Determination of the Density Distribution of Suspension Poly(vinyl Chloride) by the Density Titration Method

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Synopsis

A dynamic method of density titration for the characterization of powders of suspension poly(vinyl chloride) (PVC) and of their fractions obtained by sieve analysis is described. The method is based on the distribution of PVC particles in variously concentrated aqueous solutions of sodium nitrate according to their specific weight. Separated phases are determinated volumetrically. The method makes possible characterization of various types of PVC powders and of their anomalies.

INTRODUCTION

The quality of powders of suspension poly(vinyl chloride) (PVC) is affected by reaction conditions of the suspension polymerization of vinyl chloride. For instance, the size of primary microglobules of suspension PVC or of their agglomerates depends on the polymerization temperature and conversion. In powders of suspension PVC where the particle size varies approximately between 10 and 300 μm, difficult-to-process particles appear along with normal ones. Usually, the former are nonporous glassy compact particles[1] which have a negative effect of the quality of suspension PVC powders; their occurrence creates problems both for production and processing, because their existence becomes apparent only additionally, after the PVC powders have been processed to products. The determination of difficult-to-process particles is carried out by employing a standard method based on the use of a thin (100 μm) film made from a mixture of dry powder of suspension PVC, carbon black, plasticizer, and additives. In the black film thus obtained the unprocessible particles appear in the passing light as light or shining points called "fish eyes." The result of determination is given as the number of fish eyes per gram of tested PVC.

Some authors report the separation of unprocessible particles from normal ones by enrichment techniques, consisting in the fractionation of powders of suspension PVC swollen with dioctyl phthalate by means of aqueous solutions of zinc sulfate of various density.[2] Other authors[3] use fractionated powders of suspension PVC for morphological investigation by means of methanol-tetrachloromethane mixtures of various density. In the former case, however, the structure is changed due to the effect of plasticizer; this considerably restricts the possibility of further morphological investigation, while in the latter solvents are used which do not meet the strict health requirements concerning work with poisons and carcinogenic compounds.

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This paper reports a dynamic method of density titration by which powders of suspension PVC and their fractions obtained by sieve analysis can be compared. An advantageous procedure is, for example, to compare the tested sample with a standard which is suitable for the given application.

EXPERIMENTAL

The samples of suspension PVC were of Czechoslovak origin, trade mark Neralit (Spolana, Neratovice, Czechoslovakia). Their basic characteristics are summarized in Table I.

Fraction of PVC Samples. Dry samples (500 g) were quantitatively fractionated in an Alpine apparatus (Alpine Augsburg, FRG). Five normalized (DIN, ASTM) stainless steel sieves were used, mesh size 180, 150, 125, 90, and 63 μm.

Preparation of the Basic Aqueous $NaNO_3$ Solution. The basic solution (conc. 40%) was prepared by dissolving a weighed amount of $NaNO_3$ (Lachema, Czechoslovakia, anal. grade purity) in a corresponding amount of degassed distilled water.

Determination of Integral Dynamic Density Curves by the Density Titration Method. To 1.00 g of dry PVC powder in a calibrated centrifugal test tube with a ground closure, 10 mL in volume, 2.00 of a 40% aqueous basic $NaNO_3$ solution was added, and the powder was stirred with a glass stick, 2 mm in diameter, for 5 min (after stirring only traces of PVC may remain on the stick). After centrifugation for 5 min in a desk centrifuge (1500 rpm) the volumes of separated PVC phases were read off. Next, a calculated volume of distilled water was added to the test tube to reduce the concentration as required, and thus also to reduce the density of the $NaNO_3$ solution. Each addition of distilled water was followed by stirring of the contents of the test tube with a glass stick for 5 min, centrifugation for another 5 min, and the volumes of separated phases were then read off. The dependence of the volume of the specifically heavier PVC phase on the concentration of the $NaNO_3$ solution has been plotted in a diagram characterizing the tested sample.

TABLE I
Basic Characteristics of Samples of Suspension PVC Powders, Trademark Neralit
(Producer's Data)

Sample no.	Trademark	K_h	Bulk weight	Particle size (μm)	Note
1	N 652	65 ± 1.5	520 ± 30	90% > 63 0.5% > 250	10 fish eyes at most in 1 g PVC
2	N 702	70 ± 1.5	480 ± 30	90% > 63 0.5% > 250	8 fish eyes at most in 1 g PVC
3	N 702	70 ± 1.5	480 ± 30	archival sample containing 36 fish eyes in 1 g PVC	

RESULTS AND DISCUSSION

By using the standard method of determination of "fish eyes," the principle of which has been mentioned in the Introduction, one can adequately determine the difficult-to-process particles with the original diameter larger than, or comparable with, the final thickness (100 μm) of the tested film. A certain shortcoming of the standard method is that the difficult-to-process particles with a small diameter which may become a basic obstacle to exacting (optical) applications need not be detected in this way. We tried to find a procedure to remove this shortcoming.

In our previous paper[1] we investigated difficult-to-process particles in the powder of samples of suspension PVC prepared on a laboratory scale, as well as the morphology of these particles. We found that precursors of the "fish eyes" are, basically, nonporous, compact, and glassy particles. The glassy particles were isolated by a time-consuming search and manual selection under an optical microscope. Their specific weight was 1.387–1.391 g cm^{-3}. Under the same conditions, normal particles of the same PVC sample had a specific weight in the range 1.27–1.29 g cm^{-3}. The measurements were performed in $NaNO_3$ solutions. This gave us an idea that by using aqueous $NaNO_3$ solutions of various concentration which can be prepared in the specific weight range between 0.99 and 1.42 g cm^{-3}, it would be possible to separate adequately particles of suspension PVC. Their specific weight varies just in this range of aqueous solutions. Aqueous $NaNO_3$ solutions are inert towards PVC particles and easily wet them without changing their morphology. The expansability of $NaNO_3$ solutions is comparatively low, so that small changes in room temperature are virtually not reflected in their specific weight, and consequently do not distrub the accuracy of determination. For instance, at 18°C a rise in temperature by 10°C causes the same decrease in the density of a 20% $NaNO_3$ solution as a drop in concentration by 0.8%.

The samples of suspension PVC investigated in this study, i.e., N 652 (No. 1) and N 702 (No. 2), rank among types intended for plasticized products. The samples were characterized by sieve analysis; the results are summarized in Table II. They showed that commercial products correspond to technical conditions as given by the producer (cf. Table I). At the same time, it was found that in the case of N 702 (No. 3) which contains an elevated number of fish eyes not admitted by the standard, the weight content of

TABLE II
Sieve Analysis (% by Weight) of Samples of Suspension PVC

Fraction (μm)	Sample No.		
	1	2	3
Below 63	1.72	3.57	3.11
63– 90	7.74	11.34	10.08
90–125	47.96	65.86	45.33
125–150	32.13	16.26	24.21
150–180	9.45	2.89	15.09
Above 180	1.00	0.08	2.18

fractions had been changed in favor of larger particles at the expense of the medium fraction; the amount of the smallest fractions remained unchanged, however. For the purpose of statistical evaluation, integral weight distribution curves have been constructed (Fig. 1) which allow us to determine the basic characteristics of the average particle size (D), distribution width (R), and asymmetry of the distribution function (A). The average particle size was read off from the distribution curve as the value of an independent variable (d) corresponding to the ordinate (P) $P = 50\%$ (P_{50}). The distribution width (R) is defined by $R = (d_{P_{84}} - d_{P_{16}})/2$, the asymmetry of distribution (A) is defined by $A = [(d_{P_{84}} - d_{P_{50}}) - (d_{P_{50}} - d_{P_{16}})]/(d_{P_{84}} - d_{P_{16}})$, where P_{84} and P_{16} are statistical quantils.

The values read off from Figure 1 and the calculated characteristics of distribution functions for Samples 1–3 have been arranged in Table III. It can be seen in the table that Sample No. 1 has the largest average particle size (121 μm) and a medium wide distribution (23 μm), perfectly symmetrical around the average particle size. The average particle size of Sample No. 2 is lower by 10% (109 μm) than that of Sample No. 1. The particles of
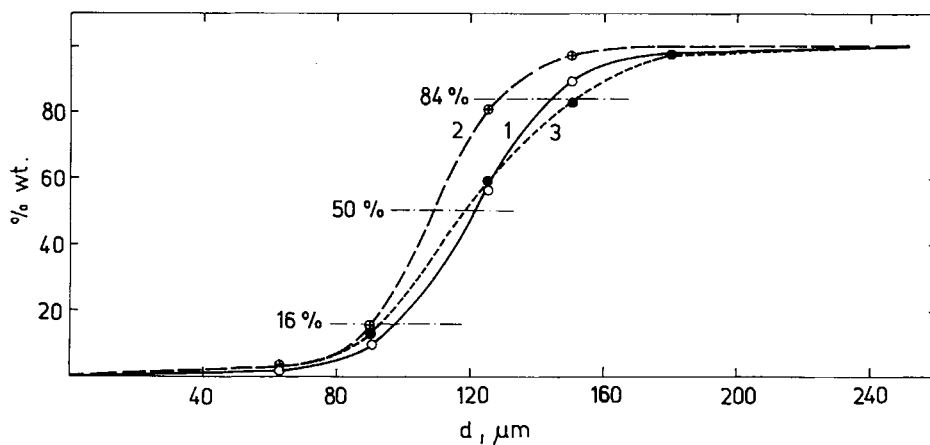

Fig. 1. Integral weight distribution curves of particle sizes of suspension PVC for Samples 1, 2, and 3.

TABLE III
Values of the Statistical Independent Variable (d_P, μm) and Characteristics of the Weight Distribution of Samples 1–3

Sample no.	1	2	3
$d_{P_{16}}$	98	91	93.5
$d_{P_{50}}$	121	109	117.5
$d_{P_{84}}$	144	127.5	152
D (μm)	121	109	117.5
R (μm)	23	18.25	29.25
A	0	0.014	0.18

Sample No. 2 (measured by the distribution width) are more uniform in size than those of Sample No. 1; the distribution curve is insignificantly asymmetrical, with a slightly higher content of larger particles. Sample No. 3 supplied from the producer's archives differs from the commercial Sample No. 2 in all characteristic data: the average particle size is larger by ca. 7% compared with Sample No. 2, the distribution width has increased by 60% and the asymmetry of the distribution function has increased to tenfold its original value, with a pronounced rise in the fraction of larger particles.

The behavior of PVC particles taken from samples of suspension PVC characterized by the above-mentioned procedure was investigated in $NaNO_3$ solutions. First, it was shown that by using aqueous $NaNO_3$ solutions the PVC powders can be distributed with respect to density, with a high content of the solid phase. After that, the procedure of density titration was worked out as described in the Experimental section. It should be pointed out that the density titration as described is a dynamic method, and the chosen working procedure must be strictly observed for obtaining comparable and reproducible results.

The dynamic method means that the test is carried out under nonequilibrium conditions and that the resuts obtained depend on the history of the examined sample. During the density titration several transport processes are operative: (i) the concentrated test solution gradually penetrates into the pores of PVC, thus changing the overall density of each individual particle, (ii) the air in the pores is dissolved in the solution, which invaded the pores, thus making possible further invasion of the solution, (iii) the dissolved air is transported by diffusion out of the particle. After addition of the required amount of water, the bulk testing solution is immediately diluted, while the concentration equilibration in the pores is time dependent, due to: (i) diffusion of water into the more concentrated solution of $NaNO_3$ present in the pores, (ii) the countercurrent diffusion of $NaNO_3$ into the bulk solution, (iii) the increased—due to the gradually decreasing concentration of $NaNO_3$ and thus increasing solubility of air in the testing solution—air transport out of the pores.

By employing the density titration method, we obtained dynamic concentration (density) volumetric curves (called below simply titration curves) as dependences of the volume (mL) of a PVC fraction specifically heavier than solution of the given composition on the concentration of the $NaNO_3$ solution for a standard weighed amount of 1.00 g PVC. The titration curves were evaluated by a procedure analogous to that used in the treatment of the particle size weight distribution of Sample Nos. 1–3 by the statistical method. The "average concentrations" were calculated similarly to the "average particle size," with the concentration range being analogous to the distribution width. The asymmetry of the titration curves was also calculated analogously to calculations of the asymmetry of weight distributions. Identical statistical quantils (16 and 84%) of cumulative function were used in the evaluation.

For the original unfractionated powders it was found (Fig. 2) that Sample No. 2 has a markedly wider concentration range than Sample No. 1, the average concentration for Sample No. 1 being the highest of all the tested unfractionated samples, in accordance with the bulk weight (cf. Table I).
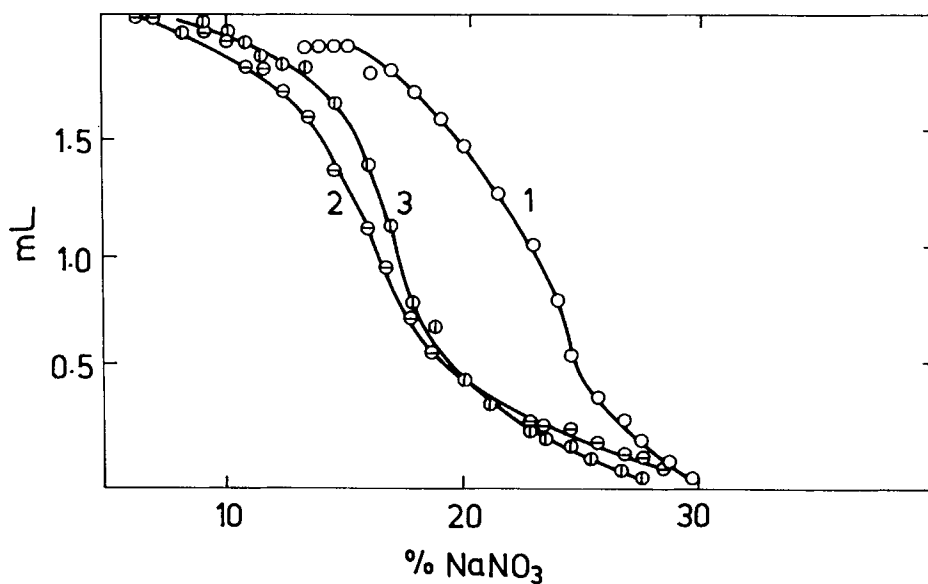
Fig. 2. Dependence of the volume of the specifically heavier PVC fraction (mL) from a standard weighed amount (1.00 g) on the concentration of NaNO$_3$ solution (% wt): 1 = Sample No. 1, 2 = Sample No. 2, 3 = Sample No. 3.

Sample No. 3 containing 36 fish eyes in 1 g PVC has the average concentration higher by 5.4% compared with Sample No. 2 of the same type, but its concentration range is narrower by 22.3%, and the titration curve is somewhat more symmetrical (its asymmetry decreased from 0.25 for Sample No. 2 to 0.21 for Sample No. 3). From Figure 2 it is possible to determine the volumes occupied by the standard weighed amounts 1.00 g PVC in the most dilute NaNO$_3$ solution in which all particles have already settled in the specifically heavier PVC phase. The volumes (for Sample No. 1, 535 g/1000 mL, and for Samples 2 and 3, 500 g/1000 mL) are in good agreement with the values of the bulk weight given in Table I.

The density titration method was then used to examine fractions of Samples Nos. 1–3 obtained by sieve analysis. The titration curves in Figure 3 characterize the individual sieve fractions of Sample No. 1; with decreasing particle diameter, the curves are shifted toward higher NaNO$_3$ concentrations, and thus also toward higher densities. According to the results obtained by the BET method, however, the specific surface is independent of particle size (Table IV).

The curves are shifted toward higher densities with decreasing particle diameter also due to kinetic effects operative during the penetration of the testing solution into pores of PVC particles and during the concentration equilibration between the composition of the liquid in the pores and the testing solution (composition of the solutions varies discretely in the course of the density titration). With the same specific surface, particles with the smallest diameter have the kinetically fastest response, because they have the most favorable ratio between the external surface and volume as well as the shortest mean diffusion paths for mass exchange.
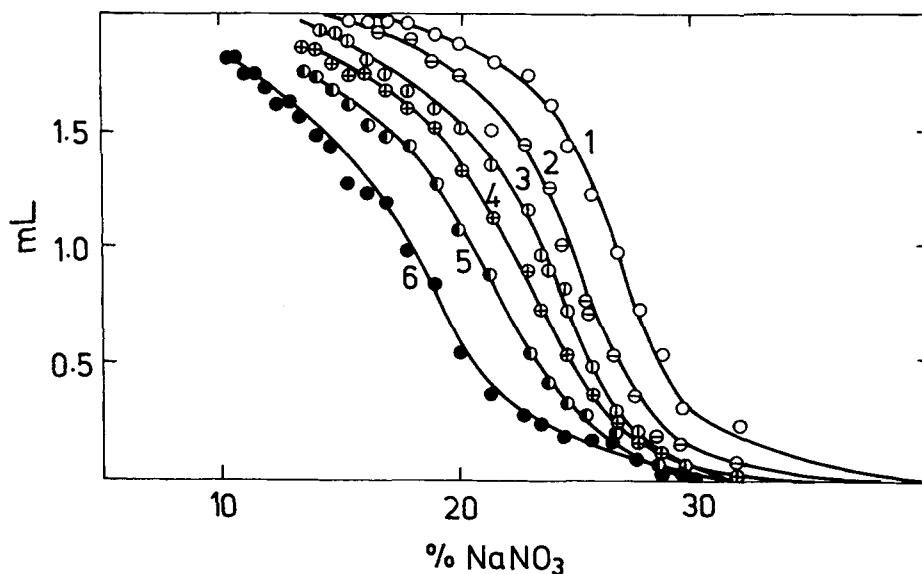
Fig. 3. Dependence of the volume of the specifically heavier PVC fraction (mL) from a standard weighed amount (1.00 g) on the concentration of NaNO$_3$ solution (% wt) for sieve fractions of Sample No. 1: 1 = (0–63) μm, 2 = (63–90) μm, 3 = (90–125) μm, 4 = (125–150) μm, 5 = (150–180) μm, 6 = above 180 μm.

TABLE IV
Specific Surface Area (S, m^{2}g^{-1}) of Sample No. 1 for Particle with Diameter d (μm)

d	below 63	63–90	90–125	125–150	150–180	above 180
S	0.50	0.47	0.53	0.53	0.56	0.66

Figure 4 shows the titration curves of fractions of Sample No. 2 obtained by sieve analysis. A comparison with Figure 3 which shows the titration curves of Sample No. 1 reveals that the concentration range of all fractions of Sample No. 2 is larger than that of Sample No. 1, and that titration curves are shifted toward lower concentration values (densities), in agreement with the lower bulk weight of Sample No. 2.

Figure 5 presents the titration curves of the individual fractions of Sample No. 3 which document the same trend in the behavior as that observed with samples in Figures 3 and 4, i.e., shifts of the titration curves toward higher concentrations (densities) with decreasing particle size. Since the type of the sample is the same as that of Sample No. 2, which however, differs in quality (an increased number of fish eyes), the titration curves were transferred to other figures for a better comparison of the individual fractions. In Figure 6 the titration curves are compared for the finest fractions with mesh size 0–63 μm and 63–90 μm. The titration curves of both fractions of Sample 3 with a higher number of fish eyes are shifted to the range of higher densities. In the case of the finest fraction up to 63 μm, Samples 2 and 3 do not differ at all in their concentration range. Though the asymmetry of the titration curves is virtually the same with respect to its absolute value, yet in Sample No. 2 the effect of specifically heavier particles (with respect to
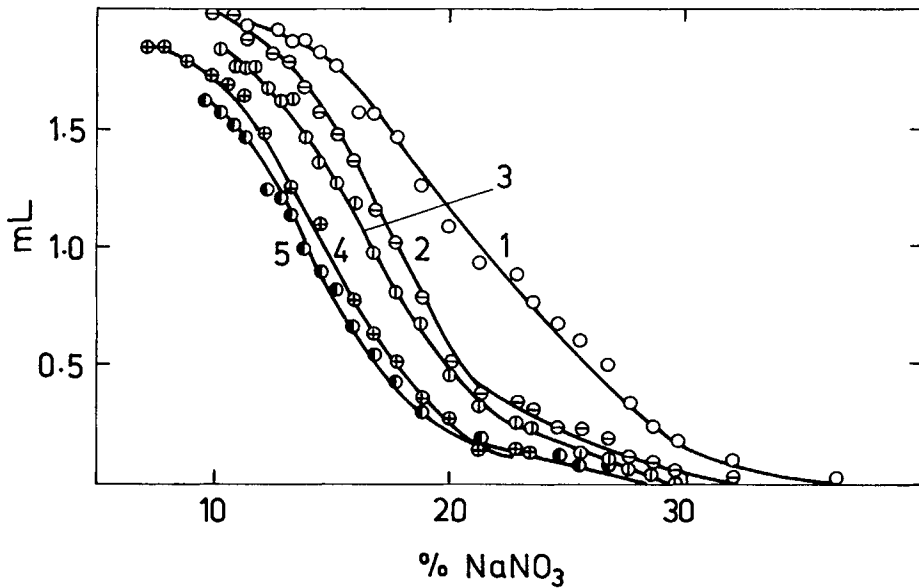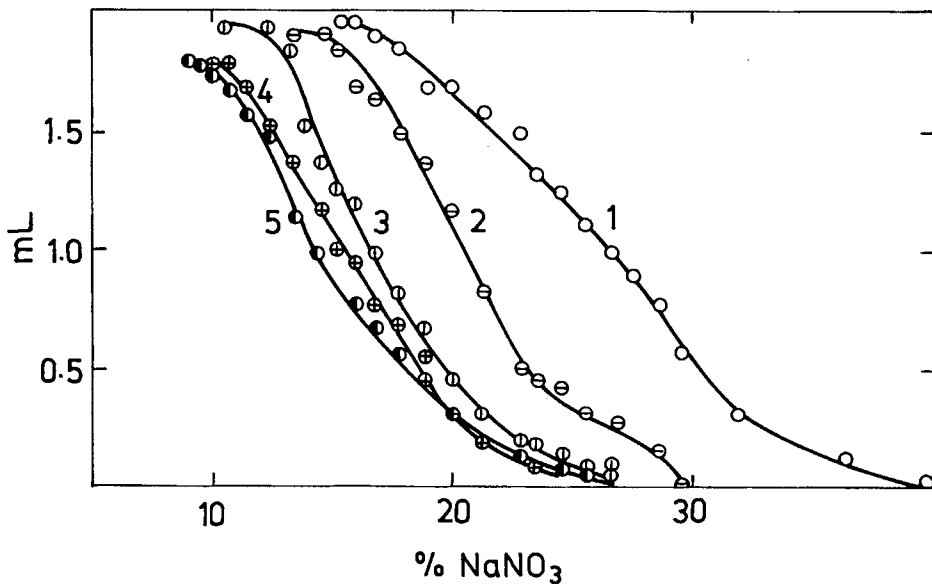
Fig. 4. Dependence of the volume of the specifically heavier PVC fraction (mL) from the standard weighed amount (1.00 g) on the concentration of NaNO$_3$ solution (% wt) for sieve fractions of Sample No. 2: 1 = (0–63) μm, 2 = (63–90) μm, 3 = (90–125) μm, 4 = (125–150) μm, 5 = (150–180) μm.
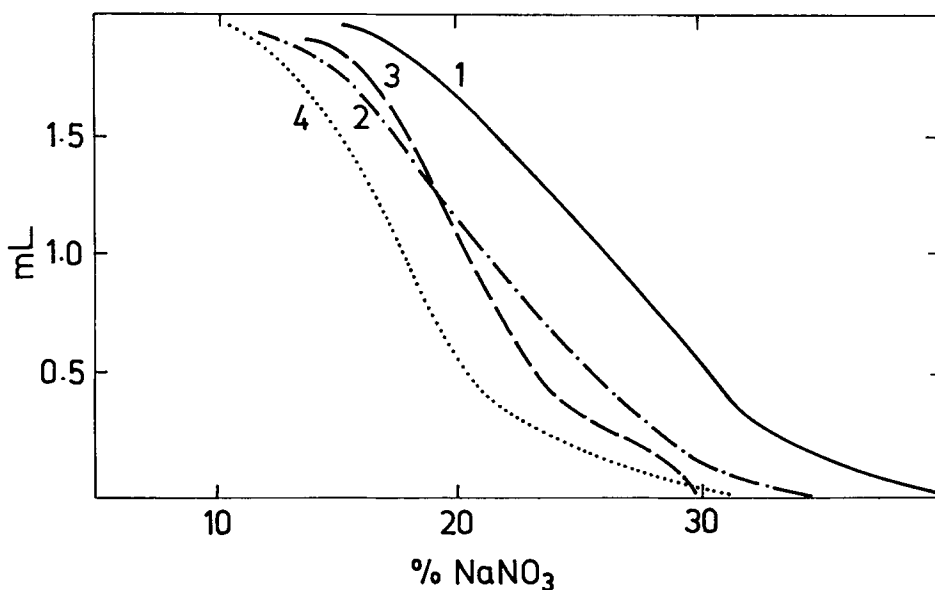

Fig. 5. Dependence of the volume of the specifically heavier PVC fraction (mL) from the standard weighted amount (1.00 g) on the concentration of NaNO$_3$ solution (% wt) for sieve fractions containing an increased number of glassy particles of Sample No. 3: 1 = (0–63) μm, 2 = (63–90) μm, 3 = (90–125) μm, 4 = (125–150) μm, 5 = (150–180) μm.

Fig. 6.   Dependence of the volume of the specifically heavier PVC fraction (mL) from the standard weighted amount (1.00 g) on the concentration of $NaNO_3$ solution for sieve fractions of Sample No. 2: 2 = (0–63) μm, 4 = (63–90) μm; of Sample No. 3: 1 = (0–63) μm, 3 = (63–90) μm.

the average value) predominates, while in Sample 3 it is the other way round. In the fraction 63–90 μm, the concentration range is virtually the same for both samples.

In the case of fractions 90–125 μm (Fig. 7), Samples 2 and 3 virtually do not differ in the average concentration value, but Sample 2 has a larger concentration range. Sample No. 3 has the titration curve six times more asymmetrical than Sample No. 2, with specifically heavier particles predominating.

With fractions 125–150 μm (Fig. 8), the titration curve of Sample No. 3 is slightly shifted toward higher concentration (density) values; the concentration range of Sample No. 3 is narrower by 7% and the asymmetry is slightly higher. In the case of the coarse-grained fraction 150–180 μm (Fig. 7) the average concentration of Sample No. 3 is somewhat higher, the concentration range is the same, and the asymmetry of the titration curve is four times larger.

The detailed analysis of the titration curves presented above allows us to infer that: (i) by using density titration, it is possible to distinguish various types of powders of suspension PVC differing in their bulk weights (the differences can be perceived for the original powders and for all size fractions), (ii) similarly, the quality of the individual samples can be distinguished for the same type of suspension PVC (in the case of considerable differences in quality, this can be done also with unfractionated samples, otherwise especially with the finest fractions where the density differences are largest).
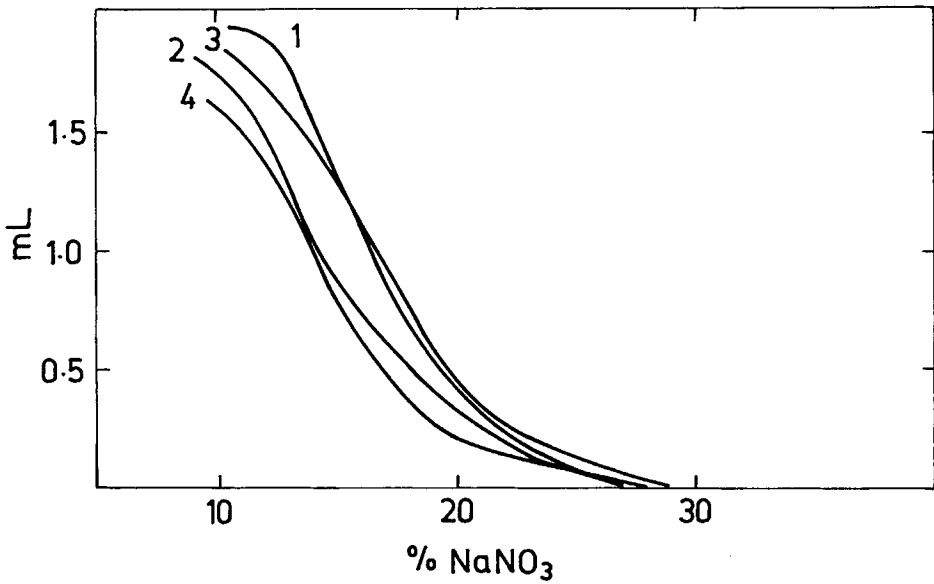
Fig. 7. Dependence of the volume of the specifically heavier PVC fraction (mL) from the standard weighed amount (1.00 g) on the concentration of NaNO$_3$ solution for sieve fractions of Sample No. 2, curve 3 (90–125) μm and curve 4 (150–180) μm, and of Sample No. 3, curve 1 (90–125) μm and curve 2 (150–180) μm.
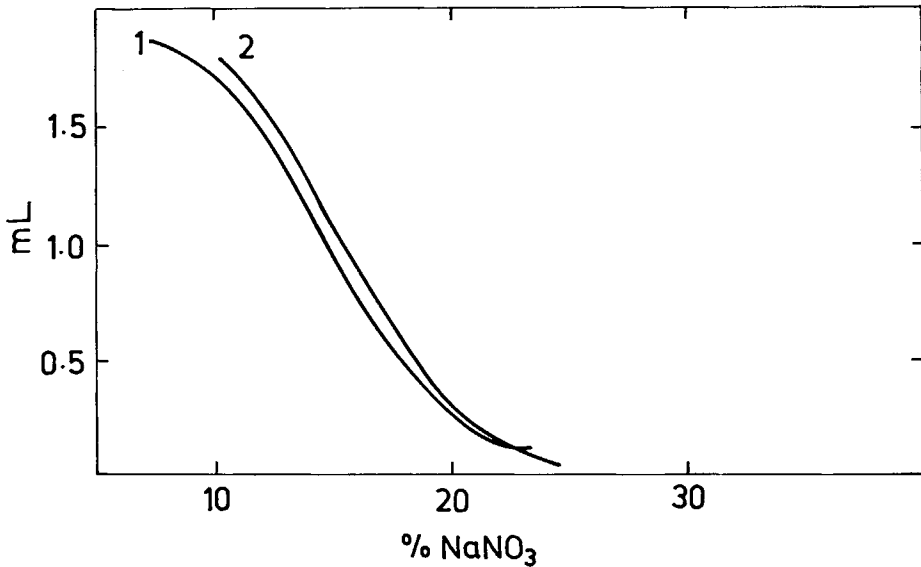

Fig. 8. Dependence of the volume of the specifically heavier PVC fraction (mL) from the standard weighed amount (1.00 g) on the concentration of NaNO$_3$ solution for sieve fractions (125–150) μm of Sample No. 2, curve 1 and of Sample No. 3, curve 2.

CONCLUSION

The density titration is a simple method, requiring no complicated devices, which depending on the purpose and on the procedure used may quickly provide valuable information on the density range of the tested samples or of their sieve fractions. In the evaluation of the quality of individual fractions, the density titration along with the sieve analysis suitably supplements standard testing of the number of fish eyes (especially for sample with fine grain size). In repeated determinations of the quality of a certain type of suspension PVC, the finest sieve fractions or their weight content and density range may be used as quality indicators: they are compared with the values of a standard which satisfies the requirements of the given application.

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