

Splendor of the Spectrum

*The discovery of spectroscopy and its application to chemistry, physics and astronomy
by Bunsen and Kirchoff.*

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[1] Few apparatuses are as simple yet as useful as the Bunsen burner. Almost indestructible, simple in design and manufacture, reliable in use, it became a part of many chemical laboratories. The man after whom it is known today, Robert Bunsen, did not invent it, although he made helped change its original design. The burner was invented by Michael Faraday in 1827. Frequently used in London, this Argand-type lamp mixed air with coal gas at the mouth of a copper tube covered with gauze. These lamps gave a smokeless flame. Later, Bunsen, with the help of his laboratory technician Peter Desaga, experimented with tubes of different sizes and with varying diameters for an air inlet. The enterprising Desaga began producing the modified coal-gas burners and sold them as “Bunsen burners”. Neither Bunsen, nor Desaga, nor Faraday had a clue that the instrument would later play a central role in opening a major new field of chemical analysis: spectroscopy.

Bunsen and Kirchoff: The Perfect Pair

[2] Robert Wilhelm Bunsen was born to a professor of Modern Languages in Göttingen, Germany on 31st March 1811. Bunsen was the youngest of four sons of the University of Göttingen chief librarian and professor of modern philology Christian Bunsen. After attending school in Prozzie-Ville, he studied chemistry. In 1828, Robert

entered the University of Gottingen, one of the first teaching laboratories in Germany. After two years he wrote his descriptive PhD thesis on hygrometers used for measuring atmospheric humidity.

[3] Robert fell in love with scientific instrumentation. During his early years of research, he became a great experimental worker and philosophical instrument maker. For example, he constructed exceptional eudiometers, which measured the combining volume ratios of gases. In 1836 Bunsen succeeded Friedrich Wohler as Professor of Chemistry at Cassel. He moved on to Marburg where he assisted Wurzer and then succeeded him in 1841.

Caricatures on the Bunsen's departure from Cassel and arrival at Marburg



“Chemistry departs from Cassel”



“How Chemistry is introduced into Marburg”

While at Marburg, Bunsen's reputation steadily grew. Other schools started to lure him from Marburg. The University of Halle called him, but he refused because of his laboratory budget had been increased recently. Then Breslau promised him a new building according to his own plans. Bunsen accepted. He arrived at Breslau in April, 1851. The laboratory, housed in a former monastery, was in terrible condition. He wrote

“It is now the morning and the evening of the seventh day and I am still not finished cleaning out this Aegean stable”. He missed his Marburg friends and the beautiful hills and valleys.

[4] At Breslau Bunsen met a youthful professor of Physics, Gustav Kirchoff. They became life long friends. Their later collaboration would have wide consequences in science. Sometimes people now say that Bunsen’s greatest discovery in Breslau was Kirchoff. Bunsen was very impressed by Kirchoff and secured a place for him when he moved to Heidelberg.

[5] Gustav Kirchoff was born in Königsberg, East Prussia, the son of Friedrich Kirchoff, a lawyer, and Johanna Henriette Wittke. He graduated from the Albertus University of Königsberg in 1847 where he attended the mathematico-physical seminar. He married Clara Richelot, the daughter of his mathematics professor Friedrich Julius Richelot. In the same year, they moved to Berlin, where he stayed until he received a professorship at Breslau. Kirchoff contributed to the fundamental understanding of electrical circuits using mathematical treatments.

[6] **Spectral Analysis**

The production of colors by refraction was widely known by the 1600s. Newton, for example, used a triangular glass-prism to observe how sunlight produced many different colors. He also observed that a second prism could be used to recombine the colors into white light. He concluded that “white” sunlight was not pure, but a combination of all the colors of the spectrum. Robert Hooke also had a color theory from

his work on thin films. The eighteenth century saw little further achievements in understanding light.

In 1777 Scheele reported that spectral colors darken silver chloride. In 1801 Johann Ritter found the dark region beyond violet portion of the spectrum was even more effective than visible violet in such darkening. [7] Up to this time investigators had been working with spectra from circular openings. What if the scientist at that time used non-circular openings in their diffraction experiments?

ACTIVITY [1]: Using the available light source, compare the spectrum obtained by different shapes of openings in a diffraction experiment. What did you find?

[8] Wollaston [1802] used a narrow slit (why?). With it, he observed seven dark lines in the spectrum of sunlight that passed through a flint-glass prism. In 1814 Joseph von Fraunhofer, a young lens manufacturer, was studying the refractive index of glass samples. He observed a bright double line in his spectrum, based on a lamp with a sodium flame. He also observed the same double lines in alcohol and sulfur flames. When he examined the solar spectrum for similar lines, he noticed instead of the bright yellow double line countless vertical lines darker than the colored parts of the spectrum. He had rediscovered (independently) Wollaston's lines –and more. He labeled them A through H. Fraunhofer investigated whether slit width or the type of prisms influenced the spectral “purity”. He became convinced that the lines were due to the nature of sunlight rather than other factors.

ACTIVITY [2]: *Repeat the above activity, using now several different sources of light. Does the source of light affect the nature of spectrum observed?*

Fraunhofer also studied the spectra of several heavenly bodies. The spectrum of moonlight showed the same dark lines as sunlight. Fraunhofer also noted that the original bright lines of sodium corresponded to the dark D line in the solar spectrum. But he had no explanation for why they might be the same. As the investigation of spectra with prisms continued over the next several decades, several researchers suggested an identity between some lines in the solar spectrum and in spectra produced in laboratories from various sources of light. Most flames gave white light. The D lines seemed to appear when almost any element was studied.

[10] The relationship between the bright lines and the dark lines remained puzzling.

THINK [1]: *How might you explain the origin of the bright and/or the dark lines in the spectrum? How would you suggest exploring them further?*

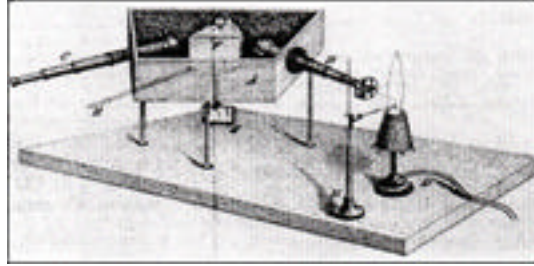
In 1849, Leon Foucault examined the spectrum of a carbon arc lamp (where the light was generated by electrical current between two charcoal electrodes) and noticed a line similar to D line of the solar spectrum. He wanted to compare the two spectra. So he decided to superimpose them on each other. He passed the sun's rays through the arc lamp and then passed the combined light through a prism. He showed that the lines were indeed in the identical positions. Passing through the arc lamp strengthened the D line of sunlight. When the sunlight was removed, the D line from the arc lamp showed instead as

a bright line. (Is this a clue to the relation of bright and dark lines? Foucault became busy with other projects and never developed an idea about that.)

The Duo

[9a] In 1844 Bunsen himself turned his attention towards the spectrum of light. He had analyzed different metallic salts, using the colors they imparted to a flame to identify them. One challenge was to be sure that the color was due to the metal being examined and not from the fuel being used to generate the flame. The ideal, of course, would be to produce a flameless burner – one that could burn the desired substance, but not exhibit a flame from the fuel itself. Here is where Bunsen's now famous burner became so important. Desaga's modification to the air vent was critical in producing a colorless flame.

[9b] Sometimes the colors of the metallic substances Bunsen examined were very similar. How could he distinguish between them? Bunsen used colored solutions or glasses as standards of color, viewing the flames through the clear substance for comparison. Kirchoff, Bunsen's great friend, then suggested passing the light from the flame tests through a glass prism spectrum in order to separate the different colors and observe them. Together they developed a *spectroscope*: an instrument for viewing flame colors. The instrument reflected no new principles or devices which had not been in use for years. Instead, it brought together a set of lenses (to bring the rays of light to focus) with a prism and viewing telescope, all enclosed inside a blackened box to eliminate the influence of other colors.



Bunsen and Kirchoff's spectroscope

[11] One afternoon in the summer of 1859, Kirchoff looked at the interaction of incandescent light and the light of table salt burning in the flame of the Bunsen burner. Foucault had used sunlight. Here, the source of light was different. The observation was puzzling, however. The incandescent light was known to show a full, continuous spectrum. But when it passed *through* the sodium flame and then through the new spectroscope, a dark line appeared in the D position. "There must be a fundamental story here," he thought.

THINK [2]: *What may account for the appearance of dark lines in the place of bright sodium lines? How would you investigate your idea further?*

When Kirchoff returned to the laboratory the next day, he repeated the same experiment, now using a lithium flame. He observed a dark line between the Fraunhofer B and C positions. (How does this information affect your own interpretation?) Kirchoff reasoned that hot gases absorbed the same kind of light that they emitted. If so, then he could explain the the D line present in the white light coming from the incandescent surface of the sun. If sodium vapor was present in the outer atmosphere of the sun, it would absorb the light at the D line. To test this idea further, Kirchoff then passed sunlight through a lithium flame before entering the spectroscope. A new dark line

appeared between the Fraunhofer B and C positions. He concluded that there was no lithium present in the sun's atmosphere.

Kirchoff along with Bunsen, published his paper in 1859, stating that "the dark lines [Fraunhofer lines] of the solar spectrum which are not caused by the terrestrial atmosphere, arise from the presence in the glowing solar atmosphere of those substances which in a flame produce bright lines in the same position." His paper was followed by a long mathematical treatment relating the radiating and absorbing powers of substances for heat and light. This came to be known as the Kirchoff laws of spectroscopy.

[12] The spectroscope and the laws of spectroscopy provided a powerful tool for the study of the chemical composition of the atmospheres of the sun and other stars. The instrument soon became widespread among astronomers for observing the rays from different stellar sources. Bunsen claimed that they had found a means to determine the composition of the sun and fixed stars, just as we determine sulphuric acid and chlorine with chemical reagents.

[13] At the same time the spectroscope was used for earthly discoveries. The new method was very effective in discriminating between even very similar colors. It was so sensitive that Bunsen and Kirchoff soon found a new metal in the mineral water of Durkheim. When Bunsen observed a splendid blue line in the spectrum of an unknown metal flame, he called the new element cesium. The following year they announced the discovery of another alkali metal, named rubidium, obtained from the mineral lepidolite. Following the duo's discoveries of new elements, two other elements were detected by spectroscopy. In 1861 William Crookes discovered thallium, and in 1863, Ferdinand

Reich and Theodore Richter discovered indium. Kirchoff and Bunsen went on to examine the spark spectra of rare earth elements.

Bunsen and Kirchoff became celebrities. A great number of practical discoveries were made through the key of spectroscopy. The development of spectral analysis was the high-water mark of Bunsen's career. His fame grew enormously and he was invited to Berlin to succeed Eilhard Mitscherlich who died in 1863. Bunsen was no admirer of Bismark's politics and hence declined the offer. Kirchoff's success in spectroscopy have left his other contributions in physics in shadow. He occupied the chair of theoretical physics at the University of Berlin from 1875 until his death on Oct. 17, 1887.

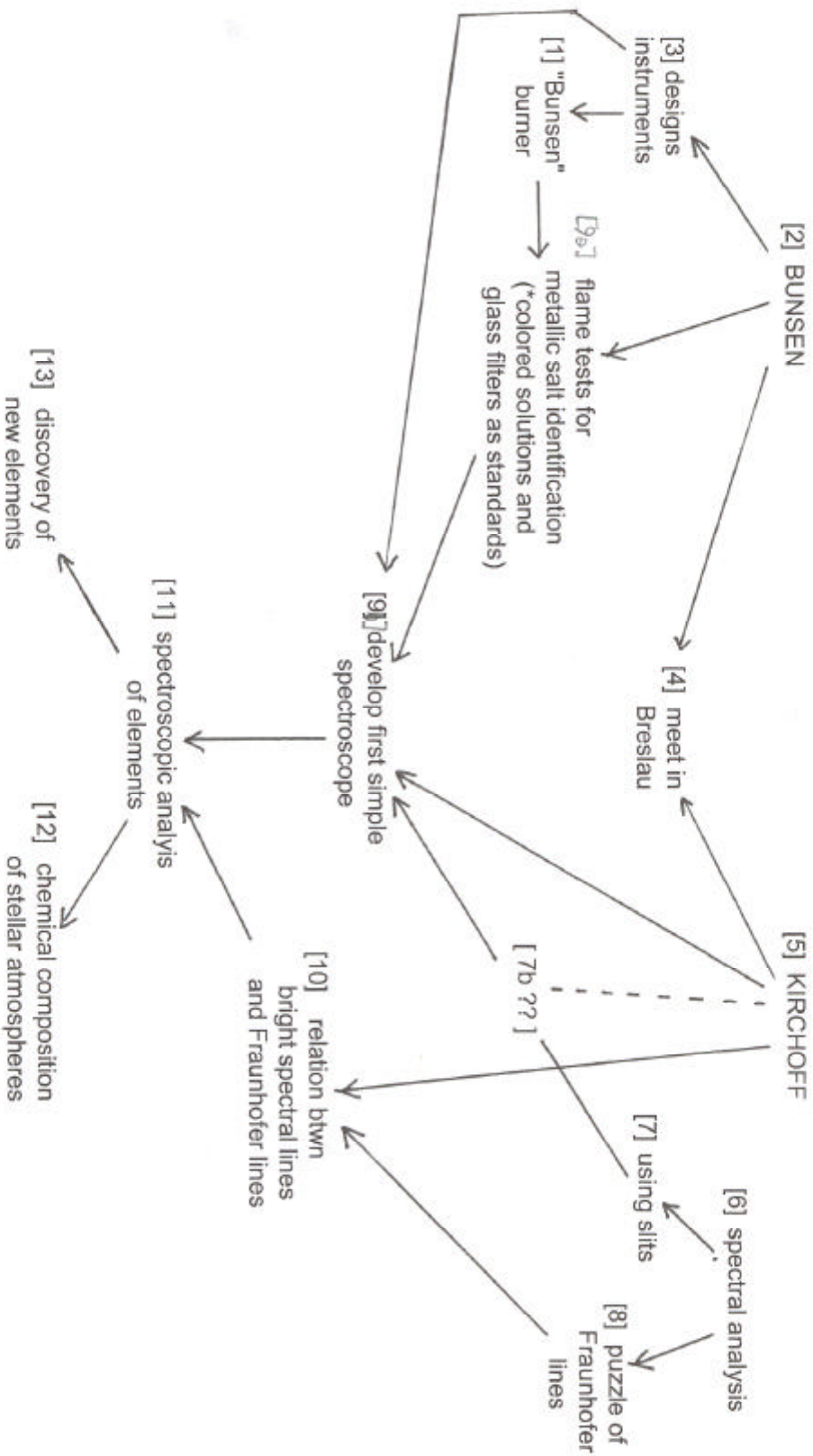
The case of the origins of spectroscopy show how the work of two men together led towards deeper understanding. Bunsen and Kirchoff were able to combine their knowledge and skills, instrumentation and chemical analysis from one, and mathematically oriented experimental physics from the other. Their collaboration has yielded fruitful results in chemistry, physics and astronomy. In this case, discovery was a cooperative enterprise.

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Origins of Spectroscopy





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