# SPECTROSCOPICAL ANALYSIS WITH DIFFUSE-SCATTERING SAMPLES

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The absorption spectroscopical investigation of scattering systems may be performed either by measuring the intensity of light after passing or reflected by the sample, in both cases the obtained data are related to the intensity of illumination as a function of the wave length.

The processes of absorption and scattering are simultaneous and depends also on each other. The two processes are expressed by a single value at any wave length. This is valid for both measuring arrangements, stressing that the data obtained at the same wave length differ without exception. The total loss of radiation is the extinction.

In processing the obtained data, radical differences from non-scattering samples (solutions) must be taken into consideration:

— the applied sample is not a homogeneous medium surrounded by plane and parallel surfaces,

— the layer thickness of great importance in optical measurements is unknown,

— the agreement between illumination and detection is problematic,

— with a given quantity of absorbing centers, the probability of absorbance, due to the scattering, differs from that under scattering-free conditions,

— the measured radiation (resp. the loss of radiation) is not identical with the effective radiation of remission or transmission, only a part of the scattered radiation reaches the detector after leaving the surface of the sample, there exists an instrumental constant which highly varies with the distance between sample and detector, the intermediate optical elements, etc.,

— losses of light occur within the sample sideways too.

The consideration of these differences is of extreme importance for well-defined measuring conditions. Else the measurement becomes irreproducible, the obtained data become uninterpretable, moreover they lead to errors both in principle and in practice.

During the last thirty years several scientists had been dealt with the investigation of filter papers with a view on analysis. Several authors discuss

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the problem of preferable measuring arrangement and the question whether — in the case of transmission arrangement — the direct measuring of the sample would serve better or the sample should be made transparent before [1].

In the following, a method for measuring the relative intensity of the light having passed the sample will be presented, with possibilities for routine measurements with modern instruments.

## Well-defined instrument conditions

According to our investigations the spectrophotometer type Unicam SP 700 guarantees the possibility for transmission measurement of scattering samples. This instrument has been designed first of all for the investigation of non-scattering systems. For our investigations the instrument had to be completed with several accessories [2]:

a) Base plate with grooves guarantees the good reproduction in positioning the different sample holders and devices for light weakening.

b) Special sample holders for different types of scattering samples. Some types of samples need extremely good reproduction in fitting, i.e. reproducible change in layer thickness or in the number of layers.

c) We put into the reference beam the device for weakening the intensity of the light beam. The screen applied by us is a new, up-to-date type of the older types. These grids are brass plates attacked by photomechanical procedure. Single grids are applied between extinction values 0.6—2.6, double ones between 2.5—4.7.

## Supervision, adjustment before measuring scattering samples

The instrumental conditions of measuring scattering systems, in all cases need an exact control. Important before scattering sample measurements:
— adjust exactly the 100% mark,
— assign the place of the sample holder throughout the measurement series,
— check the interchangeability of the sample holders in both beams,
— check the reproducibility of sample holder and grid locations.

Unicam SP 700 spectrophotometer allows measurements in the visible region with an intensity order of 5.0—6.0. In the case of scattering sample measurements this value decreases by two orders because of the distance between sample and detector (instrumental constant). E.g. we measure about 0.4% transmission instead of about 25—30% transmission of the W1 filter paper at 16.000 cm$^{-1}$ wavenumber. But even now the nearly four orders in extinction suffice to perform the measurements in good quality.

## The analytical investigation of scattering samples

It has to be taken into consideration that the Bouguer—Lambert—Beer law is not valid for the analytical investigations of scattering samples. We need a reference curve of samples prepared with standard solutions. As described in particular in previous publications [2, 3], a special dropping technique has been elaborated for the uniform dispersion of dyestuff on the filter paper. We used sheets, prepared in this way, having identical extinction values for the construction of the combined sheet systems [4].

For measuring coloured samples uncoloured paper sheets were put into the reference beam constructed of the same number of sheets as the sample.

Table I presents the extinction values of filter papers prepared with dyestuff solutions of various concentrations. The second column shows the dyestuff quantity dropped on one filter sheet. Indications 1, 2, 3, etc. refer to the number of sheets in the sheet system.

Table I

| $\mu g/ml$ | $\mu g$ | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| 6.56 | 0.264 | 0.020 | 0.125 | 0.259 | 0.426 | 0.617 | 0.820 |
| 1.64 | 0.064 | 0.008 | 0.049 | 0.103 | 0.178 | 0.259 | 0.351 |
| 0.41 | 0.016 | — | 0.014 | 0.026 | 0.046 | 0.069 | 0.098 |
| | | 7 | 8 | 9 | 10 | 15 | |
| 1.64 | 0.064 | 0.449 | 0.565 | 0.602 | 0.696 | — | |
| 0.41 | 0.016 | 0.130 | 0.164 | 0.197 | 0.239 | 0.431 | |

The analysis of these data leads to the conclusion that the extinction value increases to a higher degree than the augmentation of material effected by the increase in the number of layers. That means the extinction of two layers appears as the six-fold rather than the double of the extinction belonging to a single layer, again extinction of six layers is about seven-fold rather that the treble of the extinction of two layers. This substantial augmentation of extinction is due to the scattering and in consequence, to the increase in absorption. That means an elongation of the optical path length for the photons not absorbed by the layer, i.e. this path become longer than the geometrical layer thickness. [5]

Going on with the analysis it comes out that same E value can be achieved by using a smaller quantity of dyestuff but distributing it in a sheet system of more layers. For example the value of 0.259 E may be achieved either with a 3-layer system prepared with a solution $c_1$ (corresponding to 0.792 $\mu g$ of material) or with a 5-layer system prepared with a solution $c_2$ (corresponding only to 0.320 $\mu g$).

Table II presents the data obtained from combinations of different arrangement. It hints to the fact that concentration $c_3$ does not give any measuring datum with a single layer but in combination 3 (2) it provides the value of 0.023. Indication 3 (2) means that in a sheet system of 3 layers the second sheet is coloured. Augmenting the numbers of uncoloured layers the relative extinction also increases, although in this method the sample quantity is constant. That means an augmentation of the optical path length without increasing the quantity of material.

### Table II

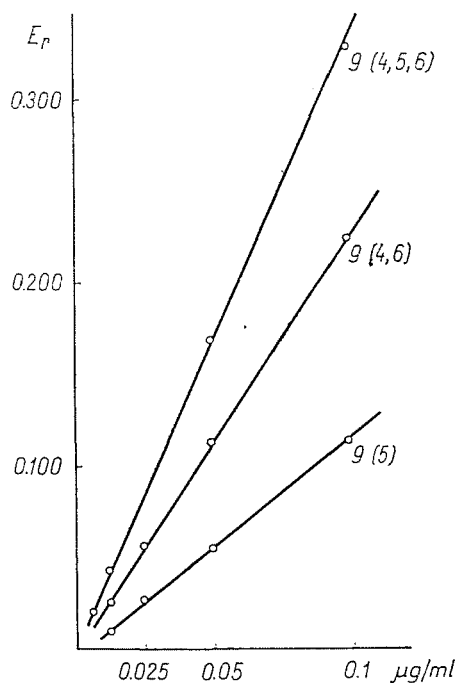| $\mu g/ml$ | $\mu g$ | 3 (2) | 5 (3) | 7 (4) | 9 (5) |
|---|---|---|---|---|---|
| 6.56 | 0.264 | 0.127 | 0.189 | 0.244 | 0.270 |
| 1.64 | 0.064 | 0.056 | 0.082 | 0.108 | 0.111 |
| 0.41 | 0.016 | 0.023 | 0.027 | 0.035 | 0.042 |
|  |  | 11(6) | 13 (7) | 15 (8) | 15 (7,8,9) |
| 6.56 | 0.264 | 0.297 | 0.310 | 0.328 | — |
| 1.64 | 0.064 | 0.117 | 0.130 | 0.140 | 0.371 |
| 0.41 | 0.016 | 0.045 | 0.050 | 0.067 | 0.123 |



*Fig. 1*

Figure presents the measuring results obtained with a 9-layer combined sheet system, containing one, two and three coloured layers. It is noticeable that the gradient of the standard curves increases according to the combination.

## Comparison of the measuring data

Measurements with solutions and with scattering systems at 16.000 cm$^{-1}$ absorption maximum (dyestuff is malachite green) have been compiled in Table III. The first column includes "A" and "E" as the values of the qualita-

Table III

| Absorbance resp. Extinction | μg/ml (10 mm) | Actual quantity of material (μg) | | |
|---|---|---|---|---|
| | | in solution | in scattering system | |
| | | (10 mm) | simple sheet (numbers) | combined system (combinations) |
| 0.020 | 0.10 | 0.35 | 0.040 (2—3) | 0.016   3(2) |
| 0.100 | 0.55 | 1.93 | 0.096 (6) | 0.048  15(7,8,9) |

tive and quantitative lower limit. The second column represents — in accordance with the BLB-law — the quantity of dyestuff in the solution necessary for gaining the given "A" value. The quantity of material is given in μg/ml, the cell thickness is 1 cm. The actual quantity of dyestuff in solutions used in routine measurements is given in the third column, using one cm cell, while the fourth and the fifth column indicate the quantity of dyestuff in scattering systems necessary for producing the given "E" values. The layer numbers and the symbol of the combination of sheets are in brackets.

We can calculate from this data the ratio of the dyestuff quantity necessary for exact measurements: namely, qualitative measurements with solutions need approximately twenty times, quantitative measurements about forty times as much material as the measuring method with combined sheet systems. Transmission measurements with scattering medium ensure much higher analytical sensitivity than spectrophotometric method with solutions. The difference at the lower measurement limit is about two orders.

## Summary

An analytical method performed with diffuse scattering systems in transmission arrangement is briefly outlined, together with the conditions required for well defined measurements.
The advantages of the measurements performed with combined sheet systems are illustrated by some representative tabulated values, selected from great many measuring data.

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