

Tyndall Spectra, Their Significance and Application

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Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

Tyndall Spectra, Their Significance and Application

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June 24, 1946

"TYNDALL spectra," i.e., the variation of light scattering with the wave-length, λ , were determined by spectrographic investigations of the resulting apparent (conservative) absorption. The value of the "wave-length exponent," n , in the formal equation

$$k = c\lambda^{-n}$$

(k , absorption coefficient, c , a factor which is constant if light scattering particles and medium have equal optical dispersion) and, in addition, the variation of n with λ were found to provide two types of significant information on light scattering systems. n was either calculated or determined graphically from the slope of $\log k$ ($\log \lambda$)-curves.¹

(1) The $n(\lambda)$ functions of exclusive apparent absorption, $n_a(\lambda)$, and of exclusive true absorption, $n_t(\lambda)$, are characteristically different. A consideration of their difference greatly facilitates the detection and delimitation of absorption bands in such complex spectra where bands of true absorption are suspected, but indistinct because of a background of strong conservative absorption.

The differences, which follow from theoretical considerations and which are illustrated in part by the juxtaposed spectra in Fig. 1, are

(a) n_t may vary between 0 and $\pm \infty$, whereas n_a can only vary between 0 and 4.0, except for large microscopic particles, where small negative values are conceivable. n -values in excess of 4.0 are, therefore, generally indicative of the presence of true absorption.

(b) n_t changes rapidly with λ , whereas n_a changes so slightly (unless the particles are microscopic) that $\log k$ ($\log \lambda$) curves are, in the latter case, practically straight lines over a spectral range of 1000Å or more. The spectral approach of true absorption can thus easily be recognized.

The wave-length at which n changes sign characterizes the exact peak of an absorption band in systems free from

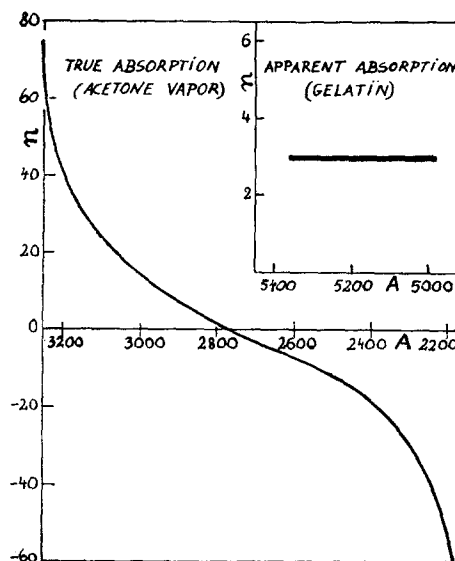


FIG. 1. Variation of n with wave-length. Main figure: Calculated from data taken from Landolt-Börnstein. (Peak of absorption: $2777 \pm 5\text{Å}$.) Inset: Six percent aqueous solution of Nelson photographic gelatin at 21.00°C (equilibrated gel).

light scattering. In light scattering systems, the approximate location of the peak is possible from considerations of the $dn/d\lambda$ -values, although the magnitude and wave-length characteristics of light scattering are altered in the spectral range of true absorption.

The application of this type of spectral analysis to strongly light scattering inorganic colloidal solutions made it possible, as will be shown elsewhere, to characterize and to define chemically the light scattering material.

(2) In absence of true absorption, n has a constant value of 4.0 as long as the diameter of spherical particles (or the longest axis of non-spherical particles) is $< \frac{1}{10}$ of the wave-lengths used (Rayleigh radiation). With an increase of the diameter (long axis) beyond this limit, the value of n decreases for reasons which follow from the theory of Mie.² This opens the possibility of determining particles sizes (or axial ratios, if the size is known) from n -measurements.

This principle of size analysis was tested in extensive spectrographic investigations on light scattering of gelatin solutions. The objective was limited to determining relative sizes and to studying the kinetics of changes in size of gelatin particles. The results were encouraging and seemed to warrant the development of the method into a quantitative method. As an example, the following table gives the variation of n in a 3 percent, 3:2 water-ethanol solution of Nelson photographic gelatin containing 100 millimoles of NaCl, with the time, t , elapsed since the solution, in equilibrium for 35°C , was brought to the lower constant temperature of 18.0°C .

t (hours):	0.17	2.25	7.5	12.75	25.0	47.5
n :	4.0	3.5	2.5	2.0	2.0	2.0

The change in size here is, as shall be explained elsewhere, caused by a reversible aggregation of molecules to so called

"geloids" which are responsible for gel formation. The size of these aggregates varies with the experimental conditions, such as temperature, protein concentration, and composition of the solvent.

¹ W. Heller and E. Vassy, *Phys. Rev.* **63**, 65 (1943).

² G. Mie, *Ann. d. Physik* **25**, 377 (1908).

The Determination of Particle Sizes from Tyndall Spectra*

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June 24, 1946

TYNDALL spectra in light scattering systems without selective absorption furnish a hitherto neglected principle for the determination of particle sizes within an important range of ultramicroscopic dimensions. The principle, based on the decrease of the wave-length exponent, n , with increasing particle diameter, above dimensions of $\sim \frac{1}{10}$ of the wave-lengths used, was outlined in a previous paper¹ and it has now been used for a quantitative method. For this purpose, particle size determinations were carried out with the slit ultramicroscope, using model systems described below. The data obtained were correlated with the wave-length exponent which was obtained, on the same systems, from spectrophotometric measurements of the conservative absorption, the latter being equivalent to spectrophotometric measurements of the global Tyndall effect. Two instruments, the visual Pulfrich spectrophotometer and the Beckman photoelectric spectrophotometer were used for the experiments. The range of wave-lengths covered was 4000–6500Å for the latter and about 1000Å less for the former. Using the principle outlined previously,¹ true absorption—which would interfere with the measurements—was found to be practically absent above 3800Å. The calibration curves, obtained on the variation of n with particle size, depend slightly on the amount of Tyndall light radiated in the direction of the primary beam. The respective solid angle was defined for the Pulfrich instrument, under the conditions used, by $\leq 4^\circ$, depending on the slit width (turbidity). The angle is larger

for the Beckman instrument where it is constant by virtue of the standard construction of the apparatus. The wave-length exponent obtained for a given particle size decreases slightly with increasing concentration of the particles. This effect was excluded by compiling n in each instance for a series of concentrations and by extrapolating to infinite dilution. The latter value generally differs by not more than 5 percent from the lower value obtained at a concentration of 0.1 percent, the latter being approximately the highest concentration used in all experiments.

The model systems used were aqueous emulsions of polystyrene, polyisoprene and styrene-isoprene copolymer. Ultramicroscopic observations showed that these particles were spherical (in contradistinction to the molecules of which they are composed). Extensive optical investigations of the authors on the locus and mechanism of emulsion polymerization, by means of a spectrophotometric-interferometric method,² and with the ultramicroscope—selected results have already been published³—showed that the size of these particles can be varied and controlled by varying the reaction time and temperature, and the nature and concentration of the emulsifier used. The information thus gained made it possible to vary the average particle diameter systematically between <500 and ~ 3000 Å, the size range desired for calibrations of n against particle sizes. Because of the courtesy of the United States Rubber Company, electron-microscopic material could be examined which showed that the size distribution curve in systems as those used is—if prepared in the presence of a stabilizer—generally fairly symmetrical and has a half-width of approximately 200Å. The results obtained for the calibration curves, therefore, do not differ appreciably from those to be expected from strictly monodisperse systems.

Figure 1 represents the calibration curve obtained with a series of polystyrene emulsions. It is valid for a refractive ratio $m = n_p/n_m$ (n_p , refractive index of the light scattering particles, n_m , refractive index of the medium) of 1.23–1.25. The total range of m covered thus far in the various series extends from 1.18–1.25. Since light scattering is, in absence of true absorption, wholly independent of the chemical nature of the particles, the data obtained may be applied for particle size determinations in any type of dispersed system with spherical particles and refractive ratio 1.24 ± 0.01 . (These refractive ratios were determined interferometrically from the refractive indices of the emulsion and of the medium, using, for the calculation of n_p , a mixture rule given recently.)⁴

TABLE I.

Reaction time (hours)	Percent conversion	n	Diameter (Å)
6	<0.5	4.0	500**
9	<0.5	4.0	570**
11	<0.5	3.95	~700**
14	~0.5	3.8	800
18	1.0	3.5	900
36	2.3	2.85	1150
60	3.0	2.5	1500
360	13.8	2.1	2300
540	44.0	2.05	2550
660	59.5	2.0	~2700

** Determined from the quantitative value of light scattering itself, reference 2.

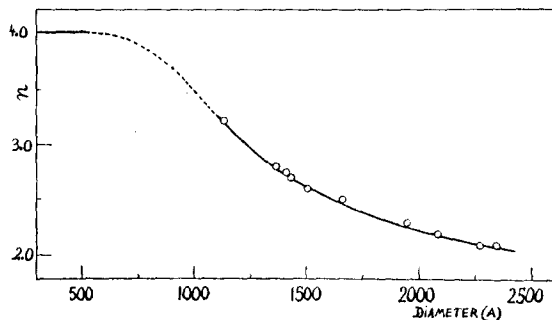


FIG. 1. Variation of wave-length exponent with the diameter of spherical dielectric particles.