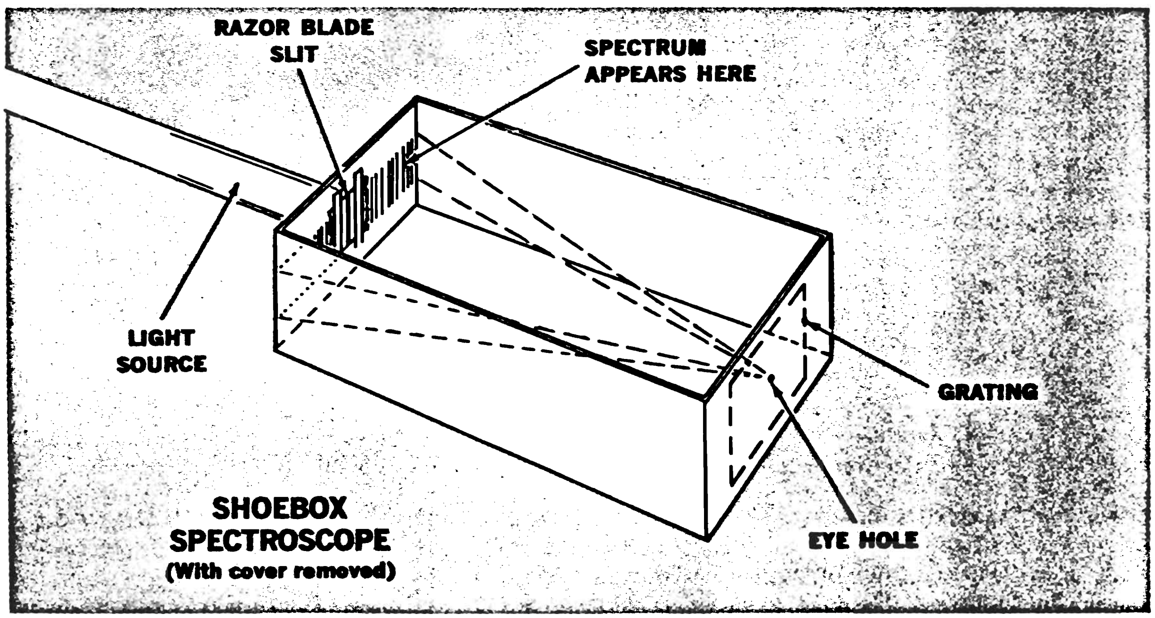
Aim the spectroscope at the sky near (NOT AT) the sun. Can you see any of the Fraunhofer lines? Do they match up with any of the lines shown in the drawing on page 12?

Use the spectroscope to observe bright-line spectra, as suggested in Activity 5.

Set up a source of white light, which gives a continuous spectrum. Put colored liquids in a thin cell in front of the slit of your spectroscope. What colors of the spectrum are absorbed by each of the colored liquids?

How is the spectrum seen through a colored liquid different from a dark-line spectrum?

Can you think of a way to improve your spectroscope so that you could measure the wavelengths of different colors of light or of certain lines in the spectrum?



SHOEBOX SPECTROSCOPE
(With cover removed)

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SOURCES OF QUOTATIONS

PAGES	
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10	From "The Place of Torricelli in the History of the Barometer," by W. E. Knowles Middleton, *Isis,* Vol. 54, 1963, p. 16. Reprinted by permission. (Translation of a Latin account of Berti's experiments in Emanuel Maignan, *Cursus philosophicus;* Toulouse, 1653.)
12, 14	From Middleton, *loc. cit.*, pp. 20–21. (Translation from the Italian of a letter of Torricelli's, in Carlo Dati, *Lettere e Filaleti di Timauro Antiate;* Florence, 1663.)
14, 16	From *Pascal: The Life of Genius* by Morris Bishop. New York: Reynal & Hitchcock, 1936. Pp. 53, 58. Copyright 1936, Morris Bishop. Reprinted by permission of Harcourt, Brace & World, Inc.
16, 18 20, 22 24, 26 30, 31 32	*The Physical Treatises of Blaise Pascal.* Translated by I. H. B. and A. G. H. Spiers. New York: Columbia Univ. Press, 1937. Pp. 3–5, 7–8, 11–13, 33–34, 34–42, 98–108. (Translation from the French of a compilation by Florin Périer, *Traités de l'équilibre des liqueurs et de la pesanteur de la masse de l'air;* Paris, 1663. Units of measure have been converted to English units for this case.)
28, 29	*UNESCO Source Book for Science Teaching,* Revised Edition. © UNESCO 1963. Paris: UNESCO, 1963, Pp. 106–107.