Photoelectric Color Measurements

New Precision Instrument Useful in Plotting Energy Curves of the Spectra of Oils[1]

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SUMMARY

PRECISION color measurements of oils, fats, waxes, etc. can be made with a Photoelectric Spectrophotometer, and their absorption or reflection determined with a degree of exactness not possible with any visual method.

Oils of similar chemical constitution, although widely different in color, give similar spectral absorption curves.

Oils of dissimilar chemical constitution, although alike when measured on the Lovibond scale, give dissimilar spectral absorption curves.

This photo-electric method of measuring color may enable the oil chemist to make use of a method of color measurement that will disclose fundamental data.

THE December, 1915, issue of the Journal of Franklin Institute, Dr. H. E. Ives said "A spectrophotometric table derived from at least 25 points (for a continuous spectrum) gives the only unique description of a color, and it appears probable to the writer that the requirements of precision color measurement are most likely to be met by the development of simple and rapid means of plotting and recording accurate spectrum plots of reflection or transmission characteristics."

The American Photoelectric Corporation, in collaboration with Eimer and Amend, is developing and building a series of instruments for the accurate measurement of the colors of all substances, gaseous, liquid or solid and transparent, translucent or opaque. By the measurement of colors, we mean the determination of the relative energy distribution throughout the entire spectrum from the extreme ultraviolet through the infra-red. Some of the ideas, upon the application of which the successful operation of this series of light-measuring instruments depends, have been advanced during the past decade by technologists working in this field, but no one, so far as we have knowledge, hitherto has developed any practicable instruments that enable one to make a complete accurate spectrum analysis wholly independent of the human eye.

Because of many patent applications pending and in course of preparation, we are unable at this time to disclose the exact workings of this series of instruments. We can merely say that by a novel utilization of photoelectric cells we have developed means whereby it is now possible to measure accurately, i.e. within 0.1%, the quantity of light transmitted by or reflected from a substance for each wave length in the spectrum. In commercial practice no such sensitivity is required, because even the trained human eye rarely can detect variations in density less than 2.0%. With these instruments the accuracy of determination of hue, saturation, etc., is many times greater than that obtainable by visual methods of measurement.

In his discussion of waves and quanta, Dr. Karl K. Darrow (*Introduction to Contemporary Physics*) says that the solution of several fundamental problems depends upon accurate measurement of the intensity of individual spectral lines and he points out further that there are no means available for making such measurements. We believe that this series of instruments, by making it possible to measure accurately differences in intensity of individual bands in the spectrum, especially those in the ultra-violet, opens the door to extensive and fundamental research on many physical and chemical problems that have baffled technologists simply because there were no means available for discovering the facts. This paper has been prepared at the suggestion of the past president of American Oil Chemists' Society, Mr. H. P. Trevithick, merely to indicate some of the possible uses of these light-measuring instruments in the particular field of oil chemistry.

Apparatus as Developed

THE first picture (Exhibit 1) is a Photoelectric Spectrophotometer designed for making color analyses of transparent substances in the visible spectrum. It consists essentially of (A) a modified Bausch and Lomb constant deviation spectrometer to which

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[1] Presented at the Third Fall Meeting of The American Oil Chemists' Society.

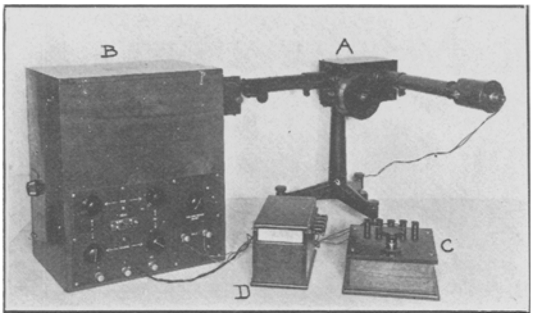

Exhibit 1

a light source has been attached; (B) a case containing the photo-electric devices, on the outside of which is provided an enclosed slide for the material to be examined; (C) a Leeds and Northrup bridge; and (D) a Leeds and Northrup galvanometer. The batteries that are required do not appear in the picture.

The second picture (Exhibit 2) is a Photo-electric Spectrophotometer designed for making color analyses of opaque substances in the visible spectrum. It consists of (A) a modified Hilger constant deviation spectrometer; (B) an opaque illuminator; (C) the case containing the photo-electric devices; (D) a Kohlrausch bridge, made by Leeds and Northrup; and (E) the same type of galvanometer as shown in the first picture.

At this time it might be mentioned that in our laboratories we recently made two color analyses of the same sample of cottonseed oil using for the different analyses different apparatus throughout; i.e. different types of light source, different makes of spectrometers, bridges and galvanometers, and even different types of photo-electric cells, and yet the two color analyses were substantially identical, the maximum variation at any point in the spectrum being less than 0.1%.

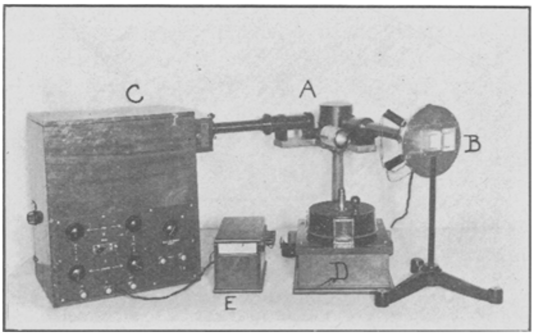

Exhibit 2

The third picture (Exhibit 3) is a Photo-electric Spectrophotometer designed for the determination of the relative energy distribution in the ultra-violet. It consists of (A) a modified Hilger quartz spectrometer; (B) the case containing the photo-electric devices; (C) a Kohlrausch bridge; and (D) a Leeds and Northrup galvanometer. It is, of course, understood that when working in the ultra-violet, whether with transparent or opaque substances, that a light source is employed which is rich in ultra-violet rays, e.g. a Cooper-Hewitt quartz-mercury arc, and that all parts of the instrument through which light passes are of quartz.

One of the daily problems of the chemist who works with animal or vegetable fats and oils is the determination of their color. For this purpose Lovibond glasses are employed, usually glasses that have been calibrated by the U. S. Bureau of Standards.

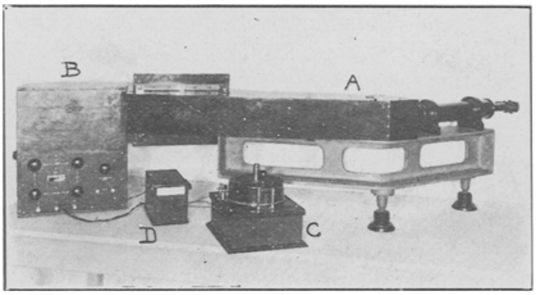

Exhibit 3

The next exhibit (Exhibit 4) shows the transmission curves of four Lovibond red glasses, which were calibrated by U. S. Bureau of Standards. We also calibrated them, using one of the several formulas proposed by U. S. Bureau of Standards. Following is a tabulation of the several values found:—

COLOR VALUES (N)

Lovibond	U. S. Bur. of Stand.	*Amer. Photoelec. Corp.
2.00	2.42	2.35
4.00	4.30	4.40
6.00	6.34	6.15
10.00	10.52	10.21

*Calculated according to one of the several formulae proposed by U. S. Bureau of Standards.

The observations at Bureau of Standards, upon which were based calculations necessary for calibration, were made visually, whereas these curves are based upon measurements made photo-electrically. The Bureau of Standards claims a degree of accuracy of observation within 1.0%, whereas our measurements were made with an accuracy within 0.1%. Even if Lovibond glasses were calibrated with

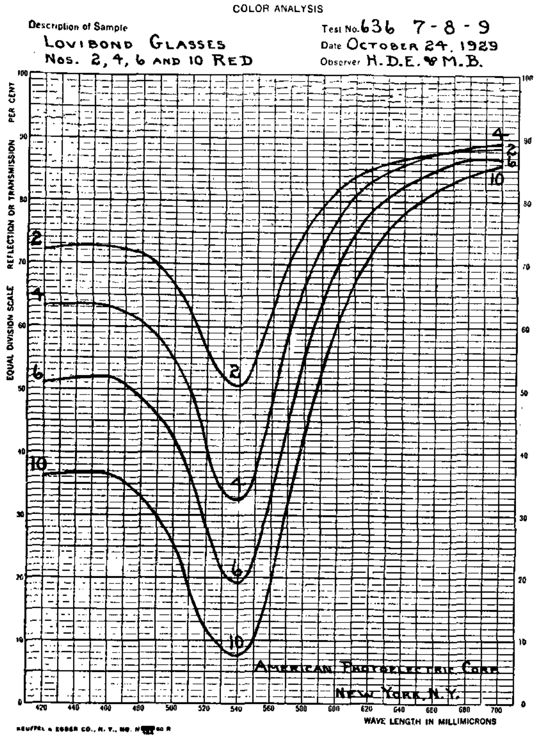

Exhibit 4

the highest degree of precision, the major sources of error would still remain. Priest has pointed out that errors may result from

(1) use of glasses without rule as to number of separate glasses used to match the oil;

(2) use of color comparators (tintometers) of widely different types;

(3) use of illuminants of widely different quality;

(4) color grading of oils by many persons whose color sense and power of color discrimination have never been tested.

In this connection, it may be of interest to note that, while the extreme defects of color vision e.g. color blindness, are more common among men than women, minor defects of color vision are more frequent among women than men, the most common being a periodic disturbance which affects their discrimination in the green and yellow, which has been investigated by Havelock Ellis. Since this is a variable function, testing the color vision would be of little value. It would seem, therefore, that a method of color analysis that develops data expressed in terms of basic physical facts, and subject to none of the sources of error indicated by Priest, would be highly desirable, and such a method is now available.

Color Analyses of Oils

FUNDAMENTALLY, an oil chemist is not interested in the color of a sample per se, but is interested only in so far as the color determination gives him some clue to the chemical or physical characteristics of the oil. The spectral absorption of any substance is a direct function of its chemical constitution and physical characteristics, but, heretofore, no practicable means has been available to industry for the accurate determination of such fundamental data.

The next exhibit (Exhibit 5) shows the absorption curves of two samples of peanut oil, which are widely divergent in color, Sample A being very much lighter than Sample B. The similarity of the curves indicates that the oils are of similar chemical nature, the difference being more of quantity than of quality of coloring matter. Attention is particularly directed to the fact that both absorption curves show sharp changes in direction at 460 millimicrons, at 540, 580, and at 675 millimicrons. If chemical differences exist we might expect them to be reflected in changes in shape of the

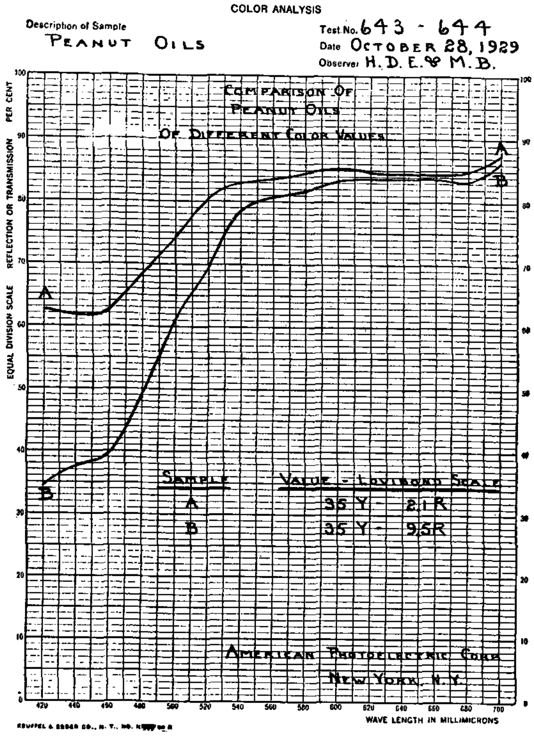

Exhibit 5

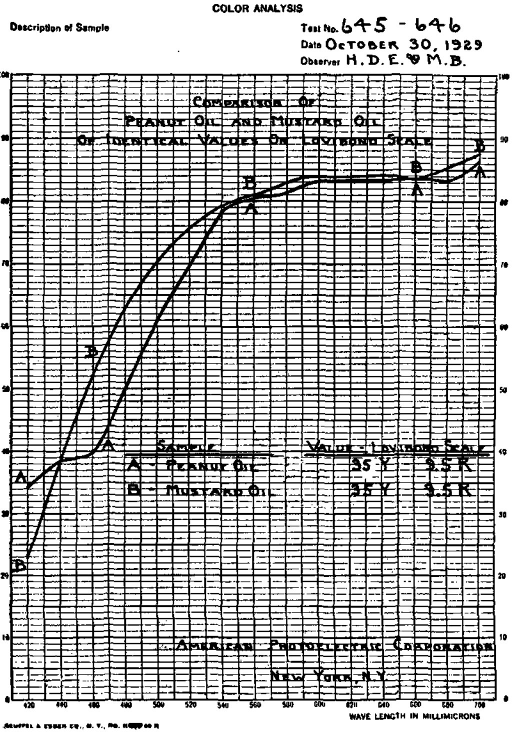

Exhibit 6

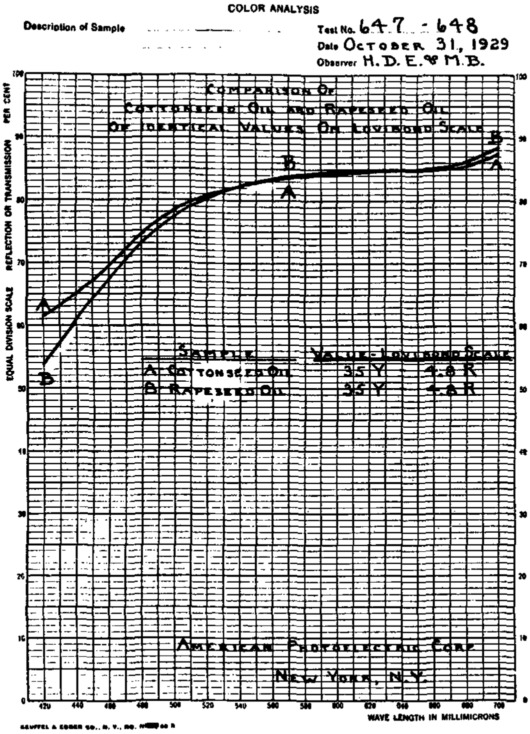

Exhibit 7

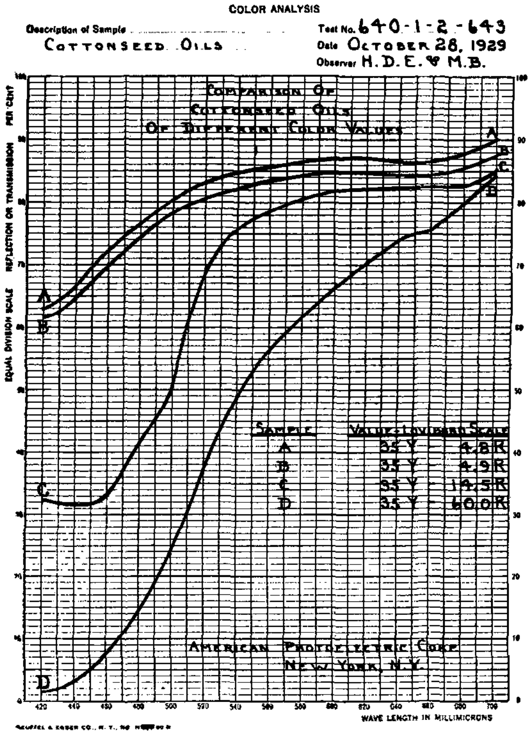

Exhibit 8

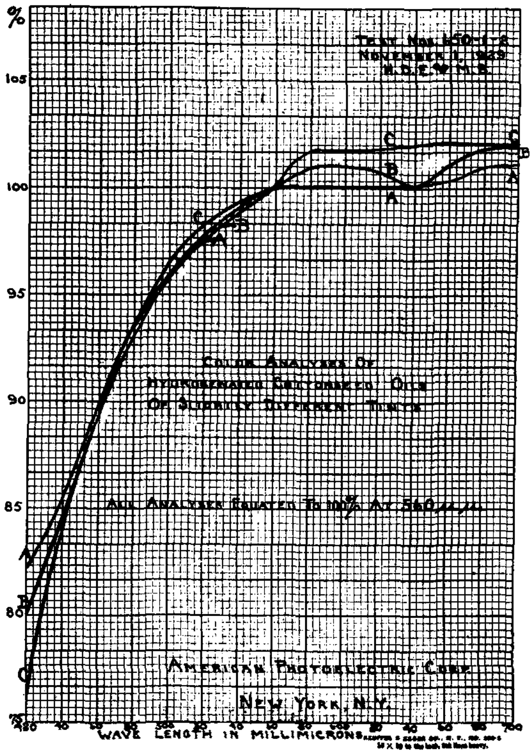

Exhibit 9

spectral absorption curves. The next exhibit (Exhibit 6) shows two different kinds of oil that have identical values on the Lovibond scale, one a peanut oil and the other a mustard oil. These curves indicate that oils of dissimilar chemical composition have distinctly dissimilar spectral absorption. This is most evident in the sharp breaks in the curve of the peanut oil at 460 and 540 millimicrons, which are not present in the curve of the mustard oil.

Another example of detection of chemical differences by the determination of absorption curves is shown in Exhibit 7. Here we have a comparison of the curves of rapeseed oil and cottonseed oil of identical Lovibond readings. While the difference is not as great as that existing between the curves of peanut oil and mustard oil, the steeper slope of the curve of rapeseed oil distinguishes it clearly from that of cottonseed oil.

Another valuable point is illustrated by Exhibit 8. Here we have the curves of four cottonseed oils. A, B and D are similar, but curve C shows marked peculiarities which indicate chemical differences. The changed spectral absorption of this sample in the blue end of the spectrum is perhaps due to overheating.

These important distinctions are not discoverable by means of visual color matching and yet they may be of primary importance in the determination of the kind of oil, or of the treatment to which it has been subjected. The compilation of reference data consisting of the curves of oils of known composition and treatment would enable the oil chemist to interpret results. Such information would make possible a more exact and efficient control of oil production.

Nor is the method limited to oils alone. The spectral absorption of such products as hydrogenated cottonseed oils, soaps, etc. may be measured equally well. Exhibit 9 shows the differences of tint between three hydrogenated cottonseed oils. A, which is whitest, is higher than B or C at the blue end of the spectrum and lower at the red end. That is to say, it most nearly approaches pure white, which would be represented by a straight line at 100%. C, which is yellowest, has opposite characteristics. That is to say, it is lowest in the blue and highest in the red, while B is of intermediate tint. The extension of this method into the ultra-violet and infra-red would be extremely valuable, and measurements in these regions may be made with a comparable degree of accuracy. Furthermore, the measurement of curves of decay of luminescence, which are of too short duration to be measured visually, may be accurately determined.

We thus see that this method enables us to determine color characteristics more accurately than the visual method, to discover facts which the visual method does not, and to extend measurements into those spectral regions where the visual method does not apply, and where, at present, the result is largely a matter of guesswork. Thus, with means available for obtaining fundamental data, it now becomes possible to set up standards, mathematically expressed and capable of reproduction, that will enable one to exercise a more rigid control over production and distribution of all sorts of products, and this series of instruments gives to pure and applied research a new set of tools having a degree of accuracy never before attained.

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Coconut Oil Industry in Cuba

The manufacture of vegetable oil compound from coconut oil is reported to be meeting with great success in Cuba, and the consumption of the product is stated to be, at present, about 2,500,000 pounds monthly. It is necessary to import the coconut oil, since the production of coconuts in Cuba has been greatly reduced by a disease which attacks the palms. *"Comercia"* of Habana states that the Secretary of Agriculture is impressed with the importance of the industry and has given orders that the Agricultural Experiment Station establish nurseries for the coconut palms and that experimental work be carried on in the cultivation of peanut, sesame and other oleaginous seeds. The foregoing information was reported by Consul Keena at Habana, Cuba.

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Exports of Palm Products from Nigeria, 1928

During the year 1928 there was exported from Nigeria 246,638 tons of palm kernels valued at £4,423,114 ($21,522,873) as compared with 257,206 tons valued at £4,438,886 ($21,599,619), during the previous year. Exports of palm oil totaled 127,111 tons valued at £3,751,484 ($18,254,721) during 1928 as compared with 113,240 tons valued at £3,374,550 ($16,420,560) during 1927. (Report from Consul Fernald at Lagos, Nigeria.)