

A CENTURY OF SPECTRUM ANALYSIS

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1. Almost three hundred years have elapsed since the first discovery of the spectrum. On February 6, 1672, Newton reported to the Royal Society on his discovery of the dispersion of light and on his explanation of the different colors. In a letter to Oldenburg, the secretary of the Royal Society, in which this discovery was announced, Newton reported that the discovery had already been made by him in 1666.* The first edition of "Opticks" appeared in 1704: "Opticks: or a Treatise of the Reflections, Refractions, Inflections and Colours of Light,"¹ which contained a complete description of numerous ingenious and delicate experiments of Newton. It is of interest that Newton had no fore-runners in his discovery, since no attention had been paid before him to the connection between color and the refraction of light. The origin of colors was ascribed to the mixing of light and darkness in different proportions.

Over a period of more than 100 years following the publication of Newton's discovery, not a single observation was made on spectra that is worthy of mention. Only at the beginning of the nineteenth century was a series of important discoveries made. In 1800, the noted self-taught astronomer Frederick William Herschel--a former musician and scholar--discovered and, for his time, thoroughly investigated the infrared part of the spectrum.² Although he even pointed out that the infrared rays possessed all the properties of visible radiation,³ (except, of course, visibility) that they were reflected, refracted, and obeyed Snell's law just as light did, Herschel ascribed to them a nature different from the nature of light and considered them a particular type of "heat rays."

The discovery of ultraviolet light followed the discovery of the infrared portion of the spectrum: in 1801, J. W. Ritter⁴ discovered that the blackening of silver chloride did not stop at the edge of the violet part of the spectrum, but was observed--and even increased in intensity--beyond the limits of the visible spectrum. In this case the invisible rays were discovered by means of their chemical effects; as a consequence it was long the mistaken

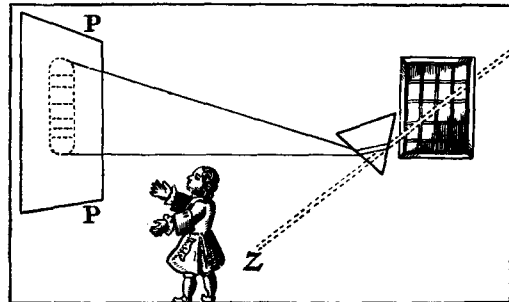


FIG. 1. Newton's experiment. From the book by Voltaire: *Elements de la philosophie de Newton. Mis à la portée de tout le monde.* Par Mr De Voltaire. Amsterdam, 1738.

idea that the ultraviolet rays were "chemical" rays.

2. In 1802, Wollaston published two important observations, the value of which was recognized only many years later. Repeating an experiment similar to that of Newton, but using a slit in a shutter in place of the circular aperture, Wollaston⁵ discovered that the sun's spectrum was crossed by several dark lines. This was undoubtedly the discovery of the Fraunhofer lines. However, this discovery did not attract any attention and in later years, no one recalled it.

At the same time, studying the spectrum of the inside of a light flame, Wollaston found that the spectrum of this part of the flame consisted of five bright lines, separated by dark intervals. This was the first discovery of the line spectrum of luminous gases.

3. Quite independently of Wollaston, both discoveries were made in much more complete and exact form almost fifteen years later by Fraunhofer, whose works marked one of the most important steps in the history of spectroscopy. First and foremost, Fraunhofer⁶ made significant improvements on the experimental method of observation of spectra. Being a skilled mechanic and a fine optician, Fraunhofer used prisms and lenses in his researches that were of the highest quality available at that time, and used accurate arrangements of the mechanical apparatus. In his first researches, Fraunhofer still used a prism as a dispersive element, and he observed the spectrum by means of the telescope of a theodolite. By means of such an arrangement, Fraunhofer first discovered the two neighboring bright yellow lines in the spectrum

*This letter was translated into Russian by S. I. Vavilov and published in the issue of "Uspekhi," devoted to Newton. See Usp. Fiz. Nauk 7, No. 2, 1927.

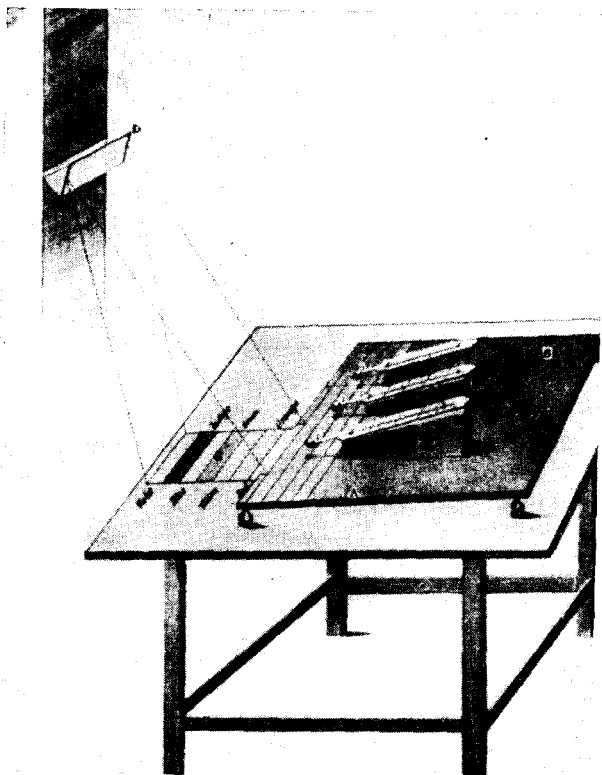


FIG. 2. Herschel's apparatus for the study of the infrared portion of the spectrum (Phil. Trans. 1800, p. 292). The thermometer 1 served to measure the increase in temperature in the different parts of the spectrum. The other thermometers served as controls.

of the flame of a tallow candle; these lines were clearly separated against the background of the continuous spectrum of the candle. Expecting to see these lines in the spectrum of sunlight, Fraunhofer employed his apparatus for the study of the spectrum of the sun. But, looking in the theodolite telescope, he was astonished by the fact that instead of bright lines, he saw "a large number of dark lines, while some appeared completely black." Fraunhofer made up a drawing of the sun's spectrum, denoting the most intense lines by the Latin letters from A to H; the violet end of the spectrum was denoted by the letter J. Between B and H, Fraunhofer observed 754 lines, of which the positions of 350 were accurately measured and put in the drawing of the spectrum of the sun. Among these dark lines, Fraunhofer noted a line located at the boundary between the yellow and orange part of the spectrum and assigned the letter D by him. This line, which upon careful observation appeared to be double, occupied the same position on the scale of the apparatus as the pair of bright lines observed by Fraunhofer in the spectrum of the flame of the tallow candle; coincidence could be established to the limit of accuracy achieved by the

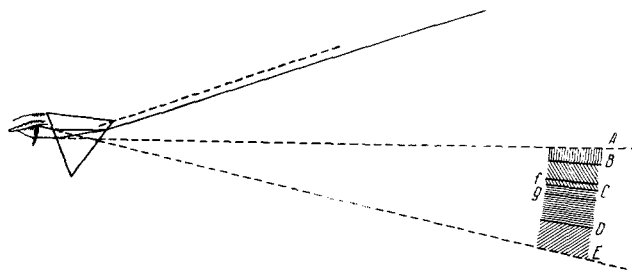


FIG. 3. Wollaston's experiment: a beam of light enters a darkened room through a slit of width $1/20$ in. and is picked up by a flint glass prism located in front of the eye at a distance 10 or 12 ft. from the slit (Phil. Trans., 1802).

apparatus of Fraunhofer. Thus an amazing fact was discovered which was to play such an important role in the future history of spectroscopy. Speaking descriptively, we might say that this fact was that the light of the tallow candle contained in abundance just those wavelengths which were absent or at least strongly attenuated in sunlight. The origin of this notable phenomenon and the origin of the dark lines of the sun's spectrum generally were not yet understood, but the important value of his discovery for practical optics was evidently appreciated by Fraunhofer, since, as a result of the measurement of the position of these lines, the possibility was discovered of measuring the optical constants of materials (the index of refraction) for specific wavelengths.⁶

After the discovery of the dark lines of the sun's spectrum, Fraunhofer investigated his second very important discovery: the diffraction grating.⁷ Fraunhofer studied the diffraction picture that is observed when parallel light rays pass through a narrow slit and through a grating consisting of parallel threads. This is how he himself describes his first observations with the grating: "In order to make it possible for a large number of identical, strongly diffracted rays to pass through the whole surface of the telescope of the theodolite, I stretched a very large number of parallel threads of the same thickness on a frame located at equal distances from one another: light would have to undergo diffraction in passing through the interstices. To assure that the threads were accurately parallel and separated by equal distances, I placed fine screws on the two opposite ends of a quadrilateral frame, each screw having about 169 threads per inch. I attached the threads in the grooves of this screw and I could thus make certain that the threads were accurately parallel and equally spaced. I focused an intense ray of sunlight on the telescope of the theodolite through a vertical slit of a heliostat of height 2 inches and width 0.01

inch. I then put the grating, which consisted of approximately 260 threads of thickness 0.002021 inch, at the center of the circle of the theodolite (the distance between the edges of the threads amounted to 0.03862 inch). I was greatly astonished when I saw that the phenomena which are observed with the grating in the tube are quite different from those which can be observed in the diffraction from a single slit."

"If the objective was so placed that the picture of the aperture of the heliostat was sharply bounded without the grating, then in the color spectra which were produced by the thread grating, one could see lines and bands which I discovered with the aid of a good prism in the spectrum of sunlight, a phenomenon which is of great interest since it permits--as will be seen below--an accurate study of the laws of modification of light which arise as a result of the interaction of a large number of diffracting rays."

With the aid of the grating just described and another finer grating of 340 lines per (Parisian) inch, Fraunhofer showed that the effect did not depend on the thickness of the thread nor on the width of the transmission space, but depended only on the sum of the thicknesses of the thread and transmission space.⁷ Furthermore, the material of the thread had no effect on the picture of the phenomenon: Fraunhofer made gratings of hair and of silver or gold wires, and in all cases observed the same phenomenon.

Later, Fraunhofer prepared gratings with a still greater resolving power. For this purpose, he shifted from gratings made of stretched parallel threads to gratings cut on glass plates: with the help of a specially constructed machine, parallel scratches were cut with a diamond. He thus succeeded in making gratings with a constant of 0.0001223 Parisian inch, while his best thread grating had a constant of 0.001952 inch.

With these gratings, Fraunhofer continued, expanded, and made more accurate his spectral observations. Kayser* has accurately characterized the value of the researches of Fraunhofer for spectroscopy: "In these researches, Fraunhofer did not advance any hypotheses on the origin of the light and dark lines of the spectra. However, the gain from these researches was enormous. In the first place, we learned that the sun's spectrum has dark lines at definite unchanging places, which permit a very exact designation of the place in the spectrum instead of such vague descriptions as 'in the beginning of the yellow part' etc. With the

help of the grating, we could now characterize each definite position in the spectrum by its wavelength. Further, we learned that other heavenly bodies have similar lines, but that these lines can be different depending on the object. Finally, we learned that terrestrial sources give bright lines. The researches of Fraunhofer are a brilliant example of what can be shown and what accuracy can be achieved by an absolutely reliable investigation, without any hypotheses but with precise definition."

4. We cannot dwell in detail here on the many researches of the forerunners of Kirchhoff and Bunsen, among whom were such outstanding scientists as John Herschel, Wheatstone, Stokes, etc. In the opinion of Kirchhoff himself, the closest of all to the discovery of spectral analysis were Talbot and Foucault.

The first work of Talbot, published in 1825,* is of interest because it shows especially clearly what difficulties were presented by the extreme sensitivity of spectral analysis in investigations toward the discovery of sodium by its yellow doublet.

Referring to his previous observations, in which the yellow light was produced on the one hand by the flame of a mixture of alcohol and water and the other by a flame of sulphur, Talbot resolved to test whether the identical spectrum is obtained in both cases. To his astonishment, the spectra were the same: "The result of these experiments," he wrote, "therefore points to the far reaching optical analogy between sodium and sulphur--i. e., two substances which according to the chemists have nothing in common." Becoming convinced that the same sodium line appears in the spectrum of flames composed of a series of other substances, Talbot came to the conclusion that this line belonged to crystallized water (!), since, in the opinion of Talbot, water was the only component common to all these bodies.

In spite of this wrong conclusion, Talbot, as a result of further experiments, became convinced of the unambiguous correspondence between a body and its spectrum. "For instance, the orange ray may be due to strontia, since Mr. Herschel found a ray of that color in the flame of muriate of strontia. If this opinion should be correct and applicable to the other definite rays, a glance at the prismatic spectrum of a flame may show it to contain substances which it would otherwise require a laborious chemical analysis to detect." (The emphasis is mine--E. Sh.)

*H. Kayser, Handbuch der Spektroskopie, Vol. I, p. 12, Leipzig, 1900.

*Original not available. The quotations are from Kirchhoff's article on the history of the discovery of spectral analysis.

In a subsequent work, Talbot described the observed spectra even more precisely: "The strontia flame exhibits a great number of red rays well separated from each other by dark intervals, not to mention an orange, and a very definite bright blue ray. The lithia exhibits one single red ray. Hence I hesitate not to say that optical analysis can distinguish the minutest portions of these two substances from each other with as much certainty, if not more, than any other known method."

We therefore see that in spite of the absence of definite data on spectra, on the difference between the spectra of solids and vapors, of individual elements and chemical compounds, Talbot guessed the possibilities of spectrum analysis. Of course, from this intuition to the discovery of spectrum analysis in the modern sense, was still a great distance.

The correct solution of the problem of the appearance of the yellow lines was given by Swan^{8a} in 1856, that is, only three years before the publication of the first work of Kirchhoff. Swan turned his attention to the fact that the same yellow line which had been observed by Fraunhofer more than forty years previously and designated by the letter R always appeared in the spectrum of the lower part of the candle flame. This line also appears when minute amounts of table salt are put into the flame of the candle. To this question Swan gave a clear answer: The yellow line which appears in the spectra of almost all flames always belongs to sodium which is present in minute quantities. Thus was finally solved the puzzle of the yellow line which had for forty years intrigued every investigator, without exception, who was interested in the study of spectra.

Leon Foucault came the closest to the discovery of spectrum analysis by performing (in 1849, i. e., 10 years before the publication of the work of Kirchhoff and 7 years before the research of Swan) the decisive experiment, and that in a particularly elegant fashion. However, it remains an historical or psychological puzzle why this outstanding physicist did not have the daring to draw a final conclusion from it in clear form. Studying the spectrum of an electric arc between carbon electrodes, Foucault turned his attention to the fact that a bright yellow line was always present in the spectrum. He compared it with the D line of the sun's spectrum and found that both lines occupied the same position in the spectrum. Furthermore he showed that if one passed sunlight through the arc, then the D line became dimmer. Finally, in a fashion that was in the highest degree ingenious, he altered the experiment so that he artificially reproduced the appearance of the D lines in the

sun's atmosphere. Projecting the incandescent carbon electrode of the arc on the slit of his apparatus, Foucault became convinced that this incandescent solid gave a continuous spectrum without any sign of dark lines. However, if with the help of a small mirror the light of this incandescent electrode was reflected and so directed that it passed through the flame of the same arc, then dark lines quickly appeared in place of the bright yellow lines. "Therefore," concluded Foucault, "the arc is itself the means which produces the D rays and at the same time absorbs them when they enter from without." Finally, he made an experiment which almost led to the solution of the problem of the origin of the yellow lines. The experiment was the following. He replaced the carbon electrodes by metal electrodes. The yellow lines reappeared but in greatly weakened form: they were strongly intensified if one of the electrodes were packed with "potash, soda or one of the salts making up lime." Instead of making one further, seemingly small (but in fact not simple) step, and stating that the yellow lines were intensified when the material put into the arc contained sodium (for example, soda, but not potash), Foucault limited himself to the remark: "Before drawing any conclusions on the almost constant presence of the D ray, it is of course necessary to be convinced that one is not perhaps always witnessing its appearance because of the presence of one and the same material dissolved in all our conductors." Finally, in connection with the possibility of the creation of a solar or astral chemistry on the basis of spectrum analysis, Foucault again made a rather indefinite remark: "Nevertheless, this phenomenon (he had in mind the experiments with the D rays, described above--É. Sh.), it seems to us, henceforth creates an insistent stimulation for the study of the spectra of stars, since, if the same ray is found there--the astronomer will draw his own conclusions from it."

We thus see that, in spite of his being close to the discovery of the inversion of spectral lines, Foucault in fact did not make this discovery, since he never gave any clear explanation of his noteworthy experiments. It is therefore not surprising that the work of Foucault remained unnoticed immediately after its appearance. It was recalled only when, in connection with the discovery of Kirchhoff, a discussion as to priority arose at the initiative of William Thomson (Lord Kelvin). In these circumstances, Foucault had the courage honestly to acknowledge* that the last decisive step

*In a paper published in the newspaper "Temps" in connection with the discovery of spectrum analysis. (Cited in Kayser.)

for the discovery of the basis of spectral analysis was not achieved by his experiments. This step, in the opinion of Foucault, was made by the two later (and independent) observations of Swan and Kirchhoff: Swan showed that the yellow lines belonged to sodium, while Kirchhoff demonstrated the inversion of spectral lines in other metals. The latter experiment Foucault characterized as "une expérience véritablement admirable,"* although in justice it should be acknowledged that his (Foucault's) experiment was no less remarkable.

5. Passing over a series of no less remarkable researches, we now turn our attention to the classic works of Kirchhoff and Bunsen.

In a work published one hundred years ago, in October, 1859, Kirchhoff wrote:**¹¹ "Fraunhofer noted that two bright lines appear in the spectrum of a candle flame which coincide with the two dark D lines of the sun's spectrum. The same bright lines are easily obtained even stronger from a flame in which cooking salt has been placed. I produced a sun's spectrum and allowed the sun's rays to pass through a strong cooking salt flame before impinging on the slit. If the sunlight is sufficiently attenuated, then two bright lines appear in place of the two dark D-lines; but if the intensity of the sunlight exceeds a certain limit, then both D-lines appear with considerably enhanced clarity than in the absence of the cooking salt flame.

*"A truly remarkable experiment."

**Fraunhofer hat bemerkt, dass in dem Spectrum einer Kerzenflamme zwei helle Linien auftreten, die mit den beiden dunklen Linien D des Sonnenspectrums zusammenfallen. Dieselben hellen Linien erhält man leicht stärker von einer Flamme, in die man Kochsalz gebracht hat. Ich entwarf ein Sonnenspectrum und liefs dabei die Sonnenstrahlen, bevor sie auf den Spalt fielen, durch eine kräftige Kochsalzflamme treten. War das Sonnenlicht hinreichend gedämpft, so erschienen an Stelle der beiden dunklen Linien D zwei helle Linien; überstieg die Intensität jenes aber eine gewisse Gränze, so zeigten sich die beiden dunklen Linien D in viel grösserer Deutlichkeit, als ohne Anwesenheit der Kochsalzflamme.

Das Spectrum des Drummond'schen Lichtes enthält der Regel nach die beiden hellen Natriumlinien, wenn die leuchtende Stelle des Kalkcylinders noch nicht lange der Glühitze ausgesetzt war; bleibt der Kalkcylinder unverrückt, so werden Linien schwächer und verschwinden endlich ganz. Sind sie verschwunden oder nur schwach hervortretend, so bewirkt eine Alkoholflamme, in die Kochsalz gebracht ist, und die zwischen den Kalkcylinder und den Spalt gestellt wird, dass an ihrer Stelle zwei dunkle Linien von ausgezeichneter Schärfe und Feinheit sich zeigen, die in jeder Hinsicht mit den Linien D des Sonnenspectrums übereinstimmen. Es sind so die Linien D des Sonnenspectrums in einem Spectrum, in dem sie natürlich nicht vorkommen, künstlich hervorgerufen.

"The spectrum of Drummond's light usually contains the two bright sodium lines, if the radiating portion of the chalk cylinder is not subjected to heating for a sufficiently long time; these lines gradually become weaker and finally disappear completely. If they disappear or are sufficiently attenuated, then an alcohol flame, in which cooking salt has been introduced, and which is placed between the chalk cylinder and the slit, produces the phenomenon of two dark lines of striking clarity and fineness at the position of the light lines; these dark lines coincide in all aspects with the D-lines of the sun's spectrum. They are therefore the D-lines of the sun's spectrum in a spectrum in which they are produced not naturally but artificially."

Kirchhoff further described how, by means of a lithium flame, he could obtain a new dark line in the sun's spectrum which is usually absent in that spectrum.*

"On the basis of these observations, I conclude that colored flames, in whose spectrum bright, sharp lines are present, so attenuate the rays of the color of these lines when these rays penetrate the colored flame that dark lines appear in the place of the bright lines as soon as a light source of sufficient intensity is placed back of the flame, a light source in whose spectrum these lines are absent. I further conclude that the dark lines of the sun's spectrum, which are not produced in the earth's atmosphere, arise because of the presence of the same material in the glowing atmosphere of the sun which produces bright lines at the same place in the spectrum of a flame. One therefore assumes that the bright lines coinciding with D in the flame spectrum are always due to the sodium content; the dark D lines in the sun's spectrum further permits the conclusion that sodium is found in the sun's atmos-

*Ich schliesse weiter, dass die dunklen Linien des Sonnenspectrums, welche nicht durch die Erdatmosphäre hervorgerufen werden, durch die Anwesenheit derjenigen Stoffe in der glühenden Sonnenatmosphäre entstehen, welche in dem Spectrum einer Flamme helle Linien an demselben Ort erzeugen. Man darf annehmen, dass die hellen, mit D übereinstimmenden Linien im Spectrum einer Flamme stets von einem Natriumgehalt derselben herrühren; die dunklen Linien D im Sonnenspectrum lassen daher schliessen, dass in der Sonnenatmosphäre Natrium sich befindet. Brewster hat im Spectrum der Salpeterflamme helle Linien aufgefunden am Orte der D Fraunhofer'schen Linien A, B; diese Linien deuten auf einen Kaliumgehalt der Sonnenatmosphäre. Aus meiner Beobachtung, nach der dem rothen Lithiumstreifen keine dunkle Linie im Sonnenspectrum entspricht, würde mit Warscheinlichkeit folgen, dass Lithium in der Atmosphäre der Sonne nicht oder doch nur in verhältnissmässig geringer Menge vorkommt.

phere. Brewster has found bright lines in the spectrum of saltpeter at the position of the Fraunhofer lines A and B; these lines indicate a potassium content in the sun's atmosphere. From my observation, according to which no dark lines in the sun's spectrum correspond to the red lithium band, it would most probably follow that lithium is either not present in the atmosphere of the sun or is present only in relatively small amounts."

Kirchhoff further emphasized that the inversion of the lines is observed only when the absorbing flame is weak.

In the work of Kirchhoff just discussed, generalizations were made without theoretical justification. This basis was provided in another work, which appeared within six weeks of the first paper.¹²

Kirchhoff based his explanation of the connection between the emission spectra of gases and vapors and their absorption spectra on a thermodynamic law pointed out by him, according to which the ratio of the emissive capability of a body to its absorptive capability for the same wavelength and the same temperature is identical for all bodies, and is equal to the emissivity of an absolutely black body for the given wavelength at the given temperature. Proof of this law was given in the second paper of 1859. It then follows that "the intensity of rays of a definite wavelength which are emitted by different bodies at a given temperature can be very different: it is proportional to the absorptivity of the body for rays of this wavelength. Therefore, for a given temperature a metal radiates more strongly than glass and the latter more strongly than a gas. A body which would remain completely transparent at the highest temperatures would never radiate."

Furthermore, Kirchhoff gave a thermodynamical explanation of the inversion of spectral lines. This explanation was received by his contemporaries with such difficulty that, as is seen from the report in the journal *Chemical News* for 1861 (pp. 130-133) on the lecture of Roscoe in the London Chemical Society, even Faraday, who was present at the lecture, found the understanding of inversion to be extremely difficult.

Kirchhoff argued as follows. Assume that a lithium flame is placed between the source giving off a continuous spectrum and the slit of the spectroscopy. In such a case the intensity of the continuous spectrum can be changed only at the point where the red lithium line is located. In fact, the lithium flame at the point in question increases the intensity because of characteristic radiation and decreases it because of absorption which the radiation passing through the flame experiences for the same length of wave. We assume that the absorptivity of the flame is equal to $1/4$. In such a case,

by Kirchhoff's law, the lithium flame should have an intensity equal to $1/4$ of the intensity for the same wavelength in the spectrum of an absolutely black body of the same temperature. Therefore, if the radiating body were an absolutely black body with the temperature of the lithium flame, then the latter would absorb $1/4$ of the intensity for the wavelength of the lithium line (in the continuous spectrum of the source), but would add the same amount as a consequence of characteristic radiation, i. e., no effect would be observed. If now the body giving off the continuous spectrum were less bright than the black body of the temperature of the lithium flame, either because its temperature was lower or because it radiated less at the same wavelength, then the lithium flame would have absorbed less than it radiated, and we would have seen a bright line on the continuous background. Finally, if the emitting source were stronger than the black body of the temperature of the flame (and for this to happen, its temperature would certainly have to be higher than the temperature of the flame), then the flame again would absorb $1/4$ of the incident radiation and since this amounts to more than the flame could radiate in correspondence with its temperature, then dark lines would appear on a light background. Therefore the necessary condition of inversion is obtained: the absorbing flame must be of lower temperature than the radiating body.

This provided at the same time a theoretical explanation of the inversion of spectral lines, which however, as we now see, was not outstanding either in clarity or in rigor. It can scarcely be doubted that usually the real guiding thread for Kirchhoff was physical intuition, while theoretical considerations were added afterwards to establish a foundation for this intuition.

The most important conclusion which Kirchhoff drew from the proof of the inversion of spectral lines given by him consisted in the confirmation of the fact that the presence of the D-lines in the sun's spectrum established conclusively the presence of sodium in the sun's atmosphere. Then, by an additional series of considerations, which show that the production of D-lines cannot be ascribed to absorption in the earth's atmosphere, Kirchhoff concluded: "Thus, a path is found for the determination of the chemical composition of the solar atmosphere and this same path makes it possible for us to draw conclusions on the chemical composition of bright, fixed stars."

Since childhood, we have become so accustomed to this generalization from school books and popular literature, that it is not an easy matter now to estimate its daring, novelty and great sig-

nificance. But this very popularity of the conclusion as to the possibility of the study of the chemical composition of heavenly bodies now, one hundred years after the appearance of the work of Kirchhoff, establishes it in the ranks of the fundamental victories of natural science for all time. The daring of the conclusion of Kirchhoff is emphasized by the fact that this conclusion stood in sharp contradiction with the opinion of the creator of the positivistic philosophy which was then popular among natural scientists, Auguste Comte, who emphasized that we can study the motions of heavenly bodies in detail but we can never know their chemical composition.

For this reason, it is probable that, from a natural desire to place an experimental foundation under the method of chemical analysis which laid claim to applicability not only in terrestrial but also cosmic chemistry, Kirchhoff undertook a special investigation together with the outstanding chemist Robert Bunsen. As a matter of fact, even before Kirchhoff, the possibility of the use of spectra for chemical analysis had been repeatedly pointed out (for example, we recall the work of Talbot, about whom we spoke earlier); however, no one had shown any available independent control in examples that such analysis could give unique and trustworthy results. No one had shown--to cite a trivial example--that sodium always appears in the spectrum in the form of the well known two yellow lines, independently of the mixture of the chemical compound in which it was present and also independent of the properties of the flames which render it luminous. After all, these were not very evident facts at this time and no one had, for example, proved that the presence of these yellow lines or of the red lithium line, in the introduction into the flame of sodium chloride or of lithium chloride, indicated the presence of the element and not its compound.

Kirchhoff and Bunsen carried out extensive research with the three then known alkali metals--lithium, sodium and calcium--and three alkaline-earth metals--calcium, strontium and barium.^{13, 14} The very simple arrangement shown in Fig. 4 was employed. Here F is a hollow prism filled with carbon bisulfide which could be rotated by means of the crank H. The mirror G served for reading the position of the prism, for which purpose a tube and scale, not pictured in the drawing, were employed. The salts to be investigated were placed in a colorless flame of a Bunsen burner D which was a useful innovation in comparison with the flame of an alcohol lamp previously employed. Furthermore, the experiments were carried out with flames of carbon monoxide and oxygen-hydrogen.

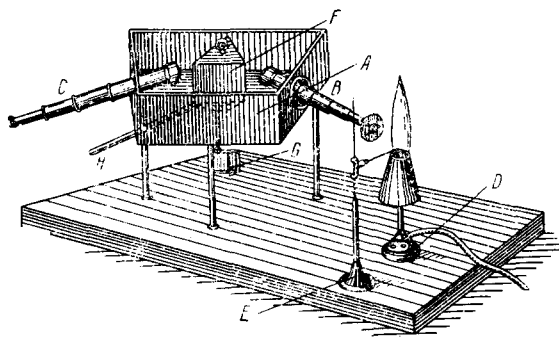


FIG. 4. The spectroscope of Kirchhoff and Bunsen [Pogg. Ann. 110, 160 (1860)].

Kirchhoff and Bunsen formulated the final conclusion of this experiment in the following way:¹³ "A variety of compounds in which the metals appear, a variety of chemical processes taking place in different flames, in a wide range of temperatures--all this had not the slightest effect on the position of the spectral lines of the different metals."

In this same research drawings of the spectra of the elements investigated were put forth which were widely known and used for some decades afterwards, numerous practical proofs of the application of spectrum analysis were given for various special cases, the sensitivity of the analysis was estimated and shown to be extraordinarily high, and numerous examples of real analyses were put forth.

In particular, the appearance of the "omnipresent" yellow lines in the spectra of materials which had no connection with sodium was explained by the following figures of fantastic sensitivity (especially for sodium) of spectral flame analysis. These figures have been cited in countless textbooks, popular works and papers from that day to our own. According to Kirchhoff and Bunsen¹³, one could detect approximately the following amounts in the Bunsen flame:

Li	$\frac{1}{60\,000}$	mg	Cs	$\frac{1}{25\,000}$	mg
Na	$\frac{1}{14\,000\,000}$	"	Ca	$\frac{1}{50\,000}$	"
K	$\frac{1}{3000}$	"	Sr	$\frac{1}{30\,000}$	"
Rb	$\frac{1}{7000}$	"	Ba	$\frac{1}{2000}$	"

In this same work, and in subsequent research, the application of spectrum analysis in the discovery of two new alkali metals was shown--cesium and rubidium, which was undoubtedly one of the clearest proofs of the value of spectrum analysis in "terrestrial" analytical chemistry. In the second paper, several improved types of spectral apparatus (with prism comparison) were described;

this apparatus is encountered in instructional laboratories up to the present date.

We now well know that the success of these classical researches of Kirchhoff and Bunsen was brought about by the conjunction of two extremely favorable properties of alkali metals and their compounds: the low excitation potential of alkali metals and the low thermal dissociation of their halide salts, thanks to which they dissociate into atoms even in the flame of the Bunsen burner.

However, the fact that the investigators had a clear picture of the limitations of their method follows from the remarks repeated below. Kirchhoff and Bunsen pointed out that although in most cases investigated by them the various compounds put into the flame usually gave the spectrum of the metal entering into the compound, it would have been a mistake to think that this would always be the case. Further, they put forward a number of examples which show that the atomic spectrum does not coincide with the molecular spectrum and, by way of an hypothesis, they advanced the following: "In every case, it is possible that the salts which we vaporized were not preserved at the temperature of the flame but were broken up so that we were always dealing with vapors of the metal itself, the metal to which the observed line belonged; furthermore it is conceivable that the chemical compound displays other lines than the elements of which it is composed."

While these observations may appear to be trivial to us today, at the time, in the extreme limitation of experimental means, in the novelty of the field, and in the inadequacy of investigated material, such a clear understanding of the situation was achieved only by outstanding observers.

In 1861, Kirchhoff published his principal research on spectrum analysis, in which he gave

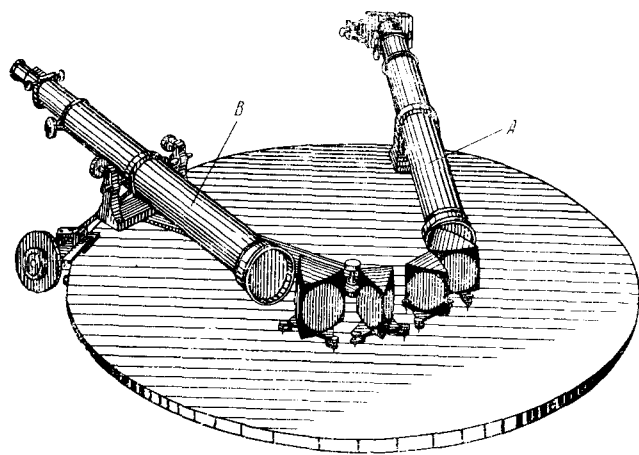


FIG. 5. The great spectroscope of Kirchhoff for the study of the solar spectrum (Abh. Berliner Akad. 1861, p. 63).

drawings of the spectrum of the sun on a large scale, along with the spectra of a large number of elements: Ag, Al, Au, Cu, Fe, etc. --in all, 22 elements. Special apparatus was constructed for the investigation; it was completed by the Steinheil firm and is shown in Fig. 5. As is seen, there are four prisms in the apparatus (three of these were of 45° and the fourth was 60°); the collimator was rigidly connected to the same disc on which the prisms were placed, while the telescope could be rotated about an axis passing through the center of the disc. For excitation of the spectrum, a condensed spark from a large Ruhmkorff coil with Leyden jars connected in parallel was passed between electrodes of the corresponding element.

By establishing the coincidence of the emission lines of particular elements with the Fraunhofer lines of the sun's spectrum, Kirchhoff could determine the presence of these elements on the sun. He thus laid the basis of the chemistry of the sun.

This work made an enormous impression on Kirchhoff's contemporaries. Roscoe who worked for some time in Bunsen's laboratory (the classic work of Bunsen and Roscoe was devoted to the photochemical combination of chlorine and hydrogen*) wrote the following in his recollections: "I had already left Heidelberg when the two friends began their classic research on spectral analysis. But when I returned to Heidelberg in the summer of 1860, I studied this work in great detail and translated it from Poggendorf's *Annalen* for the *Philosophical Magazine*. I shall never forget the surprise which I experienced when, in the back room of the old Physical Institute, I peered into the excellent spectroscope of Kirchhoff constructed there and saw the coincidence of the bright lines of the spectrum of iron with the dark Fraunhofer lines of the solar spectrum. The conviction that our terrestrial iron also existed in the solar atmosphere took hold of me with overwhelming force. And this happened within 40 years of the date when Comte in his "Systems" gave as an example of an insolvable problem, pursuit of which was a waste of time for the scholar, the attempt to learn the chemical composition of the sun, located 91 million miles away from us. But now the composition of the solar atmosphere is almost as well known to us as our own terrestrial atmosphere. And who knows what is still hidden from us in this or that atmosphere. And recently, to our astonishment, four previously unknown elements have been discovered in our terrestrial atmosphere." **

*H. Roscoe, *Ein Leben der Arbeit. Erinnerungen*, Leipzig, 1919, pp. 57-58.

**He is speaking here, of course, of the "noble gases" of the atmosphere.

6. The interest excited in spectroscopy by the researches of Kirchhoff and Bunsen was so great that Crookes set himself the task of printing and reprinting everything which appeared anywhere or at any time relative to spectra in the journal Chemical News, which he published.

Along with the recognition of the importance of the researches of Kirchhoff and Bunsen there appeared many objections; furthermore, an argument arose as to the priority of discovery of spectrum analysis.

We shall recount here one very characteristic objection. The astronomer Morren¹⁸ reproved Kirchhoff for immoderate hastiness in his conclusions. In Morren's opinion, before drawing conclusions on the presence of any particular elements in the solar atmosphere, he should have investigated the spectra of various elements far more carefully. Thus, for example, Morren observed "D-lines are excited not only by sodium, but also by other metals, for example mercury and iron also give yellow lines; and therefore the conclusion as to the presence of sodium on the sun is not substantiated." (!) This objection appears to us today to be almost anecdotal. Actually, the position of the yellow mercury line differs from the D-line by more than 40 Angstroms and therefore it is impossible to confuse them. But if we take into consideration the crudeness of the methods of determination of the position of spectral lines at that time, then this objection would appear to have been worthy of publication in a scientific journal. However, the ease of appearance of the same D lines in the presence of minute contaminations of elements investigated served as a constant source of misunderstanding in the interpretation of its applicability. Therefore one is led to complete agreement with the following comment of Kayser:* "If there had not been a universal occurrence of sodium, spectrum analysis probably would have been discovered by Herschel.** We find that even in later investigations, the sodium line was a stumbling block and led to incorrect conclusions. It is historically interesting that this light (he had in mind, of course, the yellow line of sodium--É. Sh.) which in my opinion was the chief reason for the fact that spectrum analysis was not discovered 30 or 40 years earlier--that precisely this

light in the hands of Kirchhoff and Bunsen led to a most important success, to the transition from terrestrial to solar spectra."

So far as the argument about priority is concerned, this controversy was begun by William Thomson, Lord Kelvin, who, in a letter addressed to Kirchhoff (and afterward published by Kirchhoff) pointed out that he, Kelvin, had heard ten years earlier from Stokes that Professor Miller at Cambridge had made an experiment with a high degree of accuracy which showed the coincidence of the dark D lines with the emission lines appearing in the flame of an alcohol lamp upon the introduction of vaporized salt into it. Further, Kelvin advanced a mechanical explanation of this fact as the consequence of a resonance between the frequency of vibration of the D line and the corresponding frequency in the continuous spectrum, an explanation which was given by him in a conversation with Stokes. In his final public appearances, Kelvin emphasized that everything which was done in the spectroanalytic region was to the credit of Talbot, John Herschel and Stokes. "So far as Kirchhoff is concerned," Kelvin declared in one of these appearances, "I believe that to him belongs the great credit of searching for and finding metals other than sodium on the sun."

Another English physicist, P. G. Tait, recalled* that Fraunhofer had correctly seen that the flame emits light giving a line in the same place in the spectrum where the D lines are found. This fact was more accurately shown by Miller at Cambridge. Finally, Foucault went beyond all in the experiments described on page 961. Furthermore, describing the experiments of Miller, Tait continued: "This was about 1850, and from that time the fact that sodium is found in the solar atmosphere in a heated state (as was experimentally proved to be true) was confirmed by William Thomson and others (?--É. Sh.). This was the origin of spectral analysis inasmuch as this was an application to heavenly bodies." And further: "Neither Stokes nor Thomson thought in 1850 in the smallest degree that they had come across something new--the fact was represented by them as simple and evident--and it must only be added that the circumstance that Thomson, who from that time (i. e., from 1850--É. Sh.) constantly spoke of this beginning as something well known in his outspoken lectures, did not have the slightest pretensions that his name be remembered in connection with this discovery."

*H. Kayser, Handbuch, vol. 1, p. 14, Leipzig, 1900.

**He is speaking here of John Herschel, the son of William Herschel, who discovered infrared light. In his research (1831), Herschel was the first to point out that the coloring which flames of different origin impart can serve as an easy method of the discovery of infinitesimal amounts of the material, but he wrongly concluded that at a definite temperature the flame in every case is a yellow line.

*See, for example, the still interesting lectures of Tait (citing the German translation): Vorlesungen über einige neuere Fortschritte der Physik, Braunschweig, 1877, p. 159 ff.

Inasmuch as neither W. Thomson or anyone else had put into print anywhere before the appearance of the work of Kirchhoff the fundamental confirmation about which we have been speaking (i. e., the actual discovery of spectrum analysis), the facts related by Tait must be regarded only as proof that the discovery was "floating in the air," but not as the basis of any priority claim.

It is undoubtedly true that a whole series of researches preceded the discovery of spectrum analysis by Kirchhoff and Bunsen. In these researches, their authors were close to the goal. In this connection, the investigations of Angstrom, in addition to the researches previously mentioned, are of interest. In 1855, addressing the Swedish Academy of Sciences on his researches, in which the spectrum of an electric arc between electrodes of different metals was compared with the solar spectrum, Angstrom wrote:^{10†} "The analogy between both spectra can be regarded as more or less complete if we turn aside from details; these spectra make such an impression as if one spectrum was so to speak the inversion of the other. I am therefore convinced that the explanation of the dark lines of the solar spectrum at the same time contains within it the explanation of the bright lines in the electric spectrum. Moreover, one should seek out this explanation either in the interference of light or in the capacity of the air to absorb only definite vibrations.*

As is seen from these qualitative considerations (worsened by the incorrect reference to interference as the reason for the appearance of dark lines) they were still far from a clear physical proof of the non-trivial fact of the production of Fraunhofer lines by means of the inversion of the emission lines of metallic vapors in the solar atmosphere.

From the historical point of view, the letter of Stokes addressed to Roscoe, reproduced below, is of great interest; this letter is in answer to a question of Roscoe on the relation of Stokes to the dis-

cussion on the priority of discovery of spectrum analysis. Here is the letter:*

"Dear Roscoe!

When I think of my part in the history of solar chemistry, then I must say that this part is equal to zero, since I never reported anything to anybody on this subject. If one draws attention to the story of this or that question of the discussions which a man has with his friends, then it would be impossible to connect any discovery with the name of a single individual.

However, I have attempted to recall precisely what Thomson (Lord Kelvin--É. Sh.) and I discussed on the subject of spectral lines. I recalled to him that Miller at Cambridge repeated the observation of Fraunhofer relative to the coincidence of the dark D lines of the solar spectrum with the bright lines of certain artificial flames, for example, the flame of an alcohol lamp with a wick impregnated with salt. Miller obtained such a wide spectrum that both D lines were far apart from each other and there were six intermediate lines between them; his observations were made with the greatest accuracy, and the coincidence appeared to be irrefutable. Thomson held the opinion that such a coincidence could not be accidental and asked me what I thought about this question. I illustrated my opinion by a comparison from mechanics with vibrating strings which I had recently published in the Philosophical Magazine in connection with the experiment of Foucault.** Since I knew that the bright D-line is characteristic for the salt and a negligible amount of this compound was necessary to excite the line, I connected the appearance of this line with the soda. I therefore made the assumption that there must be sodium in the solar atmosphere." . . . "Thomson then asked further whether I knew of another example of the coincidence of light and dark lines, and I told him about the observation of Brewster regarding the coincidence of a given red line in the spectrum of calcium with a group A of Fraunhofer lines . . . then Thomson replied with the impetuosity that was characteristic of him: 'Ah, in such a case we ought to establish how the metal produce the bright lines coinciding with the dark lines of the spectrum,' or something of this nature. At that time I was even inclined to follow up his suggestion, since I knew that there existed terrestrial lines which (at low elevations of the sun) undoubtedly arise in the earth's atmosphere. But the presence

†Die Analogie zwischen den beiden Spectren mag indess mehr oder weniger vollständig seyn, wenn man von allen ihren Einzelheiten absieht; in ihrer Ganzheit betrachtet, machen sie doch den Eindruck, als wäre das eine Spectrum so zu sagen eine Umkehrung von dem anderen. Ich bin deshalb überzeugt, dass die Erklärung des dunklen Linien im Sonnenspectrum zugleich die Erklärung der leuchtenden im elektrischen enthält, diese Erklärung mag übrigens entweder in einer Interferenz des Lichts oder in der Eigenschaft der Luft, nur gewisse Oscillationsreihen anzunehmen, gesucht werden.

*The explanation of the Fraunhofer lines as the consequence of interference was a widespread error before the appearance of the researches of Kirchhoff and Bunsen. -- E. Sh.

*Given in the recollections of Roscoe cited on page 965.

**He had in mind the experiments on the inversion of lines described above. -- É. Sh.

of metals in the earth's atmosphere was a doubtful matter. I therefore thought that many lines of the solar spectrum could be produced by similar absorption in the gases of the solar atmosphere.

"The idea of connecting the bright and dark lines by means of inversion theory did not belong to me. I was quite astonished upon becoming acquainted with this idea about which I first heard in a speech of Balfour-Stewart* in the Royal Society, subsequently published in Proc. Roy. Soc. The work of Stewart was performed independently of Kirchhoff but was published somewhat later; however, the same ideas were given by him in two other works which appeared in Edinb. Phil. Trans. before the work of Kirchhoff. But I did not know about these researches when Stewart delivered his address."

It is seen from the foregoing that, in contrast to the discovery of the solar spectrum, which was not prepared by the forerunners of Newton, Kirchhoff had a whole series of outstanding predecessors. The authors of these works were sometimes very close to discovery. However, none of them made the decisive step. Even Foucault, who essentially observed the inversion of the sodium lines, not only did not give the theoretical interpretation of his experiments, but did not even formulate the conclusion following from them with complete clarity, and did not have the daring to state definitely that the presence of the D lines in the solar spectrum gave evidence to the presence of sodium on the sun. As we have seen, he limited himself to a vague expression of hope for the possibility of the creation of a chemistry of the sun and of the stars by means of spectrum analysis. That is why history with complete justification connected the discovery of spectral analysis with the name of Kirchhoff, who not only established theoretically the discovery of the inversion of the D lines of sodium made by him in a quite evident form, but also applied this discovery to a whole series of metals and without any reservation drew a conclusion from this discovery as to the presence of the corresponding elements on the sun.

7. The exposition of the history of spectrum

*Balfour-Stewart was professor of physics in the so-called Owens College (later Manchester University). He was known in Russia at the end of the nineteenth century because of the translation of his popular textbook in physics written by him for the series "Elements of Science," the first volumes of which were written by Roscoe and Thomas Huxley, the noted biologist and friend of Darwin. In their day these little books achieved a great popularity. They were translated into many languages including Russian, and were very popular in Russia. Balfour-Stewart was the first physics teacher of J. J. Thomson. See J. J. Thomson, *Recollections and Reflections*.

analysis to our own day does not enter into the scope of the present paper. Therefore we shall limit ourselves only to a brief recollection of the most important steps of this history after the discoveries of Kirchhoff and Bunsen.

The most important regions of investigation of spectrum analysis up to the thirties of our own century was the investigation of the composition, physical state and motion (Doppler principle) of heavenly bodies, i. e., astrochemistry and astrophysics; in the region of terrestrial chemistry, it was the discovery of new elements. One of the most important events in the history of spectrum analysis took place in 1868, i. e., less than ten years after the publication of the basic research of Kirchhoff. In August of that year there was a total eclipse of the sun and the French astronomer Janssen,¹⁹ who observed this eclipse in Guntur (India), projected a picture of a prominence on the slit of a spectroscope by means of a telescope. Looking in the spectroscope, he saw three bright lines, i. e., an emission spectrum. He therefore immediately concluded that the prominence was a mass of incandescent gas. However, Janssen did not limit himself to this conclusion. Making use of the fact that large dispersion greatly weakens a continuous background while a line remains unchanged, Janssen, the day after the eclipse, directed his spectroscope toward the edge of the solar disc and saw the same three lines of the prominence which he had observed the day before.

The same discovery was made independently of Janssen by Lockyer²⁰ in the middle of October, 1868: By means of a high dispersion spectroscope, he saw the three lines of the prominence on the edge of the solar disc without any eclipse. Lockyer did not make his discovery accidentally. He was convinced that one could see the emission lines of the solar atmosphere at the edge of the solar disc. For several years he attempted to see this inversion of the lines, but was unsuccessful because of insufficient dispersion of his apparatus. Only in the middle of October, 1868 did he obtain a spectroscope of satisfactory dispersion and within several days, to be precise October 20, aiming his spectroscope at the sun, he saw the bright lines without any eclipse. Lockyer knew about the fact that Janssen had observed the emission lines of the prominence during a total eclipse, but he did not know that Janssen had succeeded in observing the same lines after the eclipse: A letter from Janssen giving the details of his observations was late in coming from India, and, dated August 19, arrived in the Paris Academy on October 24. The letter from Lockyer came on the same day a few hours earlier.

The French Academy immediately placed a high estimate on the discovery of Lockyer and Janssen as the discovery of the means for penetrating into the secret of the solar atmosphere. In recognition of the importance of this discovery and of the remarkable coincidence of the observation of both scientists, arranged to have a medal struck with the images of Lockyer and Janssen.

Lockyer did not limit himself to a statement of the possibility of observation of prominences in the upper layer of the sun's atmosphere outside of an eclipse. Displacing the image of the sun relative to the slit and noting the form of the spectral line in this case, he could even mark out the form of the prominence--something like a prototype of the contemporary spectroheliograph. As to the identification of the observed lines, two of the three lines coincided with the Fraunhofer lines C and F and belonged to hydrogen; the third, yellow line differed in position from the two sodium lines and belonged to a material unknown on the earth which Lockyer later named helium.^{20, 21} The full significance of this great discovery was understood only 27 years later when Ramsay discovered helium on the earth.

Lockyer was not only an outstanding observer but also an extraordinarily energetic investigator. Being an astrophysicist, he clearly understood the necessity of laboratory investigations of terrestrial spectra under different conditions in order that the resultant knowledge would permit the interpretation of physical conditions on the sun from the spectral information. To him belongs the investigation of the effect of pressure on spectral lines, the effect of temperature and other conditions in the flame or along the path on the excitation of spectral lines and many other effects. In particular, he first began the correct application of Doppler's principle in the study of radial motion in astronomy. In this connection, it should be recalled that the classical work on the verification of Doppler's principle by means of laboratory experiments was completed by the outstanding Russian astrophysicist A. A. Belopol'skiĭ.

The problem of establishing the exact values of the absolute wavelength belongs to the number of important questions which appeared in turn after the researches of Kirchhoff and Bunsen. The first measurements of wavelengths of Fraunhofer lines were made by Fraunhofer himself with the aid of the diffraction grating that he prepared.

After Fraunhofer, F. A. Nobert, a mechanic living in Bart, a small town in Pomerania, began to make gratings. Nobert succeeded in making gratings with four hundred lines per millimeter. However, their quality was low. Actually, it was impossible to obtain wavelength values with these

gratings of higher accuracy than those made by Fraunhofer. The researches of Rowland²⁷ were of outstanding importance in the development of spectroscopy; by means of a graduating machine constructed by him, he succeeded in making very fine diffraction gratings. Here is what Kayser, who studied the machine of Rowland and gave a very complete description of it, writes in this connection: "In 1882, a new period of spectrum analysis began thanks to the research of H. A. Rowland. On the basis of a new principle, he succeeded in preparing practically perfect screws and used them to construct a graduating machine for optical gratings which far surpassed anything achieved in this region to the present date. He succeeded in cutting up to 43,000 lines per English inch, i. e., 1720 lines per millimeter. But this number was too large for practical purposes, so that the machine was used for drawing 14,438 lines per inch. Later Rowland introduced several improvements and constructed two machines for 20,000 and 16,000 lines or aliquot parts of these numbers per inch. The chief contribution of Rowland was that he began to prepare gratings not only on plane surfaces, as was done exclusively before him, but also on spherically concave surfaces; gratings constructed in this manner combine the action of a grating with the action of a concave mirror, i. e., real spectra were obtained from a luminous point without any lens at all. These gratings, with more than 100,000 lines on the surface, provided a spectroscopic means of obtaining spectra with such dispersion and sharpness which could not even be conceived up to that time. For example, calculation shows that with the largest grating of Rowland such a resolution is obtained in the region of the D lines that to accomplish it with prisms would have to require such a number placed one after another that the thickness of the base of the prisms would amount to 126 cm. The chief advantage of the concave gratings was that they eliminated the necessity of using lenses: the spectroscope consisted simply of slits, gratings and photographic plates. At the same time one avoided the chromatic and spherical aberration of lenses and above all their absorption, which for a long time had prevented progress in the ultraviolet."

So far as the problem of accurate measurements of wavelengths are concerned, the greatest significance for many years following was attached to the research of Angstrom²⁵ on the solar spectrum. With the aid of a Nobert grating, Angstrom measured the absolute wavelengths of eighty of the most intense Fraunhofer lines, distributed with maximum regularity over the entire spectrum. The wavelengths of intermediate lines were deter-

mined by means of a micrometer measurement. As a result he obtained a picture of the solar spectrum with 1000 lines which were compared with the wavelengths of terrestrial elements. The work carried out by Angstrom, in part in cooperation with Talen, belonged to the number of classic works of measurement, and therefore it is just that the name of Angstrom has been perpetuated in the name of the spectroscopic unit of length.

The results of the researches of Angstrom were surpassed only by those of Rowland,²⁸ who photographed the solar spectrum with the aid of his concave grating and then photographed and measured on the photographic plates the lines of the arc spectra of almost all the elements.

8. During the first decades after the work of Kirchhoff and Bunsen, spectrum analysis gained an extremely wide and fruitful application in astronomy. In the region of terrestrial chemistry, the applications of spectrum analysis up to the twenties of the present century were extremely limited.*

As the most important application of spectrum analysis, one should recall its role in the discovery of new elements. In addition to the alkali metals cesium and rubidium discovered by Kirchhoff and Bunsen, and in addition to the discovery of helium, which staggers the imagination even to the present day, spectrum analysis was used for the discovery of all new elements, in particular gallium and germanium, which were predicted by Mendeleev. The reason for the restricted application of spectrum analysis to terrestrial chemistry lay not in the inadequacy of experimental means, but in the absence of a theoretical basis for understanding the origin of spectra and, in the same connection, the absence of criteria for clear differentiation of atomic and molecular spectra, the spectra of neutral and ionized atoms, the connection between spectra and the periodic table of elements, etc.

Theoretical ideas on the nature and origin of spectra developed slowly which, as we now understand, was the natural consequence of the unsuitability of classical ideas for the formation of a theory of spectra. The decisive step was the discovery of empirical laws relating spectral lines of a given atom. The first concrete result in this direction was obtained by Balmer in 1881.²⁹ As is well known, Balmer showed that the wavelengths of the four visible lines of the hydrogen spectrum are represented by the formula

$$\lambda = B \frac{n^2}{n^2 - 4}, \quad n = 3, 4, 5, 6.$$

*Of the researches devoted to the application of spectral analysis, one should especially recall the work of the French chemist Lecoq de Bois Baudran.²³

with amazing accuracy.

At approximately the same time, Rydberg began to look for regularities in spectra.³⁰ It must be pointed out here that for Rydberg this research was not simply a playing with numerical regularities. Rydberg's interest in spectroscopy and in spectral regularities stemmed from his interest in the periodic table of elements. This is what he wrote in this connection:* "By the discovery of the periodic system of the elements by Mendeleev, a new point of departure was obtained that was of great importance for all researches in this area. However, scarcely any use has been made of it. In order to make a beginning in these researches, I have attempted in a previous paper to determine with a little greater accuracy the periodic relation between the densities of the elements and their atomic weights. I then found that one could express this relation approximately by a sinusoidal series with variable coefficients . . . going further, one is led to the very reasonable hypothesis that cohesion, adhesion, and chemical affinity depend fundamentally on the periodic motion of the atoms. The most natural course therefore would be to study periodic motions in general and since the spectra of chemical elements are due to motions of this character, we find ourselves back in the region of spectrum analysis. It is true that we cannot know if these periodic motions are the same as what we first sought, but a study of these vibrations will give us in every case information of great value on the constitution of atoms, and will bring us closer to our goal than any other research on physical properties."

*Par la découverte du système périodique des éléments par M. Mendeleev, on a obtenu un nouveau point de départ d'une grande importance pour tous les travaux dont il s'agit ici. Cependant on s'en est peu servi. Pour donner au moins commencement à ces recherches j'ai essayé dans un mémoire antérieur de déterminer avec un peu plus d'exactitude la relation périodique entre le poids spécifique des éléments et leurs poids atomiques. J'ai trouvé alors qu'on peut exprimer approximativement cette relation par une série de sinus à coefficients variables.

. . . En remontant encore plus loin, on est conduit à l'hypothèse très vraisemblable que la cohésion, l'adhésion et l'affinité chimique dépendent au fond de mouvements périodiques des atomes. Le cours le plus naturel serait donc étudier les mouvements périodiques en général, et puisque les spectres des éléments chimiques sont dus à des mouvements de ce genre, nous nous trouvons renvoyées dans le domaine de l'analyse spectrale. Il est vrai que nous ne pouvons savoir si ces mouvements périodiques sont les mêmes que nous cherchons primitivement, mais une étude de ces vibrations nous donnera dans tous les cas des informations d'une grande valeur sur la constitution des atomes et nous conduira plus près de notre but qu'aucune autre recherche d'un coefficient physique.

The outstanding value of the research of Rydberg for spectroscopy, and through it for all quantum mechanics, is due to the fact that guided by a brilliant intuition, Rydberg began to study the regularities, not of the wavelengths as was done by Balmer, but the reciprocals of the wavelengths, i. e., the wave numbers $\frac{1}{\lambda} = 2$. The discovery of the constant differences $\Delta\nu$ in doublets and triplets was based on this happy idea of Rydberg. Turning his attention to the regularly decreasing difference of frequencies and intensity in spectral series discovered shortly before, Rydberg attempted to represent each series in the form

$$\nu = a - \phi(n + \alpha), \quad (1)$$

where a is a constant, n an integer, and ϕ some function possessing the properties that $\phi \rightarrow 0$ as $n \rightarrow \infty$. Thus a is a limit of the series expressed in cm^{-1} and ϕ is a variable term decreasing upon increase in n . Trying different expressions for ϕ , Rydberg came to the conclusion that the best result was obtained with a choice of functions

$$\phi(n + \alpha) = \frac{R}{(n + \alpha)^2}. \quad (2)$$

Further analysis revealed that even the constant a in Eq. (1) can be represented in the form

$$a = \frac{R}{(n_1 + \alpha_1)^2}.$$

Then the formula of Rydberg takes on the general form

$$\nu = \frac{R}{(n_1 + \alpha_1)^2} - \frac{R}{(n_2 + \alpha_2)^2}, \quad (3)$$

where n_1 is a constant integer for a given series.

It is evident that the Balmer formula can easily be put in the form

$$\nu = \frac{1}{\lambda} = \frac{R}{2^2} - \frac{R}{n^2}, \quad (4)$$

i. e., it can be regarded as a special case of the Rydberg formula, taking place for the simplest atom--the hydrogen atom.

The next step was taken by Ritz, who established the so-called combination principle, by virtue of which any frequency in the spectrum can be represented in the form

$$\nu = T_k - T_n, \quad (5)$$

where $T_1, T_2, \dots, T_k, \dots, T_n$ is a characteristic system of numbers for a given atom--the spectral terms.

Niels Bohr was the first to understand the full significance of this principle, seeing in it a basic law of quantum mechanics of the atom and identifying the system of terms with the system of energy levels of the atoms in such a fashion that each energy level is equal to the corresponding spectral term multiplied by hc and taken with opposite sign. As the simplest consequence for spectroscopy an explanation was immediately obtained of the apparently incomprehensible fact that only the lines of one--and in particular of the principal series--can also be observed in absorption, i. e., capable of inversion. Indeed, this fact is a direct consequence of the fact that the constant term in the principal series, which corresponds to the final state in emission and the initial state in absorption, is the energy of the atom in the lowest, unexcited state. Therefore, it follows that the constant term of the principal series must be equal to the energy of ionization of the atom--an assertion which finds direct experimental verification in experiments with critical potential (the well-known experiments of Franck and Hertz, Davis and Goucher, etc.).

One of the most brilliant consequences of the elementary theory of Bohr was the solution of the puzzle of the so-called Pickering series which is observed in the spectra of certain stars. This series is ascribed to hydrogen found on the stars in a peculiar state. But Bohr predicted--and the experiments of Paschen confirmed this prediction--that the Pickering series should belong not to hydrogen but to singly ionized helium.

These discoveries served as the basis for the solution of many complicated spectroscopic problems. The peculiarities of spectra observed in intense spark discharges, which were little understood up to that time, obtained a simple and natural explanation in the differences of spectra of neutral and singly and multiply ionized atoms.

In addition a complete development was obtained for the theory of spectra of diatomic molecules, which also explained the characteristics of spectra in the gaseous state.

All these and many other results of spectroscopy, which received a powerful impulse from the brilliant developments of quantum mechanics, in turn laid the initial stage in the development of spectrum analysis as one of the most important analytical methods. Spectrum analysis which at the beginning of its development in the second half of the previous century yielded such reliable information relative to the chemistry and physics of celestial objects, and by the same token increased without limit our knowledge of the universe, became in our time the necessary tool of physicists and chemists in the study of the structure of

matter and in carrying out rapid and exact chemical analyses. Indeed the number of analyses carried out manually on spectra in industrial laboratories, on geological expeditions and in scientific-investigatory institutes of widely varied character, is now numbered in the millions. But this contemporary development of spectrum analysis, in which the works of Soviet scientists have also played an important role, lies outside the scope of the present paper.

In the present year, one hundred years after the appearance of the classic work of Kirchhoff and Bunsen, who first began the intensive development and application of spectrum analysis, we recall the names of these founders and pioneers with gratitude.

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The largest amount of information on the history of spectroscopy can be obtained in the six-volume encyclopedia of spectroscopy: H. Kayser, *Handbuch der Spektroskopie*, I-VI. Leipzig, 1900-1910. In this monumental work there is a brief summary of the history of spectroscopy (v. I, pp. 3-128), extending to the end of the last decade of the nineteenth century and throughout all six volumes all the most important researches are set forth in a detailed fashion. Unfortunately, the entire work has at the present time only historical interest.

¹ Newton, *Opticks: or a Treatise of the Reflections, Refractions, Inflections and Colours of Light*, London, 1704. (The Russ. Transl. by S. I. Vavilov, 1927 and 1954, is of the 3d Ed., 1724).

² W. Herschel, *Experiments on the Refrangibility of the Invisible Rays of the Sun*, *Phil. Trans.* 1800, II, 284-292.

³ W. Herschel, *Experiments on the solar and on the terrestrial rays that occasion heat; with a comparative view of the laws to which light and heat, or rather the rays which occasion them, are subject, in order to determine whether they are the same or different*, *Phil. Trans.* 1800, II, pp. 293-326; III, pp. 437-538.

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