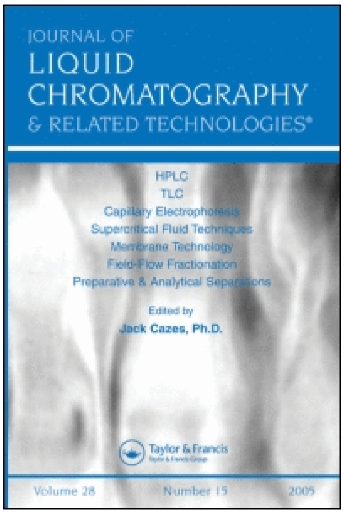

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Fischer, Christian-Herbert(1994) 'Analysis of Colloids. VI. Semiconductor Colloids of High Monodispersity by Preparative Size Exclusion Chromatography', Journal of Liquid Chromatography & Related Technologies, 17: 17, 3593 — 3611

To link to this Article: DOI: 10.1080/10826079408013979

URL: http://dx.doi.org/10.1080/10826079408013979

JOURNAL OF LIQUID CHROMATOGRAPHY, 17(17), 3593-3611 (1994)

ANALYSIS OF COLLOIDS. VI*. SEMICONDUCTOR COLLOIDS OF HIGH MONODISPERSITY BY PREPARATIVE SIZE EXCLUSION CHROMATOGRAPHY

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ABSTRACT

The recently described method of size exclusion chromatography (SEC) of very small colloidal semiconductor particles was transferred from the analytical scale to the preparative one. The particular difficulties dealing just with SEC and the special situation when working with inorganic colloids are described. The influence of flow rate, sample volume, sample concentration and fraction volume were studied using CdS-sols with particle diameters ranging from 2nm to 8nm. Up to 200mg samples were separated in less than one hour. The fractions were generally characterized by analytical SEC and in two instances by transmission electron microscopy showing excellent consistency and standard deviations down to 11%.

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* The last papers of this series were:
V: Ch. -H. Fischer, M. Giersig, T. Siebrands, J. Chromatography in press
IV: T.Siebrands, M.Giersig, P.Mulvaney, Ch.-H.Fischer, Langmuir 9,2297 (1993)
III: Ch. - H. Fischer, M. Giersig, Langmuir, 1992, 1475

INTRODUCTION

Very small semiconductor and metal particles of less than 20nm diameter to as small as 1.3nm are a relatively new and rapidly growing field of colloidal chemistry [1]. Particles of this small size are interesting because of phenomena such as a quantum size effect of absorption spectra and fluorescence spectra, possible application for solar energy conversion and electronic devices. It has been shown that size exclusion chromatography (SEC) is a fast and powerful tool for rapid size determination not only for organic polymers but also for these inorganic, so called Q-particles and especially in combination with a diode array detector for the elucidation of their basic phenomena [2]. Monodisperse colloids are of particular interest to physicochemists, because special properties can be directly correlated with a certain particle size. So it was the scope of this work to scale-up the conditions of analytical SEC, i.e. to optimize the chromatographic parameters such as polydispersity, separation time (flow rate), and sample amount (sample concentration and volume, fraction volume). Unfortunately all these parameters are connected in such a way, that improving one leads to a deterioration of another. Fig.1 demonstrates the special situation in preparative SEC of a sample with a broad size distribution. In all other chromatographic methods two or more peaks corresponding to different chemical species are separated. So the column can be overloaded easily as long as the two peaks are more or less baseline separated and only with beginning overlap the product purity decreases. However the problem in the SEC is completely different, whenever a size distribution should be separated. Then the whole peak has to be considered as a superposition of elemental chromatograms each relating to the species of one size. Thus any increase of sample amount leads immediately to a bigger overlap of the elemental chromatograms and therefore to a higher polydispersity of the product collected in the fractions. Therefore with preparative SEC it is not only a question of how much substance is needed but also of how monodisperse should it be. The performance of the separation is a necessary compromise between monodispersity and yield. Though numerous papers dealing with SEC of polymers exist [3],

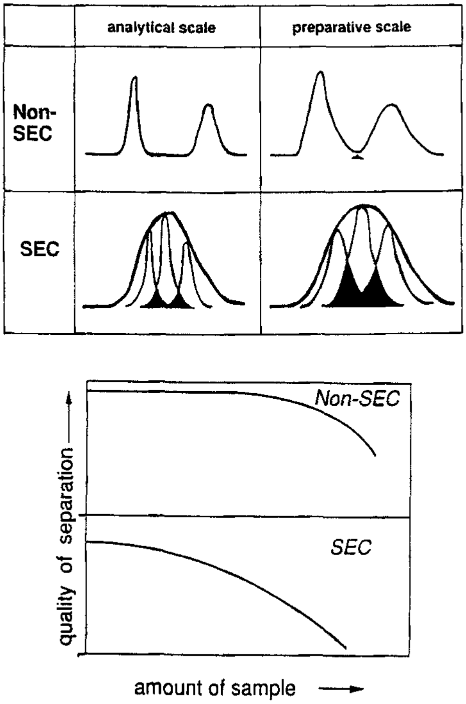

FIGURE 1. The effect of overloading in chromatography: Schematic comparison of non-SEC-methods and SEC with broad distributions. The overlapping areas of the peaks are marked in black. The SEC peak has to be considered as an overlay of numerous elemental chromatograms of one particular size. The graph on the bottom describes in principle the quality of the separation (size distribution or product purity, respectively) as a function of the amount of sample.

a rather special situation in the case of inorganic solid crystalline particles was found. For the actual investigations cadmium sulfide sols were used, because this material is one of the best known semiconducting materials. One general difficulty was the relative instability of the colloids. Despite the presence of polyphosphate as a stabilizer against coagulation in both the sample and the eluent the particle size changed with time. So all comparative experiments, such as optimization experiments had to be carried out over a short time frame in order to exclude sample changes.

MATERIALS

Cadmium perchlorate (Alfa), sodium polyphosphate (Riedel-de Haën), hydrogen sulfide (AGA) were of highest available purity and were used without further purification. Water was purified by a Milli-Q system (Millipore).

METHODS

HPLC

The equipment consisted of a Merck-Hitachi pump, type L 6000, and a Merck Hitachi L4200 UV/vis detector with a 2mm cell for the preparative work and a 5mm cell for the analytical, operating at 250nm. A set of two 125mm long Knauer columns were used, the first packed with Nucleosil 500 C4 (5µm) and the second Nucleosil 1000 C4 (5µm) from Macherey and Nagel. The mobile phase was an aqueous solution of 1×10^{-3} M cadmium perchlorate and 6×10^{-3} M sodium polyphosphate (referring to the formula $NaPO_3$) . For preparative separations the column diameter was 32mm with a flow rate of 4.5mL/min, except within flow rate optimization experiments where the sample loop volume varied from 200µL to 2000µL. Fractions were taken using an automatic fraction collector (Isco, model 328). The fraction volume was 450µL, where no other value is given. For analytical runs columns of 4mm diameter were used with a sample volume of 20µL. Concentrated original samples were diluted down to 1mM. Data collection and SEC calculations were carried out using a Bruker Chromstar system.

Preparation of colloidal cadmium sulfide

Hydrogen sulfide gas or aqueous sodium hydrogen sulfide solution was injected through a septum into an aqueous cadmium perchlorate / sodium polyphosphate solution, through which nitrogen had been bubbled for ten minutes. After shaking, the solution could be used.

RESULTS AND DISCUSSION

In the following the effects of flow rate, sample volume, sample concentration and fraction size on the separation of colloidal cadmium sulfide are discussed . The characterization of the fractionation was carried out by reinjecting fractions in the analytical column set (using the same stationary phase, the same column length, but with a diameter of only 1/8 of the preparative columns). The results were compared by the half width of the analytical peaks and/or by the diameter-polydispersity D_d determined by the chromstar computer program (as defined below). Fig.2 exemplified this general procedure. It shows the analytical chromatograms of the diluted original sample and of the fractions. The much smaller peak widths of the fraction chromatograms compared with that of the original sample were evident as well as the shift of the peak maxima with increasing fraction number. Interestingly the analytical chromatogram of the raw sol almost completely enveloped those of the fractions, when it was plotted in an adjusted size .

1. Effect of Flow Rate

In the experiment of Fig.3 the sample consisted of a cadmium sulfide sol prepared from a 5mM cadmium perchlorate and 30mM polyphosphate solution (based on the formula $NaPO_3$) by the addition of 1mM sodium hydrogensulfide. 200µl were injected three times on the preparative column the flow rate being varied from 2.25mL/min over 4.5mL/min to 9.0mL/min. 0.9mL fractions were collected and some of them re-injected in the analytical setup. In Fig.3 (top) for each run the analytical elution times of these preparative fractions were plotted over the corresponding preparative elution volumes. The slower the flow rate the higher was the initial slope and the earlier and more pronounced deflected the straight line towards saturation, i.e. the smallest particles eluted delayed in the preparative mode. They had the highest diffusion rate and were able to re-diffuse back into the same pore, if a rapid stream did not push them forward. Two reasons could be responsible for the decreasing slope with

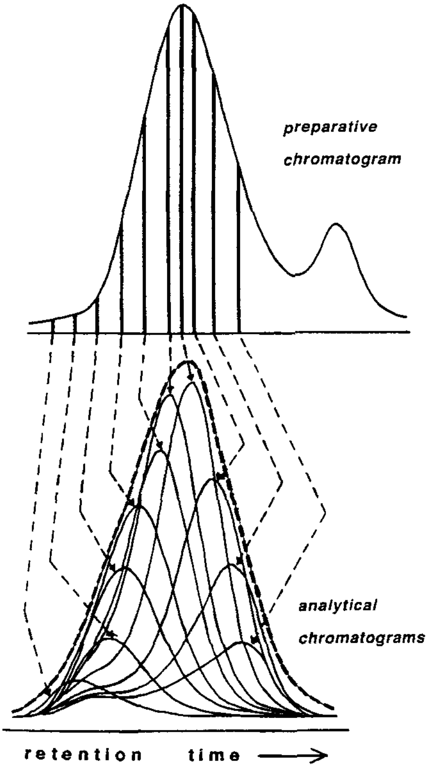

FIGURE 2. Characterisation of a preparative fractionation of a cadmium sulfide sol. Preparative chromatogram (**top**). The small peak is due to polyphosphate. Ten fractions (marked in black) were collected and re-injected in the analytical SEC (**bottom**), dashed line: diluted original sol, peak height adapted). Both time scales are different. Chromatographic conditions are given in the experimental part.

increasing flow rate: Firstly the residence time of the particles inside the pores was independent of the flow rate. But during this constant period the differing volumes of eluent, which passed through the interstitial volume, were dependent on the flow rate. Secondly, because of high flow rate fewer particles found the way into the pores, the other part is purged forward by the rapid stream. This also was obvious from the peak broadening (vide infra). The highest flow rate showed a linear relation

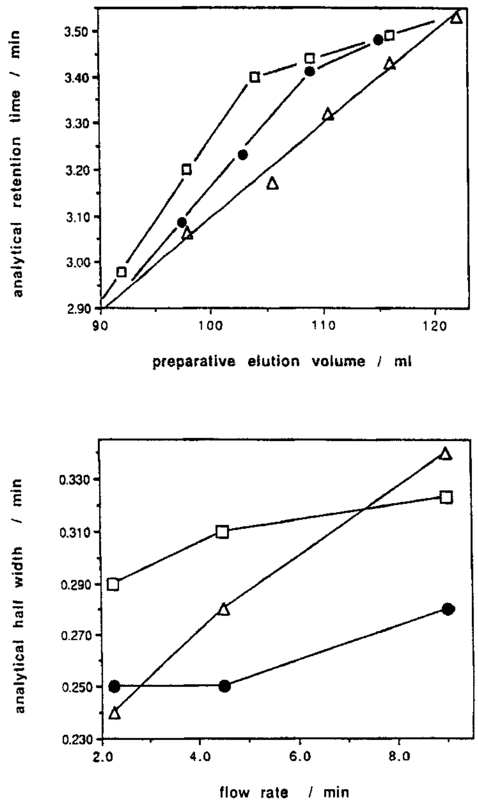

FIGURE 3. Effect of flow rates on the separation of a cadmium sulfide sol (5mM $Cd(ClO_4)_2$,30mM polyphosphate, 1mM H_2S).

Top: Analytical retention time of re-injected fractions as a function of their preparative elution volume (□ 2.25 mL/min, ● 4.5 mL/min, Δ 9mL/min)

Bottom: Half width of the analytical peak as a function of flow rate:

● fraction in the preparative peak maximum, Δ fraction at the frontal deflection point, □ fraction of the tail deflection point.

over the whole range with the smallest slope. Therefore one could be inclined to choose this condition. However, first it was necessary to characterize the quality of the separation. For this purpose three fractions of each run were analyzed: the fractions in the maximum of the preparative peak and in the two points of inflection. In Fig.3 (bottom) their analytical half widths were plotted over the flow rate. In the flow range of this experiment the peaks became broader with increasing flow rate, since there was not sufficient time for all the particles to diffuse into the accessable pore volume. Generally the peaks of the main fractions were the narrowest, while those of the smaller particles the broadest. Two exceptions were noted and both could be explained in terms of diffusion: Firstly, at the lowest flow rate the peak width of the main fraction had not decreased further, because the diffusion is dependent not only on the diffusion coefficient, but also on the concentration and the main fraction was more concentrated than the side fractions. Therefore the rate of *back* diffusion into the pores became relevant compared to the forward flow. Secondly, at the highest flow rate the peak of large particles became broader than that of small ones. The slow diffusion hindered the large particles to a higher extent to reach the pores thus causing peak broadening.

Normally the initial sol has its mean size in the desired range. Therefore the optimization of the main fraction suffices. With regard to the time consumption the medium flow rate of 4.5mL/min was used for further work.

2. Effect of Sample Volume

To study the influence of the sample volume a 10mM cadmium sulfide sol was used prepared from a 10mM cadmium perchlorate / 60mM polyphosphate solution by adding 1mM hydrogensulfide and then evaporation of the water to one tenth of the original volume. This sol was injected on to the preparative column several times using sample loops of 200µL, 500µL, 1000µL and 2000µL, respectively (constant flow rate of 4.5mL/min; 0.9mL fractions). From the normalized chromatograms (Fig.4, left part) it could be seen, that with increasing sample volume the

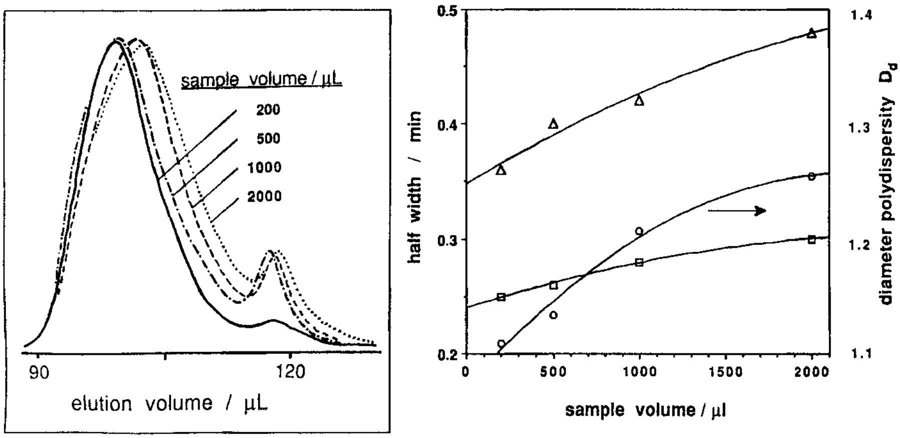

FIGURE 4. Effect of sample volume on the separation of a cadmium sulfide sol (10mM $Cd(ClO_4)_2$, 60mM polyphosphate, 1mM H_2S).
Left part: Preparative chromatograms. Loop sizes 200, 500, 1000 and 2000 µl.
Right part: Diameter polydispersity (○), half width of preparative peak (Δ) and analytical one (□) of the peak fraction as a function of the sample volume. (The preparative width was divided by ten, in order to compare all three parameters in one plot !)

peak width and the retention volume increased. The latter was shifted by 4.5mL in the case of the 2000µL loop compared to the 200µL one. This shift was much bigger than the theoretical half sample volume. Enhanced absorption was most probably the reason for the retardation. Though the sample concentration was the same in all cases, a larger sample volume was less diluted than a small one during the passage through the column. Especially the higher electrolyte concentration led the absorption increase (vide infra).

The widths of the analytical peaks of the main fractions and those of the preparative ones divided by 10 (in order to visualize both in one figure) were plotted over the sample volume in Fig.4, right part. Both values changed proportionally. For a more expressive characterization we used the *diameter* polydispersity D_d, defined in equation 1, where d_w is the weight average diameter of the particles in the sol and d_n the number average diameter, respectively, according to equations 2 and 3. n_i is the number of particles with the diameter d_i and the weight w_i. An ideal monodisperse sol would have $D_d = 1$. These expressions are very similar to the related molar weights M_w and M_n and their polydispersity D, used in polymer chemistry. However, for colloid chemists the size is a more useful value, because crystalline particles do not swell and have a measurable, constant size, independent of the solvent used, which is not the case for the coils of organic polymers. When a commercial SEC-program is fed with diameters instead of molecular weights as calibration data, d_w , d_n and D_d are automatically calculated. Fig. 4, right part, shows that the diameter polydispersities of the main fractions lay between 1.11 for the 200µL loop and 1.26 for the 2000µL loop. The peak widths reflect the diameter polydispersities. However, the latter describes the broadness of the size distribution more quantitatively, because the same peak width has a different quantitative meaning depending on the elution volume because of the logarithmic relation in SEC.

$$D_d = \frac{d_w}{d_n} \qquad (1)$$

$$d_w = \frac{\Sigma\, n_i\, d_i\, w_i}{\Sigma\, n_i\, w_i} = \frac{\Sigma\, n_i\, d_i^4}{\Sigma\, n_i\, d_i^3} \qquad (2)$$

$$d_n = \frac{\Sigma\, n_i\, d_i}{\Sigma\, n_i} \qquad (3)$$

3. Effect of Sample Concentration

For the studies of the concentration influence a colloidal cadmium sulfide stock solution was prepared from a 20mM cadmium perchlorate/

120mM polyphosphate solution by the addition of 2mM hydrogensulfide. 0.5mM and 1mM CdS sols were obtained by dilution with water and a 20mM CdS sol by evaporation of the solvent. Dilution of this concentrated sample led to 10mM, 5mM and 2.5mM sols. As checked by analytical SEC the evaporation process was not accompanied by particle growth. 500µL of all samples were injected into the preparative column (flow rate 4.5mL/min; 0.9 mL fractions). Some of these preparative chromatograms are shown normalized in Fig.5 (top). With increasing concentration the peaks became broader. That absorption played an important role revealed the inspection of the polyphosphate peak at about 29min, which could be used as an internal standard. Its size relatively to the CdS-peak increased tremendously with increasing sample concentration, though the relative concentrations were the same in all samples. This indicated the loss of particles by adsorption on the surface of the stationary phase. Following analytical SEC experiments investigating the peak area as a function of concentration also showed such a mass loss in the concentrated solutions compared to the diluted samples, when water was used for the dilution. On the other hand a linear relation between area and concentration was obtained, when the dilution was carried out with a solution of the same electrolyte composition as the concentrated solution. It is well known in colloid chemistry that high concentrations of electrolytes destabilise colloids by reducing the repelling charges on the surface of the colloidal particles. These charges do not only prevent against particle combination, but also against the adsorption of the colloidal material on any other surface carrying the same charge. The samples in question contained still electrolytes from the preparation: cadmium perchlorate, perchloric acid and polyphosphate. This was the reason for the concentration effect. The preparative peak widths and the diameter polydispersities of the main fractions were plotted as a function of CdS concentration in Fig.5 (bottom). Both parameters reflect the worse separation with increasing sample concentration. As in the case of organic polymers the slope is steeper for lower concentrations than for higher ones [4].

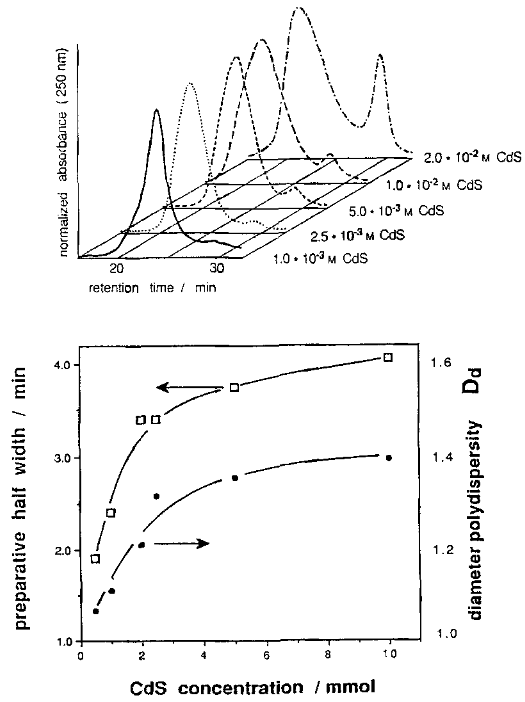

FIGURE 5. Effect of sample concentration on the separation of 500µl cadmium sulfide sol from [Cd(ClO$_4$)$_2$] : [polyphosphate] : [H$_2$S] = 10 : 60 : 1 (details in the text).

Top: Normalized preparative chromatograms from 1mM, 2.5mM, 5mM, 10mM and 20mM CdS sols.

Bottom: Preparative half width and radius polydispersity of the main fraction as a function of CdS concentration.

4. Optimization of the Yield: Sample Concentration versus Sample Volume

In order to compare both, the options of increasing amounts of sample, either higher concentration, or larger sample volume, a cadmium sulfide sol prepared from 10mM cadmium perchlorate / 60mM polyphosphate / 10mM hydrogensulfide, was separated three times: 500µL non-diluted, 1000µL diluted 1:1 by water and 2000µL diluted 1:3, respectively. So every time the same amount was injected and equal peak areas in the resulting chromatograms could be expected. Surprisingly, the peak areas were reproducibly different (Fig.6, left part) and decreased from 100% (2000μL) to 84% (1000μL) and 58% (500μL). Since the detector operated in a range, where Lambert-Beer's-law was valid, it was concluded that increase of the sample concentration led to less CdS being eluted from the column. An irreversible adsorption effect took place on the stationary phase which increased with increasing concentration. This was in accordance with the observation that precolumns had a yellow surface, when they were used for a while. The reasons for the enhanced adsorption were discussed in the previous paragraph. Fig.6, right part, shows comprehensively as a function of sample volume and sample concentration: The relative peak areas of CdS normalized on the most diluted sample, the fraction of lost CdS calculated from the relative peak area under the assumption that in the most diluted sample all CdS eluted and the diameter polydispersity of the particles. The main fractions of all three runs had the same radius polydispersity of 1.2 compared to 1.5 in the case of the original sample. This behaviour was different from normal organic polymers, which gave worse polydispersity for higher concentration [5]. The constant polydispersity can also be explained in terms of irreversible or long time adsorption of colloidal particles on the stationary phase, increasing with the concentration. Therefore the material loss in the case of higher concentrations led to lower effective concentrations and consequently to smaller differences between the sample concentrations. Obviously the effect of these remaining differences balanced just the opposit effect of sample volume. In conclusion, a larger sample volume with correspondingly lower concentration is recommended for a high yield with low polydispersity. For organic polymers the same conditions are preferred, however, there it is based on changes in polydispersity [5], whereas irreversible adsorption and yield do not play any important role.

5. Effect of Fraction Volume

200μl of a cadmium sulfide sol (from cadmium perchlorate / polyphosphate/ sodium hydrogensulfide, 10mM / 60mM / 10mM) with

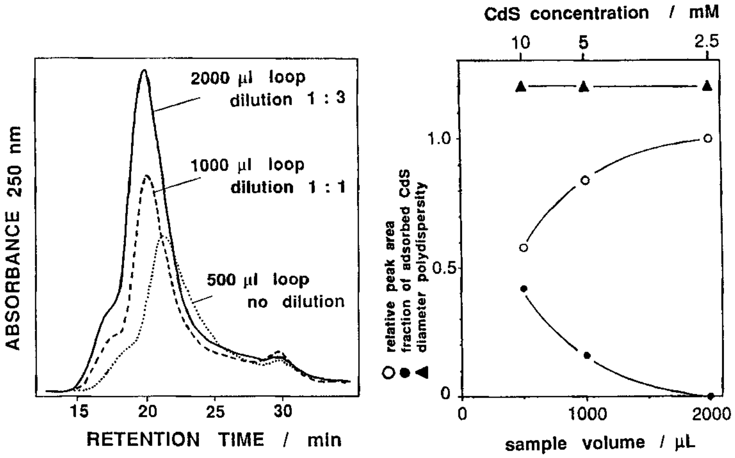

FIGURE 6. Comparison of the combined effects of sample concentration and sample volume on the separation of colloidal cadmium sulfide. The original sol was prepared from 10mM $Cd(ClO_4)_2$, 60mM polyphosphate, 10mM H_2S. The sample volumes were 500µl, 1000µl and 2000µl, but the latter two were diluted 1:1 and 1:3, respectively with water.

Left part: Preparative chromatograms of the three concentration / volume combinations

Right part: Relative peak area (non-diluted = 1), fraction of adsorbed CdS (calculated from the relative peak areas under the assumption that the most dilute sample has no loss by adsorption) and diameter polydispersity of the main fraction as a function of sample volume and concentration.

d_w = 6.9nm and D_r = 1.45 was separated, the fraction size being 0.9mL (0.2min). Analytical SEC was carried out from the collected material in the preparative peak maximum. For studying the effect of fraction volume it was expanded stepwise from 0.9mL to 8.1mL. This was achieved in one run by successive addition of the next four and the previous four fractions to the central fraction no.19 in the following sequence: 20, 18, 21, 17, 22, 16, 23, 15. After every addition an analytical run was carried out. The polydispersity increased exponentially from 1.197 to 1.272. A dramatic broadening started only when the collected fraction volume was more than 15 times the injected sample volume (Fig.7).

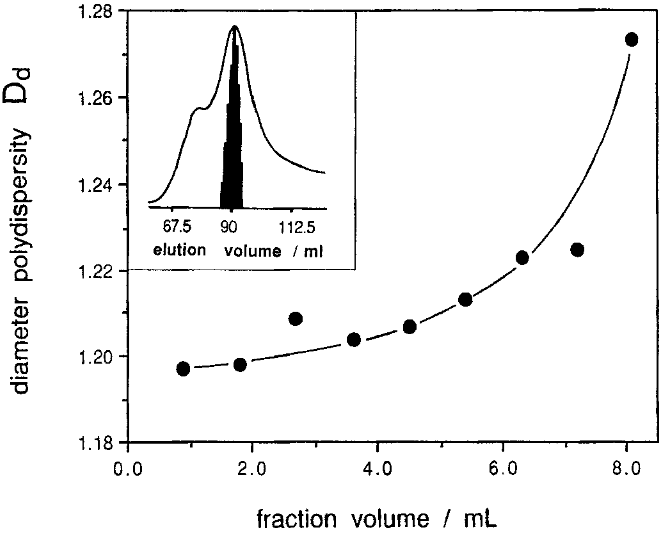

FIGURE 7. Effect of fraction volume on the separation of 200µl cadmium sulfide sol (10mM $Cd(ClO_4)_2$, 60mM polyphosphate, 10mM H_2S). Diameter polydispersity of the main fraction as a function of the fraction size. The inset shows the preparative chromatogram and the size of the fractions. Experimental details are explained in the text.

Consequently the fraction volume is the least critical point, when high yield with high monodispersities are considered.

6. Comparison of the Results by Transmission Electron Microscopy (TEM)

In order to check the efficiency of the SEC separation as well as the reliability of the SEC size analysis by a second independent method, two cadmium sulfide sols of very small and of medium size were separated (200µL sample volume). The first was prepared by mixing 5mM sodium hydrogensulfide and 5mM cadmium perchlorate/ 30mM sodium polyphosphate solution (volume /volume 4 : 1) and the latter from cadmium perchlorate/sodium polyphosphate solution and

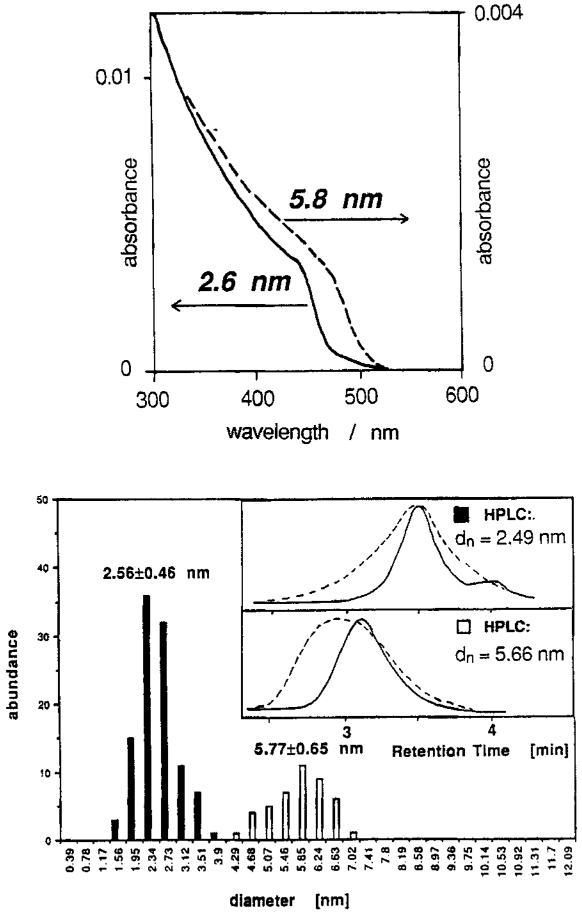

FIGURE 8. Bottom: Size distribution of two cadmium sulfide sols after preparative HPLC fractionation obtained by transmission electron microscopy (smaller particles: 5mM $Cd(ClO_4)_2$ /30mM polyphosphate and 5mM NaHS mixed 4 : 1 (v/v); bigger particles: 10mM $Cd(ClO_4)_2$, 60mM polyphosphate, 10mM H_2S). The inset shows the normalised analytical chromatograms of the diluted original samples and of the fraction analysed by TEM.
Top: UV/vis spectra of the two fractions from preparative HPLC. The shift of the onset of absorption is due to the size quantization effect. The steepness of the step indicates the narrow size distribution.

TABLE 1

Comparison of the SEC and TEM Results from the Experiment of Figure 8

sample		d_n [nm]		d_w [nm]		$D_d = d_w / d_n$	
		HPLC	ELMI	HPLC	ELMI	HPLC	ELMI
1	original	2.32		3.91		1.69	
	fraction	2.49	2.56	2.82	2.81	1.13	1.10
		σ = 0.46 (18 %)					
2	original	6.05		9.09		1.50	
	fraction	5.66	5.77	6.73	5.97	1.18	1.04
		σ = 0.65 (11 %)					

hydrogensulfide (10mM/60mM/10mM). One fraction of both separations was examined by transmission electron microscopy and also by SEC. Fig.8 (bottom) shows the histograms of the size distribution from TEM and in the insert the normalized chromatograms of the fractions in comparison to that of the original samples. On the top a typical phenomenon of nm-semiconductor particles is demonstrated: The size quantization effect (Q-effect) of the absorption spectra, i.e. the onset of absorption shifts with decreasing particle size towards shorter wavelengths [6]. It is due to the increasing energy gap between the valence band and the conductivity band. The very steep slope indicates the high monodispersity of the two fractions. Table 1 summarizes the quantitative results of this experiment. In both cases the monodispersity of the fractions increased significantly. The diameter polydispersity decreased from 1.7 or 1.5 to 1.1 or 1.04, respectively. Both fractions have size distributions with standard deviations of 11% and 18%, which is very narrow for cadmium sulfide colloids. The data of TEM and SEC were in excellent agreement.

CONCLUSION

The results have established the method of preparative SEC as a powerful tool for colloidal chemistry of nm-particles. The separation was carried out in less than one hour. With columns of 32mm internal diameter up to 200mg of sample was injected. Generally, for high yields larger sample volumes should be applied rather than higher concentrations. When larger amounts have to be separated one can work either in cycle, which is easily automated, or with larger columns, which is faster but also more expensive. In contrast to SEC, gel electrophoresis, which has also been used for the separation of CdS sols [7], needs time consuming preparation of the electrophoresis gel, the separation itself requires six hours and the column is destroyed on collection of the fractions. The analytical SEC on the other hand has been demonstrated to be a very reliable method, which is ideal just for routine size determinations because of its very short run time of less than five minutes.

ACKNOWLEDGEMENTS

The author thanks Dr. M. Giersig for the TEM-measurements, Ms. U. Michalczik and Mr. H. Seitz for their useful help in the laboratory work.

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Received: April 20, 1994
Accepted: May 6, 1994