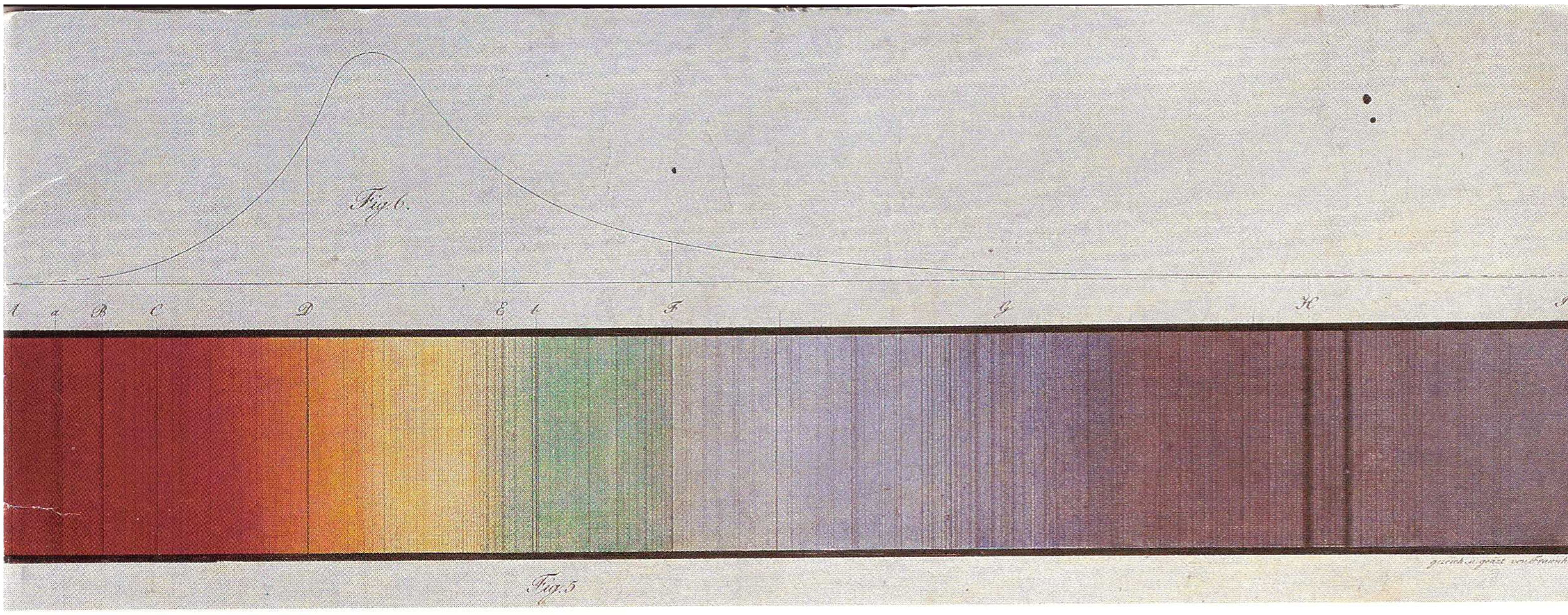
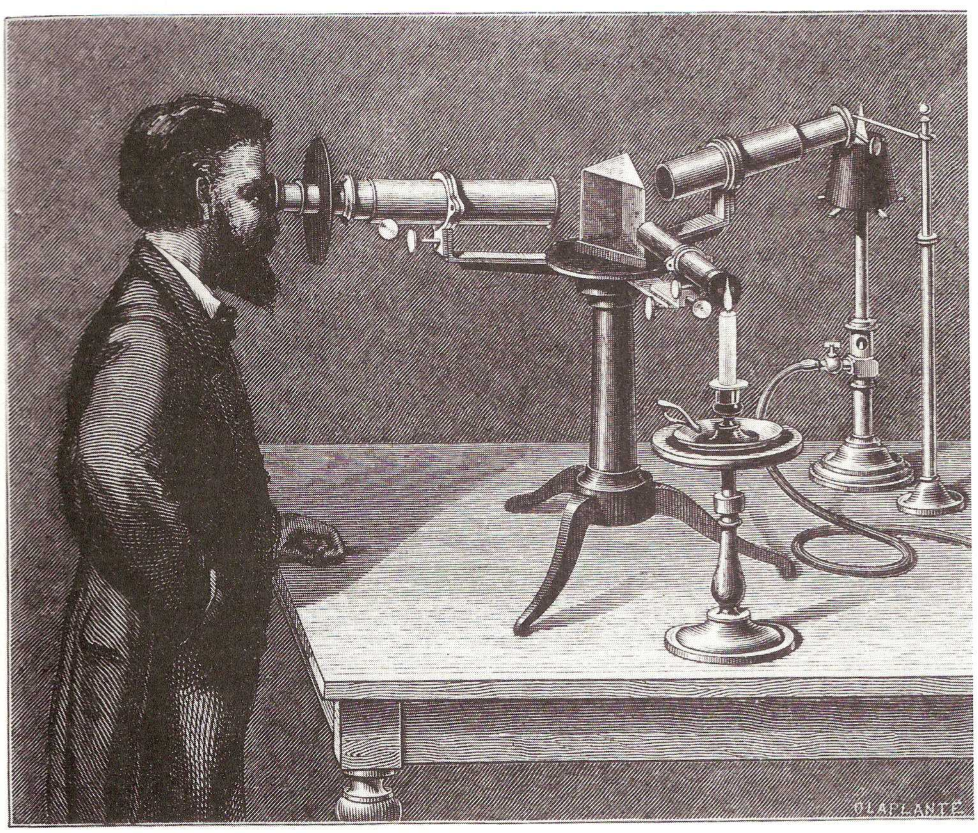


THE CELEBRATED PHAENOMENA OF COLOURS:

the early history of the spectroscope



published to accompany a special exhibition at
the Whipple Museum of the History of Science

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The spectrum on the front cover is from an original coloured by Fraunhofer and is reproduced by courtesy of the Deutsches Museum, Munich.

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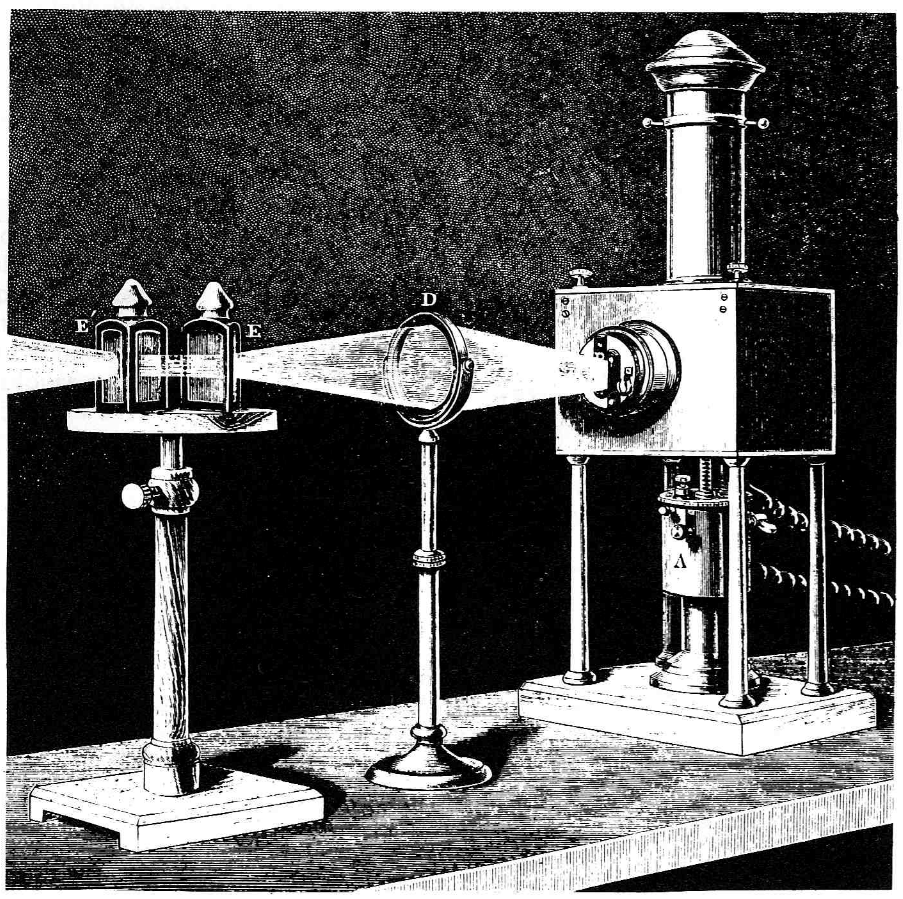
Published by the Whipple Museum of the History of Science.

THE CELEBRATED PHAENOMENA OF COLOURS:

by J.A. Bennett



The Prehistory of the Spectroscope

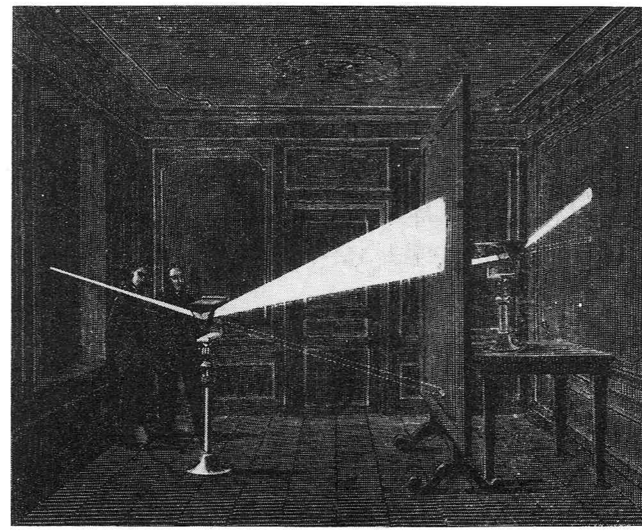
'...in the beginning of the Year 1666 ... I procured me a Triangular glass-Prisme, to try therewith the celebrated Phaenomena of Colours', Isaac Newton, 1672 (28).

When Newton began his optical researches, the production of a coloured spectrum by a glass prism was already 'celebrated'. In a carefully-reported series of experiments, he described the dispersion and re-combination of light by prisms, and the different refractive properties of the differently-coloured rays. He was led to the fundamental conclusion 'that light it self is a Heterogeneous mixture of differently refrangible Rays' (28) - in other words, that rays characteristic of every colour pre-exist in white light. Because the rays have different refractive properties, they are dispersed by the prism, but the prism is merely an instrument for separating them; it does not create the colours by modifying the incident light. It is this notion of the prism as an instrument for analyzing light that lies at the root of spectroscopy.

Not everyone agreed with Newton's conclusions. In the year before Newton (according to his own account) began his experiments, Robert Hooke had published his Micrographia (1665). Here he dealt in particular with colours seen in thin films and developed a mechanical theory whereby colours are generated - not simply revealed - by the refraction of rays of light, understood as 'pulses' or waves. This theory he judged 'capable of explicating all the Phaenomena of colours, not onely of those appearing in the Prisme, Water-drop, or Rainbow, and in laminated or plated bodies, but of all that are in the world' (14).

Whatever the theoretical differences between Newton and Hooke - differences that would be aired in a public dispute between the two men - they accepted a common domain of reference for such experiments. This domain would be accepted for almost two hundred years, until the birth of spectroscopy proper. They were concerned with what we would regard as questions of physics - with the nature, production, propagation and refractive properties of light. Certainly it occurred to various practitioners in the intervening period that this area of research, with its developing experimental techniques, could be relevant to chemical analysis. It would be some time, however, before inspired suggestions would give way to the sustained determination coupled with technical expertise that was necessary to bring the idea to practical fruition.

Some important developments in the pre-spectroscopic period of spectral studies should be mentioned. In 1800 William Herschel examined the illuminating and heating powers of different portions of the spectrum, so as to determine what coloured filters are most efficient for observing the sun. He detected the greatest heating effects with themometers placed beyond the red end of the visible spectrum, demonstrating that solar radiation was not confined to visible light.



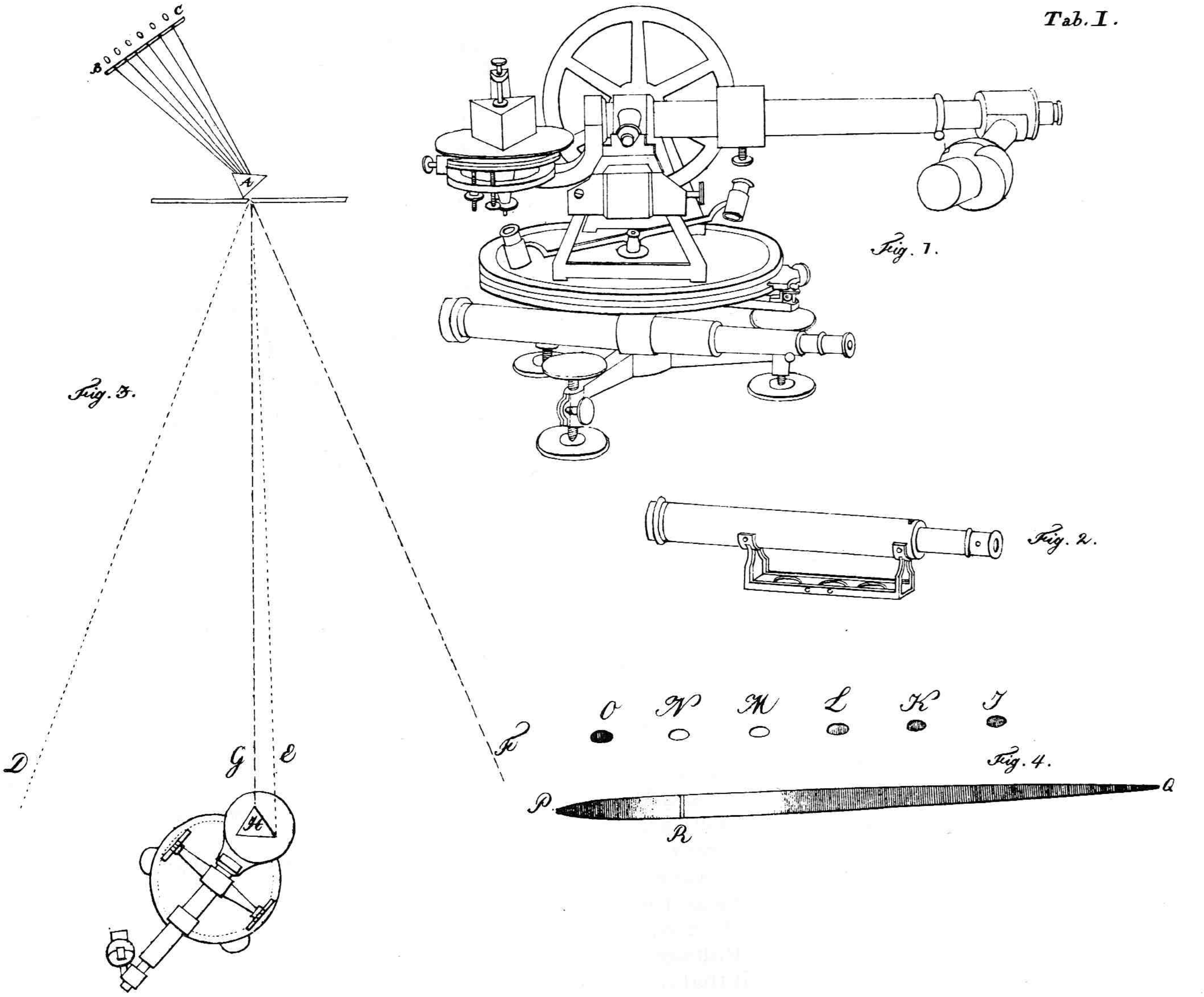
A repetition of Newton's experiment, illustrated in 1870 (36).

The experiments made by the chemist William Hyde Wollaston in 1802 were more directly related to those of Newton, except that he replaced Newton's circular aperture by a slit. He discovered that the solar spectrum was crossed by a number of dark lines, and went on to observe discontinuous spectra - with more extensive gaps - by examining, with a prism, candlelight and an electric arc.

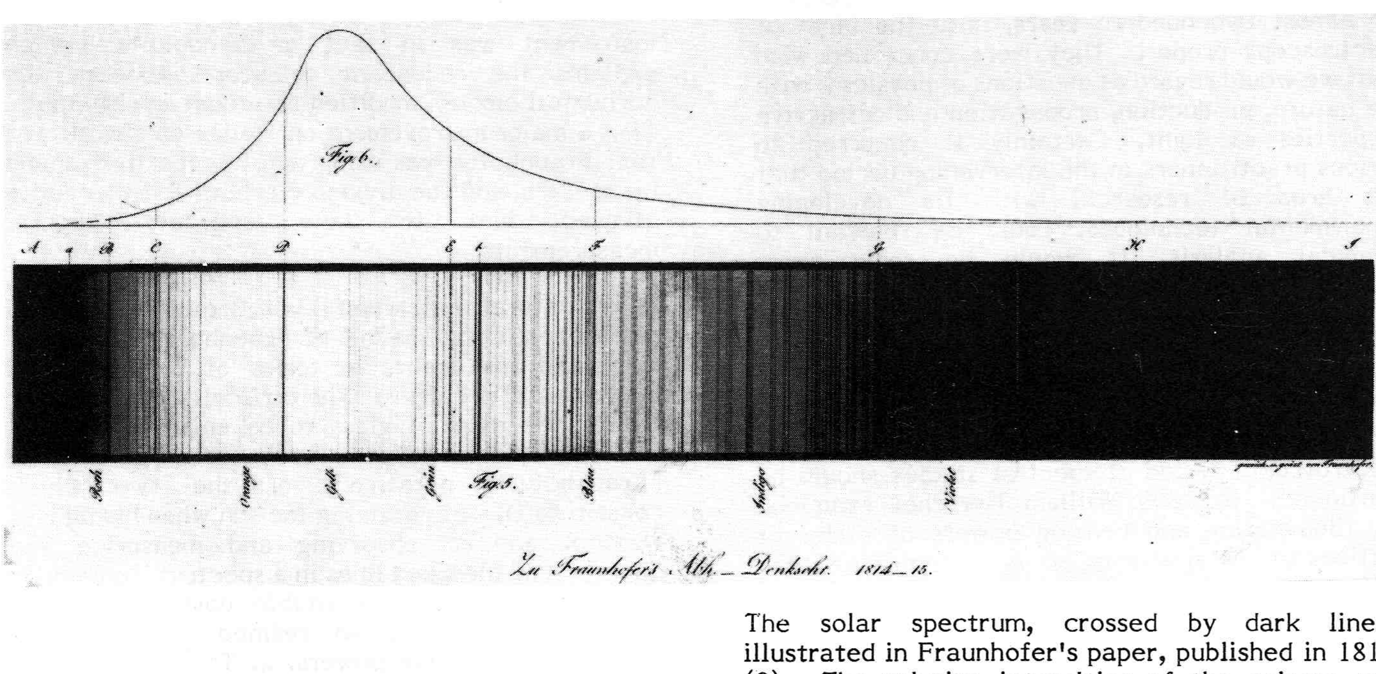
The discovery of solar lines was repeated in the much detailed and thorough work of Joseph von Fraunhofer (after whom the lines were named) in 1814. His interests in the solar spectrum and in the spectra of flames and sparks were stimulated by a practical optical concern - the need to locate a reference point in the spectrum that could be used for accurately measuring refractive indices.

Fraunhofer was professionally involved in instrument making and was better equipped - not least in the quality of prisms - than any of predecessors or contemporaries. His chief instrument was in fact a theodoloite (which explains the redundant telescope beneath the horizontal circle), modified to accept a prism table. Thus a major improvement on Wollaston's work was that Fraunhofer was using a telescope to examine his spectra, and the divided circle of the theodolite allowed him to take accurate angular measurements.

It was natural that, when David Brewster began his researches in the shadow of Fraunhofer's work, he expressed his doubts in terms of practical and instrumental problems: 'The difficulty of procuring out of the mass of glass to be employed, prisms sufficiently pure to show such narrow lines as E [Fraunhofer's notation], or the two which constitute D, - of obtaining the sun when his light is wanted, and of observing and measuring the distances of the fixed lines in a spectrum constantly in motion, are insurmountable obstacles to the general adoption of so refined a method of measuring dispersive powers. ... The magnificence of Fraunhofer's instruments, - the means of nice observation which he had at his command, - and his



An illustration of Fraunhofer's adapted theodolite and the experimental arrangement of slit and theodolite (8).



The solar spectrum, crossed by dark lines, illustrated in Fraunhofer's paper, published in 1817 (8). The relative intensities of the colours are plotted in the curve above.

great skill as an observer, were considerations which long deterred me from even attempting to repeat his examination of the spectrum'(4).

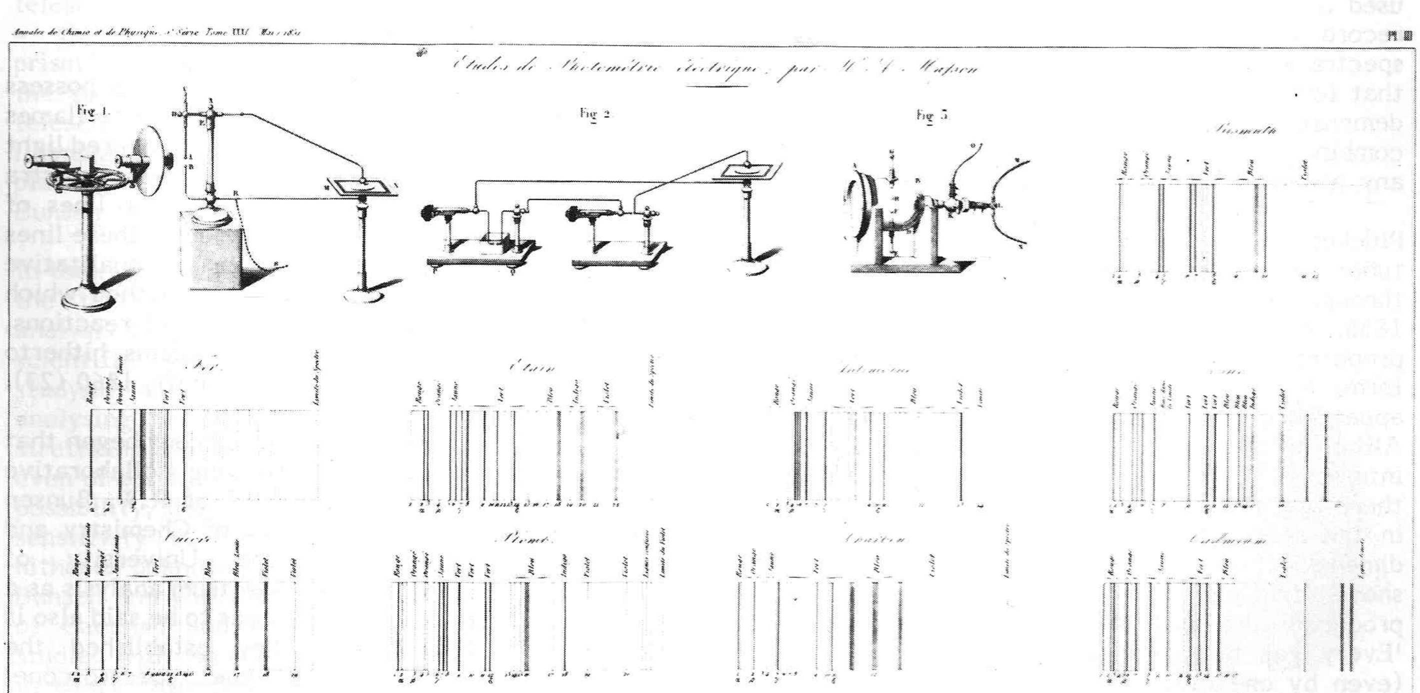
In the work of Brewster, and of W.H. Fox Talbot we see anticipations of a method of chemical analysis. Brewster, though originally concerned with the production of monochromatic light to illuminate microscopical objects and so eliminate the problem of chromatic aberration in the microscope, would come to describe 'the principal object of my inquiries' as 'the discovery of a general principle of chemical analysis, in which simple and compound bodies might be characterised by their action on definite parts of the spectrum' (4). As implied here, his technique involved observing the effects of media on transmitted sunlight. Fox Talbot in 1826 had a very clearly-projected programme of chemical analysis through flame spectra.

However the subject of the exhibition is not the history of theoretical spectroscopy, but that of the spectroscope. The distinction is artificial, but has been adopted because, while historians of science have shown considerable interest in early spectroscopy, its instrumentation has scarcely received any attention in published historical accounts.

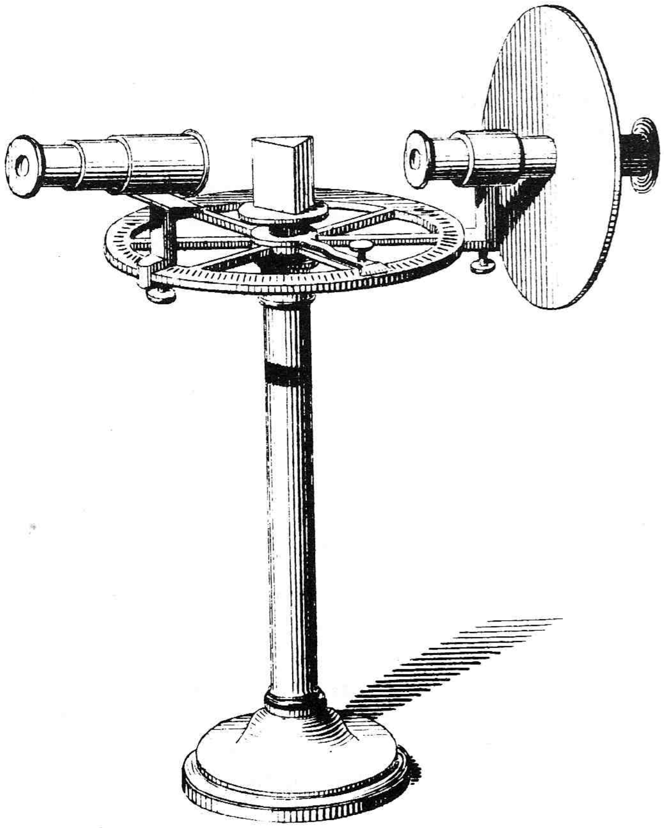
The apparatus used in the researches of Brewster, Fox Talbot, John Herchel, etc, and in the early work of their immediate successors, such as W.A. Miller of King's College, London, and J.W. Draper of New York University, were composed of disperate elements - a slit, perhaps a collimating lens, a prism table, an archromatic telescope. Research apparatus had not yet been unified into a composite instrument - a spectroscope - because it simply fulfilled the immediate needs of individual laboratory scientists. Draper, for example, tells us that he used a slit of 1/30in by 1in in a metal screen, 6 or 8 feet from his flint-glass prism, and a telescope with an eyepiece micrometer (7). W.A. miller describes a slit 1/40in by 4ins in a brass plate 20 feet from a 'prism of Munich flint glass, mounted upon Fraunhofer's plan and adjusted to an achromatic telescope' (27). Using this longer slit, Miller was able to view solar and gaseous absorption spectra in juxtaposition and make direct comparisons.

Brewster's rather more detailed account illustrates very well how he used whatever was available and had any additional elements he needed specially made up: 'The apparatus which I had at my command for this investigation were two very fine rock-salt prisms, executed by myself; a large hollow prism made of plates of parallel glass for holding fluids; a fine plate glass prism, executed by Fraunhofer, and which I owe to the kindness of Mr Talbot; a copious supply of oil of cassia and oil of cinnamon, which Mr George Swinton transmitted to me from Bengal from his usual liberality; a good archromatic telescope, by Berge; and an excellent wire micrometer by Troughton. To this apparatus Mr Robison made two important additions, which he executed with his own hands, the one a brass stand with a variable aperture for admitting the incident light, and the other a stage for holding and adjusting the prisms in front of the object glass; and I have recently been favoured, by Sir James South, with the use of his fine five-feet archromatic telescope, executed by Dollond' (4).

The work of Miller and Draper in the 1840s illustrates the increasing interest shown by professional chemists in spectra. But in the meantime another physical concern had added a new battery of instruments to spectrum studies and was also leading to a realization of the subject's



Masson's apparatus, together with his illustrations of spark spectra, published in 1851 (26).



A detail from the illustration in Masson's 1851 paper, showing a goniometer of the type made by Duboscq, used as a spectrometer (26).

potential in chemical analysis. We have seen that Fraunhofer and Brewster were both interested in the line spectra of electric sparks. Fraunhofer used a friction electrical machine; Charles Wheatstone introduced voltaic and electromagnetic sources. Antoine-Philibert Masson, in a series of experiments published between 1845 and 1855, also used a friction machine, and a camera lucida to record his spectra. Masson showed that spark spectra were uniquely characteristic of the metal that formed the electrodes, and Ångström in 1853 demonstrated that the spectrum obtained was a combination of that of the electrode and that of any gaseous medium.

Plücker used Rumkorff's induction coil and Geissler tubes to study the spectra of electric discharge through rarefied gases. 'Such tubes', he wrote in 1858, 'containing various gases and vapours, are prepared in this city [Bonn], of the most different forms by M. Geissler, and present sometimes an appearance of incomparable beauty' (29). Although the early researchers were primarily interested in the nature of sparks and of their light, there was a growing awareness - just as there was in the study of flame spectra - of the chemical dimension. This is particularly so of Plücker, who showed that a discharge through a mixture of gases produced the individual spectra superimposed: 'Every gas being characterized by its spectrum (even by one of the bands of the spectrum, the position of which is measured) we get a new kind of chemical analysis' (29).

G. G. Stokes's interest in fluoresence in the 1850s led to a further development in spectrum investigations. He discovered that quartz, unlike glass, was very transparent to ultra-violet radiation, which enabled him to investigate this invisible portion of the spectrum, detectable by fluoresence.

Masson illustrated in 1851 what we should probably call a spectroscope or spectrometer, albeit a primitive one (26). It was probably a form of universal goniometer adapted to spectrum work, but there appears to be an integrated slit, a collimator, a prism table whose position is read on a divided circle, and a telescope. Instruments of this kind were manufactured by Duboscq of Paris.

From the parallel study of flame spectra we have a further illustration of the state of instrumentation just prior to the famous research of Bunsen and Kirchhoff, in the work of William Swan, published in 1857 (39). Since Swan was seeking quantitative measures, he reverted to Fraunhofer's idea of adapting a theodolite and taking readings from the horizontal circle. The circle was 7.5ins in diameter, and was read by 2 verniers to 10 seconds. His telescope was of 1.6ins aperture with a moving-wire micrometer and an arrangement for illuminating the micrometer wires. An important development was Swan's use of a fixed collimator, resting in Y bearings in a cast stand that also held the theodolite. The collimator was thus all but integrated with the rest of the instrument, but the slit was separate - placed at the focus of the object glass. He used a Bunsen burner for his flame. Swan was one of a number of chemists in the late 1850s who were firmly committed to the idea of a programme of chemical and spectrum research that would yield a general method of chemical analysis. It was an idea that had been around for many years, but was about to become realized in practice.

Bunsen and Kirchhoff

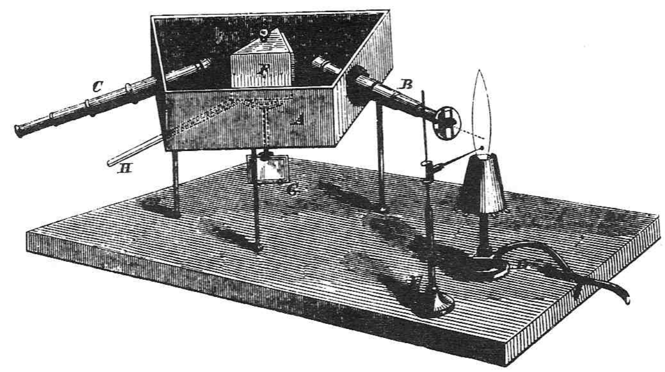
'It is well known that certain substances possess the property of imparting definite colours to flames in which they are heated. When the coloured light thus produced is analysed by a prism, spectra exhibiting differently coloured bands or lines of light are seen. Upon the occurrence of these lines of light an entirely new method of qualitative chemical analysis can be based - a method which greatly enlarges the scope of chemical reactions, and points to the solution of problems hitherto unapproachable', Bunsen and Kirchhoff, 1860 (23).

It has been recognized since the subject began that it was the careful and painstaking collaborative research between 1859 and 1861 of R.W. Bunsen and G.R. Kirchhoff, Professors of Chemistry and Physics respectively at the University of Heidelberg, that established spectrum analysis as a practical discipline. What needs to be said also is that at the same time they established the fundamental principles of the spectroscope, together with a number of individual features that would be important to the subject's instrumentation for many years to come.

R. W. Bunsen (36).

Their first apparatus, reported in 1860, has all the appearance of a composite instrument, made by combining different elements. An internally-blackened box, with a trapesium-shaped base, houses a hollow prism filled with carbon bisulphide. (Such liquid prisms avoided the problem of non-uniform glass.) The prism turns about a vertical axis and its position is measured by viewing with a telescope the image of a horizontal scale reflected in a mirror attached to the prism axis. Two telescopes are fitted to apertures in the box. One - the collimator - with its lens towards the prism has a slit substituted for the eyepiece, set at the focus of the lens. The other is used as a telescope, with cross-wires, that can be illuminated. The sample is placed on the end of a platinum wire and held by a stand in the flame of a Bunsen burner (22).

In their 1860 paper Bunsen and Kirchhoff pointed to the two spectacular applications of spectrum analysis that would create such excitement in the scientific world. One was the possibility of studying the composition of heavenly bodies by analysing their light: 'an entirely untrodden field, stretching far beyond the limits of the earth, or even of our solar system' (23). The other was the possibility, due to the 'almost inconceivable' (23) sensitivity of spectrum analysis, of detecting hitherto unknown elements. In their 1861 paper, Bunsen and Kirchhoff announced their discoveries of Caesium and Rubidium, whose spectra were studied with 'an improved form of apparatus, which in every respect is much to be preferred to that described in our first memoir' (23). In this instrument, made by C.A. Steinheil of Munich, the spectroscope comes of age and we clearly see the influence of a master instrument-maker.

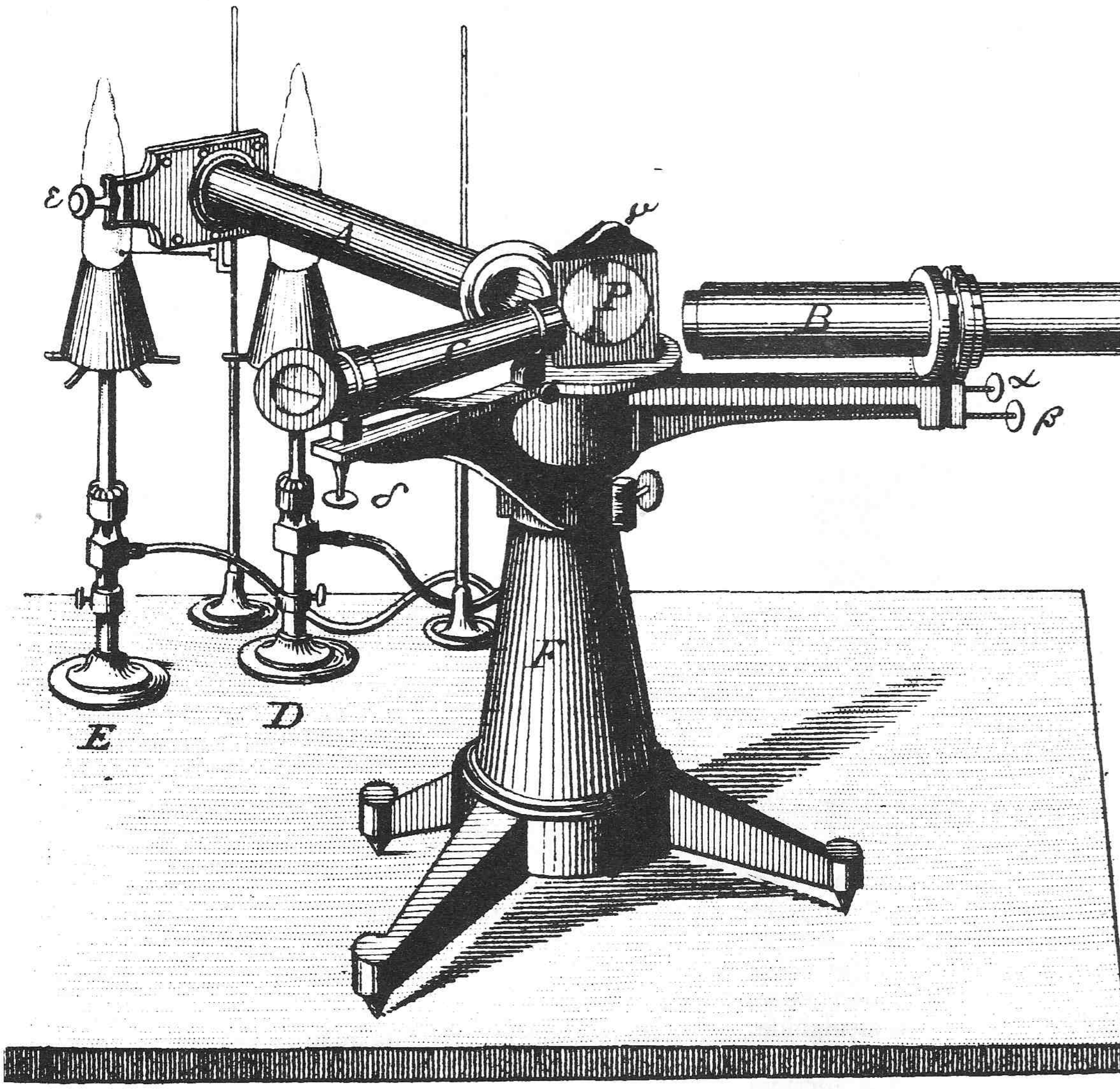


Bunsen and Kirchhoff's first spectroscope, from the illustration published in 1860 (22).

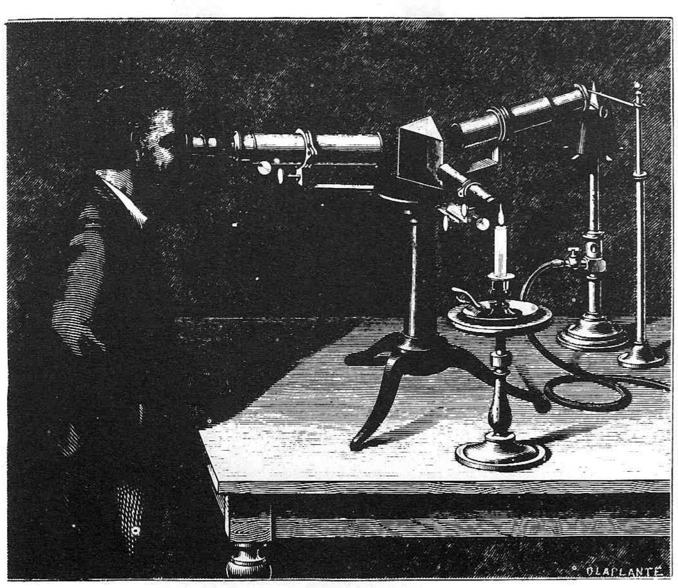
The whole apparatus is carried by a cast-iron pillar and tripod stand, which supports a platform on which is placed the flint-glass prism. The collimator is fixed to the stand and the slit - with a screw adjustment to its width - has a small reflecting prism fitted to its lower half. The small prism can reflect light from a second source into the instrument, so as to present two spectra for direct comparison. The telescope pivots about the vertical axis, as does a third tube - a form of collimator, but with a horizontal photographed micrometer scale in place of the slit. This scale is reflected into the telescope from the near surface of the prism, and can be used for taking measurements of either spectrum.

Kirchhoff's contemporaneous investigation of the solar spectrum led to his independent discovery that a substance could be arranged either to emit or to absorb light of exactly the same spectrum position. The Fraunhofer lines thus correspond to

G. R. Kirchhoff (36).



Bunsen and Kirchhoff's improved spectroscope, illustrated in 1861 (22).



The compound spectroscope of the Bunsen and Kirchhoff type illustrated in use in 1870 (36). J. N. Lockyer published a precise commentary on this illustration in 1873: '[The spectroscope] will be seen to consist of a circular table, supported by a pillar and three legs, carrying three lateral tubes; the right-hand tube is called the collimator, and holds at its outer extremity the fine slit, the width of which can be regulated to a nicety by a micrometer screw; the other end of the collimator is furnished with a lens, which serves to collect the rays of light coming from the slit and to render them parallel before falling on the prism in the centre of the table.....after passing through the prism, in which the light undergoes both deviation and dispersion, the spectrum is observed by the telescope on the left, which is simply a small astronomical telescope of low magnifying power. ... The... method of measurement ... consists of a short tube carrying at its outer extremity a small photographic scale, which is illuminated by a candle flame; the light passing from the photographic scale is rendered parallel and thrown on the surface of the prism by means of a lens in the tube, carrying the scale, and is reflected by the last surface of the prism up the observing telescope, so that it is seen as a bright scale on the background formed by the spectrum under observation' (25).

the emission spectra of the substances constituting the solar atmosphere. For this work, Kirchhoff introduced a spectroscope with a series of prisms to increase dispersive power - an idea that would be crucial to the further development of astronomical spectroscopy.

Once again the spectroscope was made, 'in the celebrated optical atelier of C.A. Steinheil of Munich' (21). Collimator and telescope were mounted on a circular iron plate - the collimator fixed, the telescope moved about the centre of the plate and fitted with a clamp and micrometer screw. Slit width could be adjusted by a screw moving against a spring and the slit adjusted to the focus of the achromatic collimator lens by rack and pinion. Four flint-glass prisms in brass mounts were positioned on the plate - their adjustment was a difficult and involved procedure - and distances between lines measured by the divided head of the telescope's micrometer screw. The sun's light was directed at the slit by means of a clockwork heliostat. Once again, small prisms were used to reflect light from a second source through half of the slit.

Through the work of Bunsen, Kirchhoff and - we must add - Steinheil, the spectroscope had made a remarkable advance. Many of the features they introduced became established in the instrument's repertoire - the integrated slit and collimator, slit width adjustable by a micrometer screw, the reflecting prism for introducing a comparison spectrum, the reflection of a comparison scale into the telescope, the use of a series or 'train' of prisms. Above all, the spectroscope was now a complete and integrated instrument and the scientific work of Bunsen and Kirchhoff had revealed its enormous potential. Optical and philosophical instrument makers would lose no time in grasping the implications for the instrument-making trade.

The International Exhibition of 1862

'...this page of the book of Nature has only just been opened ... it would be presumptuous as well as foolish to expect that we should understand it in its full bearings at once', H.E. Roscoe, first lecture in a course of three 'on Spectrum Analysis' at the Royal Institution, March-April 1862 (31).

The sudden development of the spectroscope in the 1860s was prompted by the change in status of spectrum studies from optical research to 'spectrum analysis' - a powerful and exciting new technique with widespread applications. Instrument makers

Fig. 2.

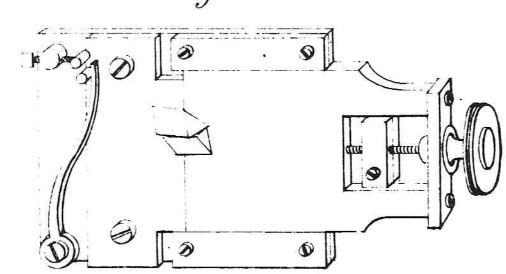
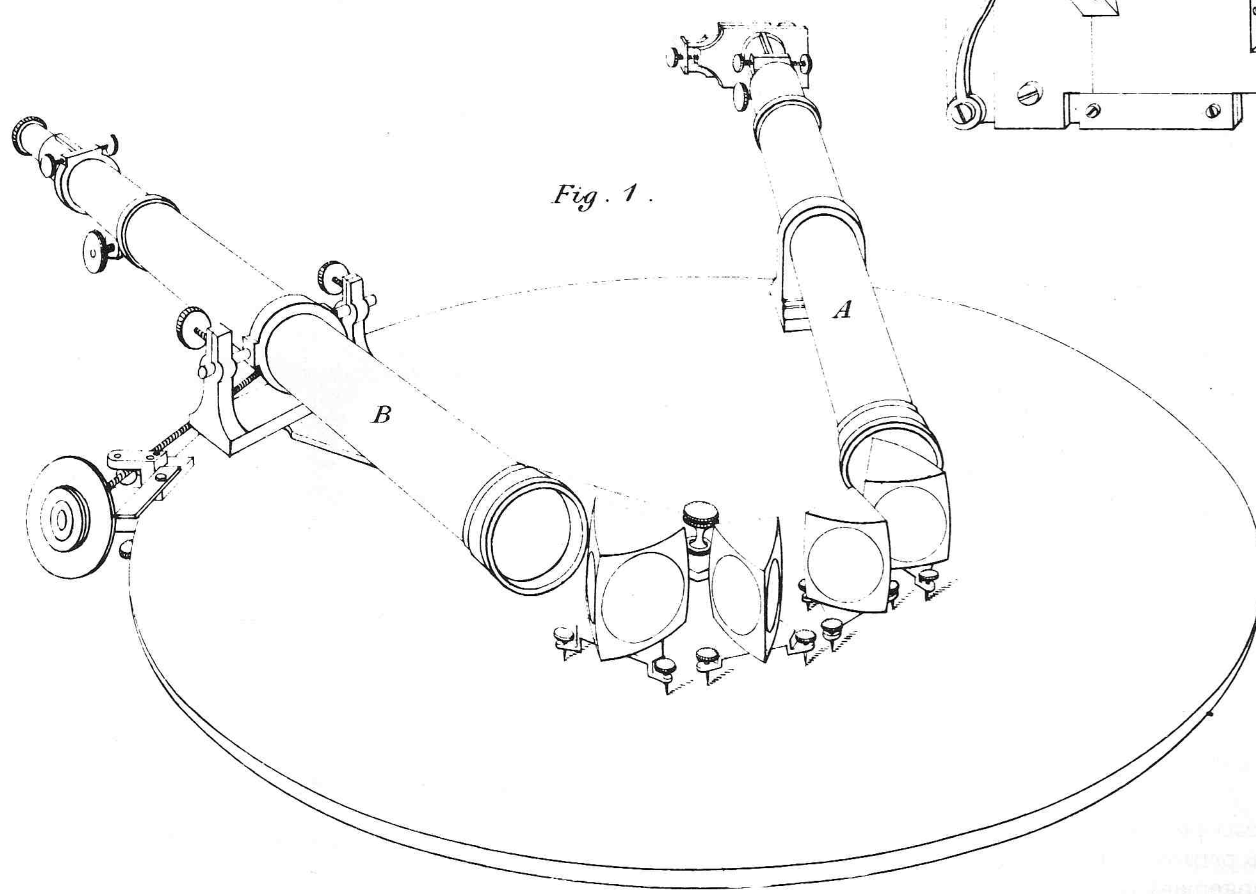


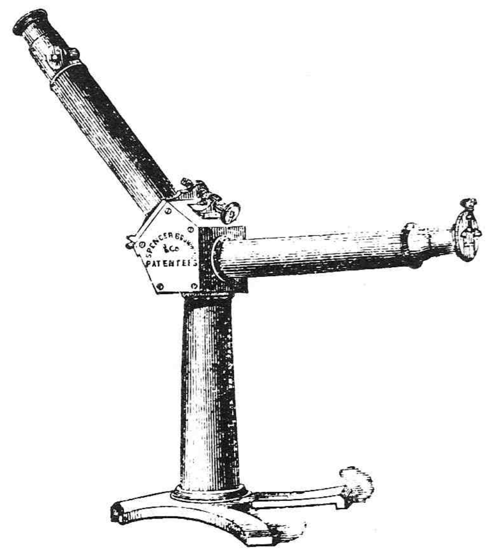
Fig. 1.



Kirchhoff's solar spectroscope by Steinheil (21).

[2962]

SPENCER, BROWNING, & Co., 111 *Minories*, *London.*—Telescopes, Crooke's spectroscopes, pocket and improved aneroid barometers, and nautical instruments.



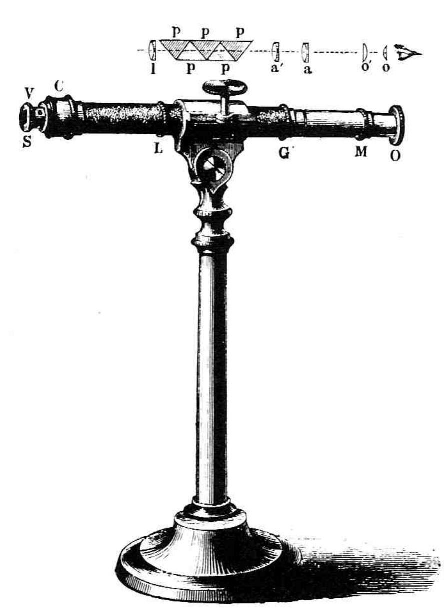
	£	s.	d.
LONG RANGE ANEROID BAROMETER, S. B. & Co.'s PATENT	2	10	0
Compensating ditto, uninfluenced by temperature	4	4	0
Long range aneroid for the waistcoat pocket, in gold case	15	15	0
Long range aneroid in silver case . .	5	5	0
Long range aneroid, in metal case . .	4	4	0
Crooke's pocket Spectroscope for "Spectrum analysis"	3	13	6
Crooke's large model "Spectroscope" (see illustration)	20	0	0

The entry in the catalogue of the International Exhibition of 1862 for Spencer, Browning & Co, showing their new spectroscope, after the design of William Crookes (17).

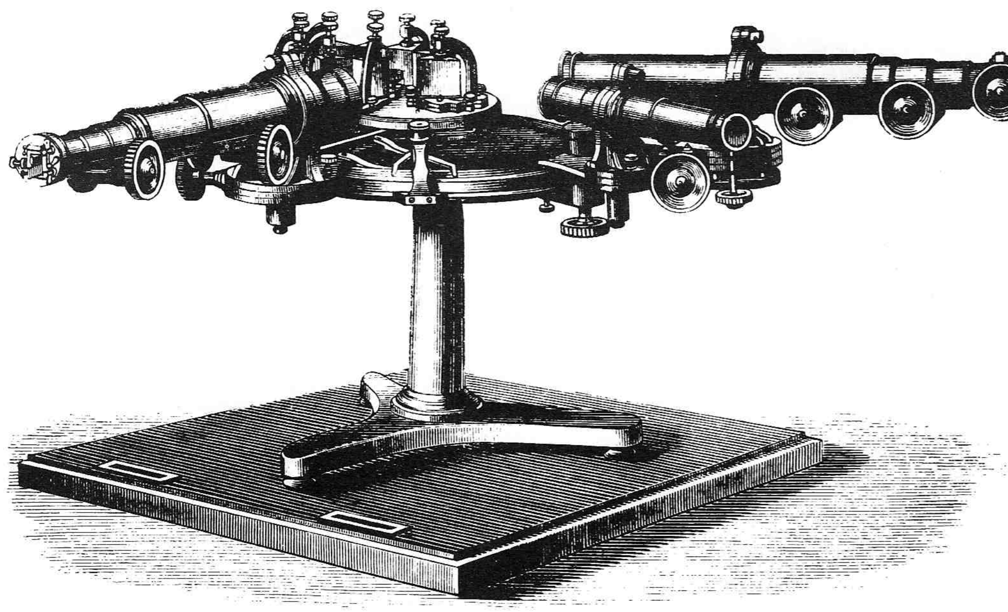
were quick to respond to the new interest in spectroscopy and there were few precedents for so sudden a development of a scientific instrument. There are several reasons why the trade was able to respond as it did. Spectrum analysis began at a time when opticians had recently made considerable advances in technique, most noteably in the achromatization and general improvement of the compound microscope. A considerable and allied growth area just prior to the advent of spectroscopy - in which Duboscq, for example, was a leading figure - was physical optics, especially polarization. In addition to this, spectroscopy from the start was applied in astronomy, and this naturally drew in the astronomical instrument makers, traditionally the most skilled makers in the trade.

At the International Exhibition in London in 1862, spectroscopes were exhibited by Duboscq, Ladd, Hofmann, Luhme and Co. and by Spencer, Browning and Co. English makers who would have less importance for the development of the spectroscope, but who still managed to exhibit examples at this early stage were Elliott Brothers, J. J. Griffin, S. Highley and Horne and Thornthwaite (17). William Ladd and John Browning of Spencer, Browning & Co. would be the leading English makers during the 1860s and 70s, and Browning for some time thereafter. Ladd exhibited at least two instruments - one had a carbon bisulphide prism, the other had optical components of quartz. Browning's chief instrument was after the design of William Crookes, who had discovered thallium by spectroscopic techniques in the same year. Crookes and Browning had applied for a patent for this instrument, which had 2 prisms and cost £20.

The spectroscope exhibited by Duboscq had no fewer than 6 prisms, after the manner of Steinheil, with an arrangement for viewing a comparison scale by reflection. Adjustment of the prism train was again difficult and, in Duboscq's absence, defeated the Jury. It is interesting that the Jury's report notes that Hofmann of Paris 'exhibited, at a late period of the Exhibition, an ingeniously-contrived pocket spectroscope, in the form of a straight tube' (18). This was Hofmann's direct-vision spectroscope, which applied an idea of Amici (1860), developed by Janssen, of combining crown and flint glass prisms to produce the effect opposite to that of an achromatic lens - dispersion without deviation. Hofmann's spectroscope had 2 flint prisms cemented between 3 crown, and its late entry to the Exhibition probably indicates its recent addition to his range.



Hofmann's direct-vision spectroscope on a stand, with a diagram above of the optical arrangement (36).



The 9-prism spectroscope made by John Browning for J. P. Gassiot in 1863 (32).

The Jury for philosophical instruments commented in their report that 'it is to the recent researches of Bunsen and Kirchoff [sic.] that we owe the present great development of this department of physical science' (18) and one of their number, J.P. Gassiot, was so inspired by what he saw that he persuaded Browning to build him an instrument with a remarkable train of 9 flint-glass prisms (9). A footnote to the Jury's report described it as 'probably the most complete, as well as most powerful instrument yet constructed' (18).

Further developments, 1860-1870

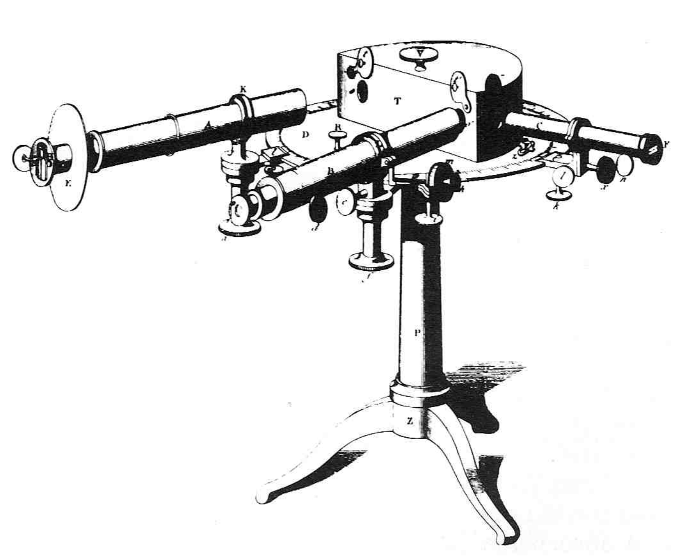
'So unexpected and important are the results of the application of spectrum analysis to the objects in the heavens, that this method of observation may be said to have created a new and distinct branch of astronomical science', W. Huggins, 1866 (15).

Two important non-technical developments during the 1860s were the beginnings of a textbook tradition and the establishment of specialist makers. Ladd and Browning have already been mentioned as leading the field in England. It was Ladd who provided the optical demonstrations at Roscoe's Royal Institution lectures of 1862 (31), and also at William Huggins's lecture 'On the Results of Spectrum Analysis Applied to Heavenly Bodies' at the British Association meeting of 1866 (15). Ladd was advertising 'Apparatus for Spectrum Analysis' by at least the beginning of 1863 (Chemical news, 7) and in 1865 his spectroscopes ranged in price from 3 guineas to £21 (ibid., 12).

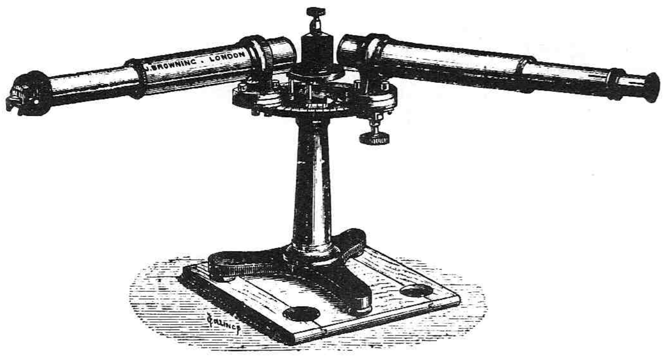
By at least February 1865 Browning was trading as 'John Browning, Optical and Physical Instrument Maker', with a list of spectroscopes from 2 guineas to £50 (Chemical news, 11), although Spencer, Browning and Co. continue to be listed in Post Office directories till 1870. By the mid-1870s Browning was established as the leading English maker, and his little book How to work with the spectroscope, first published in 1878, became a standard introduction to the subject's instrumentation. Whereas Ladd continued in business only until 1883, Browning's firm was trading well into the present century.

Textbook writers were not so forthcoming as instrument makers. As early as September 1862 a correspondent to the Chemical News felt the need of 'a "Manual", or even a comprehensive Paper, giving detailed instructions on the manipulation necessary in spectrum analysis'. The editorial staff, however, knew of no such work.

In the early French textbook, Instruction pratique sur l'analyse spectrale (Paris, 1863), Louis Grandeau illustrated a direct-vision spectroscope, with reflected scale, a Bunsen and Kirchhoff design of compound spectroscope by Gaiffe, and a table spectroscope by Duboscq with a 4-prism train and reflected scale (10).



A 4-prism table spectroscope by Duboscq, with a micrometer scale reflected into the telescope, illustrated by Grandeau in 1863 (10).



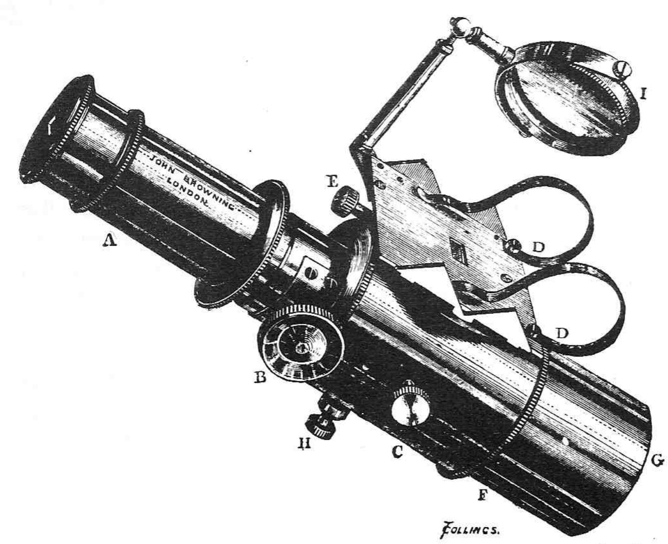
Browning's 'Student's Spectroscope' illustrated in 1878, when Browning, with reference to the Bunsen and Kirchhoff model, pointed out: 'The circle is divided, and reads with a vernier, thus dispensing with an illuminated scale: this arrangement possesses the very great advantage of giving angular measures in place of a perfectly arbitrary scale' (6). This model remained popular for many years.

The first English textbook appeared some time later with the publication of H.E. Roscoe's Spectrum analysis (London, 1869) - an expanded version of six lectures delivered to the Society of Apothecaries in 1868, illustrated by 'a variety of spectroscopes kindly lent ... by the maker, Mr Browning, one with one, one with two, one with three, and one with four prisms' (32). It was now Browning who provided the optical demonstrations for Roscoe, and Roscoe also published an illustration of the 9-prism spectroscope made for Gassiot, as well as dealing with the new Sorby-Browning micro-spectroscope.

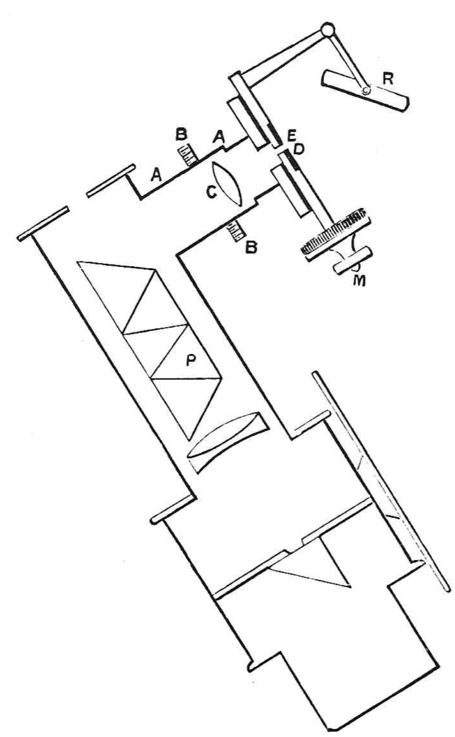
Important developments in instrumentation in the early 1860s included the use by W.A. Miller of photographic recording (together with quartz prisms) in his work on ultra-violet spectra, a number of different arrangements for direct vision and the application by H.C. Sorby, in collaboration with Browning, of the direct-vision spectroscope to the microscope.

Browning's 'New Miniature Spectroscope, with Micrometer' (6). A micrometer scale in the small tube is reflected into the field of view. 'This portable and complete instrument may be used for showing any of the leading experiments in spectrum analysis', wrote Browning, 'the Fraunhofer lines: the lines in the spectra of the metals, and the alkaline earths and alkalies; the spectra of gases; and absorption bands. Applied to a telescope, it may be used for viewing the lines of the solar prominences. It can also be used as a Micro-Spectroscope' (6).

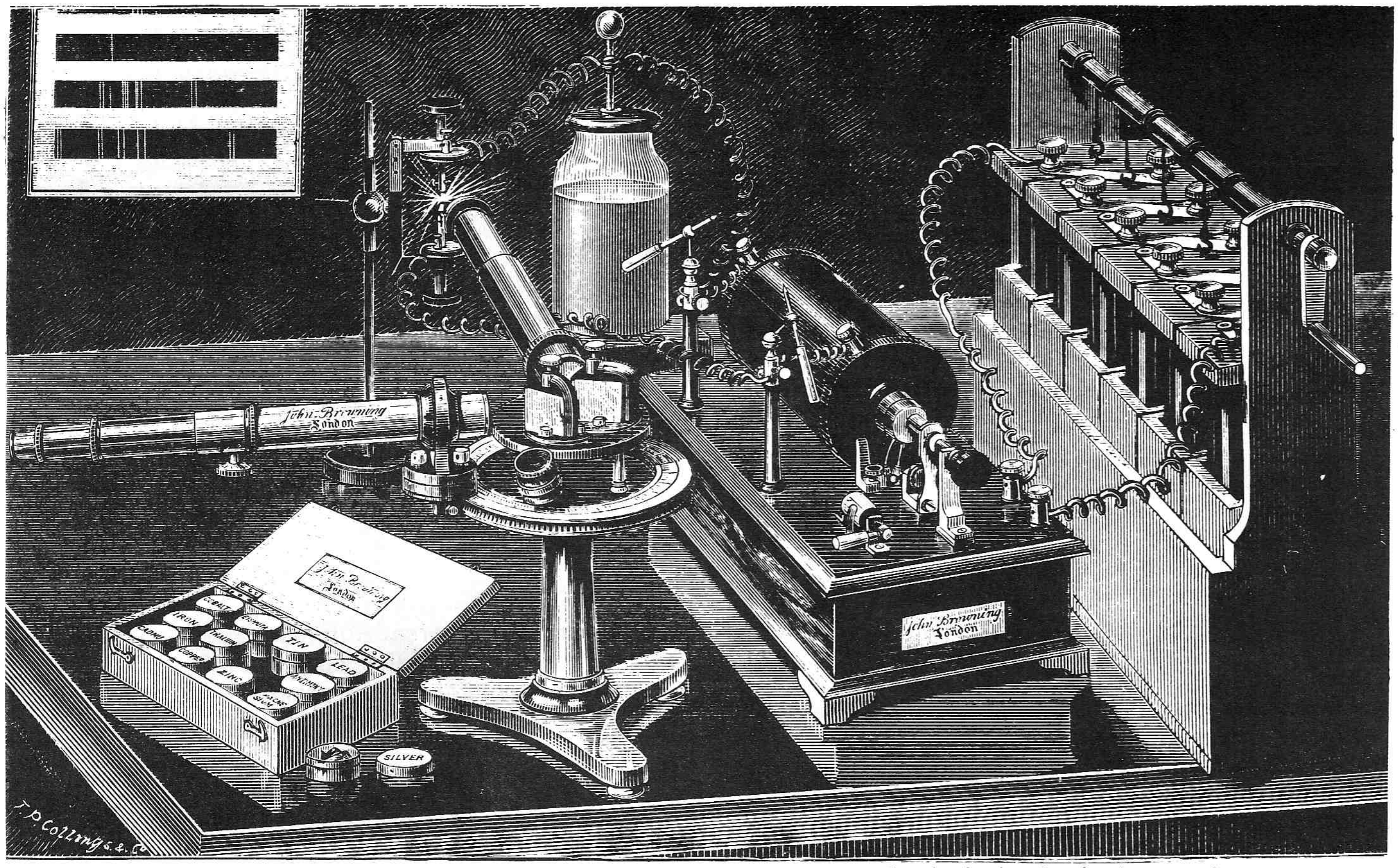
The micro-spectroscope was arranged to fit a compound microscope in place of the usual eyepiece, and comprised a slit, an achromatic lens and a short direct-vision spectroscope. Light from a second source could be introduced for comparison from the side by means of a reflecting prism and the spectroscope could, if desired, be fitted with a micrometer. 'It possesses', Browning enthused, 'the immense advantage over all other contrivances of the kind, that the spectrum of the smallest object, or a particular portion of any object, may be obtained with the greatest certainty and facility. This Micro-Spectroscope will indicate plainly the minutest quantity of blood, adulterations in wine, mustard, peppermint oil, and many other articles of food, as well as the absorption bands in the leaves and juices of plants' (6).



The Sorby-Browning micro-spectroscope, ready for attachment to a compound microscope (6). The slit in view is for introducing light from a comparative source.



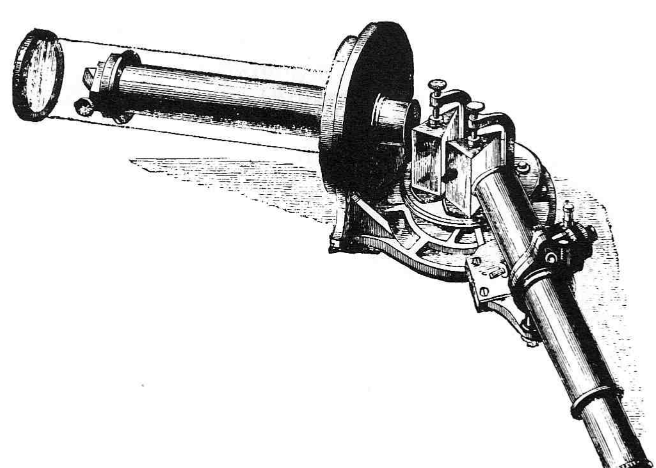
The optical arrangement of a micro-spectroscope, fitted with a bright-line micrometer (6).



'Spectrum Analysis in Action' was the caption to this engraving published by Browning in 1878 (6). A Rumkorff coil, resistance and Leyden jar are shown in the production of a spark to be analysed by a Browning 'Model Spectroscope'.

The development of the prism train was largely associated with astronomical applications of spectroscopy - an unexpected development perhaps, as astronomers are generally concerned with managing light from faint sources with maximum efficiency. The prism train, however, was well suited to solar work.

For his work on solar and terrestrial spectra, intended to provide the baseline for his astronomical work, Huggins used an instrument with a train of 6 flint-glass prisms provided by Browning and a micrometer eyepiece by Dollond. Other components were provided by Ross and by Cooke



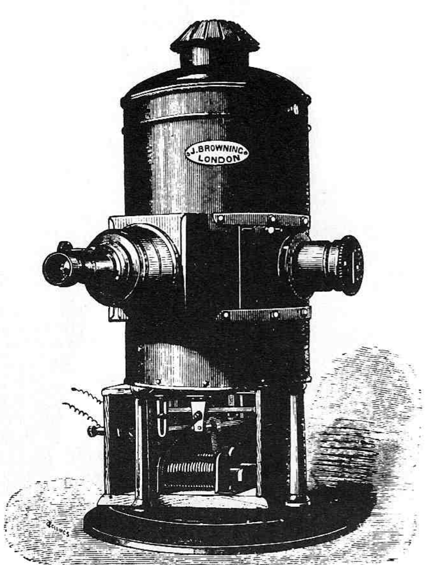
The Huggins star spectroscope manufactured by Browning (6). A cylindrical lens in front of the slit is used to produce a spectrum of finite height, and a small reflecting prism introduces light from a comparative source.

William Huggins (36).

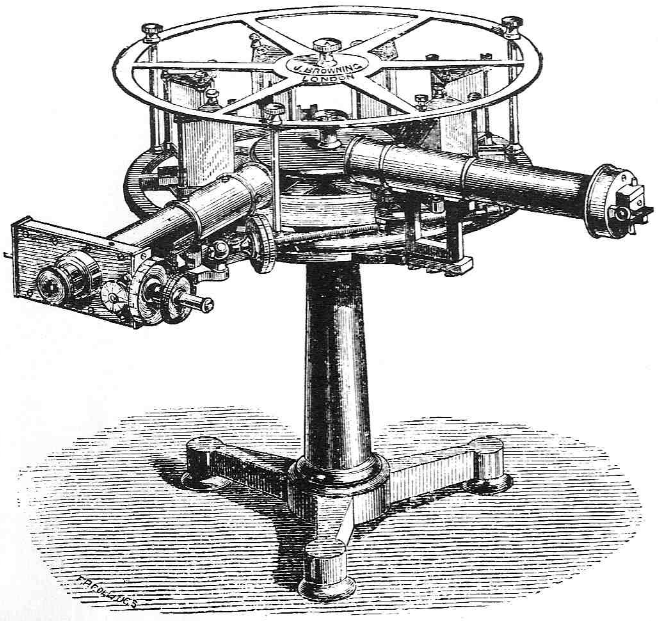
and the instrument was described by Huggins in 1864 (16). When he went on to study the spectra of stars and of nebulae, he designed a 2-prism spectroscope (also illustrated by Roscoe) to be fitted to a telescope, which was made - and subsequently manufactured - by Browning. By a small reflecting prism, covering half the slit, Huggins was able to introduce spark spectra of metals for comparison, and for making measurements the telescope could be moved by a micrometer screw (6). Working in collboration with W.A. Miller, he demonstrated that some nebulae consist of luminous gas and that there is considerable chemical similarity between the sun and other stars.

One major obstacle to the use of prism trains was the difficulty of adjusting the prisms, and this was called for frequently since the best results were obtained only under conditions of minimum deviation. The optimum arrangement of the train was thus different for every portion of the spectrum. In describing a form of semi-automatic adjustment in 1865 for a spectroscope with 6 carbon bisulphide prisms, L.M. Rutherford explained the problem with some feeling: 'In order to obtain fine definition it is necessary that the prisms should be placed at the angle of least deviation for the ray under observation. To make the adjustment with several prisms, or to change it when made, is so barbarious and troublesome a task as almost to amount to a prohibition of the use of a powerful battery for practical and extended investigations' (33).

Rutherford's solution was to hinge the prism mounts together at their corners, set them on a glass platform, and arrange a rod projecting from the back of each mount with a slot embracing a central pillar. In this way the prism backs were kept tangential to a circle centred on the pillar, whatever the position of the train. The train, and thus the ray refracted with minimum deviation, was adjusted by supplying the rod of one prism - the third - with rackwork engaging a pinion on the pillar, which was rotated by a knob above.



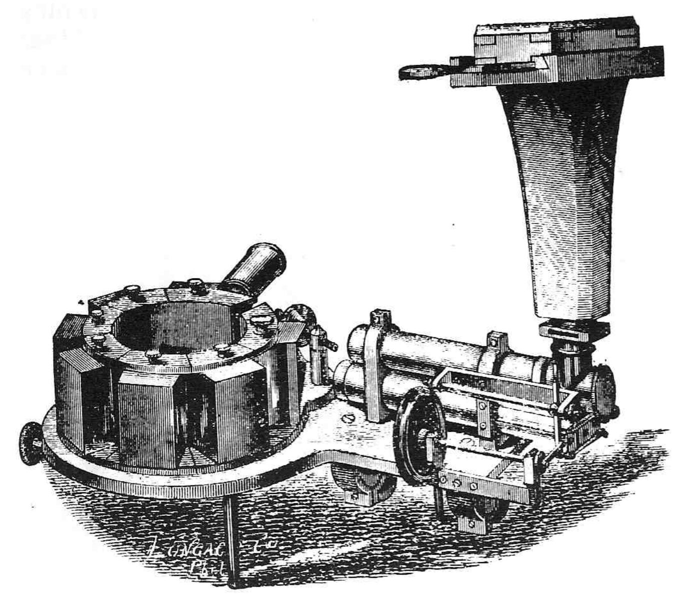
Browning's 'Screen Spectrum Apparatus' for projecting spectra to illustrate scientific lectures (6).



Browning's 'Universal Automatic Spectroscope' (6). The motion of the telescope by a micrometer screw automatically adjusts the prism train to the position of minimum deviation for the ray being observed.

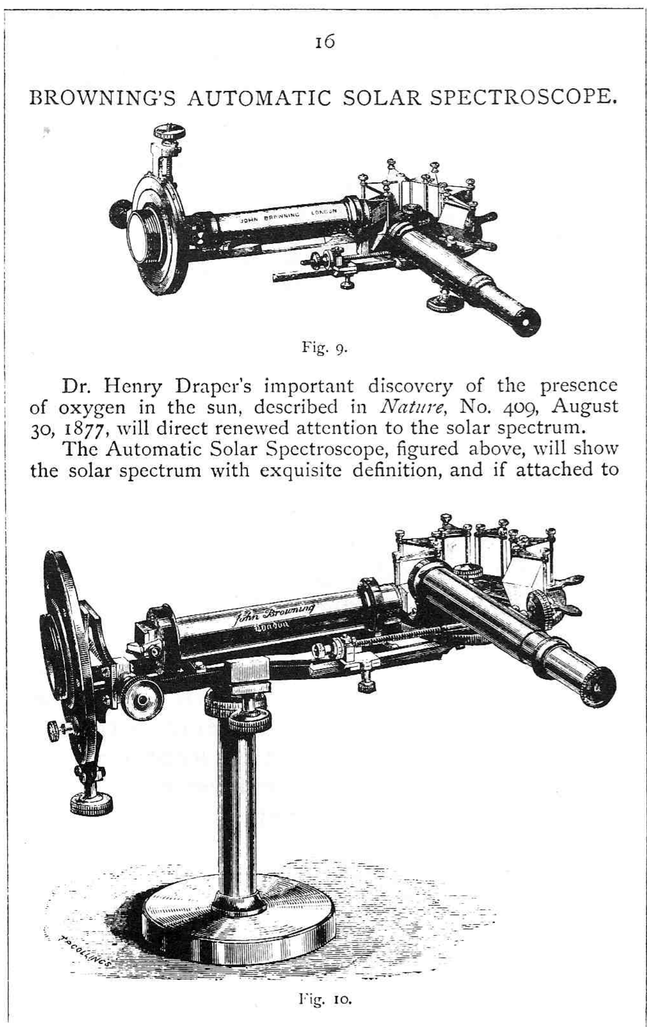
Browning made the adjustment fully automatic in an arrangement described in 1870 where the telescope was linked to the final prism, so that moving the telescope by a screw adjusted the train to minimum deviation for the ray being observed (5). In the same year also occurred the first account of an alternative arrangement by Grubb (11).

It was also in 1870 that the first account appeared of a reflecting prism being used to terminate the train, so as to pass the light back through the upper or lower halves of the prisms and double the total dispersive power. Mirrors had been employed in similar attempts by Janssen and by Littrow as early



C. A. Young's spectroscope, constructed by Alvan Clark & Sons for solar work with the 6.4in refractor at Dartmouth College Observatory (40). The prism train is terminated by a reflecting prism, which reverses the path and doubles the dispersive power.

as 1862 (24). The use of a reflecting prism was described in 1870 by C.A. Young in his account of a solar spectroscope made for an equatorial telescope at Dartmouth College Observatory by Alvan Clark and Sons (40). The seventh prism in the flint-glass train was a combination of a half prism and a right-angle prism cemented together. Browning added this idea to his existing arrangement and in his 'automatic solar spectroscope' the telescope is fixed and the portion of the spectrum observed is adjusted by moving the final prism - and thus all but the first prism of the train - by a micrometer screw (6).



16

BROWNING'S AUTOMATIC SOLAR SPECTROSCOPE.

Fig. 9.

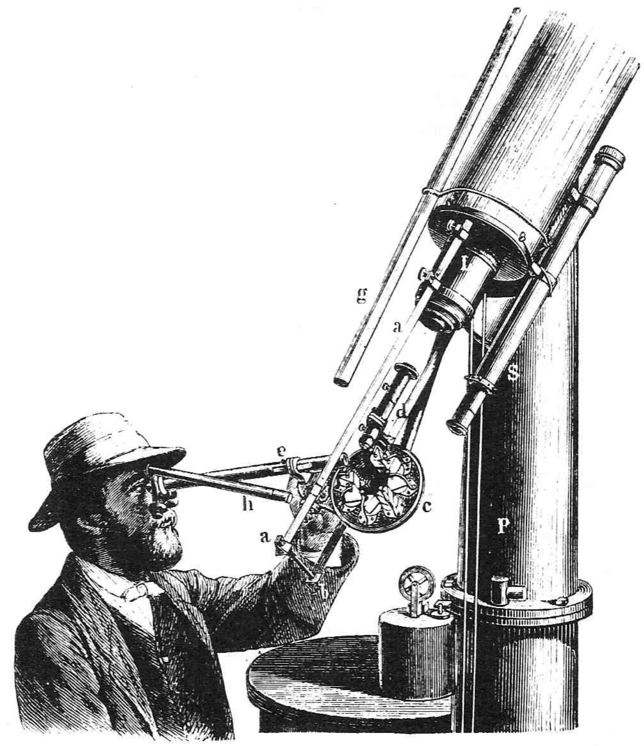
Dr. Henry Draper's important discovery of the presence of oxygen in the sun, described in *Nature*, No. 409, August 30, 1877, will direct renewed attention to the solar spectrum.

The Automatic Solar Spectroscope, figured above, will show the solar spectrum with exquisite definition, and if attached to

Fig. 10.

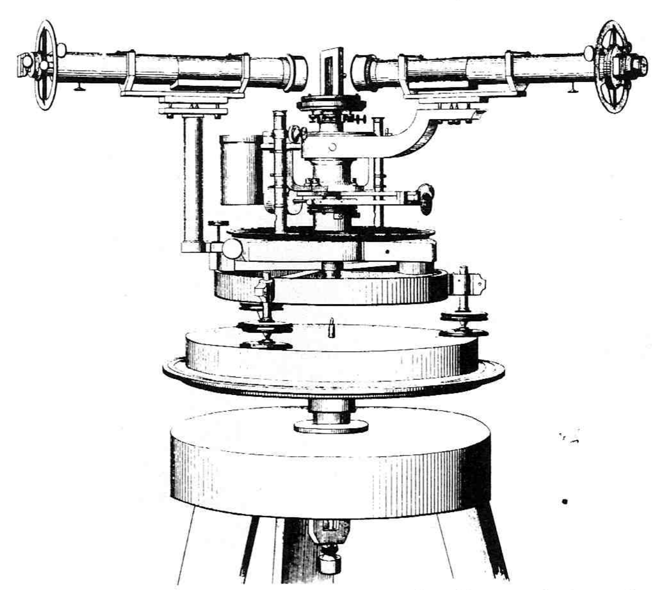
A page from Browning's handbook (6), where the two versions of his 'Automatic Solar Spectroscope' are illustrated. Collimator and telescope are fixed and the automatic train terminated by a reflecting prism. The light observed is varied by moving the train.

To confirm the years from 1860 to 1870 as a decade of remarkable innovation in the instrumentation of spectroscopy, we can cite the application of the diffraction grating to fundamental spectrum research in the work of A.J. Ångström. The only serious precedent for such work had been carried out by Fraunhofer. Ångström used transmission gratings prepared by F.A. Nobert of Pomerania, who was already famous for his glass plates ruled with finely-spaced parallel lines. They were prepared on his ruling machine as increasingly exacting test objects for microscopes. Ångström,



J. N. Lockyer using a 7-prism solar spectroscope (36).

however, commissioned gratings from Nobert in 1861, for a spectroscopic project aimed at a detailed atlas of the lines in the solar spectrum, with physical measures of their wavelengths. Kirchhoff's wavelength measures had depended on the arbitrary scale of his instrument. Ångström's result, with wavelengths expressed as ten millionths of a millimeter (the unit later named after him), was published as Recherches sur le spectre solaire in 1868 (1).



Angström's spectrometer, made by Pistor & Martins of Berlin, with a diffraction grating by Nobert (1).

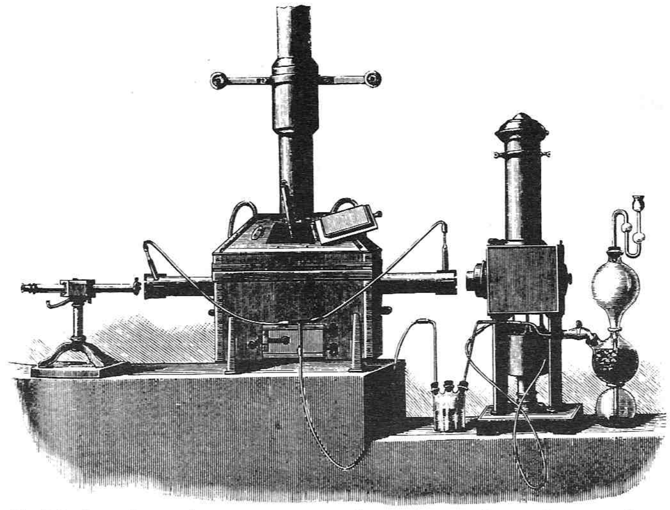
The later nineteenth century

'... I have no doubt that the time is not very far distant when, not only in the chemist's laboratory, but in a great many applications of the physical sciences, the spectroscope will be considered as necessary, and will be almost as much used, as a chemical balance, and the sooner that time comes the better', J.N. Lockyer, 1873 (25).

By the 1870s it was clear that spectroscopy had more than fulfilled its early promise. It was established as a means of chemical analysis and had created an entirely new and previously unimagined branch of astronomy that would become known as astrophysics. More spectacular than the discovery of new terrestrial elements in 1861 was Norman Lockyer's claim in the late 1860s to have discovered a new element, which he named 'helium', by analysing light from the sun. The third, and equally unimagined significance of spectroscopy, as a key to understanding the atomic and molecular world, was implicit in contemporary explanations of spectra located in molecular characteristics, but it would be some time before the full potential of this aspect of spectroscopy was revealed.

The instrumentation had made a rapid advance, now to be followed by a period of consolidation. Certainly a great many particular spectroscopes were constructed for special purposes - too many to be dealt with here - but equally the basic table spectrometer, as well as the standard direct-vision spectroscope, survived the century and beyond.

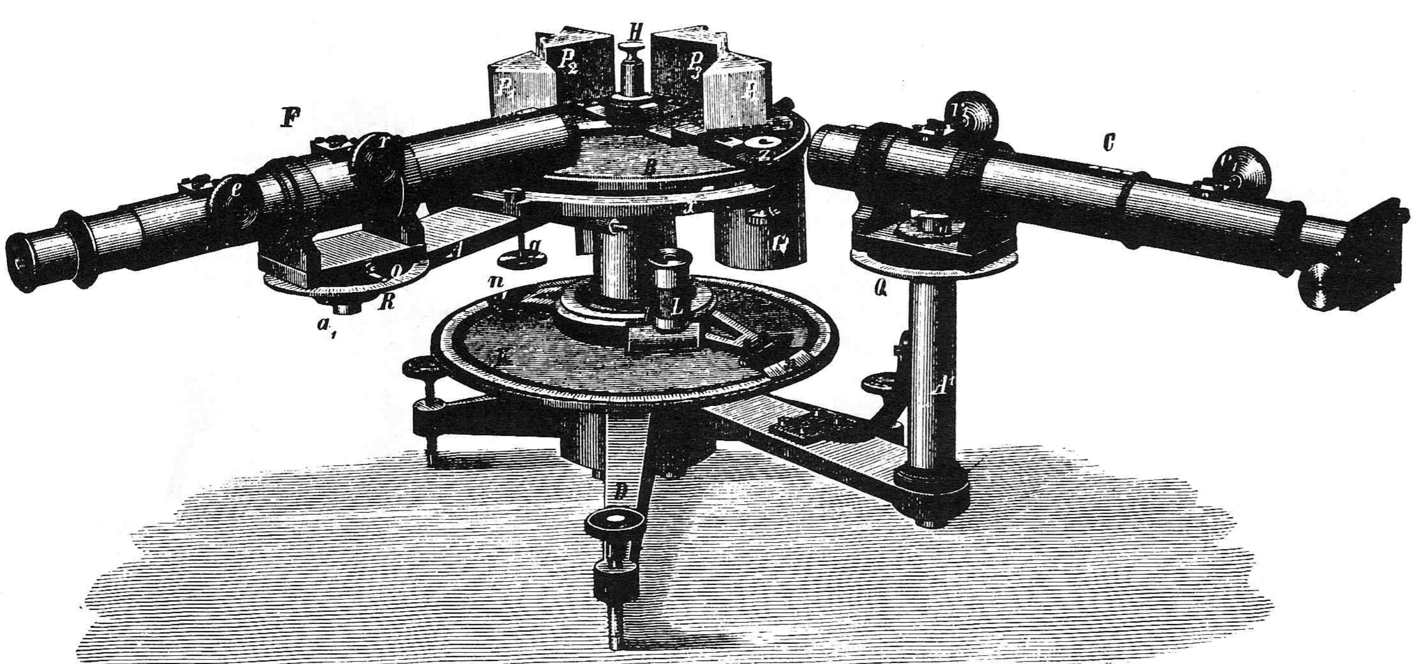
The section of the British Association report of 1881 'on our knowledge of spectrum analysis', while dealing with recent developments, recommended the Bunsen and Kirchhoff design of spectroscope for general use: 'For the ordinary purposes of chemical analysis, nothing can be better than a strongly-built spectroscope, provided with one



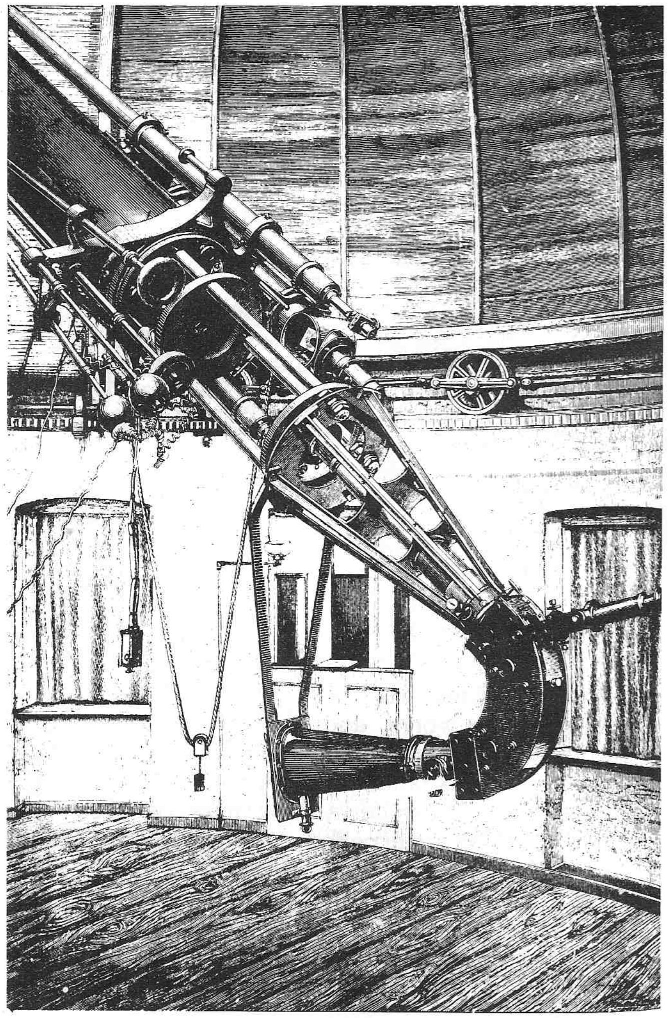
J. N. Lockyer's apparatus for observing absorption spectra (19).

prism of 60° of dense glass, and a photograph-millimetre scale, seen by reflection at the first surface of the prism' (30). The ordinary spectrometer with a divided circle and cross-wires in the telescope was 'A favourite plan with the opticians...' and recommended provided the base and support were sufficiently massive to be steady. Such strictures were not always observed in supporting the collimator and telescope, which might be 'merely screwed by one end into a slender upright of brass, further weakened at the most important point by being attenuated into some (so-called) ornamental shape' (30).

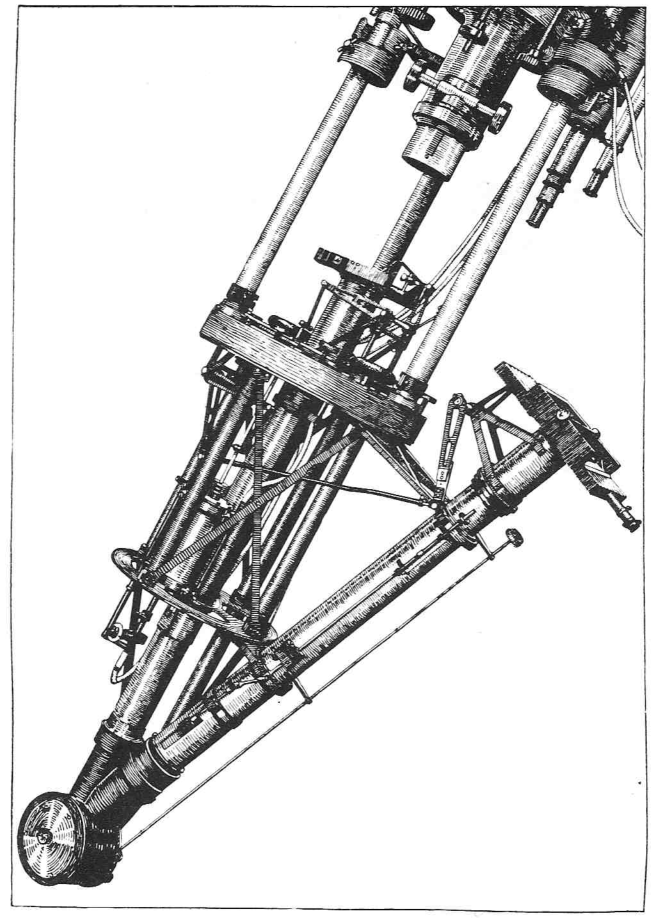
Perhaps the most important practical innovation in spectroscopy in the later nineteenth century was the development of the reflecting diffraction grating. The British Association Report of 1881 referred to the important achievements of L.M. Rutherford, who produced both silvered gratings



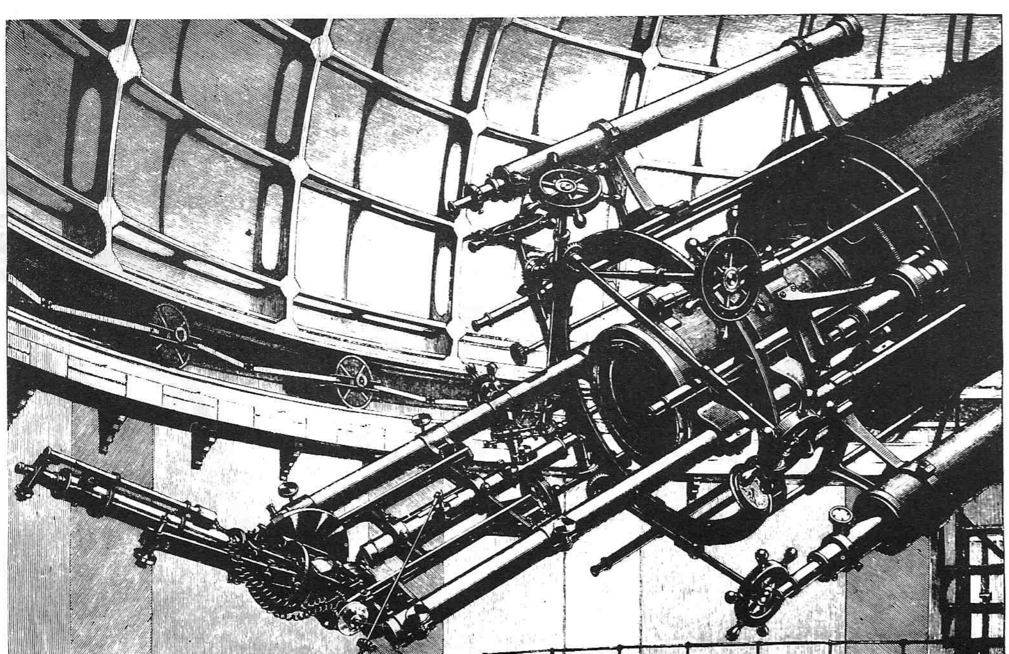
A 4-prism spectroscope by Schmidt & Haensch of Berlin, illustrated in 1883 (19).



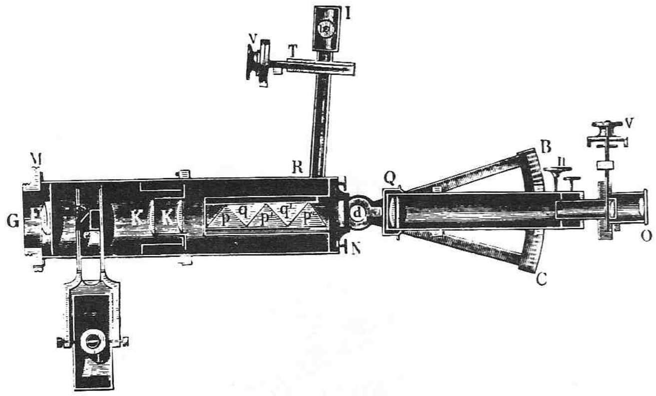
A spectrograph, with two prisms by Rutherford, fitted to an 11in refractor at Potsdam Observatory (35).



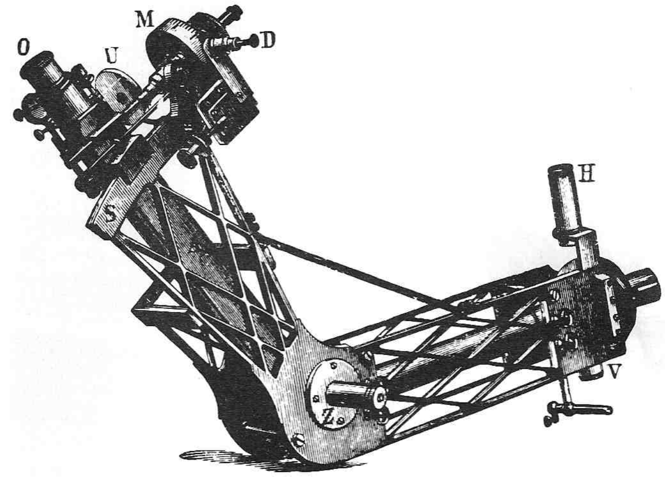
A spectroheliograph - an instrument for recording the spectra of solar prominences - devised by G. E. Hale (c.1889) and fitted to a 12in refractor at the University of Chicago (35). There are two slits - one in the usual position, which moves across the sun's image, while the other moves to expose fresh portions of the photographic plate. The light is dispersed by a reflecting grating.



A spectroscope constructed by Brashear for the 36in refractor of the Lick Observatory, California (35). It could be used alternatively with a prism or with a Rowland grating.



The direct-vision spectroscope as applied to stellar observations by Secchi (35). The components in the body of the instrument are (from the left) a cylindrical lens, a slit, a mirror for introducing light from a comparison source, a 2-lens collimator and the 5 prisms.

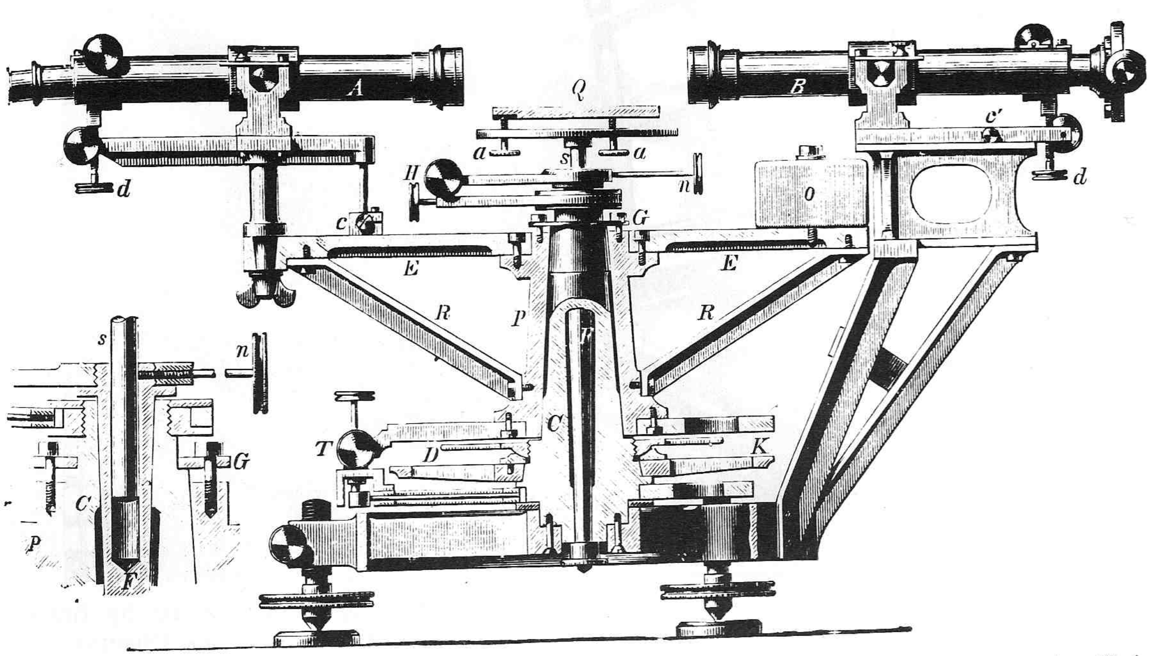


A 2-prism astronomical spectroscope, designed by H. C. Vogel and made by Adam Hilger (35).

ruled on glass, and others ruled directly on polished speculum metal: 'The splendid diffraction-gratings furnished by Rutherford give results unapproached by any other means when the source of light is sufficiently powerful' (30). But in the following year, 1882, Henry A. Rowland, Professor of Physics at Johns Hopkins University, Baltimore, produced his first reflecting grating on a remarkable ruling engine of his own design, and before long a Rowland grating became one of the most prized items of spectroscopic equipment.

Rowland's blanks were concave reflecting surfaces - of glass or, more generally, speculum metal - supplied by J.A. Brashear and Co. of Pennsylvania. By using a concave surface Rowland dispensed with the need for any lenses, and the usual arrangement was to mount both slit and eyepiece or photographic plate close to the centre of curvature. He supplied gratings at cost price to laboratories throughout the world, and they were important to the development both of astrophysics and of molecular and atomic theory. Rowland himself used them to produce a new map of the solar spectrum, which superceded the work of Ångström.

The pattern of trade in spectroscopes in England was changed significantly in the later nineteenth century by the rise of the Hilger firm as specialist instrument makers. Adam Hilger began making spectroscopes in the 1870s and by his death in 1897, when his brother Otto took over the business, Hilger were the leading spectroscope manufacturers - a position they would maintain until the mid-twentieth century.



A large laboratory spectrometer by Wolz of Bonn, illustrated in 1900 (20).

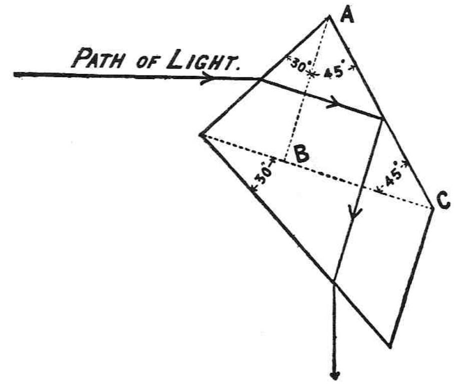
The early twentieth century

'It will be readily understood that, originating with the simple instrument used by Fraunhofer and modified by Bunsen and Kirchhoff, many methods have been adopted and corresponding designs made depending upon the particular nature of the work to which the instruments were applied', E.C.C. Baly, 1905 (2).

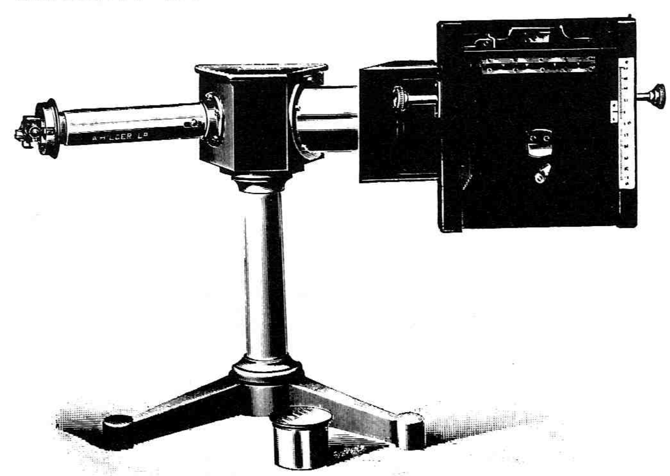
In spite of Baly's reference to the many varieties of specialized instruments - which, in fact, he declined to describe - it is clear that when the first edition of his textbook on spectroscopy was published, the essential instrumentation of at least optical spectroscopy had not changed in its important characteristics over the previous two decades. He deals, of course, with Rowland's gratings - 'this grating has proved to be one of the finest spectroscopic machines ever produced' (2) - and to emphasize the point includes a detailed account of Rowland's ruling engine, but his ordinary direct-vision spectroscope and table spectrometer had long been familiar.

The spectrograph was now more prominent and a new form of grating - the 'echelon' diffraction grating of A.A. Michelson was introduced. Designed in 1898, it was built up from parallel plates of glass of equal thickness, but each shorter than the next by an equal amount. Transmitted light was thus differentially retarded across the grating. Baly dealt also with a new form of prism - the 'constant deviation prism' recently introduced by Hilger. This was a 'combination' (in practice cut from a single piece of glass) of two 30° prisms and one 90° reflecting prism, such that the minimum deviation of every ray was 90°. Thus the collimator and telescope in such a spectroscope were fixed at right angles and the observed ray varied by rotating the prism table.

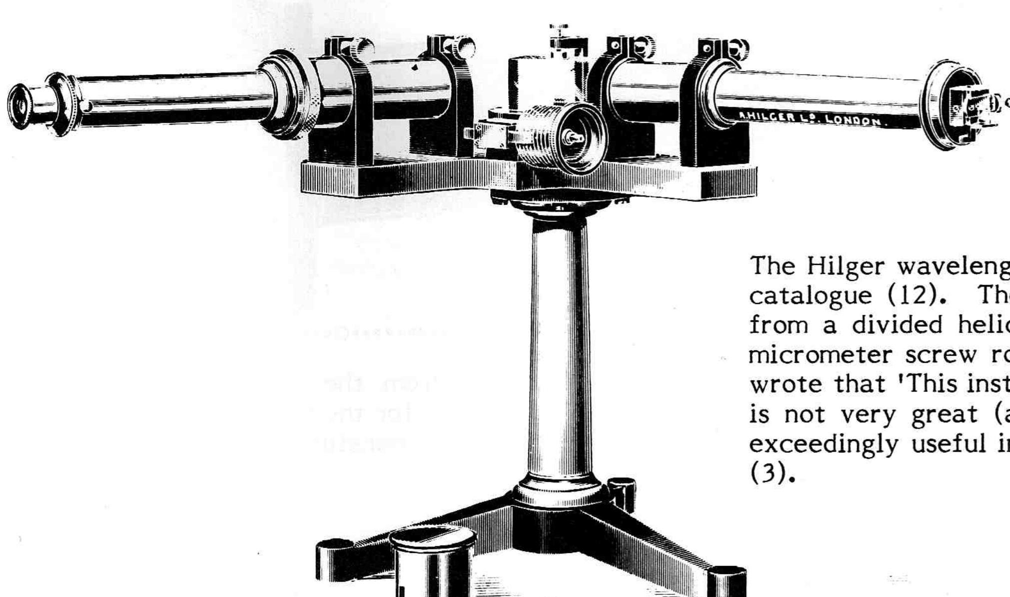
When the third edition of Baly's Spectroscopy appeared in 1924 the constant deviation prism was now applied to Hilger's ubiquitous 'wavelength spectrometer', in which the prism table was rotated by a micrometer screw, the drumhead carrying a helical line divided in wavelengths. He dealt also with the complete range of Hilger quartz spectrographs - small, medium and large - all with optical components of quartz, and the largest a 'Littrow' type instrument with a common collimating and telescope lens and a 30° prism with a reflecting back surface. Hilger, by then, dominated the British market.



A diagram of the constant deviation prism from the Hilger 1913 catalogue (12), shown as comprising two 30° and one 90° prisms. Minimum deviation for every ray is 90°.



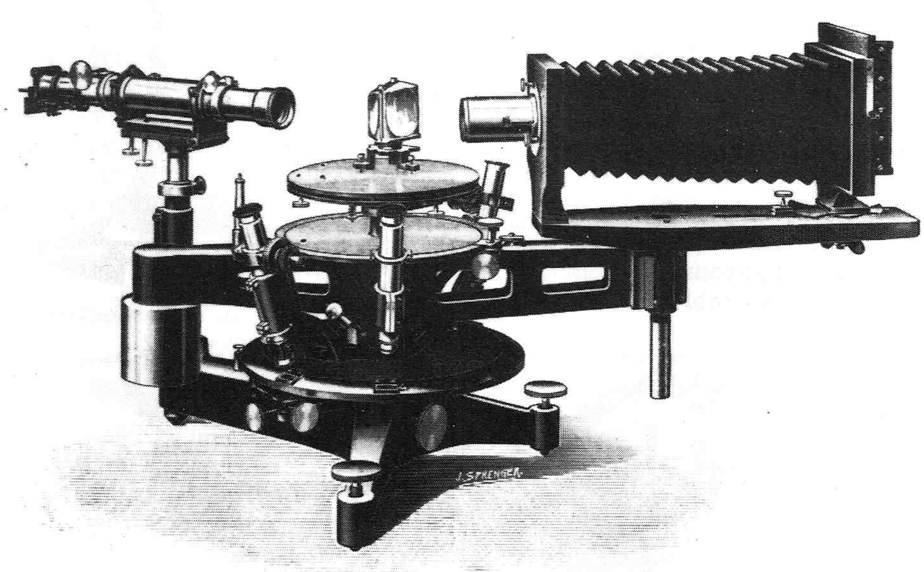
The 'small' quartz spectrograph from the 1913 Hilger catalogue (12).



The Hilger wavelength spectrometer from the 1913 catalogue (12). The wavelength is read directly from a divided helical line on the drumhead of a micrometer screw rotating the prism table. Baly wrote that 'This instrument, although the accuracy is not very great (about two Ångströms), proves exceedingly useful in ordinary spectroscopic work' (3).

The spectroscope in the early twentieth century seemed to be developing as much by improvements in design and construction as by overall changes in conception. Indeed the whole development profile of the spectroscope over time has a curious aspect. Early investigations, largely concerned with physical questions, proceeded without the help of spectroscopes proper. Suddenly - with the advent of 'spectrum analysis' - there was a flurry of inventive activity over a decade or so. Makers seemed poised to respond to the new challenge and chemists and astronomers were keen to collaborate with them in extending the new techniques and applying them as widely as possible. There followed a period of more even-paced progress, while familiarity with the spectroscope became more widespread and the ordinary laboratory instrument more commonplace.

A telling contrast can be made with the early histories of the telescope and of the microscope in the seventeenth century. Their trade origins are obscure, their acceptance within natural philosophical debate was resisted, their early development was slow, and their reference limited and controversial. The spectroscope was perhaps the next optical research instrument with widespread and fundamental applications to be introduced into science. Not only had the milieu changed comprehensively, so that its acceptance and dissemination were rapid and enthusiastic, but a great deal of technical expertise had accumulated among the specialist opticians and instrument-makers. The first decade or so of the spectroscope's development was thus characterised by the application of the makers' now considerable technical skills, under the guidance of the scientists - chemists, physicists and astronomers - and the results more than justified the early spectroscopists' enthusiasm for instrumental innovation.



SPECTROMETER No. 2206 WITH DARK CHAMBER.

A spectograph from the 1913 catalogue of the Société Genevoise for the Construction of Physical and Mechanical Apparatus (38).

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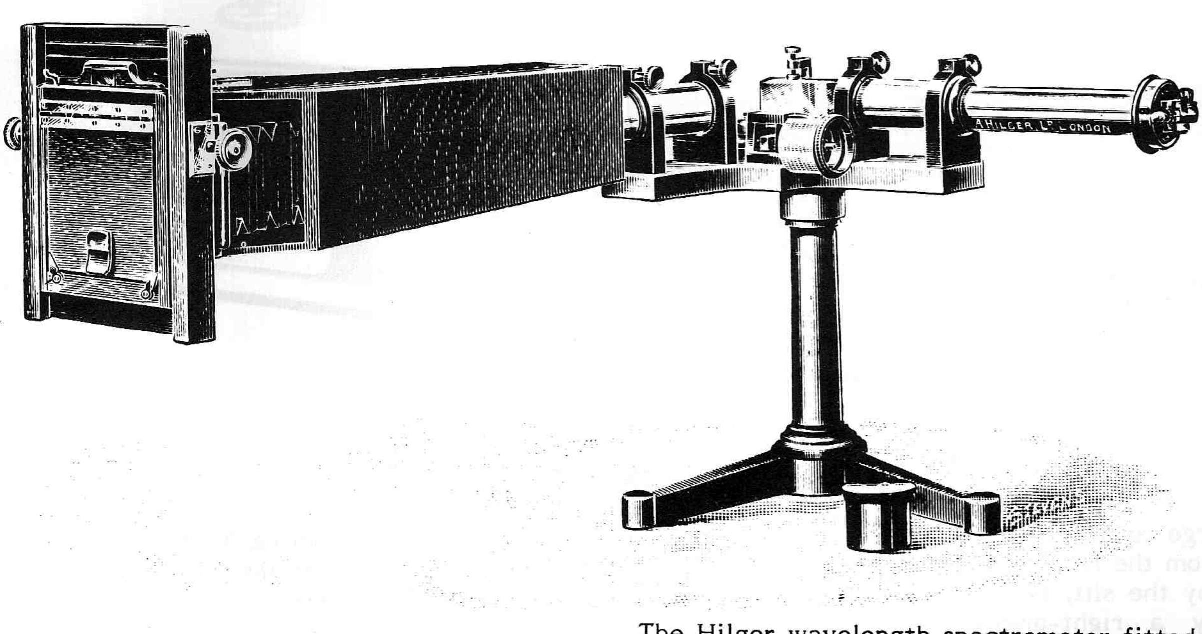
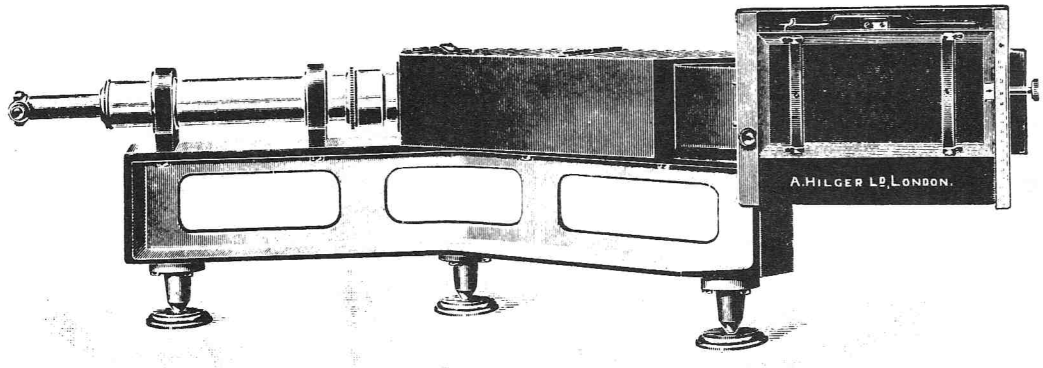


The Hilger wavelength spectrometer fitted with a camera (12).



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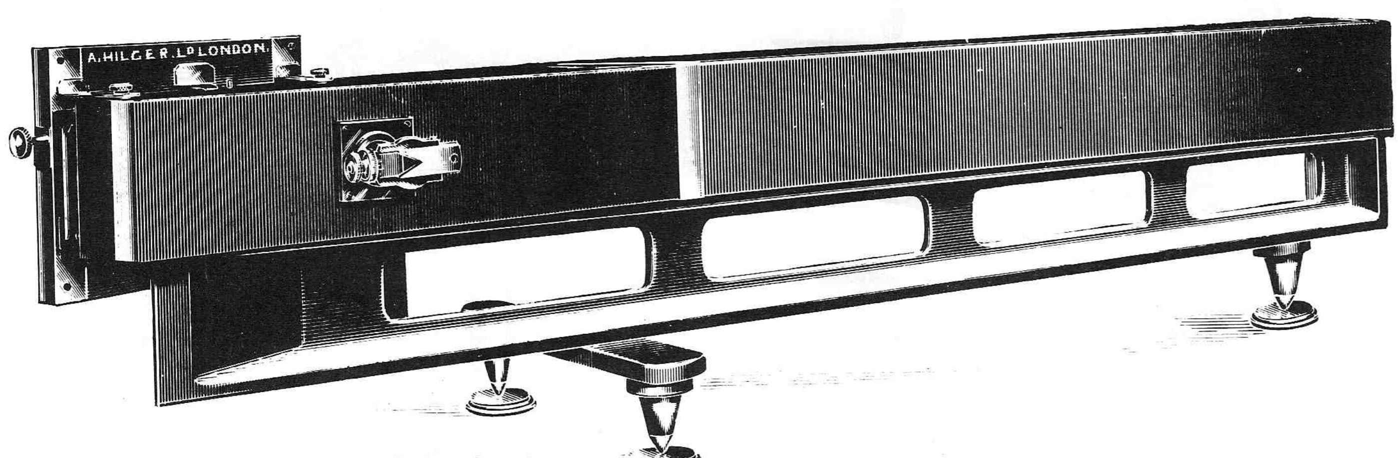
(30) 'Report of the Committee....appointed for the purpose of reporting upon the present state of our Knowledge of Spectrum Analysis'. Report of the British Association, 1881.



The 'large' quartz spectograph, of the 'Littrow' form, from the Hilger 1913 catalogue: 'The light enters by the slit, is reflected along the camera tube by a right-angled prism of quartz, is collimated by the lens, enters and is reflected back by the quartz prism [a 30° back-silvered prism], and retraces its path through the lens, an image of the spectrum being formed on the photographic plate' (12). The overall length is given as 2m.

(31) H.E. Roscoe, 'A course of three lectures on spectrum analysis', Chemical news, 5 (1862), pp. 218-22, 261-5, 287-93.

(32) H.E. Roscoe, Spectrum analysis. Six lectures, delivered in 1868, before the Society of Apothecaries of London (London, 1869).

(33) L.M. Rutherford, 'On the construction of the spectroscope', Chemical news, 11 (1865), pp. 244-5.

(34) J. Scheiner, Die spectralanalyse der gestirne Leipzig, 1890.

(35) J. Scheiner, A treatise on astronomical spectroscopy, trans. E.B. Frost (Boston and London, 1894).

(36) J. Schellen, Die spectralanalyse (Braunschweig, 1870).

(37) H. Schellen, Spectrum analysis, trans J. and C. Lassell, ed. W. Huggins (London, 1872).

(38) Société Genevoise for the Construction of Physical & Mechanical Apparatus, New spectrometers & spectrographs of the greatest exactitude with their accessories (Geneva, 1913).

(39) W. Swan, 'On the prismatic spectra of the flames of compounds of carbon and hydrogen', Transactions Roy. Soc. Edinburgh, 21 (1857), pp. 411-29.

(40) C. A. Young, 'Spectroscopic notes', Chemical news, 22 (1870), pp. 277-80.

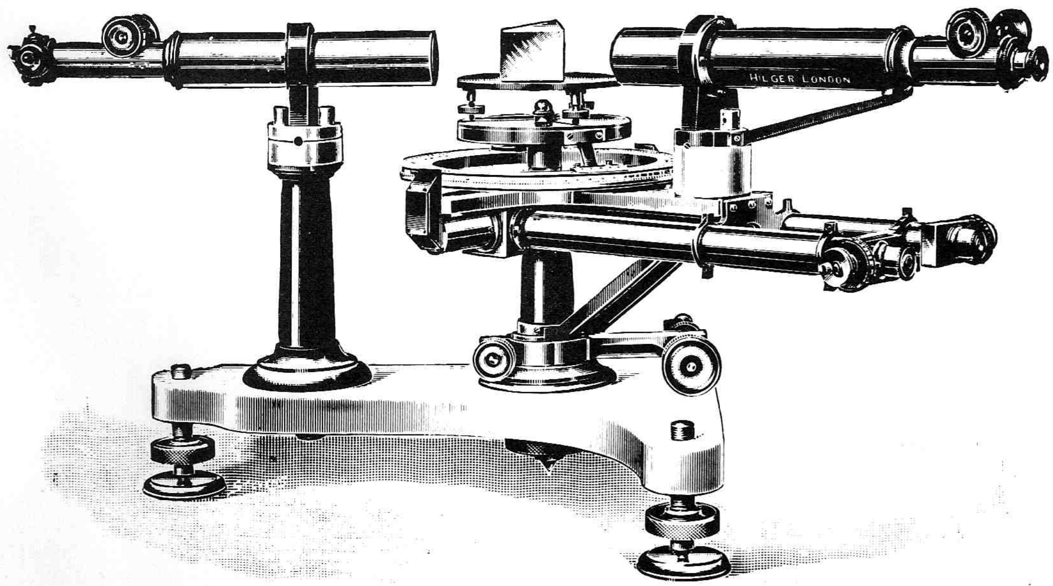


Table spectrometer by A. Hilger Ltd, illustrated in their catalogue of 1913 (12). The 10in divided circle is read from the eye-end of the telescope by two micrometer microscopes to one second of arc.

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