SPECTROSCOPIC STUDY OF PAPERS

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Summary

The paper as diffuse scattering sample was studied. In every optical datum of paper are in undifferentiated joint evidence the three factors, i.e. the basis weight of the sample, its absorption and its scattering of light. Experimental results are also included.

At a former itinerant congress on spectroscopic analyses we have offered a report about the study concerning model substances on filter paper as their carrier and concerning the possibilities of qualitative and quantitative analyses by means of spectroscopy [1]. At this juncture we think to deal with the spectroscopic study of paper itself as the generator of diffuse scattering patterns.

The domain of utilization of the optical data relevant to papers is very large indeed (above the characterization of the optical properties of paper these data can be used for the tracing of the consequences of many technological processes which affect the quality of the finished product, and are indispensable in the study of paper-structures and also in the indirect study of those properties of papers which stand in close connection with a given paper-structure, e.g. with several features of strength, density, interaction with liquids, etc).

The three factors, i.e. the basis weight of the sample, its absorption, and its scattering of light, are in *undifferentiated* joint evidence *in every optical datum*— this is manifestly so with the results of spectroscopical measurements.

The change of the *mass* of a given paper—be it characterized by means of basis weight or number of layers—characteristically changes the optical data recorded (coordination "A" [2]). Intensity figures as recorded are best recalculated to extinction figures. Extinction is the measure of "loss of light" evident in the given datum of measurement: it is the joint consequence of scattering and absorption. Up to a threshold of a critical mass extinction does not linearly change with the increase of the number of layers (the part due to transmission increases and that due to remission decreases). At critical mass remission has reached "infinite thickness of layers" and does not change any more. The extinction due to transmission, however, turns linear at a further increase of the number of layers. In respect of scattering samples this fact expresses the same correlation which is known as the Bouguer–Lambert law in solvent spectrocopy (extinction is a linear function of layer-thickness).

Paper is a heterogeneous system. One phase of it is cellulose (solid frame) perhaps with accompanying matter present; the other phase is air in the system of holes.

Scattering of light occurs at boundaries between phases of different refraction indices. In paper phenomena of light scattering are determined by the significant difference (about 1.56/1.00) at cellulose/air phase-boundaries. In comparison, the various organic additives, and kaolin, cause small changes in light scattering, owing to their refractive indices being between 1.5 and 1.6 as a rule. A filler having a high refractive index (e.g. TiO_2) may cause a substantial increase of light scattering. If a fluid, moistening the paper, occupies the place of air in it (transparentation), a significant diminution of light scattering ensues.

An essential influence upon the diffuse scattering of light is exerted by the solid structural components of the paper (first of all by cellulose fibres) and by the shape, dimension, distribution of the holes and pores of various types. 10 to 50 per cent of a natural cellulose fibre is made up of holes. The porosity (the ratio of hole-volume to paper-volume) of writing or printing paper is between 40 and 60 per cent. Something between 2 and 30 nm is the dimension of micropores in the cell walls, the distribution curve shows a maximum at 3.5 nm. Dimensions of the macropores are 10^{-5} to 10^{-3} cm with a maximum of the distribution curve at 1 μm. The average dimension of one pine cellulose fibre is 5 by 25 by 1000 μm. The surface of the fibres is not smooth, the striations on them may be deeper than even 0.1 μm.

Light in interaction with paper meets a very great number of cellulose fibres. E.g. within the area of a 1 cm² piece of a 40 g/m² paper 10^4 fibres and the intricate system of holes between them form the structure with which light interacts.

One part of the entirety of fibre-surfaces participates in the inter-fibre bonding that holds the solid frame together. When fibre-surfaces approach each other within a distance of 50 nm (this is significantly greater than bond-distance) "optical contact" can be spoken of; light passes practically without any scattering through these places. Light is scattered by surfaces not involved in bonding.

In an optical datum the wavelength (more exactly: its dimension in reference to particle-size) of the probing light decisively affects the role of light scattering. At a given wavelength scattering increases with the decrease of particle-size and reaches a maximum when particle-size is about half the wavelength; from this point on it decreases abruptly.

Based on the foregoing: the lower limit of the dimension of particles which play an intensive role in optical test-results is between 50 and 100 nm. No information with any value accessible by means of optical testing can be expected from the domain of discontinuity with dimensions smaller than this. When wavelength is shortened, newer and newer elements of paper structure

emerge which did play no role in intensity-figures recorded at longer wavelength. The diffraction index of the solid phase, the ratio of the several elementary processes of light scattering, also absorption, change with wavelength.

Thus, essential changes occur in the information-content of the test data when the wavelength of the probing light is changed. (Perhaps we might say that it is then that "optical accessibility" changes.) Therefore, in the course of optical studies, tests with monochromatic light yield the most accurate information, spectra have the most to say.

Light absorption occurs in the solid phase. According to the relevant literature, pure cellulose does not absorb light above the wavelength 200 nm practically at all. Impurities present in technical cellulose, and additives, are responsible for light absorption by paper.

Diffuse reflection and diffuse transmission spectra also characterize light absorption—under conditions of light scattering. The spectroscopy of light scattering media (paper is one of these) is an autonomous domain of spectroscopy [3, 4]. In the case of diffusely scattering systems, however, we have not yet found unequivocal quantitative correlations like the Beer-law, for instance.

Table 1 serves the illustration of some characteristics of paper-spectra, and contains *data for the R_∞-spectra of model papers.*

Spectra recorded with an SP 8-100 Pye-Unicam spectrophotometer.

Geometry of the integrating sphere: 8°/D

Reference: the white etalon ($BaSO_4$) of the instrument.

Model papers prepared on laboratory Fourdrinier machine (in 1971 and 1972).

Basis weight: 70 g/m^2, freeness: 40 SR°, machine-finished.

The correlations that can be established are as follows.

— The determinant factor in a paper spectrum is the spectrum of the fibrous substance (especially in the visible domain).

— Additives modify the spectra more or less, yet no component causes selectivity in the R_∞ spectrum (exceptions: dyestuffs may generate absorption bands in the visible and ultraviolet, optical bleachers in the ultraviolet).

— In the range studied, R_∞ continuously decreases, the slope of the curve is a function of composition:

this decrease is the least in the case of paper made of cotton (1); the highest degree of decrease of R_∞ is caused, among technical celluloses, by non-bleached pine sulphite cellulose, and straw cellulose (3, 4)

rosin-sizing causes a very great decrease of the remission of a 14-year old paper (7)

this effect is in evidence also when filler substances are present (13, 14).

Table 1

Sample number	Furnish			Wavelengths (nm)						
	Fibre	Sizing	Filler	300	350	400	450	500	600	800
1	Cotton			92.0	93.5	94.4	95.0	95.6	96.6	96.8
2	Bleached sulphite			66.1	78.3	86.5	90.3	92.1	93.0	93.2
3	Non-bleached sulphite			15.5	23.2	43.3	54.7	61.5	74.8	89.0
4	Straw			43.2	56.3	66.8	74.3	80.3	87.0	90.3
5	Bleached poplar			52.8	65.6	75.3	82.4	87.4	92.9	94.2
6	Bleached sulphate			52.1	65.6	75.5	82.8	87.2	91.0	91.6
7	Bleached sulphite	3% rosin		29.2	50.0	68.8	78.4	84.3	89.6	90.1
8	Bleached sulphite	0.5% ketene dimer		66.3	78.6	86.6	89.9	92.2	94.5	95.0
9	the same	3% rosin	10% ZnO	75.3	85.8	90.5	92.9	94.7	96.0	96.2
10	the same	the same	Kaoline	31.0	53.9	72.4	81.5	86.8	91.1	92.6
11	the same	the same	TiO_2	15.4	19.2	77.2	86.7	91.4	94.9	95.3
12	the same	the same	Talc	35.4	51.2	64.2	72.7	77.2	84.3	84.8
13	the same	the same	$BaSO_4$	60.7	71.7	81.2	87.0	91.1	94.6	95.2
14	the same	the same	$BaSO_4$	41.9	63.9	79.4	87.7	91.9	95.5	96.2
15	the same	the same	Zeolex	45.1	67.7	82.7	89.6	93.6	96.6	97.7

Filler substances cause greater decrease in the ultraviolet (10, 12, 15); especially worthy of note is the very steep section of the curve between 350 and 400 nm caused by TiO_2.

The effect of the several components on the spectra of papers is like this also in the case of papers produced on industrial equipment. The phenomenon will be more complex since papers of various basis weight have to be tested; at furnish, further additives, ever greater masses of spoilage for re-use must be reckoned with, together with the effects of comminution and other technological processes.

References

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