

Spectroscopy: Its Applications.

(Sifting the Secrets of the Universe by the Analysis of Light.)

By Everett White Melson.

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MORE than two hundred and sixty years have passed since Newton discovered that a beam of light could be separated by means of a prism into bands of violet, indigo, blue, green, yellow, orange and red. This was the beginning of a series of experiments that have supplied more information about the nature of the physical world than any other single phase of research. Whether the constitution of a star, the earth or an atom is under investigation, the analysis of light plays a constantly increasing part.

This phenomena of the separation of light is the basis of spectroscopy which, beginning with the study of the solar spectrum, now reaches into the expanding fields of metallurgy, chemistry, physics, medicine and biology.

The dispersion of light is due to the varying refrangibilities of these different colours in passing through media of varying densities. In passing through a quartz prism, for instance, violet waves have less speed than red and consequently are more retarded, or refracted. Kirchoff and Bunsen developed the following conclusions relative to the three more important types of spectra. When light from an incandescent gas or vapour is examined by means of a prism, its spectrum is seen to consist of a number of bright lines, coloured images of a spectroscopy slit, which are always the same for the same gas under the same conditions of temperature and pressure. Thus the spectrum of sodium vapour at the temperature of the Bunsen burner consists of a single pair of bright yellow lines corresponding to the Fraunhofer lines D_1 and D_2 . Lithium gives a single line of deep red. Thallium light is green and strontium emits a blue light. The light from hydrogen, the prototype of all other spectra that originate in atoms, shows four well-marked lines, one in the red and one in the blue corresponding to the Fraunhofer lines C and F, and two fainter lines in the violet. Such a spectrum is known as a bright line spectrum. Its presence indicates that the source of light is a mass of incandescent gas or vapour under a pressure so low that the gas molecules have freedom of motion to execute whatever form of vibration they will.

When the light from an incandescent solid or liquid, or from a mass of incandescent gas under high pressure, is analysed, the spectrum is found to contain all colours from red to violet, showing no discontinuance at any point. This continuous, or band spectrum indicates that the source is an incandescent solid, liquid, or gas under high pressure. The spectra from molten metals, from the filaments of incandescent lamps or from the carbon tips of an arc lamp are all continuous spectra.

In 1814, Fraunhofer made a spectroscopy and saw for the first time a pattern of many fine dark lines across the solar spectrum. In the spectra of the stars he observed these same dark lines. It was discovered that if a beam of white light is passed through a layer of gas or vapour before entering the spectroscopy, this vapour

will sift out and absorb precisely those light rays, or colour, which the gas or vapour would itself emit if incandescent. It is this absorption of light by gases which is so important in astronomic spectroscopy.

The absorption bands, whose relative positions were determined and lettered by Fraunhofer, afford a ready and accurate means of designating lights of definite colours. Many substances present characteristic absorption spectra. A piece of cobalt glass absorbs all colours, except a small strip in the red, and in the blue end of the spectrum. The absorption spectrum of chlorophyll shows a dense black line in the red, while blood, even if greatly diluted, shows two characteristic bands in the green.

Since the character of the light emitted by an incandescent gas depends first of all upon the vibrations of its constituent atoms, it follows that a study of the light emitted by a glowing gas affords direct testimony concerning its chemical composition. Consequently if the bright line spectrum of any substance is once known, whenever this spectrum presents itself, we may at once conclude that the given substance is present in the source of light, whether it is in a Geissler tube in the laboratory or from a fixed star in the vast depths of space.

The spectroscopy method of analysis is characterised by its ease and rapidity, and especially by its exceeding sensitivity. In the case of a Bunsen burner, 1/14,000,000 of a milligram of sodium is sufficient to show the characteristic sodium lines, while in the spark of an induction coil, 1/80,000,000 of a milligram of lithium may be detected. The extreme sensitiveness of the method has led to the discovery of numerous new elements which have been present in minute quantities as impurities in the substances under examination. They revealed themselves through characteristic new lines in the spectrum. Among the elements so discovered are caesium, rubidium, thallium, indium and gallium.

The instrument with which this work is done is the spectroscopy or spectrograph. Its operation is based on the dispersion of light. If sunlight is passed through three prisms having the same refracting angle, one of flint glass, one of crown glass, and one a hollow prism with plane glass sides and filled with water, the resulting spectra will be found to differ greatly in length. The spectrum from the flint-glass prism is about twice as long as that from the one of crown glass, and three times as long as that from the water prism. The various colours undergo widely different deviations through prisms of the same angle but of different substances.

A careful study of the dispersion of various refracting media is therefore a pre-requisite for the scientific construction of optical instruments. Since different glasses vary widely in relative dispersion, it is within the power of the optical glass maker to produce at will prism combinations that will give either deviation without

dispersion or dispersion without deviation, according as the need may arise. Basically all designs of the spectroscope consist essentially of four parts: the slit, the lenses, the dispersing system and the observing or recording system. Various optical and mechanical arrangements of these units are used, depending on the purpose for which the instrument is designed.

In the simple direct vision spectroscope a cemented prism of the Amici type is often used. This is composed of one flint unit and two crown-glass units, the angles and glass being so chosen that the F-line of hydrogen is undeviated. In the instruments designed for photography of the ultra-violet spectrum the sixty degree type of prism is usually employed, but in order to avoid image doubling, due to the birefringence of the material, it is composed of two thirty degree prisms, one of right quartz and one of left. The rotation produced in the first half of the prism is exactly neutralised by the reverse rotation in the second half. This type is called the Cornu prism.

If the instrument is designed for visual observation it is equipped with a cross-hair and eyepiece. If a permanent photographic record is desired, the eye-piece is replaced by a plate holder equipped with an operating mechanism. The last method is used almost exclusively in studies of the ultra-violet region, and in the case of the better visual spectroscopes the design is such that the telescope can be replaced by a camera. Certain inherent characteristics which depend on the design of the instrument determine its efficiency. Chief among these are dispersion and resolving power. To alter dispersion either the index or the angle of the prism must be altered; to alter resolving power the base of the prism must be changed, at the same time utilising its full aperture.

Perhaps the earliest and greatest use of the spectroscope until recently was in the province of astronomy. According to Dr. Edwin Hubble, of the Mount Wilson Observatory of the Carnegie Institution, the study of absorption spectra is the dominating feature of modern astronomy. "They furnish," says he, "an astonishing amount of information concerning the physical condition of stars and even of planets and nebulae. Either directly or indirectly they indicate surface temperatures of stars, surface luminosities, total luminosities, distances, and velocities in the line of sight." The spectra of over 90 per cent. of all the stars are dark line absorption spectra.

It was the study of the spectra of distant nebulae with the spectrograph which disclosed a peculiar characteristic to Dr. Hubble—the dark lines, or absorption bands, are not in their usual positions. The lines are all displaced toward the red end of the spectrum and the displacements increase with the faintness of the nebulae observed. Observations are summed up in the statement that the fainter the nebula the larger the red-shift. Since apparent faintness of nebulae is confidently interpreted in terms of distance, the conclusion is that red-shifts increase with distance. Precise investigations indicate that the relation is linear—red-shifts are equal to distances times a certain constant.

Many ways of producing such effects are known, but of them all only one will produce large red-shifts without introducing other effects which

should be conspicuous but actually are absent. This one known permissible explanation interprets red-shifts as due to actual motion away from the observer. On this interpretation the nebulae are rushing away from us, and the farther away they are, the faster they are travelling. The velocities increase roughly 100 miles per second for each million light years of distance.

It is by the accurate measurement of the colour of well-defined spectral lines that the astronomer is able to discover whether the body emitting them is approaching or receding, on somewhat the same principle that the noise emitted by an automobile horn sounds deeper in pitch when it is receding from us than when it is approaching. So the light from a receding body appears redder than that of one approaching.

Spectroscopy has become such an important study at the present time that international conferences are frequently held at which authorities report recent advances in numerous fields of investigation.

At a recent conference at Massachusetts Institute of Technology, one of the reports concerned one of the great riddles of medical science—the extreme complexity of the biological units which by their balance produce health or illness. One of these units, porphyrin, was shown by Dr. Calvin B. Coulter to be capable of analysis by the spectroscope with a sharpness, precision and simplicity which usually apply chiefly to the inorganic substances like the metals. Porphyrin is the base of red blood-cells. It is also the base of chlorophyll, the green colouring matter of plants, which they use to synthesise food through the agency of sunlight. The two porphyrins differ mainly in that the blood one is combined with iron while the green plant substance is combined with magnesium. Because of this, some scientists have speculated on the possibility that far back in evolution the green of the plants and the blood of man may have originated from the same source. This may be a link between plants and animals.

Coulter has found further evidence of this kinship of plants and men in porphyrin which he extracts from cytochrome, a pink pigment existing in the cells of virtually all those living things using oxygen. This cytochrome, he finds, is combined with magnesium, so that a porphyrin-magnesium combination is not an exclusive patent of the chlorophyll-green plants, but belongs also to the red-blooded races. This porphyrin, which he places under the light beams for spectral analysis, is obtained from bacteria. He dissolves it out of their cytochrome, which they use to obtain oxygen, somewhat as man uses his lungs to get oxygen. He studied this porphyrin when combined not only with its original magnesium, but also with copper, cobalt, nickel and tin.

At room temperature the spectroscope showed a general "curve" indicating the presence of porphyrin, but when Coulter cooled these porphyrins down to temperatures between 100 and 200 degrees below zero, the curves showed much more detail. They showed precision comparable with the spectroscopic curves which identify metals.

Spectroscopic investigation has also been of great assistance in the study of hæmoglobin, another vital body substance whose function is to transport oxygen from the lungs to various parts of the body. Dr. David Drabkin, of the University of Pennsylvania, has been able to carry out experiments far in advance of any of those previously made, and although the composition and structure of the plasma is still unknown, important work toward its solution has been done.

Just why nature has chosen a coloured pigment to carry oxygen, when there seem to be other substances which could do the job as well or better; why globin with its huge molecular weight of 68,000 is used to carry oxygen whose molecular weight of 32 seems insignificant in comparison; and how globin is attached to the other parts of the blood are problems science is anxious to solve. On the answers may hang some of the most valuable discoveries medicine has made concerning the human body.

And then there is the continuous search for a cure for cancer. Active in this is Prof. Ellice MacDonald, of the University of Pennsylvania, who has examined more than 10,000 liquids in an endeavour to find one that can be injected into a cancer to enhance the curing power of X-rays and radium. The liquid sought is one that will emit ultra-violet light of a specific wavelength when activated by X-rays or the gamma rays of radium. This secondary emanation is regarded as most important, but it is essential to have the radiation at the base of the cancer since it is almost impossible to transmit these rays any distance.

Incidentally, the most deadly radiation yet discovered, a narrow range of ultra-violet light, will destroy living cells almost instantaneously, according to Dr. MacDonald, who made these observations by means of a specially constructed quartz-microscope. In his search for the liquid which he believes will be of tremendous value in the treatment of cancer, Dr. MacDonald has discovered several which radiate the desired ultra-violet light. But the requirement that they be volatile and non-poisonous to human tissue has thus far proved a stumbling block.

The detection of cancer in its earliest stages is nearing through the discovery by Doctors A. J. Allen and E. B. Sanigar, that cancerous blood is different from that which is free of the disease. These new qualities of cancerous blood were discovered by means of the spectroscopic examination in experiments on rats—and recently on human beings. While the work is admittedly in its early stages, it may suggest to other workers in this field a new and profitable method of investigation.

Some investigators have gone so far as the accurate forecasting of death by spectroscopic analysis of the blood of diseased persons. To the great astonishment of attending physicians in Paris, P. and M. Lecompte de Nouy, of the Pasteur Institute, predicted deaths by spectroscopic examination which occurred within 24 hours, although death was not believed imminent.

In their research more than 8,000 samples of the blood of men, horses and sheep were examined and various characteristics discovered by means of spectroscopic investigation of the serum and white plasma of the blood, which were plotted

on charts. The resulting curves, similar to those on business trends, show a "remarkable constancy, so great that the curves can readily be superimposed on each other. The various fluctuations in the curves represent the various structural features of the blood as indicated by the various colours which manifest themselves by the absorption of light passed through the serum or plasma into the spectroscope."

When departures from this general trend are noted they can safely be interpreted as an indication of pathological disturbances. Such alterations must correspond to very deep chemical modifications affecting the chromophoric (colour) elements which belong to very stable chemical groups. Thus these changes in the blood show that very definite and basic chemical changes are occurring. These changes have been found for the most part to precede death.

It is also through spectrum analysis that marked progress toward the complete and positive identification of pepsin is expected. Although science has for years realised the importance and function of this important digestive juice, and has been fairly sure that it was composed of carbon, hydrogen, oxygen and other elements, just what amount of these substances constitute pepsin and how they are chemically arranged has remained a mystery.

Only recently, through the researches of Dr. Geo. I. Lavin, of the Rockefeller Institute, was it discovered that pepsin is a protein, but much additional information was needed. Now, Dr. Lavin's investigations with the spectroscope suggest that pepsin is constituted of amino-acids. His method was to compare the spectra of pepsin with those of substances of which it might be composed.

An equally fascinating phase of spectral study is the method of analysing the potency of vitamins by spectroscopic light. The eye of the spectroscope is so sensitive that it would take a pool of cod liver oil 300 feet deep to look the same as one paper-thin sheet of pure vitamin D, according to Dr. R. A. Morton.

For vitamin D, it appears, the spectroscope should not be used except with the pure vitamin, named calciferol, which is 40,000 times more potent than cod liver oil. This is because in the oil, or any substance containing vitamin D, colours which register only in ultra-violet light mask the lines which reveal the potency of the vitamin. Only biological tests with living animals are safe for testing the strength of vitamin D preparations.

But for vitamin A, the investigation shows, the spectroscope is the best method of analysis, exceeding even the biological tests. Further, the evidence of the spectroscope affords reason to believe that there is more than one kind of vitamin A. It indicates that there are probably several massive groupings of molecules, all very similar, each of them carrying the medicinal or physiological effects of vitamin A. With remarkable precision the spectroscope shows the existence of these apparently different groups, but they are so close together that there is at present no way of separating them to find out whether one group may be more potent than another.

At the University of Cambridge investigators have found that the fertility vitamin E absorbs

light in a distinct and characteristic fashion thus making positive identification possible. By dissolving vitamin E, prepared from wheat germ seeds, in alcohol, it was found that a sharp absorption occurs at a wave-length of 2900 Å. This wave-length is in the invisible ultra-violet region, near the actinic rays of light which cause sunburn. The key test in this research was to show that the vitamin E which produced this absorption really produced a biological effect when given to experimental animals. Such an effect was found, and according to Doctors Martin, Moore and Schmidt, "the vitamin caused a female rat which had shown characteristic resorption gestation to produce a litter of eight live young".

In none of the phases of spectrum analysis has more progress been made than in the examination of metals. Both in quantitative and qualitative spectrographic analysis the detection and identification of metals and alloys has shown the spectrograph to be the most sensitive instrument known, far outdistancing chemical analysis in speed and accuracy. This phase of spectrography alone is creating a new and exhaustive literature on the subject. Here, the purpose is to report the investigations that affect the lives of all of us more immediately.

And one of the most interesting reports comes from Prof. Jacob Cholak, of the University of Cincinnati, which describes the detection of lead in the human system. While qualitative determination has been possible for some time, exact quantitative measurement has been exceptional without the use of the spectroscope. Chemical analysis, heretofore employed, requires anywhere from 10 to 14 days, while the spectroscopic analysis is possible in a period varying from 24 to 48 hours.

Describing the detection of lead in the human brain, Prof. Cholak reports that a percentage of three-tenths per hundred grams has been found in the brain of an individual. Through the use of the spectroscope, he has been able to detect minute amounts in other parts of the body. Another advantage of this method over the chemical analysis is that very small amounts of fluid, tissue or bone are required for the test. Using known lead concentrations to add to the spinal fluid and establishing a relation between this ratio and the lead concentration, it is possible to detect one hundred millionth of a gram of lead per cubic centimetre. Dr. J. Stuart

Foster, of McGill University, hopes to apply this method to the study of lead as a possible cause of multiple sclerosis.

The selenium poisoning of cattle has long annoyed ranchmen in various parts of the world. There has been no way to discover the small amounts of this poisonous element in the soil. Livestock feeding on vegetation growing on this infected soil are killed. But at last both selenium and sulphur have succumbed to the spectroscope—in this case one of special design, because of a very long wave-length in the infra-red or heat region of the spectrum. By making special adaptations, and by the use of the new infra-red sensitive photographic plates, Dr. George Harrison and Dwight Merrill have found it possible to record and measure the light emitted by the atoms of sulphur and selenium. As much as one part in a million of these substances can be detected in the presence of other materials.

Not only is the result important to cattlemen and farmers, but the method is expected to prove useful to metallurgists. Recently the presence of small amounts of sulphur and selenium in certain alloys have been recognised as an important factor in determining the characteristics of the alloy. By the use of the spectrograph the amount of these elements in the alloy can be measured accurately and kept at the right specification.

Even in the field of diamond mining the spectroscope is proving exceptionally useful to the geologist. It tells whether certain rock is the kind in which diamond is likely to be found. Although diamond-bearing rock may appear on the surface like any other rock, the spectroscope is able to tell swiftly whether diamonds may be hidden there.

What the instrument actually does is to detect the presence of so-called volcanic "pipes" formed by the explosion of volcanic lava through the earth's crust. It is this explosion with its tremendous heat and pressure that is believed to be responsible for the formation of diamonds although the exact process is not known to science. Detection of the "pipes" however does indicate the proper type of rock and thus eliminates considerable hit-or-miss prospecting. The spectroscope is also used in the study of volcanoes to identify the gases from which the molten lava is formed. Further researches in this field may assist science in forming an accurate picture of the substances which comprise the inner layers of the earth's crust.