

Oesper Museum Booklets on  
the History of Chemical Apparatus

No. 6

# SPECTRO PHOTOMETERS

William B. Jensen  
University of Cincinnati

Photography by Jay Yocis



Oesper Collections  
University of Cincinnati  
2014



Oesper Museum Booklets on  
the History of Chemical Apparatus

No. 6

# SPECTRO PHOTOMETERS

William B. Jensen  
University of Cincinnati

Photography by Jay Yocis



Oesper Collections  
University of Cincinnati  
2014



## SERIES INTRODUCTION

Like most museums, only about 25% of the holdings of the Oesper Collections in the History of Chemistry are on public display at a given time. In order to make the remaining 75% available in some form, it was decided to initiate a series of short museum booklets, each dedicated to a particular instrument or laboratory technique of historical importance to the science of chemistry. Each booklet would include not only photographs of both displayed and stored museum artifacts related to the subject at hand, but also a short discussion of the history of the instrument or technique and of its impact on the development of chemistry as a whole. Several of these booklets are expansions of short articles which have previously appeared in either the bimonthly series *Museum Notes*, which is posted on the Oesper website, or the series *Ask the Historian*, which appeared in the *Journal of Chemical Education* between 2003 and 2012.

*William B. Jensen*  
*Cincinnati, OH*  
*April 2014*



## SPECTROPHOTOMETERS



Figure 1. Melvin Guy Mellon  
(1893-1993)

### **The M. G. Mellon Spectrophotometer Collection**

As indicated in the previous booklet in this series, the Oesper Apparatus Museum contains a large selection of visual colorimeters, filter photometers and spectrophotometers based on collections of these instruments donated in 1990 by the late Melvin Guy Mellon (figure 1) of Purdue University. Though additional instruments have subsequently been added, each of these collections has been named in Mellon's honor in recognition of his initial gift. The M. G. Mellon colorimeter collection was the subject of booklet No. 4 in this series and his filter photometer collection the subject of booklet No. 5. The present booklet (No. 6)

deals with his spectrophotometer collection.

Like the filter photometers in the previous booklet, many of the instruments described here were sold directly by the companies that made them rather than through standard laboratory supply houses. As a consequence, many are untraceable using standard laboratory supply catalogs. Luckily, however, Mellon also provided the Oesper Museum with a large collection of manufacturer's advertisements, brochures, and catalogs which has greatly facilitated the task of identification and characterization. Unhappily much of this material is also undated. As a result, the dating of many of the individual instruments is often only approximate and should be considered as accurate only to the nearest decade at best.

### **Filter Photometers versus Spectrophotometers**

A block diagram for a typical spectrophotometer is shown in figure 2. The difference between such an instrument and the filter photometers discussed in the previ-

## OESPER MUSEUM BOOKLETS

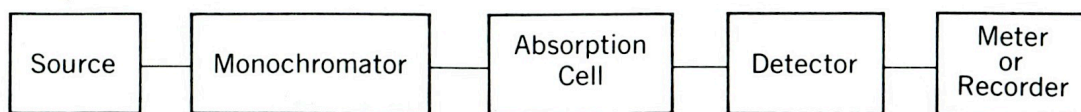


Figure 2. A block diagram for a typical spectrophotometer.

ous booklet lies in the second box in this sequence in which the monochromator is replaced by a filter of some sort. Whereas a filter restricts the light to a limited band width, a monochromator (whether a prism or a diffraction grating) supposedly restricts it to a single wavelength. As a consequence, spectrophotometers more closely obey Beer's law than do filter photometers:

$$\log(I_s/I_0) = -\epsilon bc = \log(T) \quad [1]$$

where  $I_0$  is the initial intensity of the light source,  $I_s$  is the light intensity after passage through the sample,  $T$  is their ratio – otherwise known as the sample transmittance,  $b$  is the thickness of the solution – otherwise known as the path length,  $c$  is the concentration of the solute in moles per liter, and  $\epsilon$  is the molar extinction coefficient for the species in question and varies with both wavelength and temperature. In addition, in contrast to a filter photometer, a true spectrophotometer allows one to map the transmittance of a sample over the entire range of wavelengths covered by its monochromator rather than at just one fixed band width.

In actual fact the above claim is somewhat exaggerated since the electromagnetic spectrum is continuous. It would be more accurate to say that the monochromator of the spectrophotometer allows one to isolate a far narrower band width than does the glass filter of the filter photometer. In addition, actual instrument design is far more eclectic than suggested by the block diagram in figure 2. Thus, in many of the early visual instruments the filter or monochromator was placed between between the absorption cell and the detector (i.e., the human eye) rather than between the source and the cell, and the meter or recorder was a mechanical scale on either a micrometer or potentiometer, rather than a galvanometer reading or the printout of a chart recorder.



## SPECTROPHOTOMETERS

### Visual Spectrophotometers

Solution absorption spectrophotometry is far older than most modern-day chemists realize. Though there are a few scattered anticipations, it is generally agreed that the first substantial contribution to the field is due to the work of the German, Karl von Vierordt (figure 3), as summarized in his 1873 monograph *Die Anwendung des Spectralapparates zur Photometrie der Absorptionsspectren und zur quantitativen chemischen Analyse*.<sup>1</sup> Interestingly, Vierordt was neither a physicist nor a chemist, but rather a medical doctor who



Figure 3. Karl von Vierordt (1818-1884)

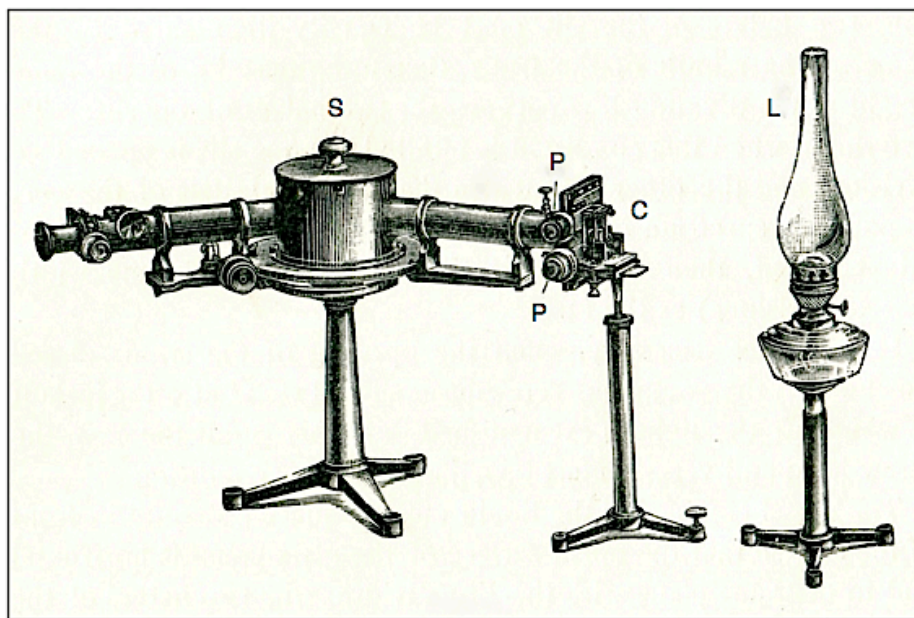


Figure 4. Vierordt's spectrophotometer as shown in the 1891 edition of G. Krüss and H. Krüss, *Kolorimetrie und Quantitative Spektralanalyse in ihrer Anwendung in der Chemie*. S is the spectrometer, L is the light source, C is the sample cell holder, and PP is the double slit photometer.

## OESPER MUSEUM BOOKLETS

was Professor of Physiology at the University of Tübingen and who specialized in the study of blood. He had previously invented an apparatus for measuring the rate of blood flow, as well as an early version of the sphygmomanometer for measuring blood pressure. His interest in spectrophotometry was apparently prompted by his desire to devise a method for accurately measuring the hemoglobin content of blood, though he was well aware that the resulting technique also had important applications in the fields of physics, chemistry, and technology.<sup>2</sup>

His apparatus is shown in figure 3. For the spectrometer he used a conventional Bunsen spectroscopy whose scale had been empirically calibrated with respect to the wavelengths of several well-established spectral lines. A special double slit on the end of the collimator tube served as the photometer. This produced a split optical field in the eyepiece, and the intensity of each half could be independently regulated by varying the corresponding slit widths using micrometer screws.<sup>3</sup> Since the Bunsen spectroscopy is so closely identified in the chemist's subconscious with the discrete line emission spectra of excited atoms, we need to remind ourselves that in the case under consideration here, where we are dealing with the room temperature absorption spectra of liquid solutions, we would instead see a continuous spectrum of varying intensity.

A summary of late 19th-century work on spectrophotometry may be found in the monograph *Kolorimetrie und Quantitative Spektralanalyse in ihrer Anwendung in der Chemie* by Gerhard and Hugo Krüss.<sup>4</sup> In its various editions, this work covers the literature through at least 1908 and surveys various refinements of Vierordt's original apparatus, as well as such optional devices as the "spectrocolorimeter," many of which were apparently made by the Krüss family apparatus firm in Hamburg.

By the 1920s several American firms were selling elaborated versions of Vierordt's apparatus. One of the earliest was the 1925 "Color Analyzer" or direct reading spectrophotometer made by the Keuffel and Esser Co. of Hoboken, NJ (figures 5 and 6).<sup>5</sup> This replaced the oil lamp of Vierordt's apparatus with an spherical electrical light source which could also be used for the study of reflectance spectra, his double-slit photometer with a rotating sector photometer,<sup>6</sup> and

## SPECTROPHOTOMETERS

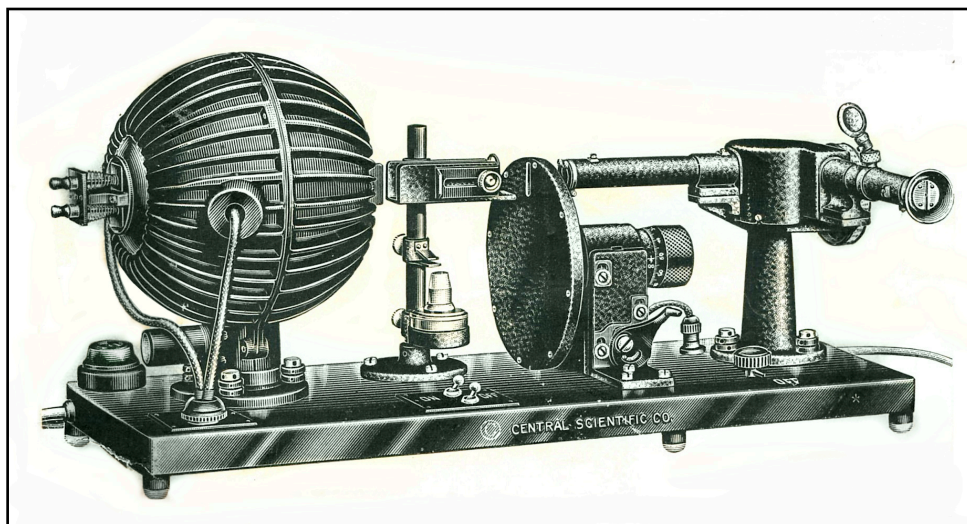


Figure 5. The circa 1925 Keuffel and Esser "Color Analyzer." From left to right: the light source, the sample cells, the rotating sector photometer, and the spectrometer.

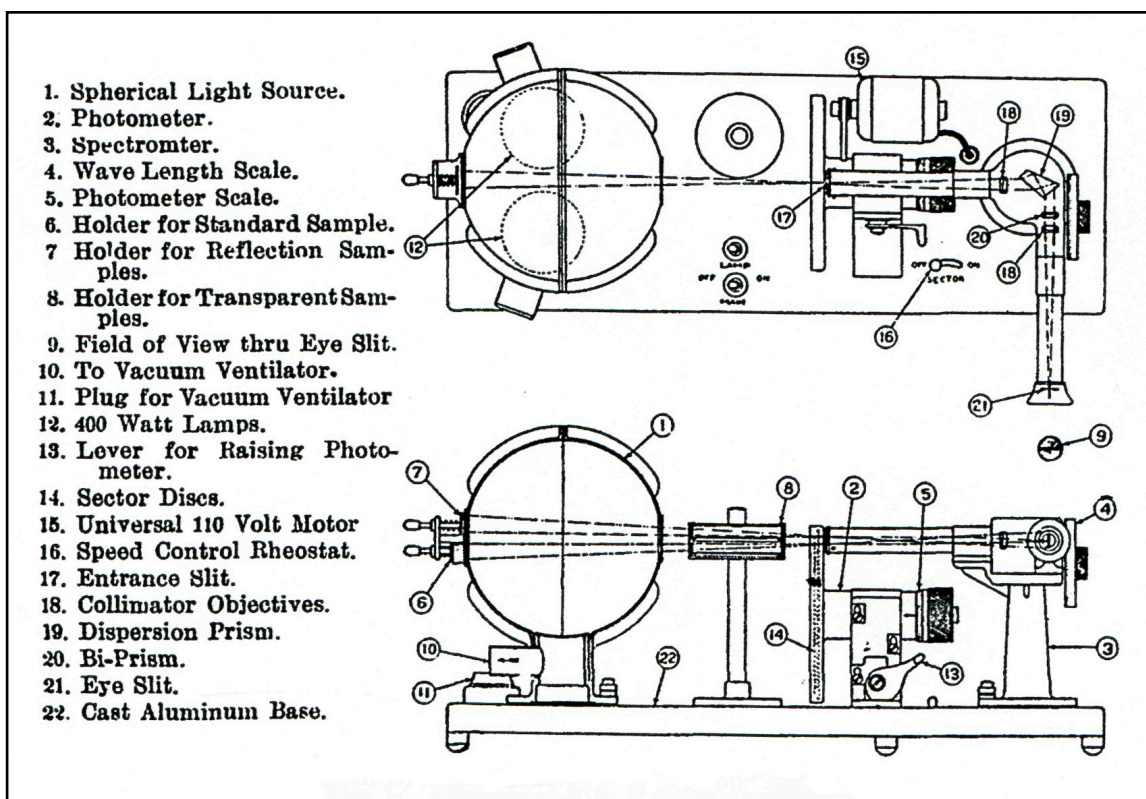


Figure 6. Cross-sectional diagram of the 1925 "K & E Color Analyzer."

## OESPER MUSEUM BOOKLETS

his empirically calibrated Bunsen spectroscope with a true spectrometer directly calibrated to read in units of wavelength. As may be inferred from its name, this instrument was directed more at physicists and technologists interested in the physics of color measurements than at chemists interested in colorimetrically determining the concentration of various solutions. Nevertheless, it came with the option of measuring the transmittance of transparent liquid samples as well as the reflectance of solids. In the former case, the sample and reference solutions were each placed in horizontal metal-jacked tubes with glass windows at each end (not unlike polarimeter tubes) and stacked on top of one another in the sample holder such that each was perfectly aligned with one of the two rotating sectors in the photometer. The rate of the rotating sector for the reference was then adjusted until the intensities of the two cells matched when viewed at a given wavelength through the eyepiece of the spectrometer. The percent transmittance could then be directly read from the speed control for the reference sector.

By the late 1920s the Bausch and Lomb Optical Co of Rochester, NY was producing a similar instrument known as the “Universal Spectrophotometric Out-

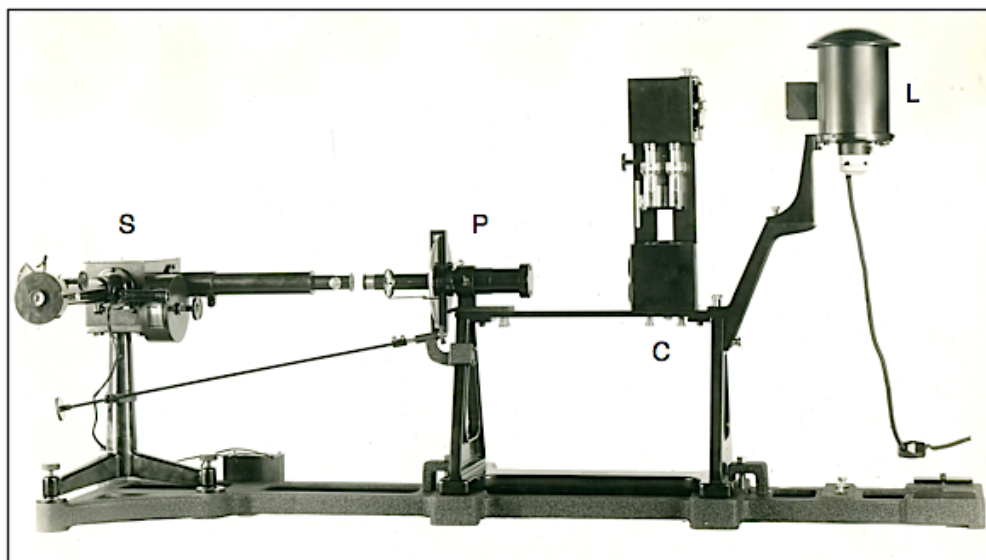


Figure 7. The Bausch and Lomb “Universal Spectrophotometric Outfit.” L is the light source, C is the special vertical holder for the reference and sample cells, P is the polarization photometer, and S is the direct-reading wavelength spectrometer.

## SPECTROPHOTOMETERS

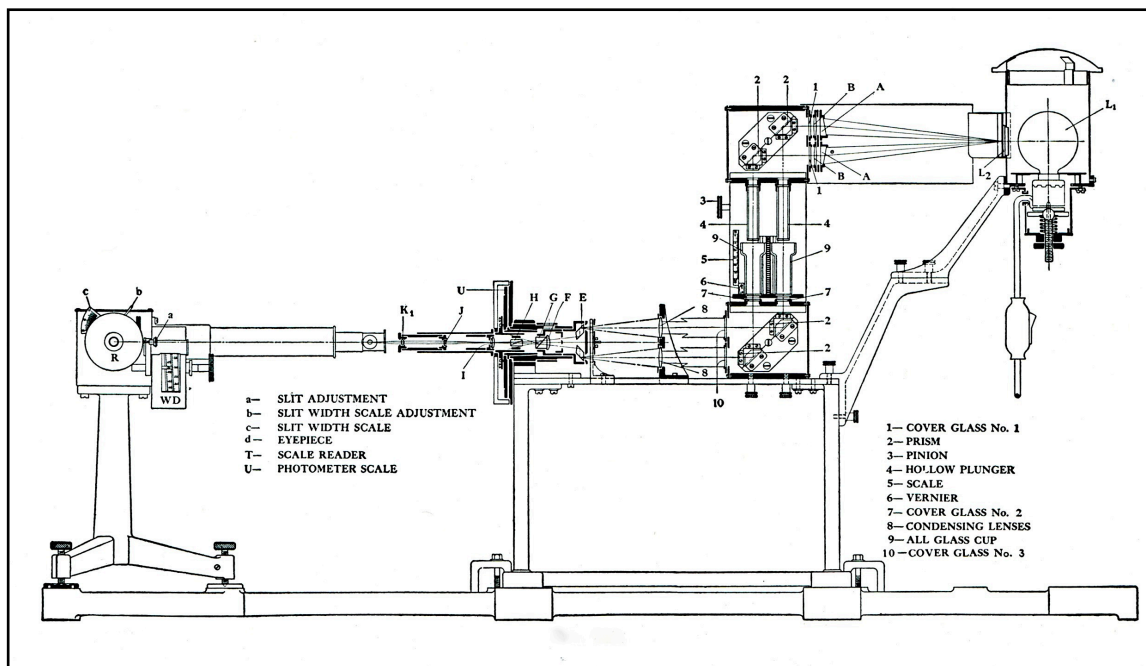


Figure 8. A diagram of the Bausch and Lomb "Universal Spectrophotometer."

fit" (figures 7 and 8).<sup>7</sup> This came with an optional light attachment for the measurement of reflectance spectra, and with a special vertical cell mount for measuring the transmittance spectra of liquids at varying depths. It also used a polarization rather than a rotating sector photometer.<sup>8</sup> By the 1930s similar "modular" visual spectrophotometers were being produced by such companies as Gaertner Scientific Corporation of Chicago and Adam Hilger Ltd. of London, photos of which may be found in the 1939 monograph on chemical spectrography by Brode.<sup>9</sup>

### Photoelectric Spectrophotometers

Just as phototubes and cells began to replace the human eye in the design of commercial filter photometers starting in the 1930s, so by 1940 that same had occurred with respect to spectrophotometers. One of the earliest of these was the single channel "Cenco-Sheard Spectrophotometer" made for the Central Scientific Co. of Chicago (figures 9 and 10).<sup>10</sup> Like the visual spectrophotometers described in

OESPER MUSEUM BOOKLETS

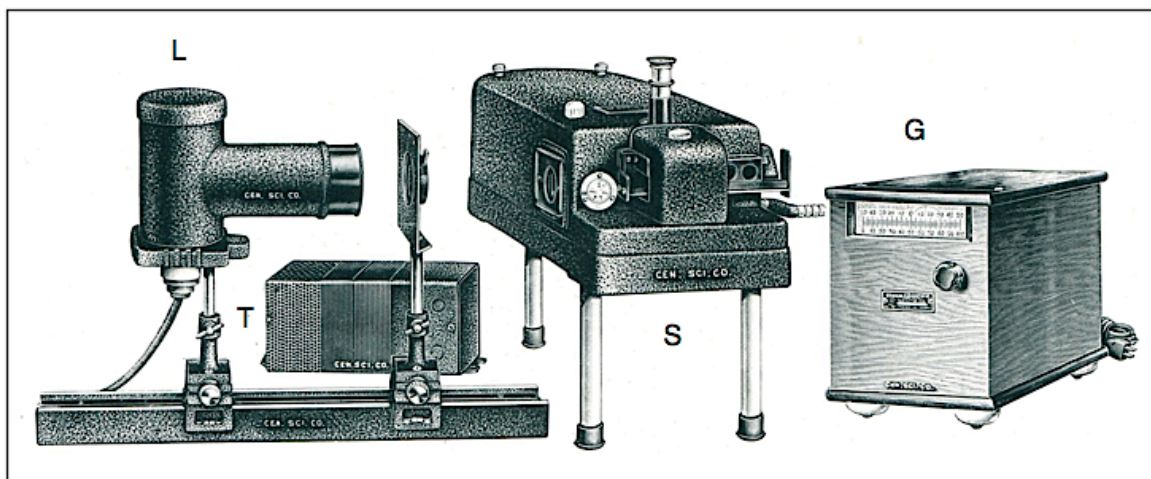


Figure 9. A circa 1941 “Cenco-Sheard Spectrophotometer.” L is the light source, T is the constant voltage transformer, S is the spectrometer, and G is the galvanometer.

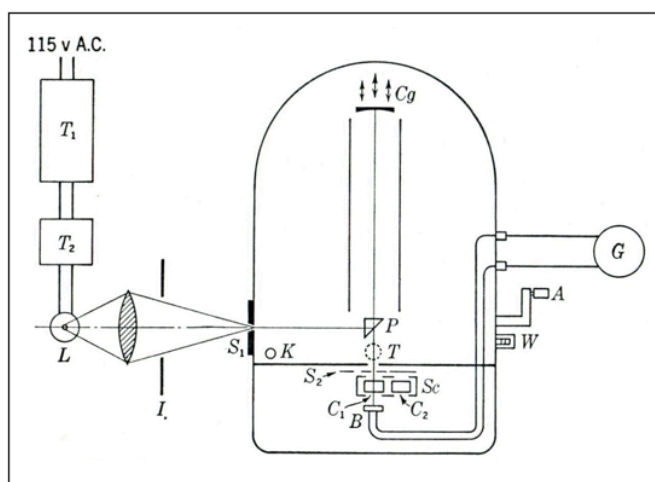


Figure 10. Diagram of the “Cenco-Sheard Spectrophotometer.”  $T_1$  and  $T_2$  are transformers, L is the light, I is an iris diaphragm,  $S_1$  is the entrance slit controlled by knob K, P is a reflecting prism,  $C_g$  is a concave reflection grating, T is a telescope for viewing the spectrum,  $S_2$  is the exit slit,  $C_1$  and  $C_2$  are the reference and sample cells, B is the photocell, G is the galvanometer, W is the wavelength scale, and A is the crank to move the grating.

the previous section, this was completely modular and required the purchase not only of the photoelectric spectrometer itself, but also of an external light source, a constant voltage transformer, and a galvanometer. The sample and reference cells could be alternately slid into the light path.

The circa 1941 “Model 10” single-channel, double-monochromator spectrophotometer (figure 11) made by the Coleman Electric Co. of Maywood, IL began the process of collapsing all of these various components into a single case.<sup>11</sup> Here the light

## SPECTROPHOTOMETERS

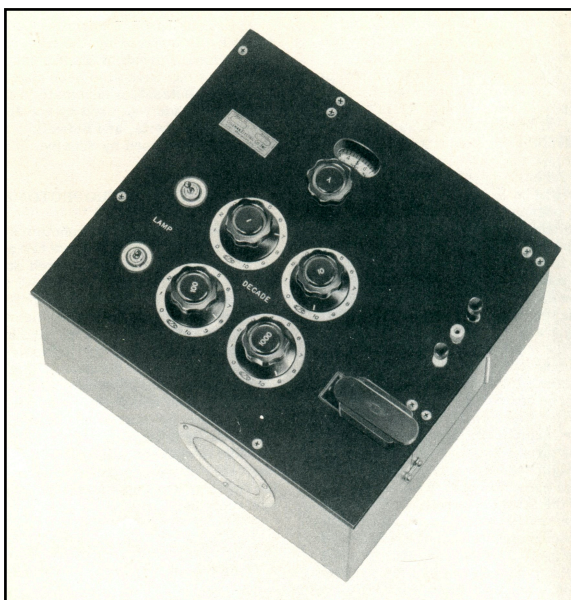


Figure 11. A circa 1940 Coleman Model 10 double-monochromator spectrophotometer sans external galvanometer.

direct reading instrument was housed in a shock resistant black plastic case and came with interchangeable blank scales for the galvanometer which could be calibrated directly in concentration units for the species of interest. Unlike the Model 10, however, it required the use of either an external battery or a constant voltage transformer.

In 1953 Bausch and Lomb introduced its "Spectronic 20" spectrophotometer (figures 13-15) which was destined to become the single most popular and long-lived of the simple desk-top

source, the DC battery, the Wood's double-monochromator (a combination prism and grating), the cell compartment, the phototube, and the variable resistors were all housed in a single wooden box, though it still required the use of an external galvanometer. Shortly afterwards the company produced an alternative "Model 11 Universal Spectrophotometer" in which the galvanometer was also enclosed.<sup>12</sup>

Around 1944 Coleman introduced its popular "Junior Spectrophotometer" (figure 12), initially for use in military field hospitals.<sup>13, 14</sup> This single channel,

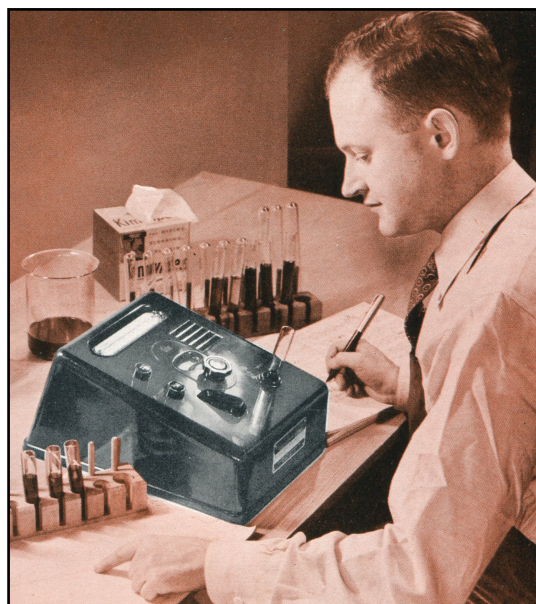


Figure 12. A circa 1945 Coleman "Junior Spectrophotometer."

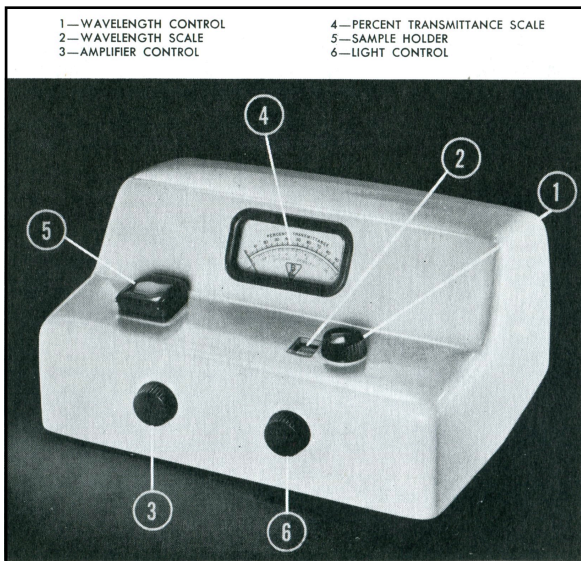


Figure 13. Bausch and Lomb’s original “Spectronic 20,” first introduced in 1953.

### UV-Visible Spectrophotometers

All of the spectrophotometers described so far – whether visual or photoelectric – had glass optics and therefore oper-

instruments.<sup>15, 16</sup> In 1985 the company sold the manufacturing rights to this instrument to the Milton Roy Company of Philadelphia, who, in turn, sold them to Spectronic Instruments in 1993. However, before doing so, Milton Roy replaced the original analog scale with a digital red LED display and a choice of alternative readouts and rechristened the upgrade as the “Spectronic 20D+.”

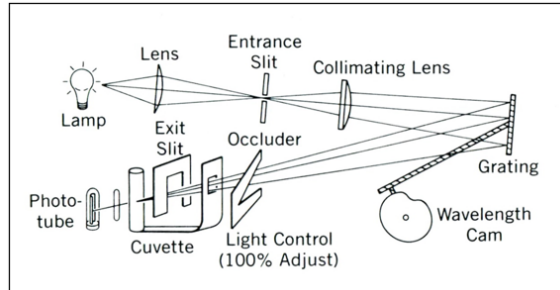


Figure 14. A simplified diagram of the internal structure of the original Bausch and Lomb Spectronic 20.

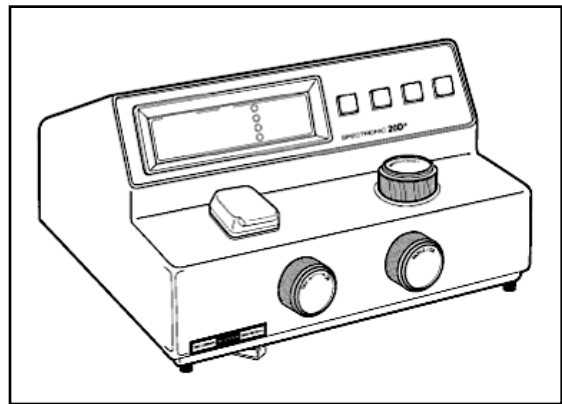
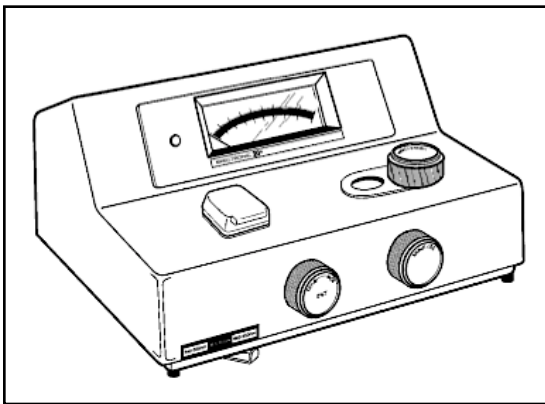


Figure 15. Line drawings of the circa 1986 Milton Roy version of the “Spectronic 20” (left) and of the later “Spectronic 20D+” (right).



## SPECTROPHOTOMETERS

ated only in the visible region of the electromagnetic spectrum. This is usually defined as extending from a wavelength of about 4000Å to around 7500Å. Since radiation in the ultraviolet (UV) region of the spectrum (100-4000Å) is strongly absorbed by ordinary glass and is invisible to the human eye, UV spectrometry requires the use of quartz optics and detection using either photography or photoelectric cells.

As with the case of Vierordt and the origins of visible spectrophotometry, the first explorations of the possibilities of UV spectrophotometry are far older than the modern-day chemist may realize and can be traced back to 1878 and the work of the British chemist, Walter Noel Hartley (figure 16).<sup>17</sup> Using a specially constructed spectroscope with a quartz prism and lenses,<sup>18</sup> Hartley attempted to correlate the photographically recorded UV absorption spectra of organic compounds with the presence of certain characteristic functional groups.<sup>19</sup> However, the special equipment required and the tediousness of the required measurements largely precluded

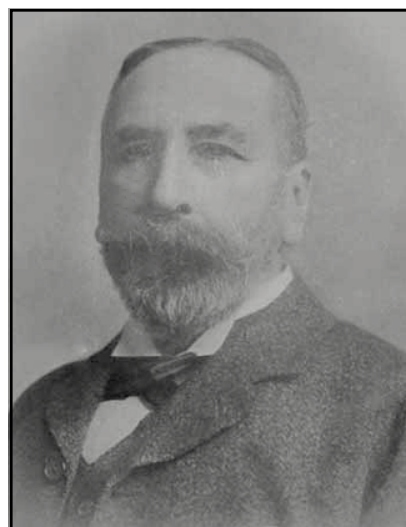


Figure 16. Walter Noel Hartley (1845-1913)

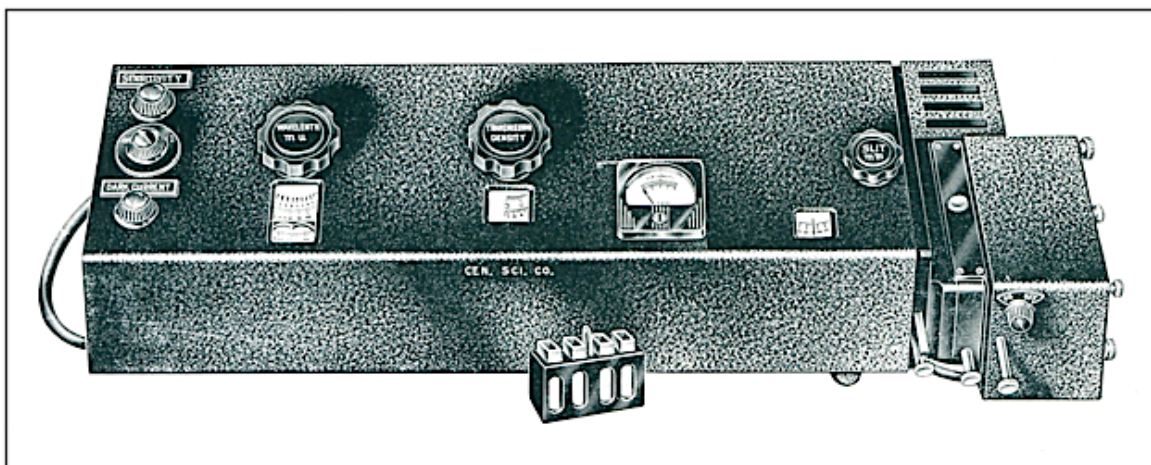


Figure 17. The original, circa 1941, Beckman DU UV-visible spectrophotometer.

OESPER MUSEUM BOOKLETS

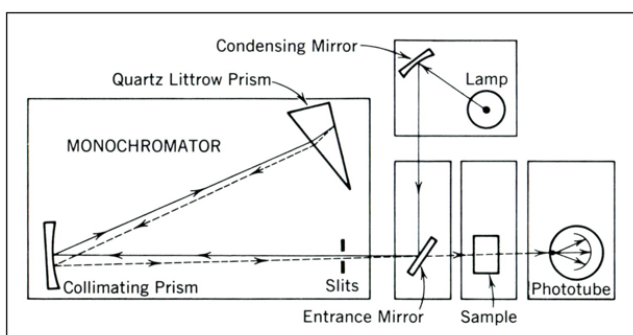


Figure 18. A simplified diagram of the internal workings of the Beckman DU spectrophotometer.

their general adoption by organic chemists as a everyday tool for structure determination, and it was not until the introduction of the first relatively inexpensive commercial UV-visible spectrophotometer (figures 17-18) by Beckman in 1941 that the technique became widely applied by organic chemists.<sup>20, 21</sup> The Beckman DU

covered the range 2000-11000Å. Between its introduction in 1941 and its discontinuance in 1976 more than 30,000 instruments were sold. By the 1950s many other companies were producing UV-visible spectrophotometers and the instruments were becoming larger, more complex, and more expensive, as typified by the circa 1963 “Hatchi Model 129 UV-Visible Grating Spectrophotometer” made by the Perkin-Elmer Corporation of Norwalk, CT (figure 19).<sup>22</sup>

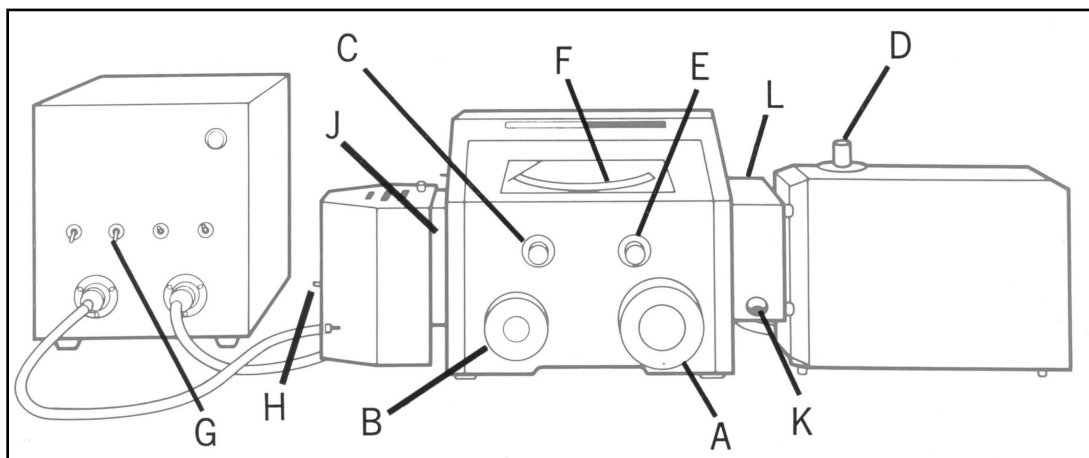


Figure 19. A diagram of the circa 1963 “Hatchi Model 139 UV-Visible Grating Spectrophotometer” made by Perkin-Elmer of Norwalk CT. G is the power supply, H is the source selector, J is the filter, B controls the slit width, C is the zero adjustment, A selects the wavelength, E selects the sensitivity, F is the transmittance scale, L is the cell compartment, K selects the cell to be used, and D controls the shutter for the phototube.

## SPECTROPHOTOMETERS

### Self-Recording Spectrophotometers

Writing in 1945, Mellon<sup>12</sup> observed that use of a visual spectrophotometer to collect sufficient data to hand-plot the transmittance curve of a species over the entire visible spectrum was very time consuming:

*[Use of] these instruments requires considerable time. Often one needs points at some 30 wavelengths for a curve extending across the visible region, and usually a reliable single value may necessitate averaging five readings.*

Though use of photoelectric spectrophotometers eliminated the need for multiple visual reading for each data point, they still frequently required that the data be plotted by hand. This was true even in cases where the data was recorded photographically, since the resulting strip photos had to be pieced together and generally showed rather diffuse absorption peaks so that much great clarity was obtained by using an ink tracing of their outline instead. A further problem was a lack of consensus as to what should be plotted versus what.

Some of these techniques and problems are illustrated in the early spectra shown in figures 20-23. Figure 20 shows early 20th-century visible absorption spectra for 11 different organic dyes taken from the monographs by Formanek<sup>23</sup> and Watson.<sup>24</sup> Here the  $x$ -axis is the arbitrary scale of a Bunsen spectroscope with the locations

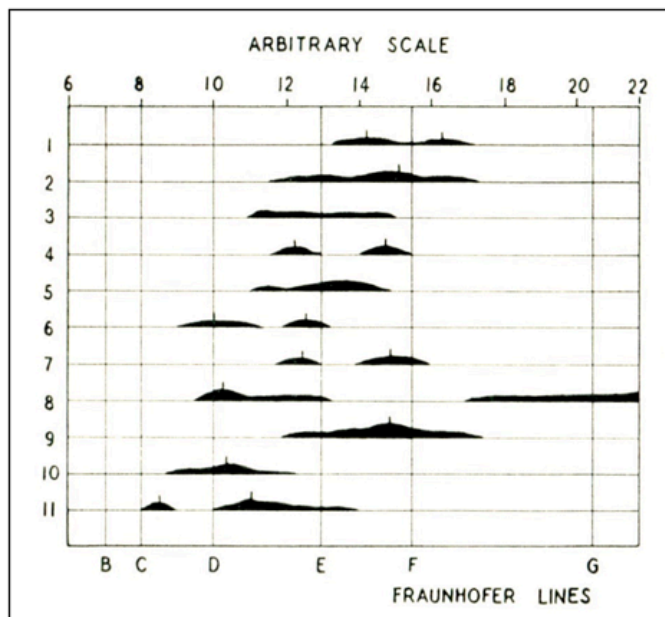


Figure 20. The hand-drawn visible absorption spectra for 11 different organic dyes, circa 1905-1919.

of several well documented emission lines (Fraunhofer lines) superimposed for calibration. There is no quantitative y-axis since the absorption envelopes have been drawn free hand.

Figure 21 shows the UV absorption spectrum of benzene as measured by Hartley in 1885.<sup>25</sup> Here the x-axis corresponds to the wavenumber or inverse wavelength in units

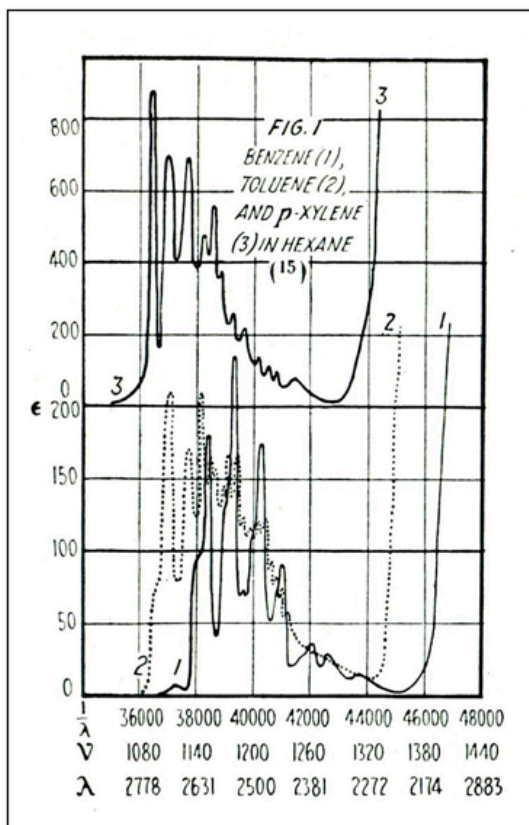


Figure 22. The hand-drawn UV spectrum of benzene (curve 1) and related aromatics as given by Henri in 1929. Note that this is the inverse of figure 21.

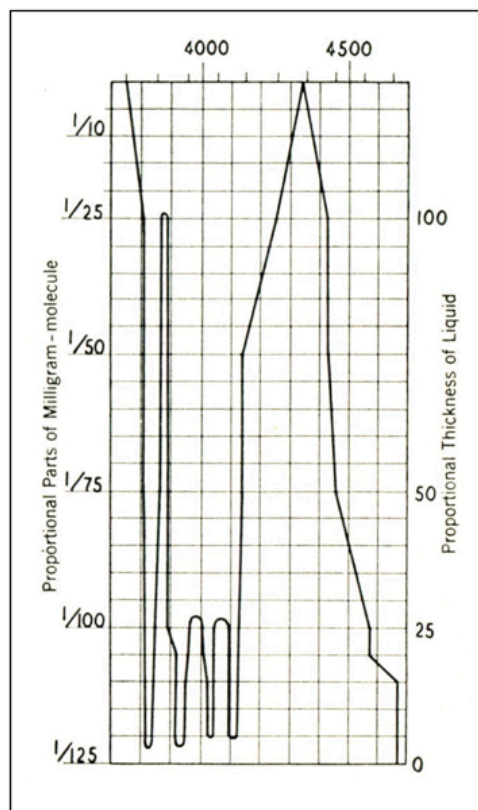


Figure 21. The hand-drawn UV spectrum of benzene as measured by Hartley in 1885 from a photographic tracing.

of  $\text{cm}^{-1}$ , and the y-axis to the transmittance as measured by the thickness of the sample required to block all light.

Figure 23 also shows the UV spectrum of benzene and related aromatics as reported by Victor Henri in 1929.<sup>26</sup> Here the x-axis is alternatively given either in wavenumber, frequency or wavelength, and the y-axis in units of  $\epsilon$ , where, via rearrangement of equation 1:

## SPECTROPHOTOMETERS

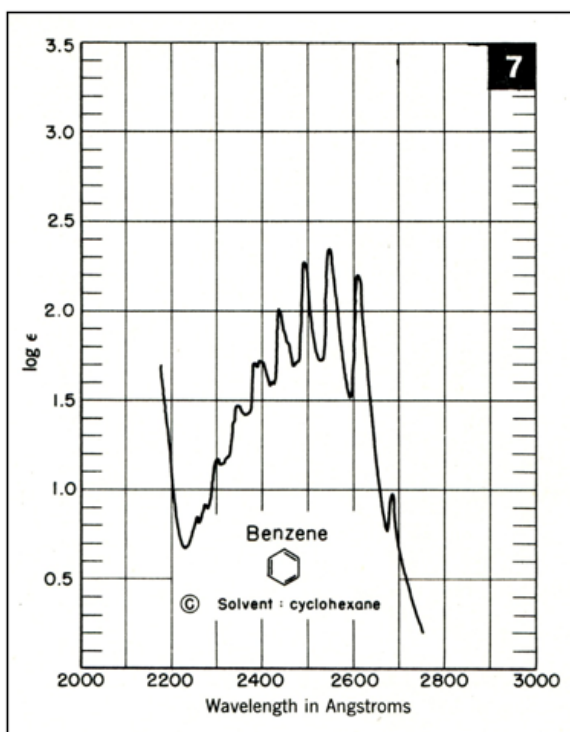


Figure 23. Hand-drawn UV absorption spectra of benzene as given by Friedel and Orchin in 1951.

$$\epsilon = -\log(T)/bc \quad [2]$$

The reason for this peculiar choice is that it allows for intercomparison of spectra collected at varying concentrations and path lengths

Finally, figure 23 once again shows the UV absorption spectrum of benzene, this time as reported in the 1951 compilation by Friedel and Orchin<sup>27</sup> and plotted by hand from data collected on a Beckmann DU. Here the  $x$ -axis corresponds to the wavelength in Ångstroms and the  $y$ -axis to  $\log \epsilon$ .

One of the earliest attempts to remedy this situation was made by A. C. Hardy of MIT.<sup>28</sup> Starting in the 1920s he began developing a sophisticated spectrophotometer in which the output from the photocells was amplified sufficiently to drive a chart recorder and thus automatically print the resulting spectrum. In the case of hand-plotted spectra one had to interpolate the graph between discrete data points and the smaller details were often lost, whereas with the chart recorder the plot was truly continuous. Hardy's instrument was commercially developed by the General Electric Company (figure 24), which began marketing it in the late 1930s.<sup>29, 30</sup> Originally restricted to the visible region of the electromagnetic spectrum, a UV-visible version was also eventually developed. Unfortunately the resulting instrument was large, complex, and quite expensive (around \$8000 in 1947 compared to \$200-\$400 for a filter spectrophotometer, and \$100-\$200 for a traditional visual colorimeter). As a result, most of them were sold either to well-funded industrial laboratories or to government laboratories. The situation was

## OESPER MUSEUM BOOKLETS

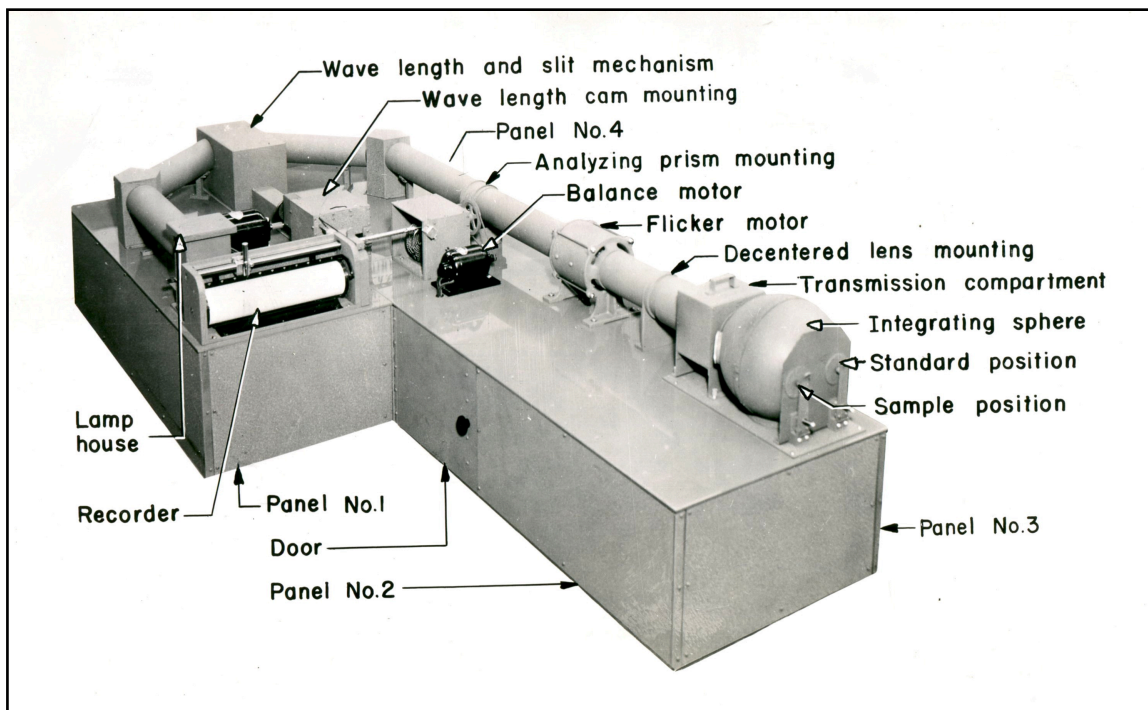


Figure 24. The circa 1938 General Electric or Hardy recording spectrophotometer.

aptly summarized by the Snells in 1948:<sup>31</sup>

*It [i.e. the GE Hardy] is so complex and expensive that only a relatively small number have been built, about 100 at the end of 1948. Such an instrument has unquestionable advantage in initial research on a specific colorimetric method, thereby determining and recording the absorption curve instrumentally over the entire range. The unit is sufficiently complicated and the sources of difficulties so varied, that a skilled operator should be in charge, although data may be obtained by a technician.*

By 1947 a more practical bench-top alternative was available in the form of the self-recording Cary-11 UV-visible spectrophotometer (figure 25)<sup>32</sup> and by the 1950s individual electric chart recorders could also be purchased, though they did not become common in laboratory supply catalogs until the 1960s.<sup>33</sup>

## SPECTROPHOTOMETERS

### IR Spectrophotometers

The infrared or IR region of the electromagnetic spectrum is usually considered to extend roughly from 7500-1000000Å. As with the UV region, IR radiation is invisible to the human eye and can only be detected using special photographic emulsions or by means such devices as thermocouples, bolometers, and radiometers. Special materials, such as rock salt, are also required for both the prism and cell windows.

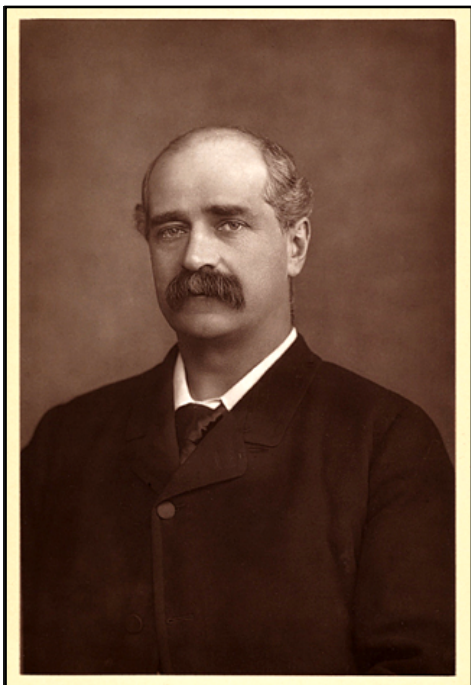


Figure 26. William Abney  
(1843-1920)



Figure 25. The circa 1947 Cary-11 recording UV-visible spectrophotometer.

The first significant attempt to explore the IR spectra of organic compounds is usually attributed to the British team of William Abney (figure 26) and Edward Festing,<sup>17, 34, 35</sup> who in 1881 succeeded in photographing the near IR spectra of various organic species and who, like Hartley, attempted to correlate the resulting absorptions with the presence of various functional groups. However, despite a few sporadic attempts by others, the first truly comprehensive study of IR spectra is due to an American physicist in the employ of the National Bureau of Standards by the name of William Coblentz (figure 27). In his two-volume study, *Investigations of Infra-Red Spectra*, published between 1905 and 1906, Coblentz hand-recorded the IR absorption

## OESPER MUSEUM BOOKLETS

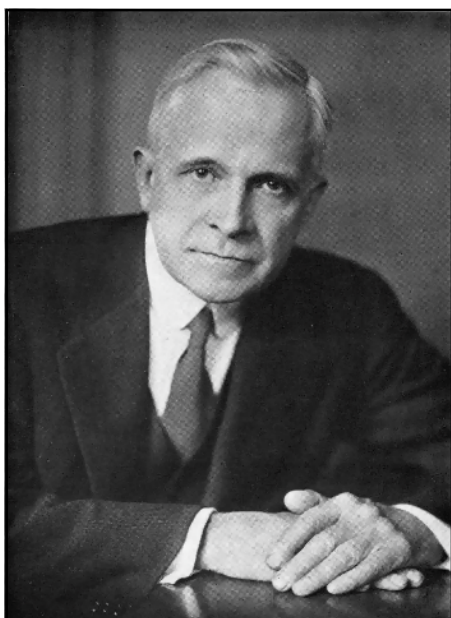


Figure 27. William W. Coblentz  
(1873-1962)

spectra of more than 132 compounds – using rock salt for the prism and cell windows, a Nichols radiometer as the detector, and a Nernst lamp as the radiation source – and noted several significant structural correlations.<sup>36</sup> Nevertheless, as with early studies of UV spectra, the specialized apparatus and the tediousness of the necessary measurements largely precluded its widespread adoption by practicing organic chemists.

This situation radically changed with the coming of World War II and the resulting concerns over petroleum and synthetic rubber production, which prompted the introduction of several commercial IR spectrophotometers by such companies as Perkin-Elmer and Beckman in the United States and Hilger and Grubb-

Parsons in England. Though some of these instruments were not self-recording, most were. UV-visible spectra, which are due to electron excitation, generally consist of only a few broad peaks, culminating in a massive charge-transfer peak at short wavelengths. Though they can yield important information on electronic trends when applied to a series of closely related compounds, they generally do

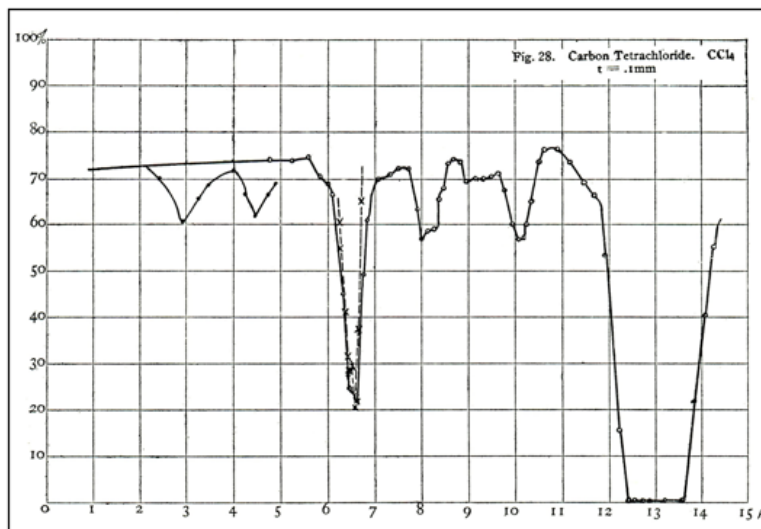


Figure 28. The IR transmittance spectrum of carbon tetrachloride as reported by Coblentz in 1905.



## SPECTROPHOTOMETERS

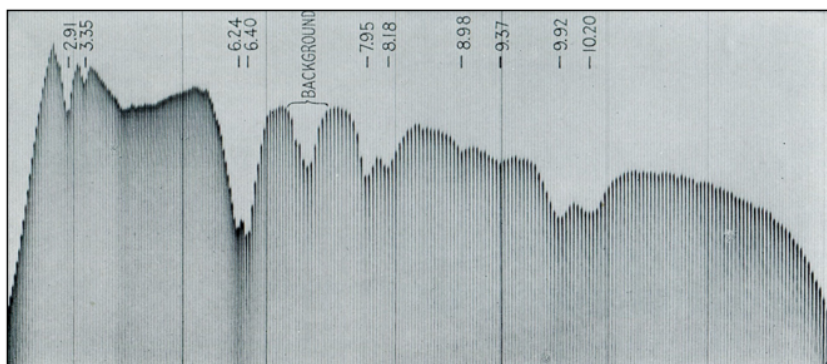


Figure 29. The IR spectrum of carbon tetrachloride as reported by Randall et al in 1949.

not contain a great deal of specific structural information about individual molecules. IR spectra, on the other hand, which are due to the excitation of molecular vibrations and rotations, are generally far more complex and contain a great deal of structural information. Here the detail provided by a chart recorder, versus the smoothed interpolations of hand-plots, is a paramount importance, as may be seen from a comparison of hand-plotted spectrum of carbon tetrachloride reported by Coblentz in 1905 (figure 28) versus the machine recorded version reported by Randall *et al* in 1949 (figure 29).<sup>37</sup>

Early recording IR spectrophotometers were rather large and bulky (figure 30), and – in the words of one science historian – it was really the introduction of the relatively inexpensive and relatively compact Perkin-Elmer “Infracord” in 1957 that finally “brought infrared spectrophotometry within the reach of the organic chemistry laboratory and, in time, even the undergraduate teaching laboratory.”<sup>17</sup>



Figure 30. The rather bulky circa 1951 “Model 21 Double-Beam Infrared Spectrophotometer” made by Perkin-Elmer. This was in fact compact compared to the earlier Perkin-Elmer Model 12-C and the Beckman IR-3.

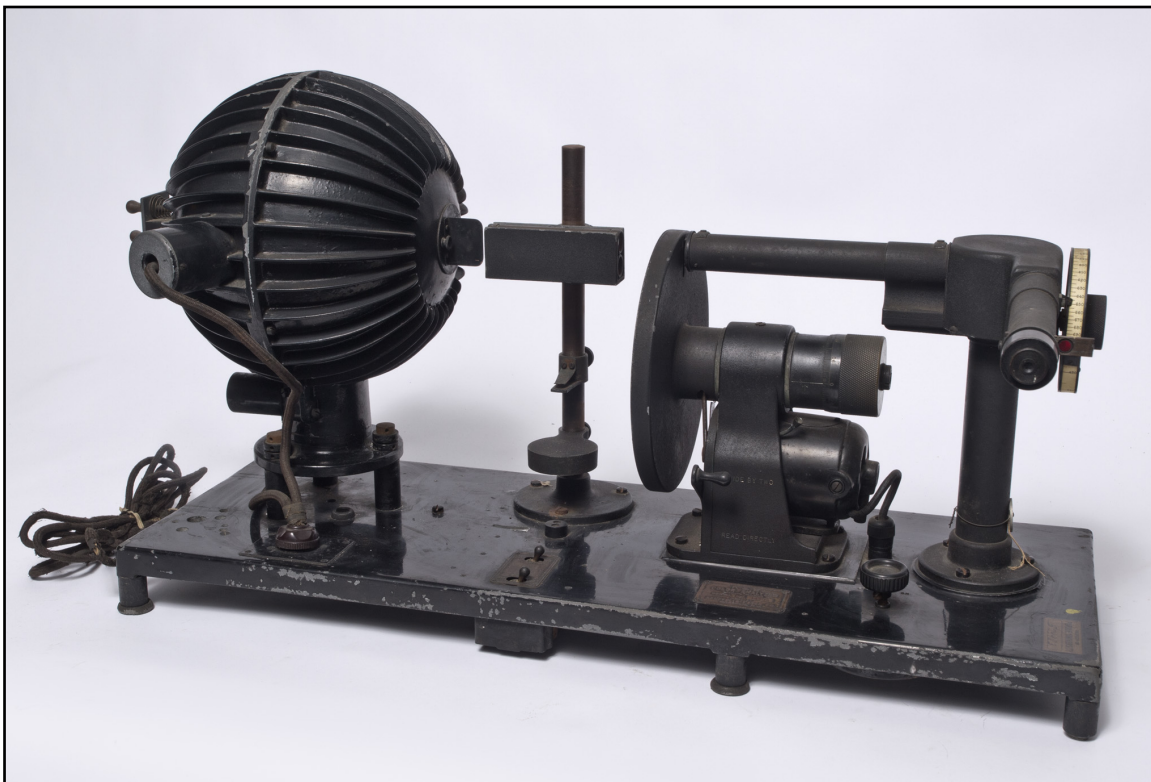
## OESPER MUSEUM BOOKLETS

### **Museum Holdings**

The Mellon Spectrophotometer Collection contains examples of American instruments roughly spanning the period 1925-1975. Though many other varieties were also produced during this period, the collection is nevertheless fairly representative of the gradual transition between the filter photometer, on the one hand, and fully computerized and digitized modern spectrophotometer on the other. Ironically, the most obvious omissions are surviving examples of both the Hardy and the Cary-11 recording spectrophotometers – ironic because both were part of the original Mellon Collection. However, both instruments were so large and so heavy that the author was unable to transport them back to Cincinnati in his car and, even if he had, we did not have the room to properly store or display them. To the best of my knowledge, both still reside in the attic of the old chemistry building at Purdue University.

## SPECTROPHOTOMETERS

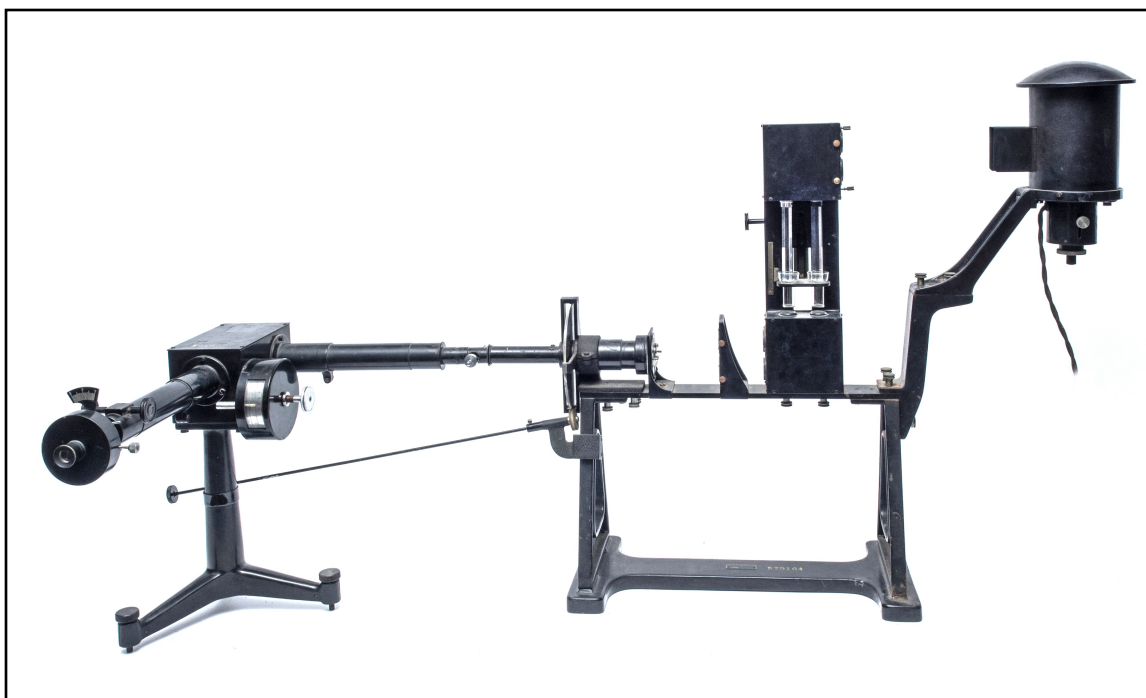
### Visual Spectrophotometers



M. G. Mellon Spectrophotometer Collection

Figure 31. A circa 1925 (29.5" x 16" x 10.75") "K & E Color Analyzer" or direct reading visible spectrophotometer made by the Keuffel and Esser Co. of Hoboken, NJ. Serial No. 44404. It can be used to measure either reflectance spectra or transmittance spectra and employs a rotating sector photometer. Compare with figures 5 and 6.

OESPER MUSEUM BOOKLETS

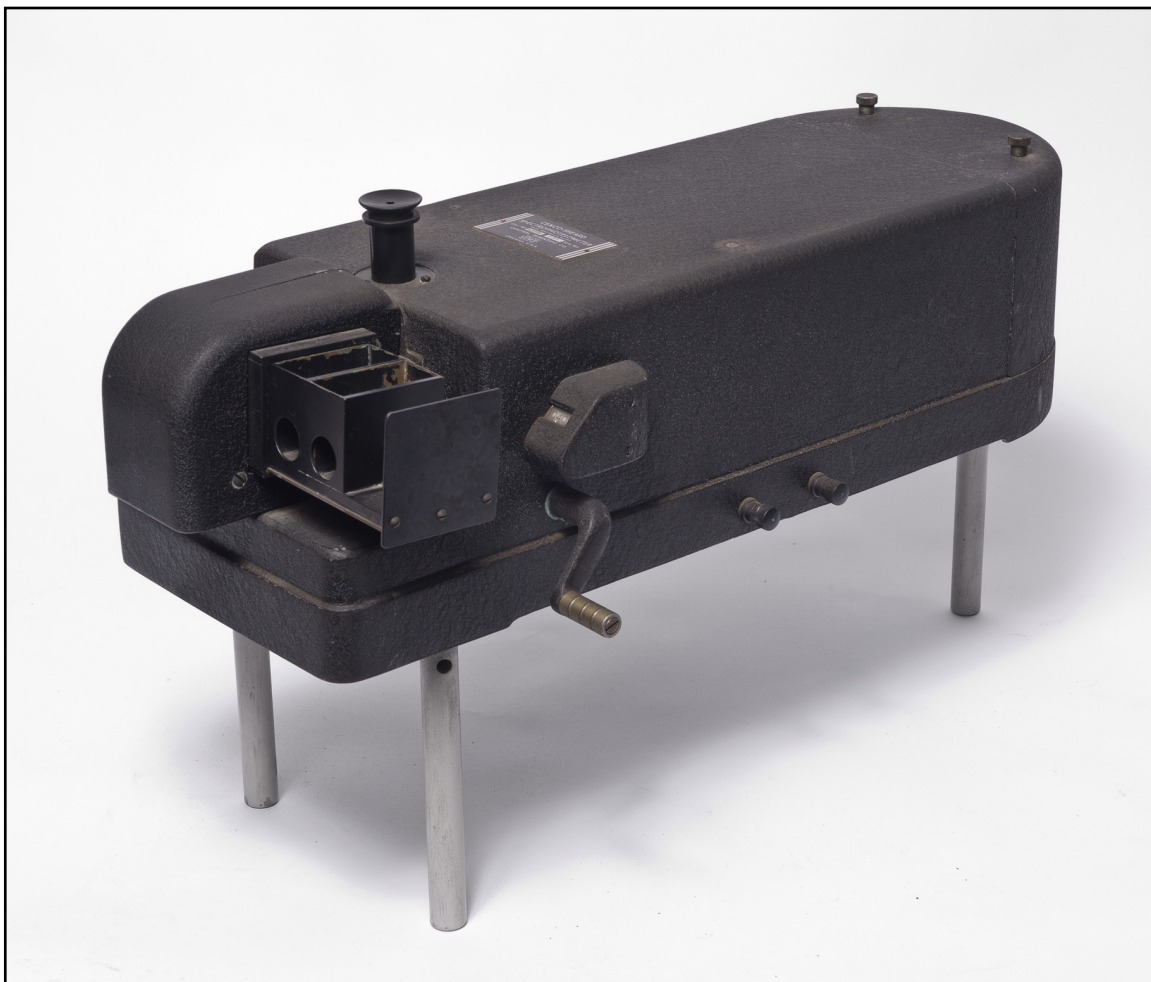


M. G. Mellon Spectrophotometer Collection

Figure 32. A circa 1930 (51" x 28.5" x 20") "Universal Spectrophotometric Outfit" for visible spectrophotometry made by the Bausch & Lomb Optical Co. of Rochester, NY. It is missing the metal base and small light attachment for illuminating both the spectrometer and photometer scales. It employs a polarizing photometer controlled by means of the rod that extends to the spectrometer. The special vertical cell attachment is shown, though optional light and cell configurations were also available for the measurement of reflectance spectra and the use of horizontal cells. Compare with figures 7 and 8.

## SPECTROPHOTOMETERS

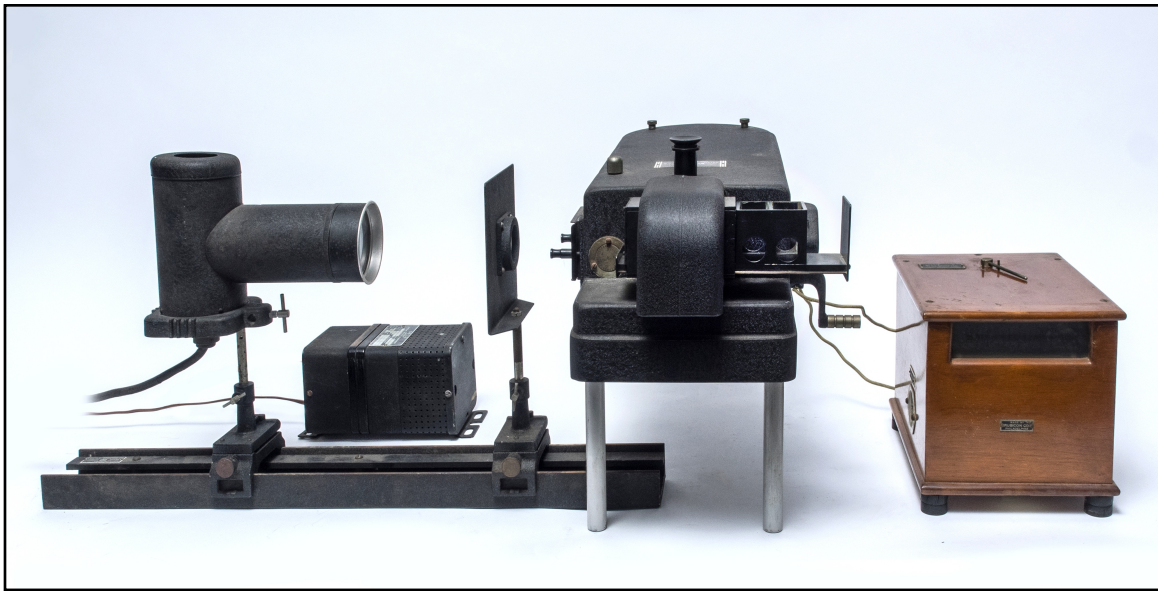
### Photoelectric Visible Spectrophotometers



M. G. Mellon Spectrophotometer Collection

Figure 33. A circa 1941 (23" x 14" x 8") "Cenco-Sheard Spectrophotometer" for visual spectrophotometry made for the Central Scientific Co. of Chicago. Serial No. 171. The crank on the right changes the wavelength which can also be visually monitored by means of the eyepiece on top. Also visible are the cell compartments for the reference and sample and the binding posts for connection to the external galvanometer. Compare with figures 9 and 10.

OESPER MUSEUM BOOKLETS



M. G. Mellon Spectrophotometer Collection

Figure 34. The previous instrument with all of the necessary externals. Besides the external light source, this single-channel instrument requires a constant voltage transformer (left) and an external galvanometer (right) for actual operation. Compare with figure 9.

## SPECTROPHOTOMETERS



M. G. Mellon Spectrophotometer Collection

Figure 35. A circa 1940 (13.5" x 12.25" x 7") "Model 10" visual spectrophotometer made by the Coleman Electric Co. of Maywood, IL. Instrument No. 3521. This single-cell instrument uses a "DM" double Wood's monochromator (a combination prism and grating). The sample and reference can be alternately slid in front of the beam. It contains its own battery as well as a wall plug and built-in rectifier for recharging, but must be connected to an external Coleman electrometer in order to read the output of the photo-tube directly as percent transmittance. Compare with figure 11.

OESPER MUSEUM BOOKLETS



M. G. Mellon Spectrophotometer Collection

Figure 36. The previous instrument with the requisite Coleman galvanometer attached. This is a circa 1940 (10" x 8" x 8") "Model 310 Coleman pH Electrometer." Instrument No. 2930.



## SPECTROPHOTOMETERS



M. G. Mellon Spectrophotometer Collection

Figure 37. A circa 1945 (13.5" x 9.75" x 6.5") "Junior Spectrophotometer" for visible spectrophotometry made by Coleman Instruments, Inc. of Maywood, IL. Model 6A. Serial No. A-11546. The detachable clear plastic transmittance scale can be interchanged with others calibrated directly in concentration units for a given solute. As a single channel instrument, it requires use of either a 6V battery or a constant voltage transformer. The monochromator is a diffraction grating. Compare with figure 12.

OESPER MUSEUM BOOKLETS



M. G. Mellon Spectrophotometer Collection

Figure 38. A circa 1950 (13.5" x 9.75" x 6.5") "Junior Spectrophotometer" for visible spectrophotometry made by Coleman Instruments, Inc. of Maywood, IL. Model 6D. Serial No. 45178. This is a later version of the previous instrument. The detachable clear plastic transmittance scale can be interchanged with others calibrated directly in concentration units for a given solute. As single channel instrument, it requires use of either a 7V battery or a constant voltage transformer.

## SPECTROPHOTOMETERS



M. G. Mellon Spectrophotometer Collection

Figure 39. A circa 1955 (13.75" x 10.5" x 7") "Spectronic 20" visible spectrophotometer made by the Bausch and Lomb Optical Company of Rochester NY. Lacquered metal case. Compare with figure 13.

OESPER MUSEUM BOOKLETS



M. G. Mellon Spectrophotometer Collection

Figure 40. A circa 1986 (16" x 12.5" x 8") "Spectronic 20" visible spectrophotometer made by the Milton Roy Company of Philadelphia, which purchased the rights to this spectrophotometer design from Bausch & Lomb in 1985. Lacquered metal case. Compare with figure 15.

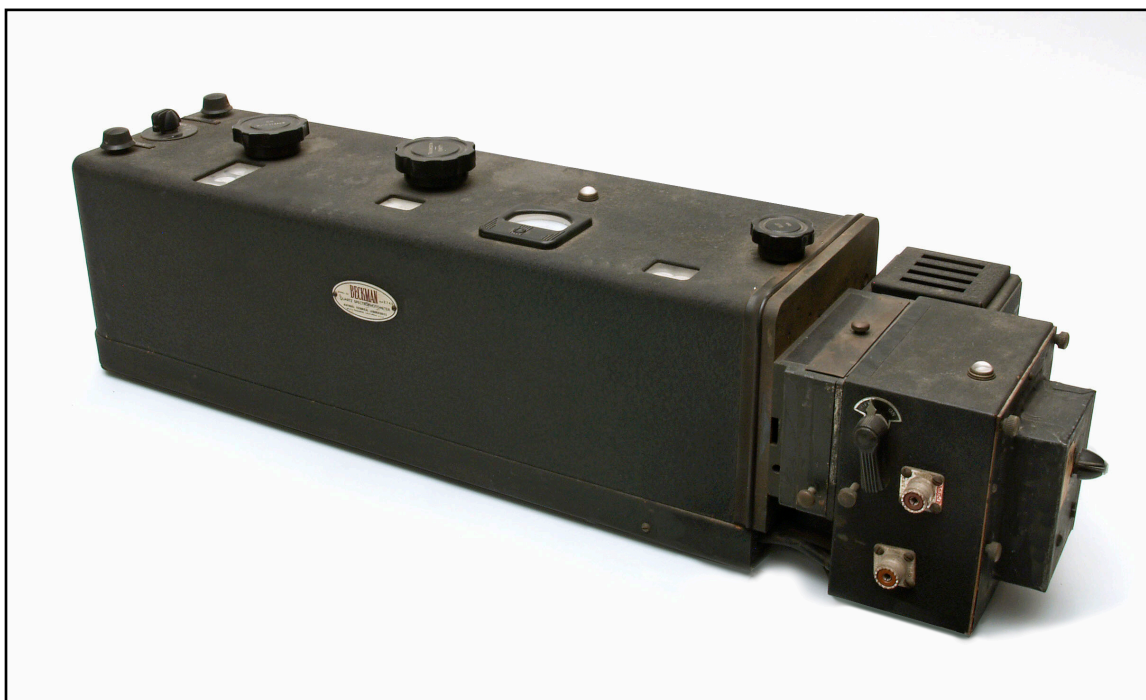
## SPECTROPHOTOMETERS



M. G. Mellon Spectrophotometer Collection

Figure 41. A circa 1996 (15.75" x 12" x 8.25") "Spectronic 20D+" visible spectrophotometer made by Spectronic Instruments which purchased the rights to this spectrophotometer design from Milton Roy in 1995. The analog scale of the earlier models has been replaced by a red digital LED display with several alternative choices of readout, and the metal case with a plastic case. Compare with figure 15.

## Ultraviolet-Visible Spectrophotometers



M. G. Mellon Spectrophotometer Collection

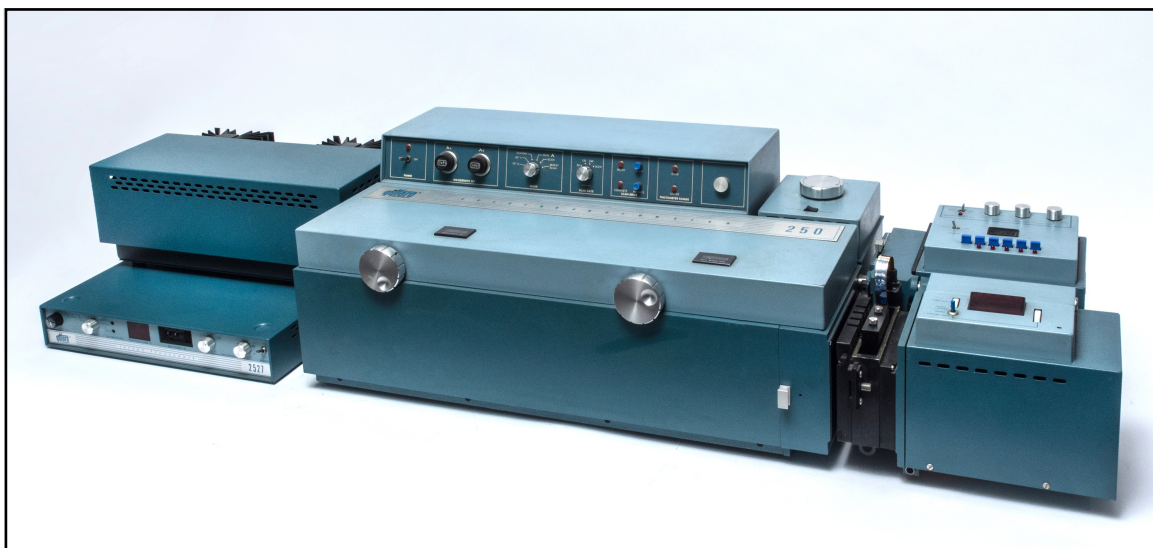
Figure 42. A circa 1945 (31" x 9.5" x 7.75") "Beckman Quartz Spectrophotometer, Model DU" for UV-visible spectrophotometry made by National Technical Laboratories of South Pasadena, CA (later renamed Beckman Instruments). Serial No. 2749. This extremely popular instrument requires use of either a constant voltage transformer or a 6 volt car battery. Compare with figure 17.

## SPECTROPHOTOMETERS



M. G. Mellon Spectrophotometer Collection

Figure 43. A circa 1963 (34.5" x 21" x 9.25") "Hatischi Model 139 UV-Visible Spectrophotometer" made by Perkin-Elmer of Norwalk CT. Compare with figure 19.



M. G. Mellon Spectrophotometer Collection

Figure 44. A circa 1976 "Model 250 UV-Visible Spectrophotometer" made by Guilford Instrument of Oberlin, OH, with an optional "Model 2527 Thermo-Programmer" (far left). The spectrophotometer portion measures 38" x 14" x 11.5".

OESPER MUSEUM BOOKLETS



Jensen-Thomas Apparatus Collection

Figure 45. A circa 1950 (13.25" x 9.5" x 8.75") portable electric chart-recorder made by General Electric of Schenectady, NY. Whether it ever occurred to anyone to connect this particular model to a spectrophotometer is unknown. Most photos from the 1950s show the use of massive floor-model recorders instead.



## SPECTROPHOTOMETERS

### Infrared Spectrophotometers



M. G. Mellon Spectrophotometer Collection

Figure 46. A circa 1958 (27" x 18.75" x 16.75") "Model 137 Infracord" recording IR spectrophotometer made by the Perkin-Elmer Corporation of Norwalk, CT

OESPER MUSEUM BOOKLETS



M. G. Mellon Spectrophotometer Collection

Figure 47. A circa 1965 (29.5" x 20" x 16.75") "Model 337 Grating Infrared Spectrophotometer" made by the Perkin-Elmer Corporation of Norwalk, CT.

## SPECTROPHOTOMETERS

### **The Spectrophotometer's Significance in the History of Chemistry**

The significance of spectrophotometry changed over time, as did the relative importance of the various instruments discussed above. As originally conceived by Vierordt, and continuing through the development of such instruments as the Coleman “Junior Spectrophotometer” and the Bausch & Lomb “Spectronic 20,” its focus remained essentially identical to that of traditional chemical colorimetry – namely the determination of the concentration of a particular colored complex by measuring the intensity of its color as a percent transmittance. As such, its greatest area of application continued to be in the field of clinical chemistry where its advantage over the traditional visual colorimeter and the filter photometer lay in its superior monochromator and consequent ability to select a wavelength that would optimize the intensity of a given characteristic absorption.

Beginning in the 1920s with the development of such visual spectrophotometers as the Keuffel & Esser “Color Analyzer” and the Bausch & Lomb “Universal Spectrophotometric Outfit,” and continuing on through the “GE-Hardy Recording Spectrophotometer,” the emphasis for physicists and technologists, at least, became the objective “fingerprinting” of various colors over the entire visible spectrum. Thus in a popular article on the early development of the Hardy recording spectrophotometer, which appeared in the September 1929 issue of *Oil & Fat Industries*, the anonymous author lauded its potential importance to industry “in nearly every branch of which control of the color of products is necessary,” and illustrated his point by reproducing the full visible reflectance spectrum of a ripe banana versus a green banana!<sup>38</sup>

Yet a third emphasis, and ultimately the most important for the history of chemistry, goes back to the 19th century and the pioneering work of Hartley and of Abney and Festing and became particularly prominent after the rise of commercial UV-visible and IR instruments, both during and after World War II, such as the Beckman “DU” and the Perkin-Elmer “Model 21” – namely the use of these instruments to fingerprint molecules rather than colors and to ultimately correlate these fingerprints with their underlying molecular structures. In keeping with this

## OESPER MUSEUM BOOKLETS

trend, chemists began amassing large collections of characteristic spectra for identification purposes. We have already noted the early collections of UV spectra by Henri (1929)<sup>26</sup> and by Friedel and Orchin (1951),<sup>27</sup> and the collections of IR spectra by Coblenz (1905)<sup>36</sup> and by Randall et al (1949).<sup>37</sup> Other early collections of IR spectra include those by Barnes et al (1944)<sup>39</sup> and the massive collections published by the Sadtler Research Laboratories (1956 and subsequently).<sup>40</sup> Initially structure determination was purely empirical and was based on lists of experimentally determined IR frequencies for various kinds of bonds. As the theory of IR spectra developed, it was also able to supplement these results with more fundamental structural insights, at least in the case of simple gas-phase molecules.<sup>41</sup>

A 1965 survey reported that between 1952 and 1965 UV-visible spectra were used in between 20% and 25% of all papers published in American chemical journals and that use of IR spectra increased from 12.5% to 36% during the same period.<sup>42</sup> Though both techniques continue to be of great importance, starting around 1970 they began to be displaced as the primary and definitive methods of choice for the instrumental determination of molecular structure by X-ray diffraction, in the case of crystalline solids, and by NMR in the case of liquids.

Yet a second index for measuring the rise of spectrophotometry and its increasing importance to chemists is through an examination of its coverage in textbooks and especially in those dealing with instrumental analysis – a topic which first made an appearance in the late 1940s. Thus the 1939 monograph on *Chemical Spectroscopy* by Brode either discusses or mentions in passing four varieties of visual spectrophotometers made by Keuffel & Esser, Bausch & Lomb, Hilger, and by Gaertner, as well as the photoelectric “GE-Hardy Recording Spectrophotometer” and several others from the research literature that were apparently never produced commercially.<sup>9</sup> The 1942 monograph on *Optical Methods of Chemical Analysis* by Gibbs discusses the visual spectrophotometers made by Bausch & Lomb, Hilger-Nutting, Schmidt & Haensch, Weigert, Walsh and Böttger, as well as such photoelectric models as the “Cenco-Sheard Spectrophotometer,” the “Coleman Models 10 and 11,” the “GE-Hardy,” the “Beckman DU,” and also mentions a half dozen more in passing whose commercial status remains ambiguous.<sup>11</sup>

## SPECTROPHOTOMETERS

Interestingly this book also states that there were still serious problems with the routine application of IR spectrophotometry and explicitly mentions only a single instrument designed Wright in 1941. The 1945 booklet by Mellon mentions five different visual spectrophotometers and eleven different photoelectric spectrophotometers, but makes no mention of IR instruments.<sup>31</sup>

It is only with the publication of the 1948 textbook, *Instrumental Methods of Analysis*, by Willard, Merritt and Dean that a detailed discussion of individual visual spectrophotometers finally disappears.<sup>43</sup> The chapter on spectrophotometry devotes only a single paragraph to these instruments and justifies its brevity by noting that they “are not widely used at present.” As for visible and/or UV photoelectric instruments, mention is made of the “Cenco-Sheard Spectrophotometer,” the “Coleman Model 10,” the “Beckman DU,” and the “GE-Hardy.” In addition, one finally encounters a brief survey of commercial IR instruments, including the “Perkin-Elmer Model 12-C,” the “Beckman Model IR-2,” and the “Baird Two-Beam Infrared Spectrophotometer.” The volume on colorimetry, published that same year by the Snells, also makes no mention of visual spectrophotometers, and discusses the same four visible and/or UV photoelectric instruments mentioned by Willard et al.<sup>12</sup> Given its special focus, this book contains, for obvious reasons, no discussion of IR spectrophotometers. From this point on, the format established by Willard et al becomes the standard pattern for such later texts as Harley and Wibberley (1954),<sup>44</sup> Ewing (1954),<sup>45</sup> and Biffin and Seaman (1956)<sup>46</sup> – all mention of visual instruments has disappeared and there are increasingly detailed discussions of IR instruments.

In summary, we see that the decade 1940-1950 was key to the development of the photoelectric spectrophotometer. It is this decade which finally saw the complete displacement of the visual spectrophotometer, whose roots can be traced back to the last quarter of the 19th-century, as well as the rise to prominence of commercial photoelectric UV and IR instruments, both of which also have late 19th-century origins. This is, of course, the so-called “instrument revolution” often spoken of by historians of chemistry. But this revolution consisted less in establishing totally new methods of instrumental analysis than in creating electronic

## OESPER MUSEUM BOOKLETS

versions of older methods that were now simple enough and convenient enough for the practicing organic and inorganic chemist, with no special interest in instrument design *per se*, to apply in the laboratory on a routine basis as a means to other ends.

### References and Notes

1. K. Vierordt, *Die Anwendung des Spectralapparates zur Photometrie der Absorptionsspectren und zur quantitativen chemischen Analyse*, Laupp: Tübingen, 1873.
2. K. Vierordt, *Die quantitative Spectralanalyse in ihrer Anwendung auf Physiologie, Physik, Chemie, und Technologie*, Laupp: Tübingen, 1876.
3. For a brief English-language summary of Vierordt's work, see J. Traube, *Physico-Chemical Methods*, Blakinson: Philadelphia, 1898, pp. 193-201.
4. G. Krüss, H. Krüss, *Kolorimetrie und Quantitative Spektralanalyse in ihrer Anwendung in der Chemie*, Voss: Hamburg, 1891; 2nd ed. 1909. See also G. Krüss, *Spezielle Methoden der Analyse: Anleitung zur Anwendung physikalischer Methoden in der Chemie*, Voss: Hamburg, 1893.
5. C. W. Keuffel, "A Direct Reading Spectrophotometer," *J. Optical Soc. Am.*, **1925**, *11*, 403-410.
6. A rotating sector photometer attenuates the intensity of a light beam by interrupting the beam with a rotating metal disk with slots cut in it. The degree of attenuation depends on the width of the slots and the speed of rotation.
7. *Universal Spectrophotometer Outfit*, undated typewritten manual plus price list presumably provided by Bausch & Lomb. Copy on file in the Oesper Collections.
8. A polarization photometer polarizes the reference and sample light beams 90° to one another and then matches their intensities via rotation of an analyzer or Nicol prism.
9. See W. R. Brode, *Chemical Spectroscopy*, Wiley: New York, NY, 1939, figures 8.18 and 8.20.
10. "A New Spectrophotometer," *Cenco News Chats*, Oct. 1941, p. 114.
11. A diagram of the circuitry in this spectrophotometer may be found in T. R. P. Gibbs, *Optical Methods of Analysis*, McGraw-Hill: New York, NY, 1942, p. 96.

## SPECTROPHOTOMETERS

12. For a diagram, see reference 11: for a photograph see G. M. Mellon, *Colorimetry for Chemists*, Smith: Columbus OH, 1945, p. 72.
13. *Operating Directions for the Model 6A Coleman Junior Spectrophotometer*, Bulletin D-174, Coleman: Maywood, IL, 1945.
14. *Coleman Junior Spectrophotometer: The Successor to Colorimeters*, Bulletin B-211, Coleman: Maywood, IL, 1948.
15. C. H. Brumley, "A New Grating Colorimeter-Spectrophotometer" Paper presented at the Los Angeles Meeting of the Optical Society of America, 14 October, 1954. Apparently never published. Transcript on file in the Oesper Collections.
16. *Spectronic 20 Reference Manual*, Bausch & Lomb: Rochester, NY, no date.
17. J. Eklund, P. Morris, "Spectrophotometer," in R. Bud, D. J. Warner, Eds., *Instruments of Science: An Historical Encyclopedia*, Garland: New York, NY, 1998, pp. 558-561.
18. A photo of Hartley's original quartz prism spectroscopy may be found in F. Greenway, *Chemical Laboratories and Apparatus from 1850*, Science Museum: London, 1966, p. 4-5.
19. W. N. Hartley, "Researches on the Relation Between the Molecular Structure of Carbon Compounds and their Absorption Spectra," *J. Chem. Soc.*, **1881**, 39, 153-168 and subsequent papers in the same series.
20. H. H. Cary, A. O. Beckman, "A Quartz Photoelectric Spectrophotometer," *J. Optical Soc. Am.*, **1941**, 31, 682-689.
21. R. D. Simoni, R. L. Hill, M. Vaughan, H. Tabor, "A Classic Instrument: The Beckman DU Spectrophotometer and Its Inventor, Arnold O. Beckman," *J. Biol. Chem.*, **2003**, 278(49), 79-81.
22. *Hitachi Perkin Elmer Model 139 Ultraviolet-Visible Grating Spectrophotometer*, Perkin-Elmer: Norwalk, CT, no date.
23. J. Formanek, *Qualitative Spektralanalyse anorganischer und organischer Körper*, 2nd ed., Mückenberger: Berlin, 1905.
24. R. E. Watson, *Colour in Relation to Chemical Constitution*, Longmans, Green & Co: London, 1919.
25. W. N. Hartley, "Researches on the Relation Between the Molecular Structure of

## OESPER MUSEUM BOOKLETS

Carbon Compounds and their Absorption Spectra, Part VII," *J. Chem. Soc.*, **1885**, 39, 685-757.

26. V. Henri, "Quantitative Determination of Ultra-Violet Absorption Spectra in Solutions of Organic Substances," in E. W. Washburn, Ed., *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. 5, McGraw-Hill, New York, NY, 1929, pp. 359-379.

27. R. A. Friedel, M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, Wiley: New York, NY, 1951.

28. A. C. Hardy, "A New Recording Spectrophotometer," *J. Optical Soc. Am.*, **1935**, 25, 305-311.

29. *Description of a Recording Photoelectric Spectrophotometer*, General Engineering Laboratory, General Electric: Schenectady, NY, October, 1935. Copy on file, Oesper Collections.

30. J. L. Michaelson, "Construction of the General Electric Recording Spectrophotometer," *J. Optical Soc. Am.*, **1938**, 28, 365-371.

31. F. D. Snell, C. T. Snell, *Methods of Colorimetric Analysis*, Vol. 1, 3rd, ed., Van Nostrand: New York, NY, 1948, pp. 66-67.

32. R. H. Munch, "Instrumentation: A New Ultraviolet Spectrophotometer," *Ind. Eng. Chem.*, **1947**, 39(April), 75A-76A.

33. Thus nine different chart recorders are offered for sale in the catalog *Scientific Apparatus and Reagents*, Arthur H. Thomas Co: Philadelphia, PA, 1968, pp. 909-914.

34. A. Dronsfield, J. Adetunji, P. Morris, "Infrared Spectroscopy – Why Did It Take so Long?," *Educ. Chem.*, **2005**, 42(2), 50-53.

35. W. Abney, E. R. Festing, "On the Influence of the Molecular Grouping in Organic Bodies on their Absorption in the Infra-Red Region of the Spectrum," *Phil. Trans.* **1881**, 172, 887-918.

36. W. W. Coblentz, *Investigations of Infra-Red Spectra*, 2 Vols., Carnegie Institution: Washington, DC, 1905-1906.

37. H. M. Randall, R. G. Fowler, N. Fuson, J. R. Dangle, *Infrared Determination of Organic Structures*, Van Nostrand: New York, NY, 1949.

38. Anon., "The Hardy Recording Spectrophotometer: New Electrically Controlled



## SPECTROPHOTOMETERS

Instrument Eliminates Visual Errors in Colorimetry,” *Oil & Fat Ind.*, **1929**, 6 (Sept.) 31-33.

39. R. B. Barnes, R. C. Gore, U. Liddel, V. Z. Williams, *Infrared Spectroscopy: Industrial Applications and Bibliography*, Reinhold: New York, NY, 1944.

40. *The Sadtler Standard Spectra*, Sadtler Research Laboratories: Philadelphia, PA, multivolume series begun in 1956.

41. P. J. Wheatley, *The Determination of Molecular Structure*, Clarendon: Oxford, 1959.

42. *Chemistry: Opportunities and Needs*, National Academy of Sciences: Washington, DC. 1965, Chapter 4.

43. H. H. Willard, L. L. Merritt, J. A. Dean, *Instrumental Methods of Analysis*, Van Nostrand: New York, NY, 1948, Chapter 4.

44. J. H. Harley, S. E. Wiberley, *Instrumental Analysis*, Wiley: New York, NY, 1954, Chapters 3-5.

45. G. W. Ewing, *Instrumental Methods of Chemical Analysis*, McGraw-Hill: New York, NY, 1954, Chapters 3-4.

46. F. M. Biffin, W. Seaman, *Modern Instruments in Chemical Analysis*, McGraw-Hill, New York, NY, 1956, Chapters 4-5.



# Oesper Museum Booklets on the History of Chemical Apparatus

No. 1  
Polarimeters

No. 2  
Melting Point Apparatus

No. 3  
Refractometers

No. 4  
Colorimeters

No. 5  
Filter Photometers

No. 6  
Spectrophotometers

*Forthcoming*

Spectroscopes

Voltaic Cells

