

The Early History of Spectroscopy

PLATINUM CONTRIBUTES TO ITS DEVELOPMENT

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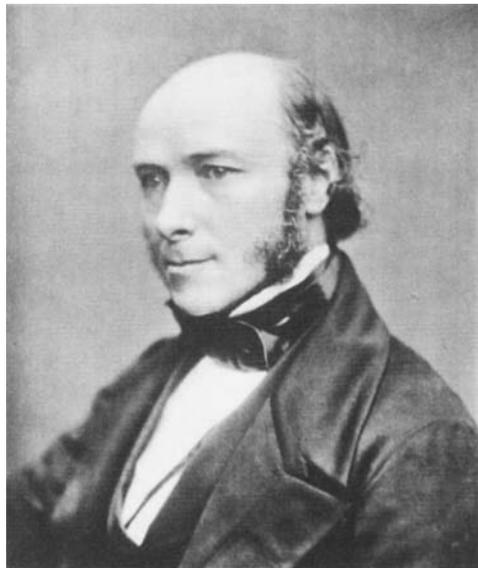
For over half a century spectroscopy has been a valuable aid in the analysis of the platinum metals (1), indeed Johnson Matthey purchased its first spectrograph in 1920 (2). For almost a century before that, platinum apparatus had played an important part in the development of spectroscopy itself. It therefore seems appropriate that William Hyde Wollaston, who developed the first practical method for working platinum (3), was also the first to publish, in 1802, a description of the distinctive patterns of bright and dark lines in the prismatic spectra of light from the sun, and from various terrestrial light sources (4).

Wollaston himself did not pursue these observations, but several other scientists did so during the first quarter of the nineteenth century. Joseph von Fraunhofer mapped the dark lines in the solar spectrum which now bear his name (5). John Herschel and David Brewster independently investigated the spectra of several coloured flames; like Fraunhofer, they had been seeking a reliable source of monochromatic light for optical experiments (6). But it was William Fox Talbot who first suggested, in 1826, that their distinctive line patterns could be used in chemical analysis (7). Talbot's method was to dip a piece of platinum foil into an alcoholic solution of the salt to be analysed, and insert it into the flame of a spirit lamp. Many subsequent experimenters used platinum for this purpose since it did not contaminate the flame.

Brewster, Talbot and Herschel all continued to experiment and publish, and in 1835 Charles Wheatstone described some spark spectra to the British Association (8), but the next major effort came from William Allen Miller, Professor of Chemistry at King's College London (9). In 1845 Miller published diagrams of the

flame spectra of a considerable number of metals. The list did include platinum, but the only line Miller attributed to it was the distinctive yellow one which coincided with Fraunhofer's dark solar "D" line. In 1856, William Swan showed that this almost omnipresent yellow line was due to contamination by small quantities of sodium. He described his experimental procedure thus:

"One-tenth of a grain of common salt, carefully weighed in a balance indicating 1/100 of a grain, was dissolved in 5000 grains of distilled water. Two perfectly similar slips of platinum foil were then carefully ignited by the Bunsen lamp, until they nearly ceased to tinge the flame with yellow



William Allen Miller
1817-1870

Born in Ipswich and educated at King's College and at Giessen, Miller collaborated with J. F. Daniell on electrochemistry. For nine years he was Treasurer of the Royal Society

Courtesy of the Royal Society of Chemistry

light; for to obtain the total absence of yellow light is apparently impossible. One of the slips was dipped into the solution of salt, and the other into distilled water, the quantity of the solution of salt adhering to the slip being considerably less than $1/20$ grain, and both slips were held over the lamp until the water had evaporated. They were then simultaneously introduced into opposite sides of the flame; when the slip which had been dipped into the solution of salt, invariably communicated to a considerable proportion of the flame a bright yellow light, easily distinguishable from that caused by the slip which had been dipped into pure water. It is thus proved that a portion of chloride of sodium, weighing less than $1/1,000,000$ of a grain is able to tinge a flame with bright yellow light . . ." (10)

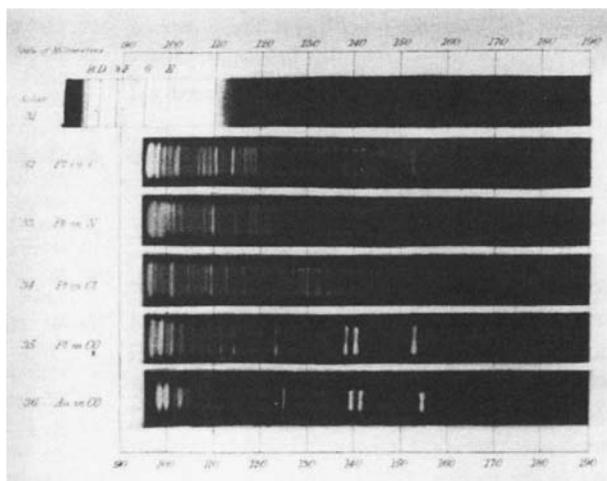
Further studies of spark spectra were published in 1859 by V. S. M. Van der Willigen who also used platinum to support his samples, having found that it contributed no lines of its own (11); but the vital significance of Swan's break-through was fully recognised by Robert Bunsen and Gustav Kirchhoff, who succeeded in converting this promising but hitherto unreliable technique into a systematic method of chemical analysis, which they publicised dramatically by announcing the discovery of a new element in 1860 (12). Caesium was isolated from mineral water by the precipitation of its platino-chloride; with this, as with all Bunsen's samples for spectrum analysis, purity was ensured by recrystallisation (sometimes up to fourteen times) in platinum vessels – a

necessary precaution, as the spectra might be affected even by the minute quantities of salts dissolved from glass containers.

These ultra-pure samples were ignited in Bunsen's gas burner, which gave a much hotter flame than the old spirit-lamps; but as in most previous experiments, they were supported on a platinum wire to avoid contaminating the flame. Whether the wire was dipped into a solution of the salt to be analysed, or tipped with a bead of fused crystals, the relatively short duration of the coloured light remained a handicap. In 1862 Alexander Mitscherlich described an ingenious means of overcoming this difficulty. It consisted of an "L" shaped glass tube, open at the top so that it could be refilled as necessary and closed at the bottom with a plug made of fine platinum threads twisted around a thicker wire, so that a steady supply of the solution was drawn into the flame by capillary action (13).

Many further technical refinements were developed in the next few years, as other physicists and chemists responded to the challenge thrown down by Bunsen and Kirchhoff; new elements were discovered, and new theories of radiation, and of the internal structure of matter, were debated (14). One of the most exciting initiatives was the application of spectrum analysis to the stars, this had been attempted by Fraunhofer but it was only with the more accurate instruments now available that

Some examples of line spectra photographed by Huggins and Miller in the early 1860s: from Sir William Huggins, *Philos. Trans.*, 1862, 152, 888. The top band is the solar spectrum, then is descending order the others are platinum in carbon, platinum in nitrogen, platinum in chlorine, platinum in carbon dioxide and finally gold in carbon monoxide



the project became feasible. In the late 1850s William Huggins had become

“... a little dissatisfied with the routine character of ordinary astronomical work, and in a vague way sought about in my mind for the possibility of research upon the heavens in a new direction or by new methods. It was just at this time, when a vague longing after new methods of observation for attacking many of the problems of the heavenly bodies filled my mind, that the news reached me of Kirchhoff's great discovery of the true nature and the chemical constitution of the sun from his interpretation of the Fraunhofer lines. This news was to me like the coming upon a spring of water in a dry and thirsty land.” (15)

Shortly afterwards, Huggins encountered W. A. Miller at an evening meeting of the Pharmaceutical Society on the subject of spectrum analysis. Being neighbours, they walked home together, continuing the discussion as they went; this chance event led to a joint research project, and to a series of important papers (16). They devised an instrument which compared directly the spectrum of light from a celestial source with that of a flame or spark in the laboratory, and with it they began to explore the chemistry of the sun and the stars. Their publications included diagrams and photographs of the flame and spark spectra of many elements. Since the purity of the samples was of concern to anyone who might be repeating their work, they were careful to cite their sources: thus Huggins records that “I have procured from Messrs. Johnson and Matthey tellurium, palladium, osmium, rhodium, iridium and pure platinum”. (17) The purity of the platinum was particularly important, since many other metals were electrodeposited on platinum wires for spark spectroscopy.

The achievements of Huggins and Miller marked the beginning of the systematic investigation of stellar chemistry. By the early 1870s spectroscopy had become widely accepted as a valuable astronomical technique (18); the era of the pioneers was over, and a period of consolidation had begun. Today, when the platinum metals are still important in the exploration of outer space (19), we should not forget their part in earlier attempts to reach out to the stars.

Acknowledgement

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