MODIFICATION OF ANDREASEN'S GRAIN SIZE DETERMINATION METHOD I

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In spite of the spreading use of expensive picture analyzers and apparatuses operating on Coulter's principle, in certain cases grain size must be determined on the basis of sedimentation rate. It is namely well known that particle size analysis will be really informative, if the determination is carried out under the same experimental conditions as actual use. Thus, for example, by sedimentation experiments the optimal additive composition can be selected for a given system (dispersed phase and dispersion medium), and in the limit case the complete elimination of electrostatic and other forces causing agglomeration can be achieved. These investigations are of particular importance in the formulation of drugs and pesticides.

In sedimentation analysis sensing can be undertaken by photometric or by gravimetric method. In the last ten years, photosedimentometers working with electromagnetic waves of various energy gained wide-spread use. However, these instruments must often be calibrated, results frequently depend on shape and size, so that these apparatuses are suitable mainly for laboratories, where a great number of routine analyses are to by carried out on substances of the same type.

In many working places still apparata based on gravimetry are used, however, an instrument is needed for the weighing with sedimentation balance, and one weighing per day can be performed at the most with the balance.

In several cases, grain size analysis belongs to those measurements, which are needed only periodically. In this case, institutions will find it impractical to procure expensive apparatus, and either comission other places with the measurement, or perform it in their own laboratory, but use a process which does not claim high investment.

Thus, notwithstanding the wide-spread use of large-instrument particle size analyzers, in certain cases particle size determination will be carried out with Andreasen's pipette method, because

— measurement must be performed in suspension,
— the reproducibility of the method is good,

— Andreasen's apparatus is simple and cheap,
— thus, one working place may be equipped with several apparatuses,
— analysis being thus finally more rapid.

These are the aspects, which justify even today the use of Andreasen's pipette method, involving cheap glass devices.

The principle of the method is known [1, 2, 3], the apparatus is shown in Fig. 1.

From the initially homogenous suspension a given volume is sucked off at the points of time t_1, t_2 . . . . t_n. The solids content of the sample sucked off is determined by some suitable method (drying, titration), measuring thus at points of time t_1, t_2 . . . t_n the quantity of the still suspended particles in the suspension.

From these measuring results the curve of the settling rate is plotted, and from this the integral or differential distribution curve can be calculated on the basis of Stokes' law.

It can be seen even from this brief description of the procedure that the method is subject to systematic error, because sedimentation is disturbed by each sampling.

The object of our modified process is to maintain the advantages of the method and eliminate or restrict to a minimum this disturbance.

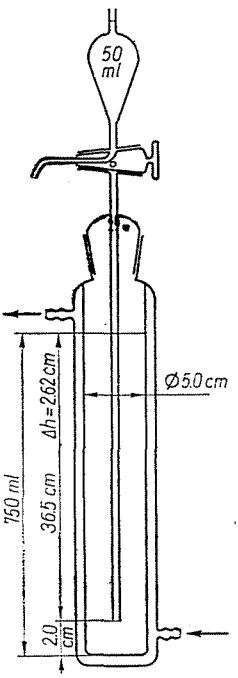

Fig. 1. Andreasen's apparatus

For this two possibilities are offered:

— Modification of the apparatus

— Sucking off only one sample from one suspension column.

Owing to the said insufficiencies, the apparatus of Andreasen saw several modifications in the last 50 years, which aimed at the development of more reliable, representative and rapid methods by a change in measuring conditions and methodics [4—10]. With our work we wish to contribute to these results, our aim being a further improvement of sedimenting and sampling conditions.

Modification of Andreasen's method

According to our experiences results obtained by Andreasens method are readily reproducible, but on comparing our measurements with results obtained by other methods, we found in our case a finer granulation for the test samples. The reason for this is obviously the disturbing of sedimentation by sampling.

Representative sampling is presumably affected by the geometric data of the apparatus and by the concentration of the suspension. Therefore, before the changing of the design of the apparatus, we investigated to what measure settling rate is changed by:

— the concentration of the suspension,

— the site of sampling in the sedimentation column, and

— the diameter of the sedimentation column.

It was established by preliminary investigations that settling rate does not change:

— if the concentration does not exceed 5 mg/cm^3,

— if the site of sampling is at a distance of at least 2.5 cm from the bottom of the column, and

— if the diameter of the column is larger than 2 cm.

We were of the opinion that sucking off by vacuum, or flow conditions established, or possibly both are responsible for the finer granulation.

First, the effect of vacuum on settling rate has been investigated. We think it namely as an acceptable explanation of the above irregularities that on sucking the pipette with vacuum the settled layer is stirred up, and this increases the real concentration of the suspension. Translating this error to particle size language: at each point of time more substance is measured in the suspended state, settling rate diminishes, the system seems to be of finer distribution.

It has been investigated in which way this error can be eliminated in a modified Andreasen apparatus. The apparatus of different sampling system

designed by us is shown in Fig. 2. From the "modified Andreasen's apparatus" shown in the figure the sample is not sucked off by vacuum, but is forced by the hydrostatic pressure of the liquid column into the sampling pipette.

In the further work the effect of a change in flow conditions on sedimentation has been investigated. For this purpose a so called "integral settling tube" was constructed on the analogy of Oden's [11, 12] sedimentation balance.

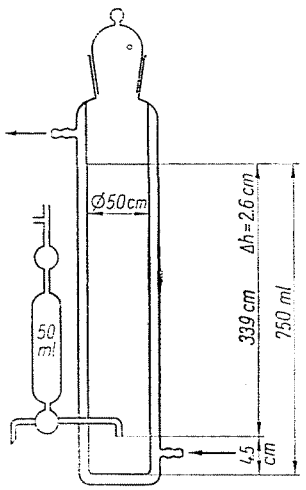

Fig. 2. Modified Andreasen's apparatus

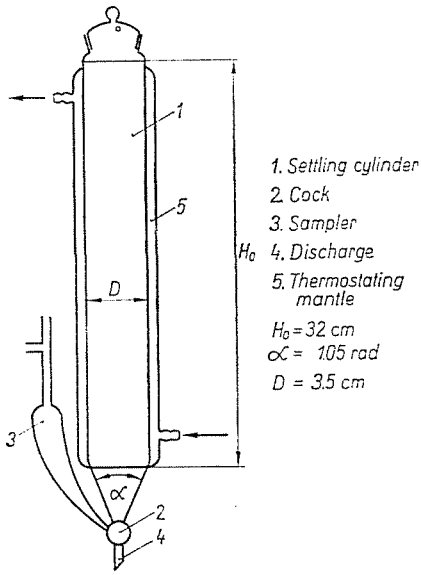

Fig. 3. Integral settling tube

Our modification was made on the basis of the following considerations:

— Settling shall be less disturbed on sampling.

— Measurement shall be more accurate, the condition of which is that in the case of complete sucking off:

— the sum of the solids content of the samples shall approach the weighed in quantity, i.e. it shall not adhere to the apparatus,

— the solids content of the sample shall be measurable at adequate accuracy, that is to say even in more dilute suspensions, providing for better settling conditions, the quantity weighed back shall be more than 10 mg.

The integral settling tube designed on the basis of these considerations is shown in Fig. 3. Measurements performed with the two different apparatuses and results obtained are reported in the following.

Experimental part

Test sample

Aluminium oxide p.a., manufactured by Reanal, was chosen as model substance. Density of the test sample: 3.82 g/cm^3. The pore structure of the mildly porous sample was determined with a mercury porosimeter Carlo-Erba. The pore distribution of the sample, plotted in an integral pore volume — pore radius coordinate system is shown in Fig. 4.

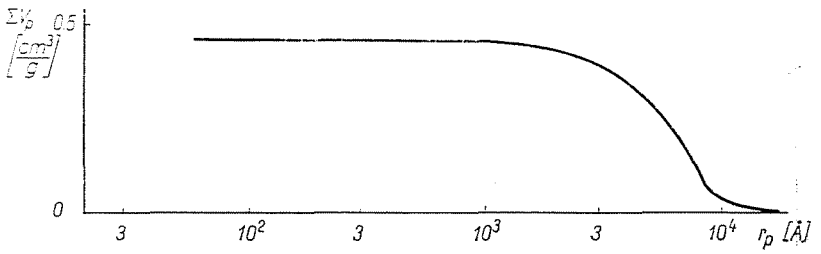

Fig. 4. Pore distribution of the sample

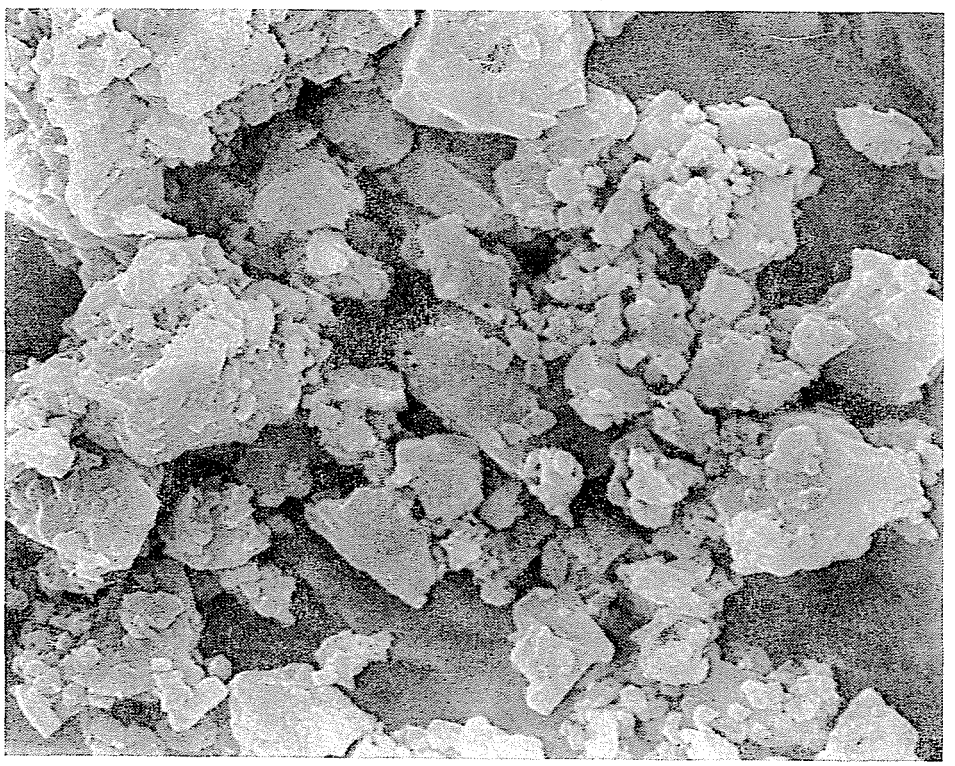

Fig. 5. Scanning electron microscope picture 4400× magnification

Conclusions on the shape of the grains can be drawn from the scanning electronmicroscope picture of 4400× magnification shown in Fig. 5.

The grain size of the test sample has been determined by the following methods:

1. With Andreasen's apparatus shown in Fig. 1 (measured in the laboratories of two institutions)
2. With the sedimentation balance of Sartorius (measured in two laboratories)
3. With photosedimentometer (Fritsch's apparatus)
4. with OPTON automatic picture analyzer.

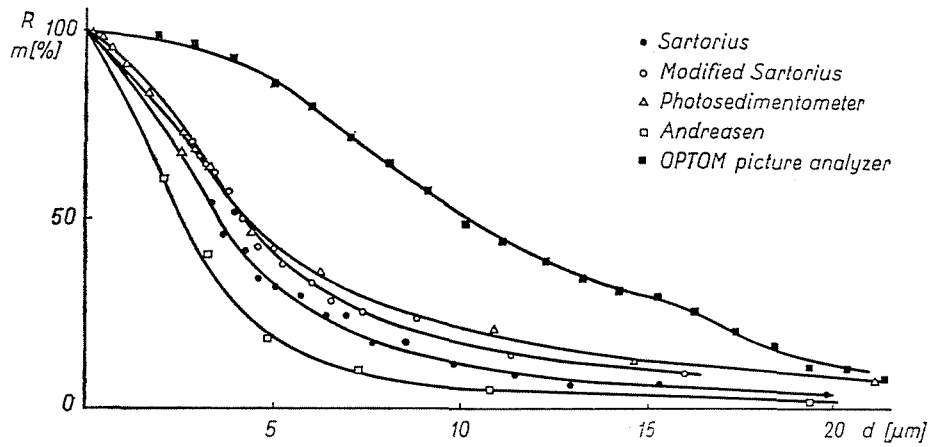

Fig. 6. Granulometric curves of the standard substance, measured by different methods

Plotted uniformly in mass — size dimensions, the distribution curves obtained are shown in Fig. 6. In the sedimentation methods the concentration of the suspension ranged from 0,5 to 2 mg/cm^3. Sodium pyrophosphate in a concentration of 1—0.1 mmol/dm^3 was used as stabilizing agent. Measurements were carried out at 25 ±0.5 °C.

Apparatus and measuring methods used

The parameters of Andreasen's apparatus are given in Fig. 1. Measurement was carried out as customary in Andreasen's method. To increase the accuracy of weighing, sampler bowls were made of aluminium foil. Schematic picture and geometrical data of the modified Andreasen apparatus are shown in Fig. 2. Measurements were carried out in the same way as in the case of the original apparatus.

Schematic picture and geometrical data of the integral settling tube are shown in Fig. 3.

It can be seen from the figure that settled particles collect at the conic bottom of the tube. Dimensions of the conical part were selected so that the volume shall be less than 10 cm^3, and the angle of inclination is of a steepness which makes the settled particles collect above the cock. The settling height is calculated thus from the edge of the cone, its maximal value being the height of the settling tube. When sampling, the aering stub is covered, the cock plug is turned, and the whole quantity of substance (m_i) settled during time t_i and still suspended in the conical part is sucked by vacuum into the sampler of 10 cm^3. The further handling of the samples is the same as customary in the Andreasen method.

The greatest problem in the design of the apparatus was to get the whole quantity of the particles settled into the sampling pipette. In the ideal case the part settled slips down along the walls of the cone, and collects above the cock. (This is promoted by washing the settling tube with chromic sulfuric acid.) However, the efficiency of suction is determined on the one hand by the quantity of the substance settled, and on the other hand, by the strength of suction.

The quantity of the sample settled can be regulated by the sampling times and by the quantity and concentration of the suspension. According to our experiences suction will be optimal, if the quantity of the substance sucked off during one suction ranges between 10 and 50 mg.

The strength of suction and the efficiency of sucking off can be improved by producing turbulent flow in the throat of the cone, which is washing off the substance. This has been achieved by the restriction of the opening of the cock. Even in this case the time of the single samplings did not exceed 2—4 seconds.

Evaluation of measuring results

It will be noted from Fig. 6 that the granulometric curves determined with the photosedimentometer and with the sedimentation balance are located in one group, while the standard sample measured with the picture analyzer seems to be of coarser, and that measured by Andreasen's method of finer structure. Results obtained with the picture analyzer can be explained by the sticking together of the sample, indeed, measurements by the other methods were carried out in suspension.

According to our assumption, the finer granulation is due to the systematic error of Andreasen's method, to the disturbance of sedimentation, thus, our aim was the design of an apparatus, where this error can be reduced to a minimum.

First it has been investigated in what measure sedimentation is disturbed by the vacuum applied for sucking off the sample. The modified

Andreasen apparatus shown in Fig. 2 has been constructed, in which sampling proceeds without application of vacuum.

Our measuring results, obtained under identical experimental conditions, are presented in Fig. 7. It can be seen from the figure that though the granulometric curve taken with the modified apparatus lies closer to the results obtained with the other methods, the effect is not substantial.

Thus, the basic difference is obviously caused by the fact that during each sicking off a suspension layer of thickness h is removed from the column, and when the layer above it flows into the place of the sucked-off layer, ascending streams are generated, which carry away substance also from the settled, i.e. the most concentrated layer. (This assumption could be proved

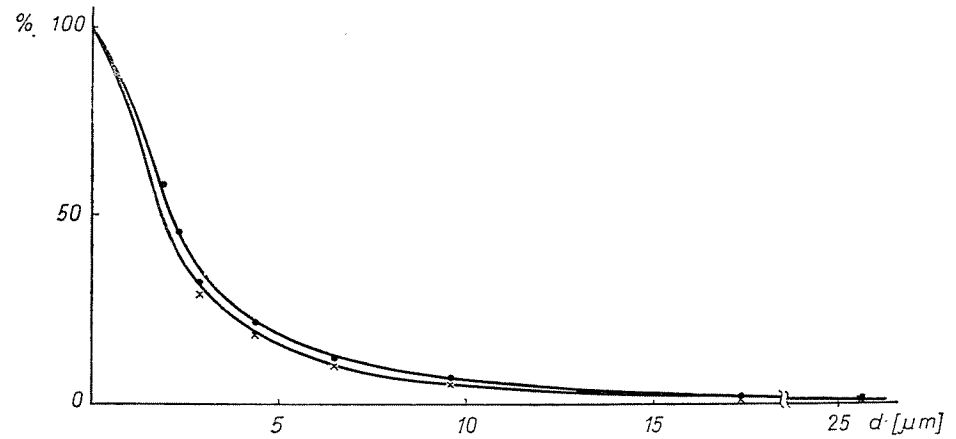

Fig. 7. Granulometric curves of the standard sample measured with × Andreasen's and ● modified Andreasen's apparatus

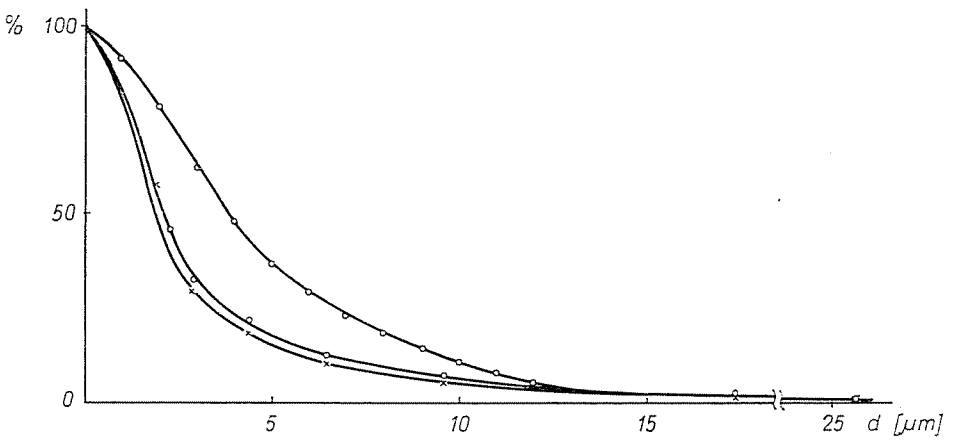

Fig. 8. Granulometric curves of the standard sample measured with × Andreasen's, ● modified Andreasen's and ○ integral settling tube methods

rather convincingly by the superlayering and subsequent sucking off of liquids of various colour.)

To avoid the stirring up of the concentrated layer, the integral settling tube shown in Fig. 3 has been constructed.

Advantages of the apparatus:

— the whole quantity of the substance settled in time t_i is sucked off, and thus, the stirring up of the more concentrated suspension layers is avoided,
— the quantity of substance weighed back can be virtually adjusted even in the case of dilute suspensions to a discretional value by the suitable selection of sampling times.

Measuring results obtained by the settling tube method are evaluated in the usual way, after forming from the weighed m_i values in turn the sums $\sum_{i=1}^{i} m_i$.

Measuring results are shown in Fig. 8. Granulometric curves taken in Andreasen's, the modified Andreasen and the integral settling tube are plotted in the figure.

It can be seen from the figure that our assumption proved true, because measurements with the integral settling tube actually yielded the grain size values determined with other methods.

The wide applicability of the apparatus is proved by the fact that under consideration of the maximal quantity which can be sucked off (50 mg, as determined in the design of the apparatus), the sedimentation rate is independent of the height of the column and of the concentration of the suspension. The reproducibility of the measurements has been checked at three different concentrations (0.5 mg/cm^3, 0.66 mg/cm^3, 1.0 mg/cm^3) and at three different column heights (20 cm, 30 cm and 32 cm).

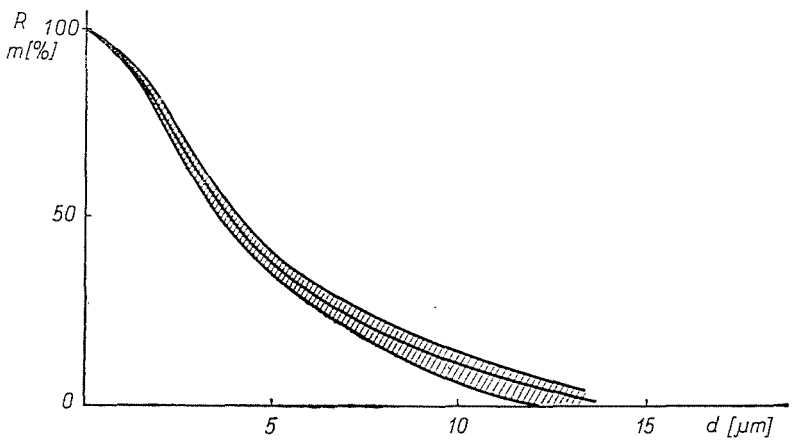

Fig. 9. Band of scattering of the measuring accuracy of the integral settling tube

Results obtained are shown in Fig. 9.

It can be seen from the figure that scattering range broadens toward larger diameters, which presumably can be attributed to the fact that this is the steepest section of the integral curve, and therefore, inaccuracy of reading is the highest, and errors in sample preparation occur also mostly in this region

Summary

On determining the grain size distribution of a given sample by different sedimentation methods, it has been established that measurement with Andreasen's method gives a finer distribution for the system. It has been assumed that this is due to the fact that in Andreasen's method sedimentation is disturbed by sampling. Disturbance of sedimentation can be caused by sucking off under vacuum, by currents produced by suction or by both.

To elucidate the problem, two apparatuses were constructed. As concerns the principle of measurement, one of these is identical with Andreasen's method, but sampling is undertaken without vacuum (modified Andreasen's apparatus), while in the other apparatus the mode of sampling has been changed, sucking off the whole quantity of the substance settled during time t_i, and preventing thereby the stirring up of the most concentrated layers. This apparatus was named integral settling tube.

According to measurements performed, this second arrangement proved to be good. Particle size determined with the integral settling tube was (within the limits of error) the same as particle sizes determined by other sedimentation methods. The reproducibility of results obtained with the apparatus has been checked, and scattering was found to be of a value between 0.75 and 1, depending on the particle size, which can be considered as a very good result in the usual grain size determination methods.

The use of the integral settling tube is particularly recommended for the grain size analysis of dilute suspensions (0.05—0.25%).

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