Chem. Pharm. Bull. 25(5)1113—1120(1977)

UDC 546.824.03.08 : 615.2.011.4

Determination of the Particle Size Distribution of Titanium Dioxide by the Measurement of Turbidity

Akira Takamura, Shun-ichi Noro,[1a)] and Masumi Koishi[1b)]

Meiji College of Pharmacy[1a)] and Faculty of Pharmaceutical Sciences, Science University of Tokyo[1b)]

(Received July 29, 1976)

In this paper, the particle size distribution of TiO_2 measured by a turbidimeter is compared with that of the micron photo sizer and, in succession, the validity of turbidimetry is discussed. After changes of the turbidity with time were measured, the particle size distribution was then evaluated indirectly from above data. Furthermore, the approximate formula of particle size distribution was calculated from an aspect of statistical analysis.

In result, it was clearly observed that the particle size distribution calculated from the approximate formula was closely agreement with the ones measured by the turbidimeter and the micron photo sizer. It was, therefore, ascertained that the particle size distribution of powder was possible to be exactly measured by the method of turbidimeter.

Keywords——electron microscope; particle size; particle size distribution; pycnometer; sedimentation velocity; sodium phosphate; Stoke's law; titanium dioxide; turbidimeter; Zeta potential

It is considered as one of the most important subjects on the preparation of suspension to determine the particle size distribution of powder suspended or to research the physical stability of suspension. Many unique techniques have already been studied and employed into the measurable instruments of particle size distribution.[2-6)] For example, the sedimentation balance method was extensively employed in the many laboratories and factories.[7)] On the measurement by this method the particle size distribution can be calculated from the data of the relationship between the weight of sedimentation particles and sedimentation velocity. However, in this method, as the weight of particles must be directly measured, a certain degree of particle weight concentration is necessary. Accordingly, the considerable predispersion of powder particles is required to prevent the primary particles adhering to one another in suspension.

On the other hand, compared with above method, the turbidimetry has several advantages that particle size distribution can be exactly measured by using only a small amount of powder.

In this paper,[8)] therefore, particle size distribution measured by a turbidimeter is first compared with that of other method and, in succession, the validity of turbidimetry is discussed.

The powder of TiO_2 of which size distribution had been already measured under the micron photo sizer was picked up and examined by a turbidimeter. After changes of the

1) Location: *a) 1-22-1, Yato-cho, Tanashi-shi, Tokyo; b) 12, Ichigaya Funakawara-machi, Shinjuku-ku, Tokyo.*

2) S. Loyd and S.L. Green, *J. Colloid Interface Sci.*, **26**, 175 (1963).
3) P.C. Hiemenz and R.D. Vold, *J. Colloid Interface Sci.*, **21**, 479 (1966).
4) R.A. Dobbins and G.S. Jizmagian, *J. Opt. Soc. Amer.*, **56**, 1345 (1966).
5) M.J. Groves and D.C. Freshwater, *J. Pharm. Sci.*, **57**, 1273 (1968).
6) T. Kubo, S. Tskiyama, A. Takamura, and I. Takashima, *Yakugaku Zasshi*, **91**, 518 (1971).
7) R.E. Wachtel and V.K. Lamer, *J. Colloid Sci.*, **17**, 53 (1962).
8) A. Takamura, S. Noro, and M. Koishi, Presents at the 29th Annual Meeting of Colloid Discussion (Chemical Society of Japan), Matsumoto, September, 1976.

turbidity with time were measured, the particle size distribution was then evaluted indirectly from above data. Furthermore, the approximate formula of particle size distribution was calculated from an aspect of statistical analysis.

Theory

Relation between Particle Size and Turbidity

The relations between the particle size of powder and the turbidity produced by a suspension can generally be represented as shown bellow,[9]

$$\log I_0 = k\sum_0^{\infty}\pi d_i^2 \cdot n_i \tag{1}$$

$$\log I = k\sum_0^{i}\pi d_i^2 \cdot n_i \tag{2}$$

where log I_0 is turbidity of initial stage, log I is turbidity of optional time, k is constant of turbidimeter, n_i is particle number of powder, and d_i is particle diameter of powder.

Namely, when the particles of powder suspended are naturally sedimenting in a liquid, the incident light is scattered at the surface of each particle. At an optional time the scattering or reflecting intensities are proportional to the total cross area of particles in suspension.

Here, the ratio of Eq. (2) to Eq. (1) is represented as

$$\tau_s = \frac{\log I}{\log I_0} = \sum_0^{i} d_i^2 n_i / \sum_0^{\infty} d_i^2 n_i \tag{3}$$

where τ_s is the surface percentage of particles in the range from $d_i=0$ to $d_i=i$. In practical, if the weight percentage of particle is required, τ_s can be easily connected to the equation concerning the weight percentage of particle, τ_w is given by

$$\tau_w = \sum_0^{i} d_i \sum_0^{i} d_i^2 n_i / \sum_0^{\infty} d_i \sum_0^{\infty} d_i^2 n_i$$

$$= \sum_0^{i} d_i^3 n_i / \sum_0^{\infty} d_i^3 n_i \tag{4}$$

Moreover, the concentration of suspension can be written as:

$$C = \frac{\pi}{6}\rho \sum_0^{\infty} d_i^3 n_i \tag{5}$$

where C is concentration of powder(mol/l), and ρ is density of powder. Now, combining Eq. (1) and (5), the following relations can be obtained,

$$\frac{\log I}{C} = \frac{k\sum_0^{\infty} d_i^2 n_i}{\rho\frac{\pi}{6}\sum_0^{\infty} d_i^3 n_i} = k' \frac{\sum_0^{\infty} d_i^2 n_i}{\sum_0^{\infty} d_i^3 n_i} = k' \frac{1}{d_{vs}} \tag{6}$$

where k' is constant of Eq. (6), and d_{vs} is mean surface-volume diameter of powder. The equation shows that, if the turbidities of suspension are measured at various concentrations, the mean surface-volume diameter of particle is obtained from Eq. (6).

The Apporoximate Formula of Logarithmic Particle Size Distribution

If the particle sizes in the size frequency-particle size plot are replaced by their logarithms an asymmetric, or skew, particle size distribution appears approximately symmetrical one. This logarithmic normal distribution curve is defined by,

$$F(d_i) = \int \frac{1}{\sqrt{2\pi}\log\sigma_g} \exp\left[-\frac{(\ln d_i - \ln d_g)^2}{2\log^2\sigma_g}\right] d\ln d_i \tag{7}$$

where $F(d_i)$ is a function of particle size, d_g is the geometric mean diameter, and σ_g is the logarithmic standard deviation, respectively.

9) P. Bagchi and R.D. Vold, *J. Colloid Interface Sci.*, **53**, 194 (1975).

$$\log d_g = \sum \log d_i / \sum n_i \tag{8}$$
$$\log^2 \sigma_g = \sum (\log d_i - \log d_g)^2 / \sum n_i \tag{9}$$

Here, if the value of t is defined as Eq. (10), Eq. (7) is rewritten as Eq. (11),

$$t = (\log d_i - \log d_g)/\log \sigma_g \tag{10}$$
$$F(t) = \int \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{t^2}{2}\right) dt \tag{11}$$

where $F(t)$ is function of t.

As $\exp(-t^2/2)$ cannot be represented as an indefinite integral form, $F(t)$ is represented as the following approximate formula derived by Taylor's theorem.

$$g(t) = \exp(-t^2/2) \tag{12}$$
$$g(t) = g(0) + \frac{g'(0)}{1!} t + \frac{g''(0)}{2!} t^2 + \cdots + \frac{g^{(n-1)}(0)}{(n-1)!} t^{(n-1)} + \frac{g^n(0)}{n!} t^n \tag{13}$$

where $g(t)$ is function of t.

Now, the coefficients of these terms are given in Table I.

$$g(t) = \left(1 - \frac{1}{2} t^2 + \frac{1}{8} t^4 - \frac{1}{43} t^6 + \frac{1}{384} t^8 - \frac{1}{3840} t^{10} \cdots\right) \tag{14}$$

Integrating the above equation, the following Eq. (15) can be obtained.

$$F(t) = \frac{1}{2} + \frac{1}{\sqrt{2\pi}} \left(t - \frac{1}{6} t^3 + \frac{1}{40} t^5 - \frac{1}{336} t^7 + \frac{1}{3456} t^9 - \frac{1}{42240} t^{11} \cdots\right) \tag{15}$$

When a particle having d_i falls naturally in the fluid, the Stoke's law is applied to the sedimentation velocity of a particle, as given by

$$d_i = \left[\frac{18\mu_c}{(\rho_p - \rho_c) g} u\right]^{1/2} \tag{16}$$

where g is gravitational acceleration, u is sedimentation velocity, μ_c is viscosity of continuous phase, ρ_p is density of particle, and ρ_c is density of continuous phase. Now, the sedimentation velocity u is defined as a transfer distance h of particle in an unit time intervals T.

$$u = h/T \tag{17}$$

Thus, Eq. (16) can be rewritten as the equation

$$d_i = \left[\frac{18\mu_c h}{(\rho_p \text{-} \rho_c)}\right]^{1/2} (1/T)^{1/2} = k'' T^{-1/2} \tag{18}$$

This equation means that the particle size d_i can be connected with sedimentation time T and constant k''.

Here, if T_m is defined as the sedimentation time required for the turbidity to be reduced to one-half its initial value, d_g is given as follow.

$$d_g = k T_m^{-1/2} \tag{19}$$

Still more, the geometric standard deviation, σ_g, is the intervals of particle size that the weight percentage of particle exists between 84.2% and 50.0% or 50.0% and 15.8%,

$$\log \sigma_g = \log d_\sigma - \log d_m = \log T_\sigma - \log T_m \tag{20}$$
$$T_\sigma = T_m \sqrt{T_{0.158}/T_{0.852}} \tag{21}$$

where d_m is mean diameter of particle, d_σ is particle diameter at $d_m \pm \sigma$, and T_σ is sedimentation time at $50 \pm \sigma$ percent.

Substituting Eq. (18), (19) and (20) into Eq. (10), the value of t given by the equation.

$$t = \frac{\log (T_m/T)}{\log (T_m/T_\sigma)} \tag{22}$$

Eq. (22) is substituted in Eq. (15), then

$$F(d_i) = F(T) = \frac{1}{2} + \frac{1}{\sqrt{2\pi}}\left[\frac{\log(T_m/T)}{\log(T_m/T_\sigma)} - \frac{1}{6}\frac{\log^3(T_m/T)}{\log^3(T_m/T_\sigma)} + \frac{1}{40}\frac{\log^5(T_m/T)}{\log^5(T_m/T_\sigma)} - \frac{1}{336}\frac{\log^7(T_m/T)}{\log^7(T_m/T_\sigma)} + \cdots\right] \tag{23}$$

where $F(T)$ is function of sedimentation time.

Consequently, T_m, T_σ and T are firstly obtained from the change of turbidity, log I, in the course of sedimentation, and in succession, the approximate formula of particle size distribution can be calculated from Eq. (23).

TABLE I. Calculated Coefficient of the Function of $y=\exp\left(-\frac{t^2}{2}\right)$ (Taylor's Theorem)

$f^{(n)}(t)$	Coefficient	Normal type	Integral type
$f^{(2)}(t)$	$-\frac{1}{2!}$	$-\frac{1}{2}t^2$	$-\frac{1}{6}t^3$
$f^{(4)}(t)$	$\frac{3\cdot1}{4!}$	$\frac{1}{8}t^4$	$\frac{1}{40}t^5$
$f^{(6)}(t)$	$-\frac{5\cdot3\cdot1}{6!}$	$-\frac{1}{48}t^6$	$-\frac{1}{336}t^7$
$f^{(8)}(t)$	$\frac{7\cdot5\cdot3\cdot1}{8!}$	$\frac{1}{348}t^8$	$\frac{1}{3456}t^9$
$f^{(10)}(t)$	$-\frac{9\cdot7\cdot5\cdot3\cdot1}{10!}$	$-\frac{1}{3840}t^{10}$	$-\frac{1}{42240}t^{11}$
$f^{(12)}(t)$	$\frac{11\cdot9\cdot7\cdot5\cdot3\cdot1}{12!}$	$\frac{1}{46080}t^{12}$	$\frac{1}{599040}t^{13}$
$f^{(14)}(t)$	$-\frac{13\cdot11\cdot9\cdot7\cdot5\cdot3\cdot1}{14!}$	$-\frac{1}{645120}t^{14}$	$-\frac{1}{9676800}t^{15}$
$f^{(16)}(t)$	$\frac{15\cdot13\cdot11\cdot9\cdot7\cdot5\cdot3\cdot1}{16!}$	$\frac{1}{10321920}t^{16}$	$\frac{1}{175472640}t^{17}$
$f^{(18)}(t)$	$-\frac{17\cdot15\cdot13\cdot11\cdot9\cdot7\cdot5\cdot3\cdot1}{18!}$	$-\frac{1}{185794560}t^{18}$	$-\frac{1}{3530096640}t^{19}$
$f^{(20)}(t)$	$\frac{19\cdot17\cdot15\cdot13\cdot11\cdot9\cdot7\cdot5\cdot3\cdot1}{20!}$	$\frac{1}{371589120}t^{20}$	$\frac{1}{78033715200}t^{21}$

Experimental

Equipment and Specimen——The specimen used in our work was rutil type bare Titanium dioxide named as R-310 of Sakai Chemical Co., Ltd. The data of particle size distribution of TiO_2 is given in Table II. The specimen was first dispersed by homomixer for 5 min and then the particle size distribution was measured by MSKK type of micron photo sizer (Seishin Kigyō Co., Ltd.). In this preparation, the suspension was diluted with a water until the concentration of it was about 0.050 g/liter. 10 ml of sodium metaphosphate (5.0 g/liter) was added to this suspension as a dispersing agent.

A sketch of the apparatus employed is shown in Fig. 1. The turbidimeter used was PT-201 type of Nihon Seimitsu Kōgaku Co., Ltd. Since the turbidimeter adopts the sphere method of electrophotometer, the intensity of turbidity could exactly be measured regardless of coloured sample. The value of turbidity could be changed in the three ranges of 0—5 ppm, 0—50 ppm, and 0—500 ppm. The cell used was made of the special coated glass. The specimen box was surrounded and circulated with the air controlled at 30.0° by thermostat in order to keep the temperature of stable suspension at 30.0°. The changes of turbidity and temperature with time were simultaneously recorded, respectively, on the B-281H type recorder of Rika Electro Co., Ltd.

Experimental Procedures——Titanium dioxide was sufficiently dried at 105° and kept in a desiccator before used in this experiment. After 1.50 mg of TiO_2 was sampled and dispersed in 400 ml of distilled water, and then 10 ml of sodium metaphosphate (5.0 g/liter) was added as a dispersing agent. The total volume of suspension was adjusted to 500 ml with adding distilled water. The pH of suspension was 7.1. The ultrasonic beam (30 kHz) was emitted to the suspension for 10 min, in order to disperse homogeniously powder particles into a water. 5 ml of sample suspension was gently placed by a pipette into the cell. The depth from a liquid surface to an optical axis was settled to 13.0 mm to keep a measurement position of turbidity constant. After 30 seconds sedimentation time, the measurement of turbidity was started and recorded. The observation of turbidity was continued for 48 hr. Then, the analyses of these data were employed and the approximate formula of particle size distribution was calculated by using a Seiko-S-301 electronic computer.

Measurement of Physical Properties of Suspension——A particle density of TiO_2 was measured by a pycnometer. The density of TiO_2, ρ_p, was equal to 4.214 (g/cm³).

The viscosities of continuous phase were measured by the rotating viscometer (Shibaura System Co., Ltd.) a constant at 30.0°. The viscosities were extended in the range of 0.80—1.00 centi poise in this experiment.

The electrophoretic velocity of TiO_2 in suspension used for turbidity measurement was measured with moving boundary method by using U-shaped tube under the constant 200 V, attached to potentiometer (Tōyō Science Co., Ltd.), and Zeta potential of TiO_2 was calculated by usual equation. The value is −37 mV and it shows the very good stability of TiO_2 suspension.

The shapes and sizes of powder particle were observed and photographed by transmission electron microscope (NEM-100B type, Nippon Electron Co., Ltd.). Figure 2 shows the electron micrograph of Titanium dioxide.

TABLE II. Particle Size Distribution from the Micron Photo Sizer Method

Subdivision of particle size μ	Weight distribution[a]		Surface area distribution[b]	
	%	Σ %	%	Σ %
2.5—3.0	3.2	100.0	0.6	100.0
2.0—2.5	6.8	96.8	1.6	99.4
1.5—2.0	6.6	90.0	2.0	97.8
1.0—1.5	17.1	83.4	7.3	95.8
0.9—1.0	5.4	66.3	3.0	88.5
0.8—0.9	4.5	60.9	2.8	85.5
0.7—0.8	6.3	56.4	4.5	82.7
0.6—0.7	5.9	50.1	4.8	78.2
0.5—0.6	8.4	44.2	8.1	73.4
0.4—0.5	12.1	35.8	14.3	65.3
0.3—0.4	11.2	23.7	17.0	51.0
0.2—0.3	8.8	12.5	18.7	34.0
0.1—0.2	3.4	3.7	12.1	15.3
—0.1	0.3	0.3	3.2	3.2

note: a) measured by Micron Photo Sizer and these technical information data received from Sakai Chemical Co., Ltd.
b) values were calculated in this experiments

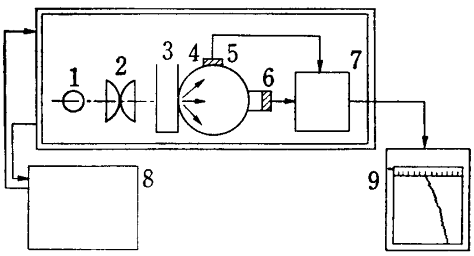

Fig. 1. Apparatus

1. lamp
2. condenser
3. cell
4. integral sphere part
5. detector (scatter transmission light)
6. detector (parallel transmission light)
7. amplifier and calculater
8. thermostat
9. recorder

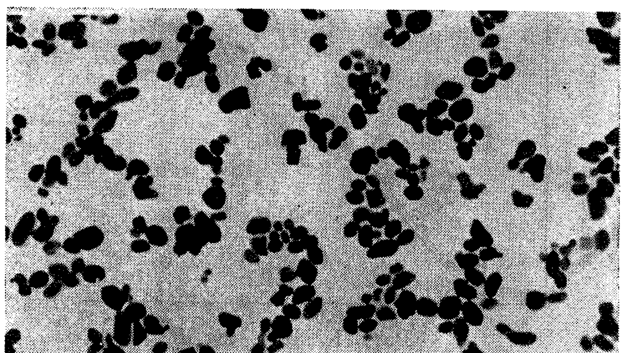

Fig. 2. Electron Micrographs of Titanium Dioxide

Results and Analyses

Calculation of the Particle Size Distribution from the Intensity of Turbidity

Figure 3 shows the change for the turbidity of Titanium dioxide at the initial stage in the course of sedimentation. A little fluctuation was found in this curve, and the turbidity decreased gently according as the sedimentation time passed.

Figure 4 shows the change of relative turbidity, $\log I/\log I_0$, in the course of sedimentation. The values of relative turbidity were 96.9, 88.8, and 41.0% at 20 min, 100 min, and 1000 min, respectively.

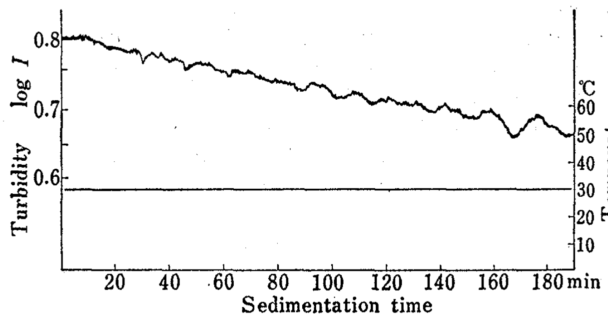

Fig. 3. Recording Curve of Turbidity of TiO_2 Suspension with Time at 30.0°

Relation between particle size of powder and sedimentation time are shown in Fig. 5. In this experiment, the values such as the viscosity of continuous phase, μ_c, the liquid depth, h, the density of particle, ρ_p, and the density of continuous phase, ρ_c, were 0.8 cP., 13.0 mm, 4.214 g/cm³, and 1.000 g/cm³, respectively. Then, after these values were substituted into Eq. (18), the value of d_i was calculated. The intercept of tangent to this curve gave the value of k'' equal to 9.55.

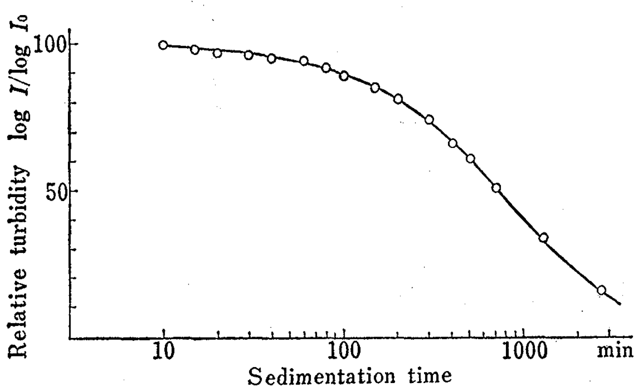

Fig. 4. Change of Relative Turbidity with Sedimentation Time

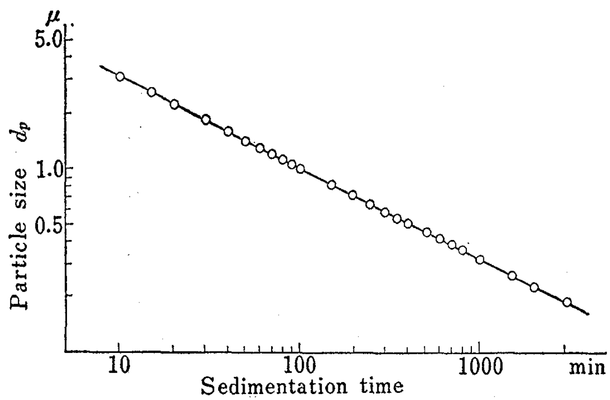

Fig. 5. Relation between Particle Size of TiO_2 and Sedimentation Time

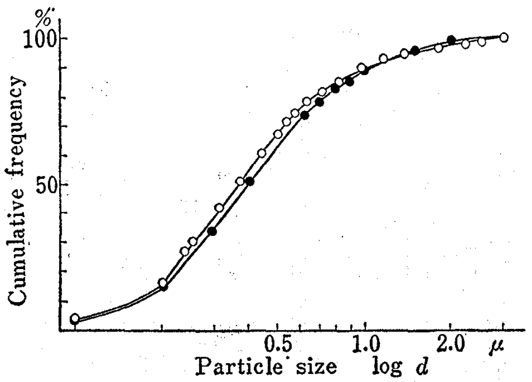

Fig. 6. Particle Size Distribution[a] of TiO_2

key: (○) calculated by data from turbidimeter
(●) calculated by data from micron photo sizer
note: *a*) corresponds to surface area distribution

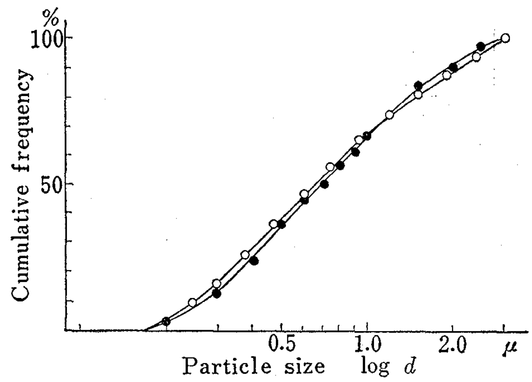

Fig. 7. Particle Size Distribution[a] of TiO_2

key: (○) calculated by data from turbidimeter
(●) calculated by data from micron photo sizer
note: *a*) corresponds to weight distribution

Relations between particle size and cumulative frequency for the surface area of particle were shown in Fig. 6. Particle size was calculated from Eq. (18), and cumulative frequency of the surface percentage of particle was required from the data of log I/log I_0.

In Fig. 6, it was obviously found that the skewed curve from the measurement of the turbidity was good agreement with the curve obtained from the micron photo sizer.

Table III gives the weight percentage of particle converted from the surface percentage of particle. The particle size in Fig. 6 was firstly divided in equal 12 parts on the logarithmic scale. In succession, multiplication of the medium of particle size at each part by the surface percentage of particle gave weight percentage of particle.

Figure 7 shows the relation between particle size and cumulative frequency of TiO_2 weight. In this figure, the values calculated from the measurement of the turbidity agreeded very closely with that obtained by the micron photo sizer.

TABLE III. Calculation of Weight Percentage of Particle Calculated from Surface Percentage of Particle

	Maximum particle size μ	Medium μ	Cumulative percentage %	Surface percentage %	Medium × Surface percentage	Weight percentage %	Cumulative weight percentage[a] %	Cumulative weight percentage[b] %
12	3.000	2.692	100.0	1.0	2.69	5.17	100.00	100.0
11	2.400	2.138	99.0	1.4	3.17	6.09	94.73	95.5
10	1.910	1.700	97.6	2.1	3.70	7.11	88.64	90.0
9	1.515	1.350	95.5	2.5	3.52	6.77	81.53	83.5
8	1.205	1.072	93.0	4.5	4.82	9.27	74.76	74.0
7	0.995	0.851	88.5	5.5	4.68	9.00	65.49	63.8
6	0.760	0.676	83.0	7.0	4.73	9.09	56.49	54.0
5	0.600	0.537	76.0	11.5	6.18	11.88	47.40	44.5
4	0.480	0.427	64.5	13.0	5.55	10.58	35.52	33.0
3	0.380	0.339	51.5	13.0	4.41	8.48	24.94	22.0
2	0.300	0.269	38.5	12.5	3.36	6.46	16.46	12.5
1	0.240	0.200	26.0	26.0	5.20	10.00	10.00	7.2

note: a) calculated by data from Turbidimeter
b) calculated by data from Micron Photo Sizer

TABLE IV. Calculation of Weight Percentage of Particle from Eq. (23)

	Maximum particle size μ	Medium μ	t	$F(t)$	Cumulative weight percentage[a] %	Cumulative weight percentage[b] %
12	3.000	2.692	1.766	96.2	100.00	100.0
11	2.400	2.138	1.505	94.5	94.73	95.5
10	1.910	1.700	1.238	89.3	88.64	90.0
9	1.515	1.350	0.968	83.4	81.53	83.5
8	1.205	1.072	0.700	75.8	74.76	74.0
7	0.995	0.851	0.476	68.3	65.49	63.8
6	0.760	0.676	0.161	56.4	56.49	54.0
5	0.600	0.537	−0.115	45.4	47.40	44.5
4	0.480	0.427	−0.376	35.2	35.52	33.0
3	0.380	0.339	−0.649	25.8	24.94	22.0
2	0.300	0.269	−0.925	16.0	16.46	12.5
1	0.240	0.200	−1.19	11.5	10.00	7.2

note: a) calculated by data from Turbidimeter
b) calculated by data from Micron Photo Sizer

Calculation of the Approximate Formula of Logarithmic Size Distribution

Equation (22) can be replaced by next equation.

$$t = \frac{\log (T_m/T)}{\log (T_m/T_\sigma)} \frac{\log (d_i/d_m)}{\log (d_\sigma/d_m)} \tag{24}$$

$$d_\sigma = d_m\sqrt{d_{0.842}/d_{0.158}} \tag{25}$$

The values such as d_m, $d_{0.842}$ and $d_{0.158}$ obtained from Fig. 7 were given by following.

$$d_m = 0.662\mu,\quad d_{0.842} = 1.71\ \mu,$$
$$d_{0.158} = 0.309\ \mu \tag{26}$$

These above values were substituted into Eq. (25) and Eq. (24), d_g and t could be calculated as follows:

$$d_\sigma = 0.662\sqrt{1.710/0.309} = 1.557 \tag{27}$$

$$t = \frac{\log (d_i/0.662)}{\log (1.557/0.662)} = \frac{\log (d_i/0.662)}{0.3716} \tag{28}$$

The both values t and $F(t)$ are calculated by using the computer of Seiko-S-301. In this case, the particle size was divided in equal 12 parts on the logarithmic scale. These calculated values are given in Table IV.

Figure 8 shows the distribution of weight percentage of particle. In this occasion, the particle size was classified into 6 parts on the logarithmic scale. It was clearly observed that the curve calculated from Eq. (18) was closely agreement with the ones measured by the turbidimeter and the micron photo sizer.

It was, therefore, ascertained that the particle size distribution of powder was possible to be exactly measured by the method of turbidimeter.

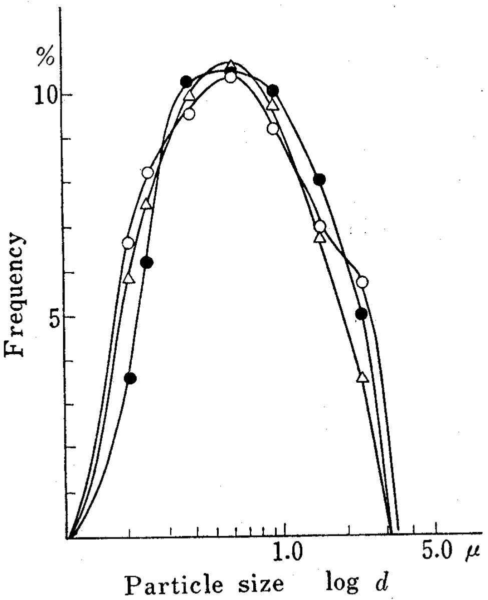

Fig. 8. Particle Size Distribution of TiO_2

key: (○) calculated by data from turbidimeter
(●) calculated by data from micron photo sizer
(△) calculation

Accordingly, this measurement method will be very useful for the observation of the particle size distribution and then it will be good guide for the studies on the preparation and stability of suspension.

Acknowledgement The authors are indebted to Dr. C. Inoue, lecture of Meiji College of Pharmacy, for suggesting this problem and for stimulating interest in it. The authors also wish to thank Mr. H. Takebayashi, Faculty of Pharmaceutical Sciences, Science University of Tokyo, who kindly supplied us their electron microscope photograph of TiO_2.