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Integral and Differential Turbidity Ratio Methods Applied to the Analysis of Changes in the Size and Number of Scatterers

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Summary

Integral (ITR) and differential (DTR) turbidity ratio methods are shown to be simple and efficient techniques suitable for estimation of the size and number of scatterers in the static and dynamic systems, mainly during processes consisting in the formation or disappearance of a single component in a complex macromolecular or colloid system. The DTR method exceeds the ITR method in the resolving power and reliability; however, their combination seems to be the optimal approach.

1. Introduction

The turbidity τ contains intact information about scatterers in the system, provided that their contributions are mutually independent (VAN DE HULST 1957, KERKER 1969). This holds also for the turbidity ratio methods (cf. SEDLÁČEK 1967, 1979; DUŠEK and SEDLÁČEK 1969, SEDLÁČEK et al. 1979); also some other limitations competent for application of the Lorenz-Mie theory (HELLER and PANGONIS 1957, VAN DE HULST 1957, KERKER 1969) must be obeyed.

In this paper, the integral turbidity ratio method (ITR) has been extended to provide some analytical data characterizing a two-component system (cf. Example 2). For an analysis of complicated systems, a new simple technique called the differential turbidity ratio method (DTR) has been described in detail (cf. Example 3).

2. Estimation of the Size of Scatterers

The usual ITR method consists in measuring the turbidities τ_a and τ_b (absolute or relative, i.e. direct photometer readings) at the two wavelengths λ_a and λ_b, which yields

$$T_{ab} = \tau_a(\lambda_a,\alpha_a,m)/\tau_b(\lambda_b,\alpha_b,m) = \kappa^{-2(b-a)} S_a(\alpha_a,m)/S_b(\alpha_b,m) ; \quad (1)$$

λ is the wavelength in the medium, $\alpha = \pi L/\lambda$ is the relative size and L is the diameter of the spherical or equivalent scatterers, m is their relative refractive index and S is the turbidity function identical with Heller´s Σ). Pairs of λ_a, λ_b and α_a, α_b are bound by the sequence condition of a constant quotient $\kappa = 1.2531$, e.g. λ_0 (= $\lambda_0\kappa^0$) = 326.7 nm; $\lambda_1 = \lambda_0\kappa^1$;

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$\lambda_2 = \lambda_0\kappa^2$ (corresponding to the wavelengths in vacuo, Λ_0 = 435.8; Λ_1 = 546.1; Λ_2 = 684.3 nm), which allows us to use the same tables* for all pairs of wavelengths. In this way, three turbidity ratios T_{01}, T_{12}, T_{02} and adequate sizes L_{01}, L_{12}, L_{02} may be obtained (for details see SEDLÁČEK et al. 1978, 1979, ZIMMERMANN and SEDLÁČEK 1981). If the L´s are nearly equal, the system may be seen as monodisperse or slightly polydisperse, and vice versa.

3. Estimation of the Concentration of Scatterers

The required concentration c_e (g/100 g) and/or the number N_e (cm^{-1}) of scatterers can be obtained by inserting the experimental turbidity τ_e (absolute only) into an appropriate relation

$$c_e=\tau_e/[\tau/c]; \quad N_e=\tau_e/[\tau/N]=\tau_e/R=2\pi\tau_e/\lambda^2 S=4\pi\tau_e/\alpha^2\lambda^2\kappa \qquad (2)$$

where the subscript e is used to discern the experimental quantities from the theoretical ones (extrapolated for $c \to 0$); R is the scattering cross-section, $S = 2\pi R/\lambda^2$ and κ is the scattering coefficient. The theoretical values of $[\tau/c]$, R, S and κ corresponding to the respective scatterer size (obtained by the turbidity ratio method) can be calculated or found by interpolation from appropriate tables (HELLER and PANGONIS 1957, PANGONIS et al. 1957, VERNER et al., ZIMMERMANN and SEDLÁČEK 1981, etc.).

4. Integral Turbidity Ratio Method: An Extension

The ITR method deals with a summation of the individual (usually unknown) turbidity contributions of the components present in a complex system. Thus, at best an average size of all the scatterers may be found (being representative for a system with the known distribution or definite for a monodisperse system); if the postulates of the Lorenz-Mie theory are not fitted, only an apparent or equivalent size is to be expected. The averaged data may differ significantly from those for the individual components as is demonstrated in Example 1.

EXAMPLE 1: A system is available of two monodisperse components, A and B, their sizes found by the ITR method at λ_0 and λ_1 being $L^A_{ab} = L^A_{01}$ = 208 nm (= $2\alpha_0$) and L^B_{01} = 624 nm (= $6\alpha_0$), and their mass fractions x_A = 0.80 and $x_B = 1-x_A$ = 0.20 of the total concentration $c = 1\times10^{-3}$ g/100 g. The ratio of the measured integral turbidities $\tau^i \equiv \tau^{AB}$ is defined by (for the given case $T^{AB}_{ab} = \tau^{AB}_a/\tau^{AB}_b$, $a\equiv0$, $b\equiv1$)

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*By inadvertence, the basic wavelength given in the tables was λ_1 = 409.3 nm instead of the correct value, λ_0 = 326.7 nm.

$$T^{AB}_{ab} = \{x_A[\tau/c]^A_a + (1-x_A)[\tau/c]^B_a\}/\{x_A[\tau/c]^A_b + (1-x_A)[\tau/c]^B_b\}. \qquad (3)$$

As the $[\tau/c]$'s are the limiting values ($c \to 0$) and (τ/c) is usually not concentration dependent, we may use $(\tau/c)^A$, $(\tau/c)^B$ or directly τ^A, τ^B instead (SEDLÁČEK 1979). Inserting into eq.(3) the appropriate values* of specific turbidities related to the sizes L^A_{01} and L^B_{01} given above, we obtain $T^{AB}_{01} = 1.600$ which corresponds to $L^{AB}_{01} = 402$ nm ($= 3.87\ \alpha_0$). The size found in this way is certainly useful for preliminary considerations, but can be hardly seen as really representative for a system of the two components $L^A_{01} = 208$ and $L^B_{01} = 624$ nm.

Nevertheless, also the ITR method may, under favourable conditions, render more information than the average size of all the scatterers only. This is shown in Example 2 where from four characteristics to be found (sizes of the components A and B, total concentration and mass fraction of individual components) only one is known (sizes of the component A or B).

EXAMPLE 2: The same system as above is considered in this example, except that only the size of A (= 208 nm) is known or may be estimated (e.g. under conditions when the component B is not yet or no longer present in the system). The measured quantities are the integral turbidities only (obtained for λ_0 and λ_1): $\tau^{AB}_0 = 0.252$ and $\tau^{AB}_1 = 0.157_5$; their ratio $T^{AB}_{01} = 1.600$ corresponds to $L^{AB}_{01} = 402$ nm as above. Using the tables of specific turbidities,** we find for $L = 402$ nm ($= 3.87\ \alpha_0 = 3.1\ \alpha_1$) the value of $[\tau/c]^{AB} = 256$. As (τ/c) is usually independent of concentration, we may calculate the total concentration c by inserting the experimental value of $\tau^{AB}_0 = 0.252$ in eq.(2); thus $c = 0.252/256 \approx 1\times10^{-3}$ g/100 g, which is nearly identical with that comprised originally in the simulated example. Using the tables, we estimate $T^A_{01} = \tau^A_0/\tau^A_1$ (from the known size $L^A_{01} = 208$ nm $= 2\alpha_0 = 1.596\alpha_1$) and we find the respective $[\tau/c]^A_0 = 173.8$ and $[\tau/c]^A_1 = 98.2$. Now we follow the instructions and obtain data as given in Table 1. Since the size found for a mixture of A and B is considerably higher than that of the component A ($L^{AB} > L^A$), component B must be represented by much larger scatterers than component A ($L^B > L^A$). The concentration of A should prevail over B if $L^B > 596$ nm. However, from a calculation made for $\tilde{x}_A = \tilde{x}_B = 0.5$

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*They are: $[\tau/c]^A_0 = 173.78$, $[\tau/c]^A_1 = 98.24$; $[\tau/c]^B_0 = 565.67$, $[\tau/c]^B_1 = 394.81$. **Tabulated for λ_1; $[\tau/c]_0 = 1.2531\ [\tau/c]_1$.

we obtain $\alpha_0^B = 4.66$, i.e. $L^B = 485$ nm only. This is why we choose $\tilde{x}_A > 0.5$ for a set of simulated compositions of A and B. Then we continue to calculate functions (given in the left column) for the individual compositions; instructions for calculation are given in the right column. For $[\tau/c]^{AB}$ "experimental" values, $[\tau/c]_0^{AB} = 252$ and $[\tau/c]_1^{AB} = 157.5$, are used in the calculation.

TABLE 1: Integral turbidity ratio method: data and procedure

$\tilde{x}_A$(sim)	0.5	0.6	0.7	0.8	0.9	fraction of A
$\tilde{x}_B$(sim)	0.5	0.4	0.3	0.2	0.1	fraction of B
$\tilde{x}_A[\tau/c]_0^A$	86.9	104.3	121.7	139.0	156.4	
$\tilde{x}_B[\tau/c]_0^B$	165.1	147.7	130.3	113.0	95.6	$= [\tau/c]_0^{AB} - x_A[\tau/c]_0^A$
$\tilde{x}_A[\tau/c]_1^A$	49.1	58.9	68.7	78.5	88.4	
$\tilde{x}_B[\tau/c]_1^B$	108.4	98.6	88.7	78.9	69.1	$= [\tau/c]_1^{AB} - x_A[\tau/c]_1^A$
T_{01}^B	1.523	1.498	1.468	1.431	1.384	$= [\tau/c]_0^B / [\tau/c]_1^B$
α_0^B	4.66	5.10	5.49	$\underline{6.03}$	6.60	for T_{01}^B
$[\tau/c]_0^B$	485.3	518.2	542.1	566.4	584.9	for α_0^B
$[\tau/c]_1^B$	318.6	345.9	369.2	395.7	422.8	$= [\tau/c]_0^B / T_{01}^B$
x_A(calc)	0.595	0.679	0.745	$\underline{0.800}$	0.846	from eq.(3)

Final data for x_A were calculated according to the relation (obtained by a rearrangement of eq.(3))

$$x_A^{-1} - 1 = (\tau_a^A - T_{ab}^{AB}\tau_B^A)/(T_{ab}^{AB}\tau_b^B - \tau_a^B) = Y \qquad (4)$$

(where τ is used instead of $(\tau/c) = [\tau/c]$), from which the quantities of interest may be obtained: $x_A = (1 + Y)^{-1}$, $x_B/x_A = Y$; for the given case $a \equiv 0$, $b \equiv 1$. By comparison of the simulated and calculated x_A, the best accordance was achieved for $x_A = 0.8$. Generally, when differences $x_A(\text{calc}) - \tilde{x}_A(\text{sim})$ are plotted against $\tilde{x}_A$(sim), the intersection may give the desired fraction $\tilde{x}_A$. Thus, the data searched for are as follows: $c = 1\times10^{-3}$ g/100 g; $L^B = 624$ nm ($= 6.03\ \alpha_0$); $x_A = 0.8$, $x_B = 0.2$.

5. Differential Turbidity Ratio Method

The DTR method (called alternatively the turbidity difference method) is based on a measurement of the difference between the "original" and "final" turbidities (through which any information about the respective states of a system is mediated) *anywhere on the time scale* coordinated to the changes occurring in the system. Suitable for being treated by this method is a system composed of various types of scatterers, where only one component is responsible for the process observed leading to its formation or disappearance, and/or to its increase (decrease) in size.

To reach the aim, we measure the integral turbidity as a function of time (continuously or successively); thus, data are obtained representing the summation of contributions of all the scatterers acting at each definite time t (or a temperature θ, etc., if correlated with t) within the available interval. For the sake of a step by step analysis of the process, the whole interval is to be divided into several subintervals, the number of which depends on the course and specificity of the process. Obviously, the data must be corrected by isochronous interpolation to be applicable for this purpose. As a result, a set of integral turbidities $\tau^{i}_{(0)}$, $\tau^{i}_{(1)}, \ldots, \tau^{i}_{(n)}$ is obtained coordinated to the respective times $t_{(0)}, t_{(1)}, \ldots, t_{(n)}$ (subscripts in parentheses delimit the individual time intervals correlated with the states of the system under investigation). Now, the turbidity differences $\Delta\tau^{i}$ are calculated for whatever time interval and between any pairs of integral turbidities τ^{i}: these data are related to the process only, which has led to the turbidity differences within the given time interval. As the trend of τ^{i} values is obvious, absolute values of the turbidity differences may be used. The differential turbidities $\tau^{d} = \Delta\tau^{i}$ so obtained carry encoded information about changes in the size and concentration (or number) of scatterers within the individual intervals, and thus about the mechanism of the process studied. To excerpt these two characteristics, the differential turbidities τ^{d} instead of the integral turbidities τ^{i} are evaluated in terms of the turbidity ratio method. The preferential use of just this method is substantiated by a crucial fact that the turbidity ratios are usually independent of concentration; this makes possible an estimation of the size and concentration of scatterers in general and during the process in particular.

The procedure just described may be illustrated by the following simulated example:

EXAMPLE 3: With a change in temperature, a process leading to an increase in turbidity sets in a complex system. We assume that the turbidity increase is correlated with the rising concentration of the component B, while the turbidity of the remaining one or more components being designed as a whole by A remains nearly constant. A question arises whether this picture is correct and, if so, what are the sizes and concentrations of the components A and B or whether the two or more components are present. This should be answered by the turbidity ratio method in a simulated experiment.

In the "experiment", integral turbidities are measured at the end of each of four time intervals (I) chosen, (0) being related to the original system. The results obtained by the ITR method are in Table 2.

TABLE 2: Integral turbidity ratio method: data

(I)	τ_0^i	τ_1^i	T_{01}^{AB}	α_0	L,nm	$10^3 c_{app}$
(0)	1.390	0.786	1.768	2.00	208	8.0
(1)	1.956	1.181	1.656	3.03	315	6.2
(2)	2.522	1.576	1.600	3.88	403	6.1
(3)	3.653	2.365	1.545	4.42	460	7.8
(4)	5.913	3.944	1.499	5.08	528	11.5

All data are calculated from the integral turbidities τ_0^i and τ_1^i: information is now available on the average size of scatterers and on their apparent concentration.

Corollary 1: With increasing integral turbidities τ^i the average size of scatterers is rising, which means that either the scatterers already present become larger, or new, much larger scatterers are formed continuously, so that at least two components different in size contribute to the effect observed. The apparent concentration does not follow the increase in turbidity and the average size of scatterers, and thus confirms that the system is not homogeneous.

Ten differential turbidities τ^d may be obtained from all combinations of pairs of the five integral turbidities τ^i. Using these data, the sizes and concentrations of scatterers may be calculated (cf. Sections 2 and 3), responsible for the increase in turbidity within the individual intervals Δ (Table 3).

TABLE 3: Differential turbidity ratio method: data for scatterers responsible for the increase in turbidity

Δ	$\tau_0^d=\Delta\tau_0$	$\tau_1^d=\Delta\tau_1$	T_{01}	α_0	L,nm	$10^3(\Delta c)$
(1)-(0)	0.566	0.395	1.433	6.0	624	1.0
(2)-(0)	1.132	0.790	1.433	6.0	624	2.0
(3)-(0)	2.263	1.579	1.433	6.0	624	4.0
(4)-(0)	4.523	3.158	1.432	6.0	624	8.0
(2)-(1)	0.566	0.395	1.433	6.0	624	1.0
(3)-(1)	1.697	1.184	1.433	6.0	624	3.0
(4)-(1)	3.957	2.763	1.432	6.0	624	7.0
(3)-(2)	1.131	0.789	1.433	6.0	624	2.0
(4)-(2)	3,391	2.368	1.432	6.0	624	6.0
(4)-(3)	2.260	1.579	1.431	6.0	624	4.0

Corollary 2: The scatterers responsible for the respective differential turbidities τ^d are homogeneous in size (L = 624 nm) within the intervals (1)-(0), (2)-(1), (3)-(2), (4)-(3) and also (1)-(0) to (4)-(0); this is confirmed also by data for the remaining intervals. The total concentration c

(g/100 g) of the newly created scatterers (component B) increases from 1×10^{-3} to 8×10^{-3}. Should the size found for individual intervals be rising (decreasing), a continuous increase (decrease) in the size of the component B or appearance of a third component C with larger (smaller) scatterers is to be expected.

Now, let us suppose that the original system measured at (I) = (0) is identical with the homogeneous component A; then $\alpha_0 = 2.00$ (L = 208 nm), $[\tau/c]_0^A = 173.8$ and $[\tau/c]_1^A = 98.2$ ($T_{01}^A = 1.769$). Component B, as estimated by the DTR method, is characterized by $\alpha_0 = 6.00$ (L = 624 nm), $[\tau/c]_0^B = 565.7$ and $[\tau/c]_1^B = 394.8$ ($T_{01}^B = 1.433$). By inserting these data into eq. (4) we calculate x_A for the systems related to (I) = (1) to (4) (Table 4) using the ITR data (T_{01}^{AB}) from Table 2.

TABLE 4: Estimation of fraction x_A, concentration c_A and homogeneity of the component A

(I)	x_A	x_B	x_A/x_B	10^3c_B	10^3c_A	10^3c
(0)	1.000	-		-	8.00	8.00 (8.0)
(1)	0.887	0.113	7.85 (8.0)	1.0	7.85	8.75 (9.0)
(2)	0.798	0.202	3.95 (4.0)	2.0	7.90	9.90 (10.0)
(3)	0.667	0.333	2.00 (2.0)	4.0	8.00	12.00 (12.0)
(4)	0.495	0.505	0.98 (1.0)	8.0	7.84	15.84 (16.0)

Correct data for x_A/x_B and total concentration c are given in parentheses.

Corollary 3: The concentration of B in the system related to (I) = (1) (Tables 3 and 4) is 1×10^{-3} g/100 g; thus, the concentration of A must be 7.85×10^{-3} g/100 g which is nearly identical with that found in Table 2. Data for systems corresponding to (I) = (2), (3), (4) behave in a similar manner. The homogeneity of the component A may be regarded as proved (Table 4, column c_A). Should different concentrations be found instead of their approximate identity, heterogeneity of the component A is to be expected.

6. Concluding Remarks

The model examples given in this paper cannot respect experimental errors usual in this type of measurements. Also, differences between the expected and really found values (due to their rounding off during evaluation of the primary data) cannot substitute the role of experimental errors which may be decisive for the applicability of the method tested. However, more persuasive are the results obtained by using both methods for the analysis of the swelling-deswelling processes in the poly(2-hydroxyethyl methacrylate) gel swollen in butanol, induced by an increase (decrease) in temperature (SEDLÁČEK and KOŇÁK 1982).

It was shown that the ITR method is able to solve more complicated problems than expected but, when applied to dynamic systems, it can hardly compete with the DTR method which exceeds the former especially in the resolving power, accuracy and reliability. A combination of the ITR and DTR methods seems to be the most efficient approach.

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