SCIENCE

VOL. 91 FRIDAY, MARCH 8, 1940 No. 2358

SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. MCKEEN CATTELL and published every Friday by

THE SCIENCE PRESS
New York City: Grand Central Terminal
Lancaster, Pa. Garrison, N. Y.

Annual Subscription, $6.00 Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the Association may be secured from the office of the permanent secretary in the Smithsonian Institution Building, Washington, D. C.

NEW METHODS IN SPECTROSCOPY[1]

By Professor GEORGE R. HARRISON
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

IN expressing my appreciation of, and gratitude for, the high honor which is bestowed in the award of the Rumford Medals, I am mindful of the obligation which is laid upon a medallist to hold in mind the true significance of such an award. In all human affairs there are values which are of so intangible a nature as to require frequent concrete symbolization if we are to keep their import before us; this is an occasion of such symbolization. I accept these medals, not as a reward for accomplishment, but as symbolic of a vast array of aspirations which we are gathered here to celebrate: the determination of our society that the search for truth shall be prosecuted diligently; the desire that men shall be encouraged in that prosecution; the hope that opportunity for such search may continue in constantly increasing measure; the conviction that every addition to our knowledge of the world in which we live, no matter how slight, brings one step closer the day when men shall be freed from the terrors which have beset them all through the ages—terrors which, though at times they may seem overwhelming, do in fact gradually become less.

Not the least of our duties of realization this evening is the appreciation of the progress which has taken place since 1839 in one of those branches of physical science which Count Rumford desired to further when he arranged for the provision of medals in recognition of researches on heat and light. Later it will be my pleasant duty to recount some of the recent developments in the study of light with which I have had the good fortune to be associated, but before I come to the specific portion of my address which deals with

[1] Address on the occasion of the Award of the Rumford Medals, of the Academy of Arts and Sciences, Boston, October 11, 1939.

"New Methods of Spectroscopy" I should like to think back for a moment to that period of 100 years ago.

Light was then a very mysterious agency, by some scientists supposed to be corpuscular in nature, but showing increasing evidence of an undulatory character. A period of great technical development in optical instruments, and in the control and measurement of light beams, was just beginning; but in so far as the nature of light was concerned the period was one of transition and controversy, and regarding the origin of light almost nothing was known. Newton, 173 years before, had split a beam of white light into its component colors by means of a prism and had recombined these colors into white light with another prism. Most important for our present discussion, however, is the fact that the later days of Count Rumford coincided with the period of greatest activity of Joseph von Fraunhofer, perhaps the inventor of, and certainly the first active experimenter with, the diffraction grating, and constructor of one of the first real spectroscopes.

During the 120-year period which has intervened, the spectroscope has been developed into what appears to be the most powerful single tool which has yet been developed by the hand and mind of man, and one which is suited to a wide variety of purposes. Henry Norris Russell has called the spectroscope the "master key of science," and an examination of the uses of the instrument reveals an astonishingly wide variety of applications. Recently I had occasion to list the various uses of the spectroscope; I found that it has been applied to such remarkably divergent purposes as the measurement of the ratio of the charge of an electron to its mass; the detection of atoms present in a mixture of other atoms in amounts smaller than one in ten million; the measurement of the amounts of lead, arsenic, and other poisons in foodstuffs; observation of the numbers of atoms entering and leaving molecules in a solution or vapor; calibration of the vitamin potencies of food samples; determination of the atomic constitution of complex molecules, such as those of hormones and vitamins; measurement of the temperatures, sizes, distances, weights and ages of stars; observation of the number and arrangement of electrons in atoms and of atoms in molecules; the identification of criminals from traces left at the scene of a crime or carried from it; the study of the colors and discolorations of pigments and papers and ceramic glazes; the investigation of the origins and constitutions of minerals; and so on and on.

To the astronomer the spectroscope is at once a yardstick, a thermometer, a chronometer, a stethoscope for star-pulses, an analyzing microscope, a chemical balance and a super-telescope of the heavens. Though without the telescope the spectroscope would have little value to the astronomer, the spectroscope in its turn has multiplied the power of the telescope by perhaps twenty—for though it is the function of a telescope to gather light and focus this in an image or a spot, a spectroscope can separate this light into its component parts and thus lay bare a hundred meanings hidden from the eye.

To the physicist the spectroscope has served as a powerful atomic probe, for with its aid in analyzing the light emitted by atoms he has deduced much about their structures. He has found that light is emitted when atoms or molecules lose energy as the result of transitions of an electron from a position involving greater energy to one involving less; the spectroscope reveals the exact size of the photon which an atom emits under such circumstances, and by means of the quantum theory the physicist can picture what is going on in a tiny atomic system which is not more than ten or twenty billionths of an inch in diameter.

To the chemist, the biologist or the metallurgist, the spectroscope serves as a sensitive analytical instrument, to detect small amounts of impurities or to analyze the atomic constitution of a speck of matter from its emission of light, or its molecular constitution from its absorption of light. Nor is the use of the instrument as a thermometer confined to the astronomer, for the engineer who wishes to determine the temperature of engine flames need only put a transparent window into the cylinder of a motor and use the spectroscope to study the light which is emitted.

Whence spring this wide adaptability and great power of the spectroscope? No detailed analysis is needed to see that they arise from its ability to attack fundamentals; with it the world and the heavens can be studied in terms of the single particles of which they are composed, and these particles in terms of the energy which is their very life. And this power is rendered the greater because it is not merely of a qualitative sort, but is quantitative as well. The human eye can distinguish at best several hundred different wave-lengths or hues of color; the spectroscope can be used to distinguish more than a million. By using an interferometric spectrograph (by a spectrograph is meant a spectroscope arranged to record spectrum lines photographically) it is possible to measure the relative lengths of light waves, themselves less than 1/50,000 of an inch in length, to closer than one part in forty million; thus measurements are obtained which are precise to one trillionth of an inch.

The precision of spectroscopic methods results directly from the fact that light waves can be made to interfere with one another—to reinforce here, giving extra brightness, and to destroy one another at some other point, giving darkness. Great heaps of waves can be piled up to give a bright spectrum line in one position and complete darkness elsewhere, and from the location of such a spectrum line the length of the waves in it can be uniquely determined.

One very powerful form of spectrograph contains a concave diffraction grating, which may consist of as many as 180,000 narrow grooves ruled uniformly in the space of six inches on the surface of a concave mirror by means of a diamond point. If light which has passed through a narrow slit falls on an array of such grooves which has been ruled with sufficient nicety, the light will be split into rays and sent in directions such that each ray will contain waves of only one length. The rays of various wave-lengths may then be caught on photographic plates spread around a vast circle. The photographic plates, after development, then show the different rays as spectrum lines. When these spectrum lines are located on the plates to within 1/25,000 of an inch, the wave-lengths of the light can readily be determined to less than a billionth of an inch.

The concave diffraction gratings which make this possible have been available for fifty years, but are continually being improved. With their aid extensive study and cataloguing of the spectrum lines emitted by the chemical elements have been carried out. Every atom can emit light waves whose lengths are definite and characteristic of only that type of atom. Any atom or molecule will emit light if struck a hard atomic blow, and since any material object—a star, a drop of blood or a speck of putty—is composed of atoms, any material object can be induced to emit light by heating it until it becomes an incandescent vapor. Thus the presence or absence of atoms of any sort can be determined in any material by a spectroscopic study of the light emitted by it.

Now we approach the specific topic of this discussion. If one is to be able to identify any sort of atom from its pattern of spectrum lines, it is necessary that the wave-lengths of these lines be known accurately and be available for immediate use. The cataloguing of spectrum lines has engaged the attention of many persons during the past fifty years, until now a quarter-million lines produced by the 88 available chemical elements (elements 43, 61, 85 and 87 are in somewhat uncertain states of discovery, but in very definite states of non-availability) have been measured, though not completely catalogued.

Two types of catalogue are needed; one should list the wave-lengths and relative brightnesses of all the spectrum lines which each atom emits, filed under the respective atoms in order of wave-length; the other should list in order the wave-lengths of all known spectrum lines, each entry containing the atom responsible for the emission of that line. Then to identify the atom responsible for some line whose wave-length has been measured, one need only consult a catalogue of the second or dictionary type; to know what lines to expect a given material to emit, one would consult a catalogue of the first or encyclopedia type.

There is a sad lack of up-to-date catalogues of either type. The most extensive catalogue of the first type is that contained in the monumental "Handbuch der Spectroscopie" of H. Kayser, which lists data on about 120,000 lines, though for some forty elements it contains no data determined since 1912. The most extensive catalogue of the second type was also compiled by Kayser and his colleagues, and contains the 27,000 strongest lines of the elements. An extensive search through the spectroscopic literature recently carried out under my direction by a corps of clerks of the Works Progress Administration has revealed that data are now available for some 250,000 atomic spectrum lines. I have recently calculated (and Professor Henry Norris Russell of Princeton informs me that he has arrived at a similar result) that data on about one million atomic lines should be provided to fill the present needs of science for information of this sort. We are therefore forced to conclude that observation and measurement of atomic spectrum lines are at present not more than one fourth complete, with the compilation of spectroscopic data in available form but one eighth complete for the encyclopedia type of information, and one fortieth complete for the dictionary type. This applies only to spectrum lines produced by atoms; for lines produced by molecules the situation is considerably worse.

Hope for rapid improvement in this situation has been somewhat limited by the fact that discovery and measurement of further spectrum lines becomes not merely progressively more difficult, but progressively less interesting. Naturally the stronger lines are discovered first, and a few thousand lines account for nine tenths of the light usually emitted by atoms. As the needs of other sciences for spectroscopic data have come closer to being met, the physicist has found himself with continually widening interests and hence with continually lessening time available for measurements which were becoming increasingly of a routine nature, yet with some three quarters of a million lines, whose wave-lengths and intensities and parent atoms he would like to know, remaining to be discovered and studied.

Progress in the accumulation of spectroscopic data has been doubly slow because the work has been of such a precise and tedious character. A spectrum plate, perhaps 20 inches long, is put on a measuring engine and, by means of a screw accurate to 0.001 mm, is moved until each spectrum line in turn has been centered on the cross-hair of a measuring microscope.

The readings of the screw scale are recorded by hand to six or seven figures for each line. The measurement of one plate containing a thousand or more lines may require two or three full working days, but even then no wave-length figures are available. By using standard lines whose wave-lengths are well known, usually from iron atoms, all the measurements in millimeters must be converted by interpolation into wave-lengths in angstroms, using a factor which is constantly varying; since this interpolation must be to seven-figure accuracy it is carried out manually with computing machines. Often a week or more of hard work elapses before the wave-lengths of the lines on a single plate are reduced and tabulated.

Only persons of skill, training and boundless perseverance have been suited for such work, and it is not surprising that, owing to the calls of less routine work in other fields, the interest of young physicists in this branch of their science has gradually been lessening, though many important results await the accumulation of further spectroscopic data.

I wish that I might state at this point that such considerations induced me to try to do something to remedy this situation, and that as a result the various automatic measuring, computing, recording and sorting devices which I am about to describe were constructed. Such would be far from the truth; even at the risk that the Rumford Committee may wish to reconsider its recommendation and the Academy its award, I must confess that the chain of events which led to these devices arose from what may well have been pure inertia—at any rate, from a disinclination to face a future filled largely with the prospect of turning the handle of a screw with my left hand, while with my right hand I wrote down six-digit numbers obtained by peering alternately through a reading microscope with one eye and at a rather illegible scale with the other.

A brief consideration showed that such a future was not necessary. The first step in avoidance was substitution, for the antiquated scale, of a modern counter device similar to that used on gasoline-station pumps, and a brightly-flashing light and a camera filled with motion picture film for the pen and paper with which the numbers were previously recorded. This cut the time of measuring a plate by two thirds. The next step was the realization that any operation of multiplication, division, subtraction or addition, carried out with much labor even on the best electric calculating machine, could be done instantly and constantly by means of gears during the very process of measurement. Such calculating methods have, of course, been applied in other fields, though perhaps not with the precision required by seven-figure accuracy; however, it will soon be apparent that I have little to report this evening other than the application, to spectroscopic problems, of methods used in radio-telephony, in television, in stroboscopy, in photography and in various other branches of applied physics and of mechanical and electrical engineering. The devices which I shall describe have arisen entirely as the result of the combination of a need with the availability at the Massachusetts Institute of Technology of experts in almost any branch of science or technology whom I had need to consult.

As a result of this combination of circumstances my colleagues in the spectroscopy laboratory and I now find ourselves the still somewhat surprised possessors of a group of machines with which routine operations that previously required much of our time can be carried out on a wholesale basis by non-technical assistants with little training. For example, a spectrographic plate can now be placed on an automatic measuring engine, and an electric motor will cause it to be scanned from end to end by a beam of light which locates the center of each resolved spectrum line somewhat more precisely than was previously done by the eye, instantly computes the wave-length of each line to seven figures in angstroms, and records this wave-length, together with an intensity trace of the contour of the line, on motion picture film. Once the machine is set up as many as 3,000 lines can thus be recorded in 120 seconds. WPA clerks have during the past four years done yeoman service in reading data from the films which came from such machines, correlating and averaging these data and otherwise assisting in the preparation of more complete, uniform and precise catalogues of wave-lengths than were available previously. Only a few weeks ago the first volume[2] appeared of what we hope will be a series of new tables of spectrum lines; this contains the necessary data on the 109,275 strongest lines emitted by the chemical elements in the range 10,000 to 2,000 A, 75,000 from our own measurements, and the remainder from the best measurements of others. In addition, many thousands of lines not previously reported have been discovered and measured, and the work is being carried on with a precision and uniformity which we could hardly have expected in advance.

I shall pass now to a description of the mode of operation of the automatic comparators, and of two other devices which assist in the determination of atomic energy states.[3]

[2] M.I.T. Wavelength Tables. New York: John Wiley and Sons, Inc., 1939.

[3] The material covered in the second half of the acceptance address has been published in the following papers: G. R. Harrison, *Rev. Sci. Inst.*, 3: 753, 1932, and 4: 581, 1933 (interval sorter); *Jour. Opt. Soc. Amer.*, 28: 290, 1938 (interval recorder); *Jour. Opt. Soc. Amer.*, 25: 169, 1935, and *Rev. Sci. Inst.*, 9: 15, 1938 (automatic comparators).