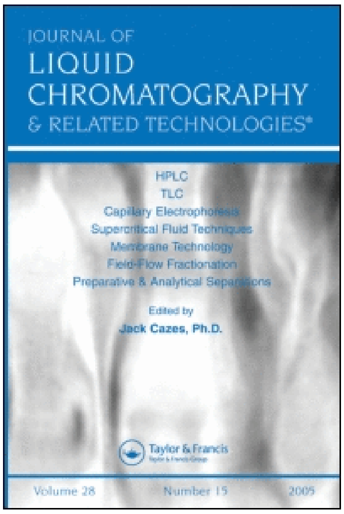

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Sedimentation Field-Flow Fractionation: A New Methodology for the Concentration and Particle Size Analysis of Dilute Polydisperse Colloidal Samples

Athanasia Koliadima[a]; George Karaiskakis[a]
[a] Physical Chemistry Laboratory, University of Patras, Patras, Greece

To cite this Article Koliadima, Athanasia and Karaiskakis, George(1988) 'Sedimentation Field-Flow Fractionation: A New Methodology for the Concentration and Particle Size Analysis of Dilute Polydisperse Colloidal Samples', Journal of Liquid Chromatography & Related Technologies, 11: 14, 2863 — 2883

To link to this Article: DOI: 10.1080/01483918808076766

URL: http://dx.doi.org/10.1080/01483918808076766

JOURNAL OF LIQUID CHROMATOGRAPHY, 11(14),2863-2883 (1988)

SEDIMENTATION FIELD-FLOW FRACTIONATION: A NEW METHODOLOGY FOR THE CONCENTRATION AND PARTICLE SIZE ANALYSIS OF DILUTE POLYDISPERSE COLLOIDAL SAMPLES

ATHANASIA KOLIADIMA
AND GEORGE KARAISKAKIS*
Physical Chemistry Laboratory
University of Patras
Patras, Greece

ABSTRACT

It is shown that the on-channel concentration procedure for the analysis of dilute monodisperse colloidal samples in sedimentation field-flow fractionation, as established in a previous work(1), provides an accurate methodology for the concentraion and particle size analysis of dilute polydisperse colloidal samples.In order to test the methodology experiments are described using polyvinyl chloride (PVC) latex beads in the diameter range 0.173-0.334 μm. A series of fractograms were run in which the amount of the PVC sample was held constant while the volume in which it was contained was varied over a 20,000-fold range. The weight average particle diameters and the particle size distribution curves (histograms or cumulative distribution curves), determined by the on--channel concentration procedure at various experimental conditions,are in excellent agreement with those obtained under normal experimental conditions, in which a small concentrated volume of the same sample is injected directly into the column. Moreover, varying the density of the carrier solution, apart from the weight average particle diameter or the particle size distribution curve, the density of the PVC latex beads was obtained in accordance with that found by a common method.

INTRODUCTION

Field-Flow Fractionation (FFF) has progressed rapidly in the last years in theory and in practical applications. This progress is naturally accompanied by the appearance of new problems that have to be solved. One of them is related to the characterization of dilute polydisperse colloidal samples and to the development of new methodologies for the on-channel concentration of dilute polydisperse colloids, since most sedimentation FFF(SFFF) studies have been limited to materials for which fairly concentrated samples (1 to 10% solids) are available. These methodologies are of paramount importance in the study of fine particles in natural waters, since these polydisperse particulates, act as the main carriers for many important water contaminants.

A brief review of SFFF theory is presented here to help in interpretation of results. Detailed theory for several FFF techniques(2) and SFFF in particular (3-6) has been published.

In the same manner as chromatography, SFFF retention ratio, R, can be defined as the ratio of the column void volume V^o to that of the component under study retention volume (the mean volume necessary to sweep the given particles through the channel) V_{R_i} Thus:

$$R = \frac{V^o}{V_{R_i}} \qquad (1)$$

The theory of SFFF shows (3) that at moderately high levels of retention, R is a simple function of the dimensionless parameter $\lambda(=\ell/w$, ℓ is the characteristic thickness of the layer in which the particles are found at equilibrium and w is the channel thickness).

$$\lim_{\lambda \to 0} R \simeq 6\lambda = \frac{6\ell}{w} \tag{2}$$

By considering the steady-stage mass-transfer balance between the applied gravitational field and the opposing natural diffusion forces, Giddings (3) has shown that in SFFF

$$\lambda = \frac{kN_A T}{M\omega^2 rw(\Delta\rho/\rho_s)} = \frac{6kT}{\pi d_i^3 Gw\Delta\rho} \tag{3}$$

where k is Boltzman's constant, N_A is the Avogadro number, T is the absolute temperature, M is the molecular weight of the solvated macromolecules or particle mass in $g.mol^{-1}$, ω is the centrifuge speed ($rad.s^{-1}$), r is the radial distance from the centrifuge rotating axis to the SFFF channel, $G = \omega^2 r$, $\Delta\rho$ is the density difference between the sample (ρ_s) and the carrier solution (ρ_o), and d_i is the spherical particle diameter. It must be pointed out that the second equivalence in Equation (3) is valid only for spherical particles.

Combination of Equations (1), (2) and (3) gives:

$$d_i = \left(\frac{36kTV_{R_i}}{\pi GwV^o\Delta\rho}\right)^{1/3} \tag{4}$$

SFFF has significant advantages over existing non chromatographic methods for determining the particle size distribution of colloidal materials in the 0.001 - 1 μm range. It is a flow-modified equilibrium separation method. Solute layers that are poorly resolved under static equilibrium sedimentation become well separated as they are eluted by the laminar-flow profile in the carrier phase. Moreover, SFFF is simpler to operate, is more definite in terms of quantitative analysis,and is capable of a much large particle fractionation range. SFFF exhibits also significant advantages over conventional non-separation approaches, e.g. microscopy and light-scattering methods, for particle size measurement.

In summary, polymers, colloids, inorganic and organic particulates suspended in aqueous solution, pigments, viruses, liposomes, other vesicles, DNA, RNA, and other polynucleotides of biochemical interest have been already characterized by the SFFF (5-14).

EXPERIMENTAL

Materials

The sample used was a suspension of polyvinyl chloride (PVC) latex beadss with a continuous size distribution in the range 0.173-0.334 um from B.F.Goodrich Inc., Avon Lake, Ohio.The average density of the PVC particles was determined to be 1.4 $g.cm^{-3}$ by the lyophilization (freeze drying) to constant weight of an aliquot having known weight and volume.The solid content of the original suspension was 52.8% (w/w).

The suspending medium was triply distilled water containing 0.5% by volume of a low foaming, low alkalinity, phosphate, chromate and silicate-free detergent FL-70 (Fisher Scientific Co.) and 0.02% by weight sodium azide (Fluka AG) as a bacterioside (carrier A).A carrier liquid containing 40% (v/v) glycerol in 0.5% by volume FL-70 (carrier B) was also used in order to obtain simultaneously the particle size and density of the PVC sample. The densities of the two carrier solutions mentioned above were determined at 25°C by a WESTPHAL balance. The densities of the carrier liquids A and B were found to be 1.00 and 1.11 $g.cm^{-3}$,respectively.

Preliminary experiments with well characterized monodisperse polystyrene latex beads with nominal diameter 0.620 μm (Dow Chemical Co.) verified the functionality of the SFFF equipment.

Apparatus and procedure

A description of the SFFF column and the method of operation have been presented elsewhere (1,5,14,15).The channel dimensions in this study were 37.1X2.0X0.0267 cm. Channel void volume as measured by the elution of the non-retained peak of sodium benzoate was 1.82 cm^3. The channel was positioned 6.85 cm from the center of rotation. A Gilson Minipuls 2 peristaltic pump was used to feed the sample during the concentration step and to maintain flow during the separation step. A Gilson model 111 UV detector was used for detection at 254 nm.A Goerz model RE 541 recorder was used to record the fractograms.

Diluted samples were prepared by adding 1 μl of the 10% solids PVC sample to 1,2,5,10,15 and 20 cm^3 of carrier solution A . In the first (concentration) step these diluted samples were pumped at a rate of $v_f = 5.0\ cm^3h^{-1}$ into the channel while it was rotating at 1800 rpm. When the samples were consumed, pumping was continued at the same rate with 2.25 cm^3 of carrier solution to clear the sample from the pump. Finally the flow was stopped to relax the sample for 12 min. Then in the second (separation) step the field was reduced (600, 750, 800 and 1000 rpm) and the flow rate increased (v_s = 15-49 cm^3h^{-1}) to elute the sample.

The fractograms obtained by the above described concentration procedure were compared with that obtained by the normal procedure of injecting 1 µl of the undiluted 10% solids sample onto the column, stopping the flow to relax the sample for 12 min at 600 rpm,then to elute the sample at flow-rate 31 cm^3h^{-1}.

RESULTS AND DISCUSSION

There are three ways of presenting a description of a polydisperse system, such as the PVC colloidal sample, in terms of the diameters d_i in each fractogram (see Fig.1) calculated from Equation(4). First is the weight average particle diameter, second the histogram and third the cumulative distribution curve.

Weight Average Particle Diameter

The elution curve (see Fig.1), which is a "raw" fractogram, i.e. a plot of the observed detector response, which is proportional to concentration, versus the elution volume V_R, is divided in about fifteen areas in which the elution volume δV is constant. Supposing that the particle diameter d_i corresponding to the medium of each interval is constant in every volume interval, we can calculate the weight average particle diameter, d_w along with its standard deviation, σ_{d_w}, in each fractogram by using the known relationships:

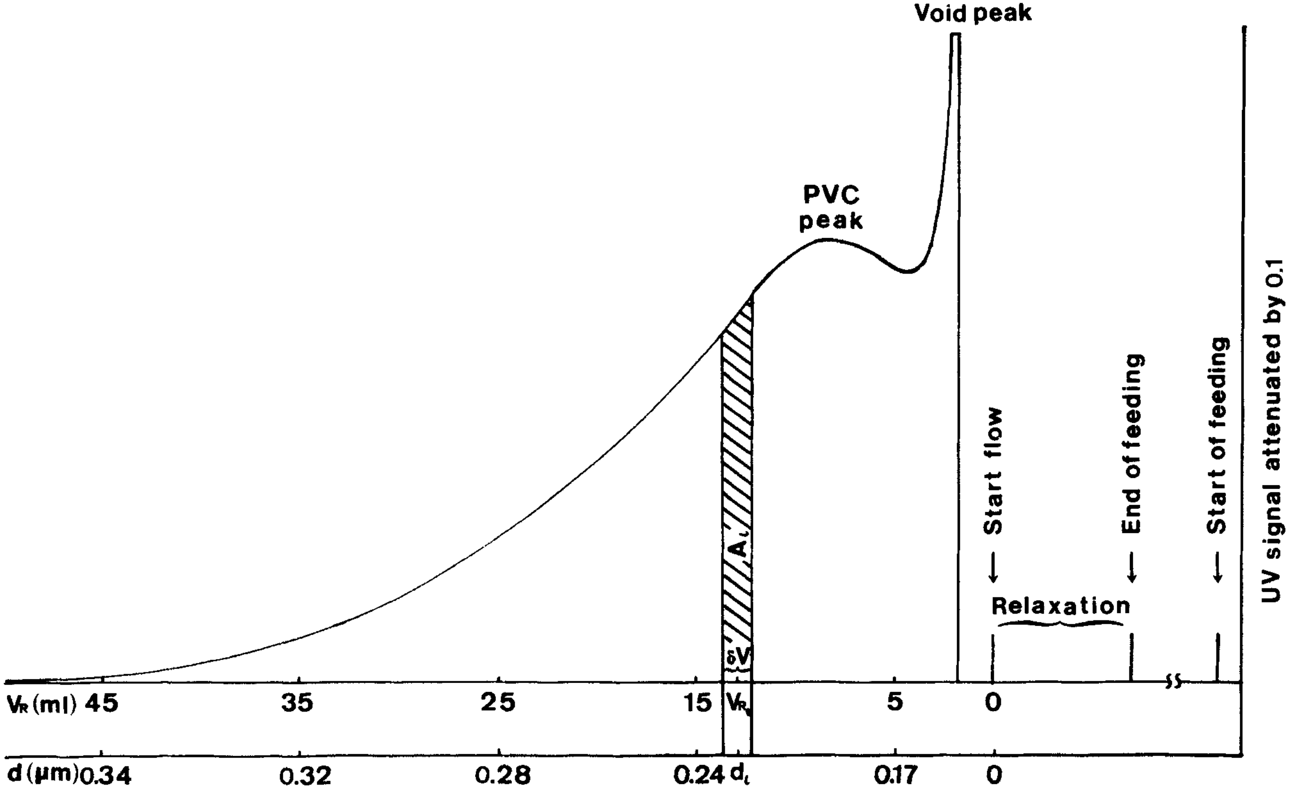

FIGURE 1. Fractogram and particle diameter scale of PVC particles obtained by the concentration procedure in SFFF. $V_f = 2\ cm^3$, $(rpm)_f = 1800$, $(rpm)_s = 600$, $v_f = 5\ cm^3h^{-1}$, $v_s = cm^3h^{-1}$.

$$d_w = \frac{\sum_i d_i A_i}{\sum_i A_i} = \frac{\sum_i d_i A_i}{A} \tag{5}$$

$$\sigma_{d_w} = \left[\frac{\sum_i (d_i - d_w)^2 A_i}{\sum_i A_i}\right]^{\frac{1}{2}} \tag{6}$$

where A_i is the area under the elution curve of the particles N_i having constant diameter d_i -which is proportional to the weight of the N_i particles- and A is the total area of the whole eluted particles.

Since in the "raw" fractogram the d scale is nonlinear because of the nonlinear relationship of V_{R_i} to d_i in Equation (4), the area A_i, which is a frequency factor, must be corrected to remove the d dependence. Using the correction factor given in Equation (4) of reference (6), the Equations (5) and (6) are transformed as follows:

$$d_w' = \frac{\sum_i d_i Q A_i V_{R_i}^{2/3}}{\sum_i Q A_i V_{R_i}^{2/3}} \tag{7}$$

$$\sigma'_{d_w'} = \left[\frac{\sum_i (d_i - d_w)^2 Q A_i V_{R_i}^{2/3}}{\sum_i Q A_i V_{R_i}^{2/3}}\right]^{\frac{1}{2}} \tag{8}$$

where

$$Q = \left[\frac{3\pi G w \Delta\rho V^o}{4kT}\right]^{1/3} \tag{9}$$

Particle Size Distribution Curves

As mentioned before the "raw" fractogram representing the direct recorded output from the detector, requires a correction, which compensates for the change in scale from elution volume based read out to the appropriate particle diameter scale. For detectors in which the signal is influenced from the particle size and concentration a second correction is necessary to remove the size dependence. This correction requires light scattering data for the sample used which are not available in any case. Fortunately these two corrections offset one another in the PVC sample (6), thus making possible the use of uncorrected (raw) elution curves as true particle size distribution curves.

Figs.2 and 3 show the "raw" histograms and cumulative distribution curves, respectively, for the direct injection (a) and the proposed concentration procedure by feeding the channel with 2 cm^3 of diluted PVC (b). It can be seen that the two distribution curves (a and b)in both Figs.2 and 3 are almost identical, showing that one could analyse almost accurately dilute polydisperse colloidal samples by the proposed methodology.

Correction Due to On-Channel Concentration Procedure

During the feeding of the column with the large volumes of diluted samples, a sample slug of finite length at the head of the channel is introduced. This reduces retention volumes because the center of gravity of the sample is moved into the channel before separation starts.

There are two processes contributing to the formation of the sample slug. First is the relaxation procedure, which affects differently particles in different parts of the channel cross section. While particles close to the outside wall of the channel do not migrate significantly during relaxation, particles at the inside wall of the channel are moved with an average linear velocity v_f as they traverse the channel. Thus, during relaxation time, τ, particles migrate a distance:

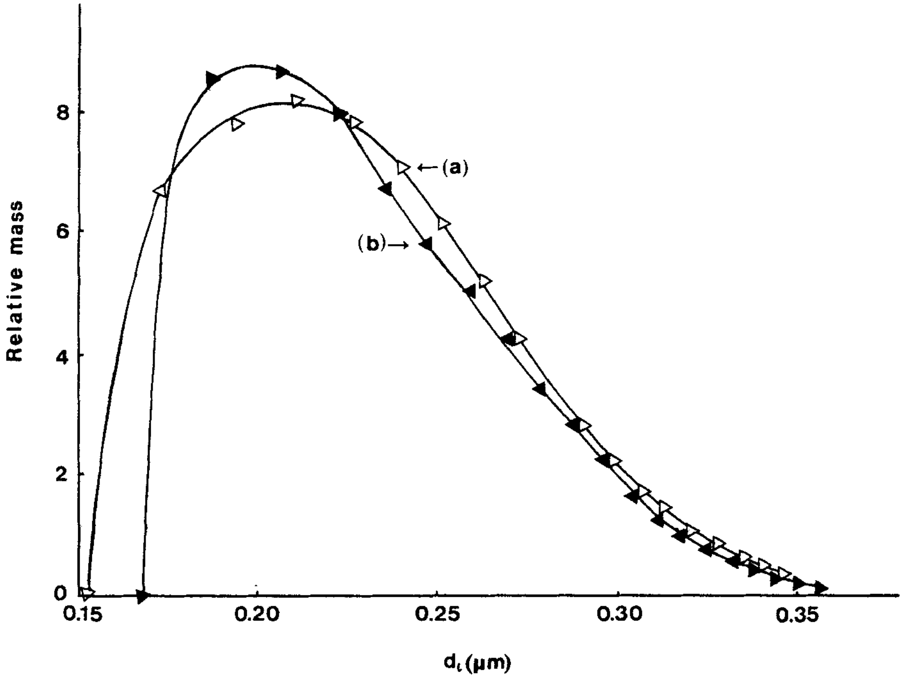

FIGURE 2. Size distribution curves for the PVC particles obtained in SFFF (a) by direct injection and (b) by feeding the channel with 2 cm^3 of diluted PVC. The experimental conditions are the same as those of Fig.1.

$$L_1 = \frac{v_f}{\tau} = \frac{v_f G \Delta\rho d_i^2}{18nw} \tag{10}$$

where n is the viscosity of the carrier solvent.

The second process contributing to the sample slug is the continuous migration of the initial part of the deposited slug during the period in which the latter is fed into the channel. During the feed step time, t_f, a sample with retention ratio R_f will distribute itself along a fraction of the column length, L, equal to

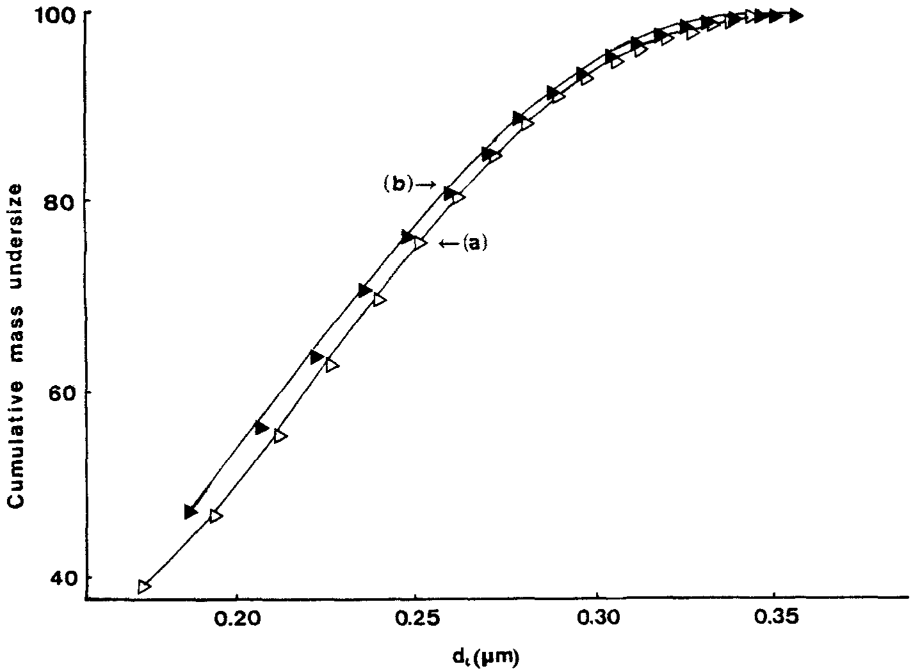

FIGURE 3. Cumulative distribution curves of the diameters for the PVC particles obtained in SFFF (a) by direct injection, and (b) by the concentration procedure. The experimental conditions are the same as those of Fig.2.

R_fV_f/V^o, where V_f is the sample feed volume. Thus, the column length of the sample occupancy is:

$$L_2 = \frac{R_fV_fL}{V^o} \tag{11}$$

The result of these two processes on the sample relaxation leads to the positioning of the center of gravity of the sample slug at a distance L_{cg} from the head of the channel:

$$L_{cg} = \frac{L_1+L_2}{2} = \frac{v_f}{2\tau} + \frac{R_f V_f L}{2V^o} \qquad (12)$$

Therefore the apparent retention volume, R_a, measured from the elution volume, will be higher than the true, R_t, by the ratio γ:

$$\gamma = \frac{R_a}{R_t} = \frac{L}{L-L_{cg}} = \frac{2L}{2L-L_1-L_2} \qquad (13)$$

The last equation shows that the true retention ratio R_t can be found from the relationship:

$$R_t = \frac{R_a(2L-L_1-L_2)}{2L} \qquad (14)$$

The values of R_t found from Equation (14) are used in Equations (4) and (5) for the calculation of the corrected values of d_i and d_w. The obtained results will be given later in Table 1, in which apart from the uncorrected values of d_w, the corrected, due to the on-column concentration sample slug, values of d_w will be also presented.

Fig.4 shows two almost identical particle size distribution curves obtained by the on-channel concentration procedure. Curve (a) is uncorrected while curve (b) is corrected for the on-channel concentration sample slug.

Self-Consistency of FFF Results

In order to show if the results are independent of experimental parameters it is important to compare size distribution curves and weight average particle diameters

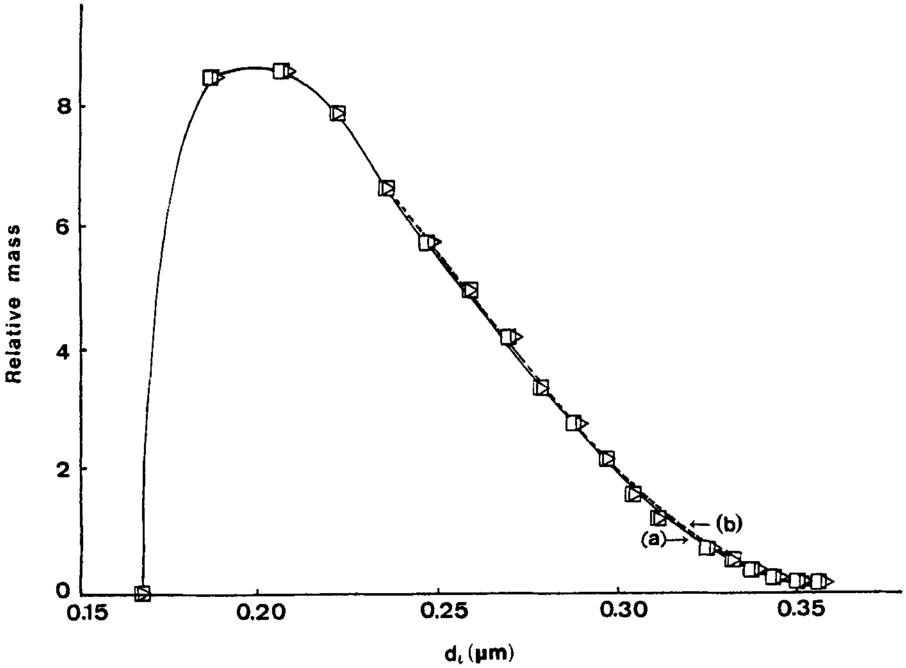

FIGURE 4. Size distribution curves of the diameters for the PVC particles obtained by the concentration procedure in SFFF. (a) Uncorrected curve (□), (b) corrected curve due to on-channel concentration sample slug (▷).The conditions are the same as those of Fig.1.

obtained by the proposed methodology in SFFF under a variety of experimental conditions. In the present work one can vary either the experimental conditions during the feed step or/and those during the separation step. So we have made runs in which we have systematically varied the feed volume and the field strength during the feed step, the flow velocity and the field strength during the separation step and finally the carrier density in both steps of the proposed concentration procedure.

First, we compare results obtained by using different feed volumes of diluted samples. This test is very important, since one can find the resolution of the proposed concentration procedure in the analysis of highly diluted samples. It is noteworthy that although the carrier volume, in which the sample was contained, was varied over a 20,000-fold range, and even the larger of these volumes ($V_f = 20$ cm^3) is about 11 times the channel volume ($V^o = 1.82$ cm^3), the weight average particle diameters obtained by the concentration procedure are in excellent agreement with that determined by the direct injection of a small (= 1 µl) concentrated volume sample onto the column (see Table 1). In Table 1 a value of weight average particle diameter calculated from Equation (7) is also given. This is identical with that determined from Equation(5), thus making possible the use of Equation (5) for all d_w calculations.

Table 1 and Fig.4 show that the correction due to on-channel concentration sample slug is non significant, since the corrected due to this factor size distribution curves and weight average particle diameters are absolutely identical with the uncorrected ones. This is due to the fact that a relatively large error in retention ratio or volume produces an error only one third as large in particle diameter. For this reason in Tables 2 and 3 are given only the uncorrected d_w values.

A second parameter, which was varied during the feed step, was the field strength. Reducing the spin rate from 1800 to 1500 rpm, while the rest experimental conditions were held constant, led to lower weight average particle diameter than those determined by the direct injection and when the spin rate during feeding was 1800 rpm. This fact indicates that this motor speed (1500 rpm) is not enough to assure that the particles are concentrated at the head of the column. For his reason all of our experi-

TABLE 1

Weight Average Particle Diameters (Corrected Due to On-Channel Concentration Procedure and Noncorrected) for the PVC Sample Obtained by the Concentration Procedure in SFFF at Various Feed Volumes V_f. The Field-Strengths During the Feeding and the Separation Steps were $(rpm)_f = 1800$ and $(rpm)_s=600$, respectively. $v_f=5\ cm^3h^{-1}$, $v_s = 31\ cm^3h^{-1}$.

$V_f(cm^3)$	Uncorrected	
	d_i range (μm)	$d_w(\mu m)$
1	0.176-0.353	0.240±0.042[a]
2	0.187-0.356	0.243±0.040
5	0.155-0.338	0.237±0.045
10	0.182-0.357	0.243±0.043 (0.243±0.043)[b]
15	0.183-0.359	0.244±0.043
20	0.174-0.349	0.234±0.043
Direct injection	0.173-0.334	0.241±0.043

$V_f(cm^3)$	Corrected	
	d_i range (μm)	$d_w(\mu m)$
1	0.177-0.352	0.240±0.042
2	0.188-0.357	0.244±0.040
5	0.159-0.339	0.239±0.045
10	0.175-0.355	0.243±0.040
15	0.191-0.361	0.249±0.042
20	0.187-0.352	0.242±0.042
Direct injection	-	-

a :Standard deviations calculated from Equations (6)

b :Calculated from Equation (7) -all other d_w values was calculated from Equation (5).

ments were done with a rotor speed of 1800 rpm during the feeding step.

Table 2 gives the results obtained at various flow velocities in the separation step, while the rest conditions are held constant. Although the flow velocity has a strong and well understood effect on band broadening, as was shown elsewhere(4), the weight average particle diameters are virtually identical.This fact indicates that the inherent high resolution of SFFF prevents,under present conditions, band broadening of sufficient magnitude to disturb the weight average particle diameters measured.

The results obtained at different field strengths during the separation step are presented in Table 3. It can be seen that this parameter has a relatively significant effect on the particle size measured. Moreover the correction due to on-channel concentration procedure did not give any significant correction to the weight average particle diameter. More complicated phenomena related with the variation of the solute layer, such as particle-wall interactions (16) and steric effects (15, 17) might be responsible for this deviation.

Density and Particle Size

By using two different carrier solutions having various densities ρ_o and ρ_o' we are able to determine from the two fractograms, apart from the d_i values, density values, ρ_i, of the suspended matter (PVC) from the relationship:

$$\rho_i = \frac{\rho_o' V_{Ri} - \rho_o V_{Ri}'}{V_{Ri} - V_{Ri}'} \qquad (15)$$

TABLE 2

Weight Average Particle Diameters (Uncorrected) with their Standard Deviations for the PVC Sample Obtained by the Concentration Procedure in SFFF at Various Flow Rates in the Separation Step. $(rpm)_f = 1800$, $(rpm)_s=600$, $v_f = 5\ cm^3h^{-1}$.

$V_f(cm^3)$	$v_s(cm^3h^{-1})$	d_i range (μm)	d_w(μm)
2	15	0.171-0.340	0.247±0.045
2	31	0.182-0.357	0.243±0.040
2	49	0.182-0.336	0.238±0.038
Direct injection	31	0.173-0.334	0.241±0.043

TABLE 3

Weight Average Particle Diameters (Uncorrected) for the PVC Sample Obtained by the Concentration Procedure in SFFF at Various Field Strengths During the Separation Step. $(rpm)_f=1800$, $v_f=5\ cm^3h^{-1}$, $v_s=31\ cm^3h^{-1}$.

$V_f(cm^3)$	$(rpm)_s$	d_i range (μm)	d_w(μm)
2	600	0.182-0.357	0.243±0.040
2	750	0.162-0.300	0.220±0.036
2	800	0.156-0.320	0.225±0.042
2	1000	0.139-0.273	0.197±0.036
Direct injection	600	0.173-0.334	0.241±0.043

From the experimentally measured values of V_{Ri} and V'_{Ri} corresponding to mobile phases with densities ρ_o and ρ'_o, respectively, the unknown values of ρ_i can be computed via Equation (15). Using the found values of ρ_i in Equation (4), the particle diameters d_i can be also determined. From all these ρ_i and d_i values (see Table 4),an average

TABLE 4

Particle Diameters and Densities for the PVC Sample Obtained by the Concentration Procedure in SFFF by Varying the Density of the Carrier Solution. V_{Ri} and V'_{Ri} are the Elution Volumes of Fifteen Equal Volume Intervals of two Fractograms Obtained when the Densities of the Carrier Solutions were 1.00 and 1.11 $g.cm^{-3}$, respectively. $(rpm)_f=1.800$, $(rpm)_s=600$, $v_f=5\ cm^3h^{-1}$, $v_s=31\ cm^3h^{-1}$, $V_f=2\ cm^3$

$V_{Ri}(cm^3)$	$V'_{Ri}(cm^3)$	$d_i(\mu m)$	$\rho_i(g.cm^{-3})$
6.54	4.62	0.186	1.376
9.50	6.93	0.205	1.408
12.33	9.24	0.218	1.439
15.29	11.56	0.232	1.450
18.13	13.87	0.242	1.468
20.97	16.18	0.252	1.482
23.80	18.49	0.261	1.493
26.76	20.80	0.271	1.494
29.60	23.11	0.279	1.502
32.56	25.42	0.288	1.502
35.40	27.73	0.295	1.508
38.48	30.04	0.304	1.502
41.19	32.36	0.309	1.513
44.03	34.67	0.315	1.517
46.99	36.98	0.322	1.516
Average values	:	$d_w = 0.230$	$\rho_s = 1.478$
Direct injection	:	$d_w = 0.241$	-
Density measured	:	-	$\rho_s = 1.400$
Relative % error	:	4.8	5.3

density, $\rho_s = \sum_i n_i\rho_i/\sum_i n_i$, and a weight average particle diameter, d_w, can be calculated from Equation (5).

Table 4 gives the average density and the weight average diameter of the PVC particles obtained simultaneously by the proposed methodology in SFFF. For comparison purposes the average density measured by the method described in the experimental section and the weight average particle diameter obtained by the direct injection onto the FFF channel are also presented. The relative percentage error of d_w is 4.8, while that of ρ_s is 5.3. More precise value of the suspended solid density one could determine by performing more than two experiments with carrier solutions having different densities (18).

CONCLUSIONS

Weight average particle diameters and particle size distribution curves for dilute polydisperse colloidal samples, determined by a new methodology in SFFF, are in excellent agreement with those obtained by the direct injection of small volumes of highly concentrated samples onto the column. Varying the density of the carrier fluid, apart from the particle size, the density of the dilute polydisperse colloidal sample was found. The method has considerable promise for characterizing particle size and density parameters in dilute complex colloidal materials, such as those of natural water, where particles are present in low concentration.

ACKNOWLEDGMENTS

We are grateful to Prof.J.Calvin Giddings(University of Utah), who supplied the SFFF system and to Mrs.M.Barkoula for her kind assistance.

REFERENCES

1. Giddings, J.C., Karaiskakis, G. and Caldwell, K.D., Concentration and Analysis of Dilute Colloidal Samples by Sedimentation Field-Flow Fractionation, Separ.Sci.Technol., 16, 725, 1981.

2. Giddings, J.C., Myers, M.N., Caldwell, K.D. and Fisher, S.R., in Methods of Biochemical Analysis, Vol.26, D.Glick (ed.), J.Wiley and Sons, New York, 1980, p.79.

3. Giddings, J.C., Yang, F.J. and Myers, M.N., Sedimentation Field-Flow Fractionation, Anal.Chem., 46, 1917, 174.

4. Karaiskakis, G., Myers, M.N., Caldwell, K.D. and Giddings, J.C., Verification of Retention and Zone Spreading Equations in Sedimentation Field-Flow Fractionation, Anal.Chem., 53, 1314, 1981.

5. Giddings, J.C., Karaiskakis, G., Caldwell, K.D. and Myers, M.N., Colloid Characterization by Sedimentation Field-Flow Fractionation I. Monodisperse Populations, J.Colloid Interf.Sci., 92, 66, 1983.

6. Yang, F.S., Caldwell, K.D. and Giddings, J.C., Colloid Characterization by Sedimentation Field-Flow Fractionation II. Particle Size Distribution, J.Colloid Interf. Sci., 92, 81, 1983.

7. Yang, F.S., Caldwell, K.D., Myers, M.N. and Giddings, J.C., Colloid Characterization by Sedimentation Field-Flow Fractionation. III. Emulsions, J.Colloid Interf. Sci., 93, 115, 1983.

8. Kirkland, J.J., Yau, W.W. and Doerner, W.A., Sedimentation Field-FLow Fractionation of Macromolecules and Colloids, Anal.Chem., 52, 1944, 1980.

9. Kirkland, J.J. and Yau, W.W., Sedimentation Field-Flow Fractionation:Applications, Science, 218, 121, 1982.

10. Caldwell, K.D., Karaiskakis, G. and Giddings, J.C., Characterization of Liposomes by Sedimentation Field-Flow Fractionation, Colloids and Surfaces, 3, 233, 1981.

11. Caldwell, K.D., Karaiskakis, G. and Giddings, J.C., Characterization of T4D Virus by Sedimentation Field-Flow Fractionation, J.Chromatogr., 215, 323, 1981.

12. Caldwell, K.D., Karaiskakis, G. Myers, M.N., and Giddings, J.C., Characterization of Albumin Microspheres by Sedimentation Field-FLow Fractionation, J.Pharmac.Sci., 70, 1350, 1981.

13. Karaiskakis, G., Graff, K.A., Caldwell, K.D. and Giddings, J.C., Sedimentation Field-Flow Fractionation of Colloidal Particles in River Water, Intern. J.Environ.Anal.Chem., 12, 1, 1982.

14. Karaiskakis, G. and Dalas, E., Characterization of Dilute Colloidal Samples by Frontal Sedimentation Field-Flow Fractionation, J.Chromatogr.Sci., 26, 29, 1988.

15. Dalas, E. and Karaiskakis, G., Characterization of Inorganic Colloidal Materials by Steric Field-Flow Fractionation. I. Determination of Particle Size distribution, Colloids and Surfaces, 28, 169, 1987.

16. Hansen, M.E. and Giddings, J.C., Retention Perturbations Due to Particel-Wall Interactions in Sedimentation Field-FLow Fractionation, Submitted for publication.

17. Myers, M.N. and Giddings, J.C., Properties of the Transition from Normal to Steric Field-FLow Fractionation, Anal.Chem., 54, 2284, 1982.

18. Giddings, J.C., Karaiskakis, G. and Caldwell, K.D., Density and Particle Size of Colloidal Materials Measured by Carrier Density Variations in Sedimentation Field-Flow Fractionation, Separ.Sci.Technol., 16, 607, 1981.