



ELSEVIER

Journal of Chromatography A. 707 (1995) 189–197

JOURNAL OF  
CHROMATOGRAPHY A

## Analysis of colloids

### VIII. Concentration- and memory effects in size exclusion chromatography of colloidal inorganic nanometer-particles<sup>☆</sup>

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First received 1 December 1994; revised manuscript received 31 December 1994; accepted 8 March 1995

#### Abstract

Colloidal cadmium sulfide with diameters of ca. 17 nm was used as a model substance to study the effects of sample concentration on elution time and peak area in size exclusion chromatography (SEC) of colloidal inorganic particles in the low nm-size regime. A clear distinction had to be made between the pure particle concentration and that of the accompanying electrolytes. The effects were astonishingly high taking into account that particles and small electrolytes are separated immediately in SEC. The reasons for these phenomena are discussed. The electrical double layer was found to play an important role. The results obtained for solid particles were compared with those for organic polymers in SEC. A memory effect of the column was observed due to temporarily adsorbed particles.

#### 1. Introduction

Colloidal inorganic particles of metals as well as of semiconductors present a very exciting and rapidly growing topic in physical chemistry because of their extraordinary properties [4]. After size exclusion chromatography (SEC) had been applied to the characterization of organic polymer latex samples down to a size of 100 nm [5], it has been shown that this method is also a powerful tool for the research on particles with a diameter ranging between 2 nm and 20 nm. It not only provides rapid information about the

size distribution [3,6], but also about the size depending properties, when appropriate detectors are used, e.g. UV–Vis spectra with a diode-array detector [7]. Colloidal silica [8], cadmium sulfide [3,6,9], zinc sulfide [3] and gold [10] have been investigated. From the differences between the particular calibration curves the relative thickness of the electrical double layer could be estimated [3]. The study of rigid solid particles, which do not swell or shrink as polymer coils do, could also be helpful in understanding the mechanism of SEC of organic polymers. Preparative SEC is useful when very monodisperse colloids have to be prepared from polydisperse ones [2]. During the studies carried out for the optimization of the conditions of the preparative separations, anomalies were found. The present work

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<sup>☆</sup> For part VII see Ref. [1], for part VI see Ref. [2] and for part V see Ref. [3].

was performed on an analytical scale in order to elucidate and explain these effects in detail. In SEC of organic polymers strong effects of the concentration on the recovery and the elution time were found [11]. It was also the aim of this work to compare the inorganic particles with the polymers in this respect.

## 2. Experimental

The equipment consisted of a Merck-Hitachi L 6000 pump (Merck, Darmstadt, Germany), and a Merck Hitachi L4200 UV-Vis detector operating at 250 nm or a Waters 990 diode-array detector (Milford, MA, USA) and a Merck-Hitachi autosampler using a 20- $\mu$ l sample loop. Under standard conditions a set of two 125  $\times$  4 mm I.D. Knauer columns (Berlin, Germany) were used in most cases, the first packed with Nucleosil 500 C<sub>4</sub> (7  $\mu$ m) and the second with Nucleosil 1000 C<sub>4</sub> (7  $\mu$ m) from Macherey and Nagel (Düren, Germany). For the estimation of the adsorption a 250  $\times$  4 mm I.D. column packed with Nucleosil 120 C<sub>4</sub> (5  $\mu$ m) was applied. The mobile phase was an aqueous solution of 6 mM sodium polyphosphate (the molarity refers to the phosphate units) (Riedel de Haen, Seelze, Germany) and 1 mM cadmium perchlorate (Ventron, Karlsruhe, Germany). In some experiments these concentrations were higher or sodium chloride (Merck) was added. The flow-rate was 0.5 ml/min. Data were collected either with a Bruker Chromstar system or with a 990 Waters system.

Colloidal cadmium sulfide was prepared from 12 mM cadmium perchlorate, 72 mM polyphosphate and 12 mM hydrogen sulfide gas (Messer Griesheim, Düsseldorf, Germany). The details were described in the previous papers [1–3].

## 3. Results and discussion

Studies on the effect of concentration were carried out with aqueous cadmium sulfide sols, because they belong to the best known inorganic colloids. In general, colloids have to be stabilized

in order to prevent coagulation and even precipitation. In this case polyphosphate was used. It covers the surface of the particles, forming complex bonds [12].

When in preparative SEC sample concentration and sample volume were varied in such a complementary way that the injected sample mass was kept constant, large differences in the resulting chromatograms were found (Fig. 1). The higher the concentration the smaller the eluting peak. This result led to the conclusion that larger sample volumes and low concentrations should be used rather than the opposite, when high yields are required [2]. The following experiments were carried out on an analytical scale with a combination of two C<sub>4</sub> modified-silica columns with 50 nm and 100 nm pore size. The eluent consisted of an aqueous solution of 1 mM cadmium perchlorate and 6 mM polyphosphate (referring to phosphate units) as described previously [7]. The colloidal CdS samples had a relatively large particle size of ca. 17 nm. The reason was that a wide concentration range had

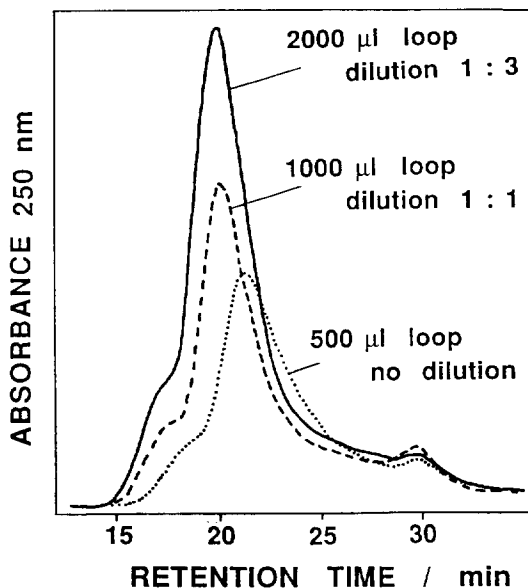


Fig. 1. Preparative chromatograms of a CdS sol (standard conditions as in the present work except for an 8-fold column diameter). The same sample amount was injected three times using different concentrations and correspondingly different volumes as indicated. Compare [2].

to be investigated and smaller particles could not be obtained in high concentrations.

### 3.1. Peak area recovery

A very concentrated cadmium sulfide sol (12 mM CdS) was diluted stepwise with water and injected. Fig. 2 shows three normalised chromatograms of this series. With increasing concentration the peak width increased dramatically and also the elution time. The small peak at 4.3 min was due to polyphosphate. Its extinction coefficient is very low at 250 nm and it can not be detected when its concentration is the same as in the eluent.

In this section, the area and shape of the CdS peak will be discussed. In Fig. 3 peak width and area were plotted versus the CdS concentration. Astonishingly the latter function had a pronounced maximum at 10 mM CdS and decreased thereafter. It is necessary to stress that in this low nm-range the colloidal particles do not show any significant scattering [4]. Moreover the extinctions were quite low and in the range of Lambert–Beer's law. So the measured extinctions were proportional to the CdS concentration. Therefore it must be concluded that with increasing concentration an increasing amount of colloidal particles was lost in the column. If the

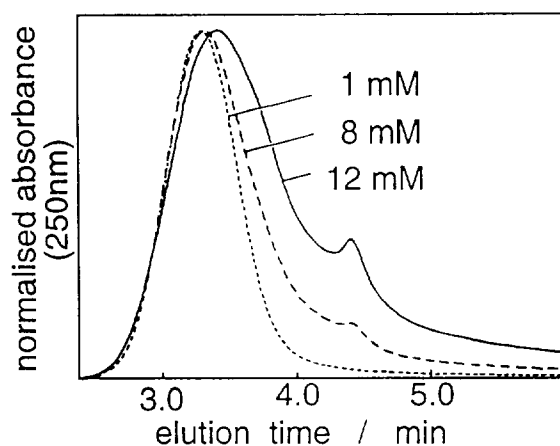


Fig. 2. Normalised chromatograms of a CdS sol of different concentrations as indicated (standard conditions; dilution medium: water).

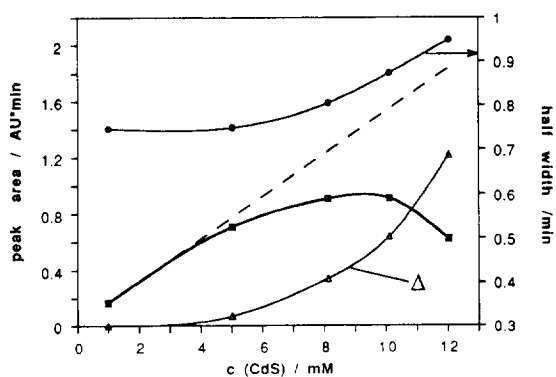
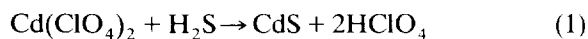


Fig. 3. SEC of a 12 mM CdS sol stepwise diluted with water (standard conditions). Area (■) and half width (●) of the CdS peak as a function of the CdS concentration.  $\Delta$  Area ( $\Delta$ ) is the loss of CdS calculated as the difference between the area curve and its extrapolated initial slope.

loss is assumed to be negligible in the lowest concentration range, the lost amount at higher concentration can be estimated from the difference  $\Delta A$  between the measured peak area and the linear extrapolation of the initial slope (Fig. 3). The only explanation for this effect can be an irreversible adsorption of the CdS particles on the surface of the stationary phase. A strong adsorption at high concentration was also indicated by increased tailing (see half peak width, Fig. 3) and finally by the fact that after many CdS injections (after several months) the first part of the column was turning yellow. The effect of electrolyte concentration on adsorption, aggregation and flocculation is well known [13]. Examples for such an exponentially increasing adsorption are described in the literature [14] for multilayer adsorption when the first layer is complete. Taking the small sample volume of 20  $\mu$ l and the low particle concentration (not molar CdS concentration, *vide infra*) into consideration, such a multilayer adsorption is very unlikely. Moreover, in the section dealing with the memory effect, it will be shown that the adsorption activity of a CdS covered surface was lower than that of a clean surface. Nevertheless, some change in the system has to occur. The eluent composition and the stationary phase remained the same. Therefore the reason for this anomaly has to be found in the sample itself. A

similar effect was observed in SEC of organic polyelectrolytes, e.g. proteins in an ionised form. Potschka [15] and Hearn et al. [16] described the lower recovery at high concentrations in these cases. Solid particles carrying surface charges might be considered as a special case of a polyelectrolyte. Now it should be noted that in the preparation of the CdS sols, hydrogen sulfide gas was added to a cadmium perchlorate/polyphosphate solution. According to Eq. 1



two molecules of perchloric acid per molecule cadmium sulfide are formed. When the dilution was carried out with water, of course all of the electrolytes present were also diluted. It is well known in colloid chemistry that electrolytes decrease the stability of sols. The surface charges of the colloidal particles cause a repulsion from each other. Oppositely charged ions from the solution are adsorbed onto the particles, thereby diminishing the net charge and thus the repelling forces. Consequently, adsorption among the particles (= coagulation) and enhanced adsorption on other surfaces occurs.

If this assumption is right, it is clear that electrolytes in the eluent should have an even worse effect, because particles are in contact with the eluent during the whole passage through the column. In the experiments of Fig. 4 a concentration series (dilution medium: water) was injected onto the HPLC system using different eluent compositions: (a) 1 mM cadmium perchlorate–6 mM polyphosphate (standard condition); (b) 1 mM cadmium perchlorate–6 mM polyphosphate–10 mM sodium chloride; (c) 8 mM cadmium perchlorate–48 mM polyphosphate.

An addition of 10 mM sodium chloride to the normal eluent reduced the CdS peak area by roughly 25%, whereas an eight-fold increase of the normal cadmium perchlorate/polyphosphate concentration led to a loss of about 80% cadmium sulfide. The reason for this was that the multiple-charged electrolytes destabilise colloids more than single-charged electrolytes (see also electrical double layer in the next paragraph).

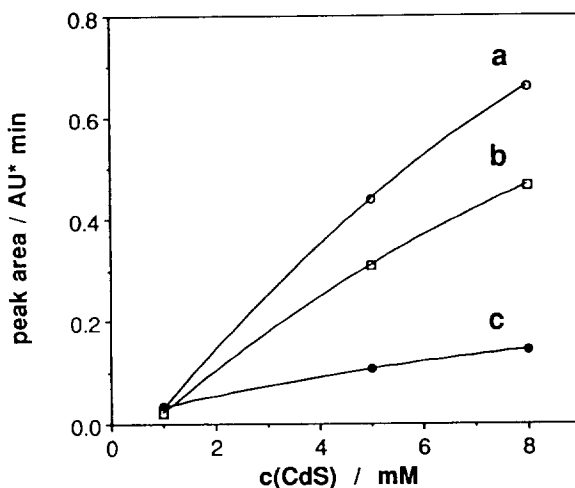


Fig. 4. SEC of a CdS sol using three different eluent compositions: (a) 1 mM cadmium perchlorate–6 mM polyphosphate (standard condition); (b) 1 mM cadmium perchlorate–6 mM polyphosphate–10 mM sodium chloride; (c) 8 mM cadmium perchlorate–48 mM polyphosphate. CdS peak area as a function of the CdS concentration (dilution medium: water).

These latter experiments show the strong effect of electrolytes and explain also the change in the recovery in one series in terms of electrolyte content.

In order to study the effect of the particle concentration, further dilution series with different dilution media were performed: (a) water, i.e. the electrolytes were diluted by a factor of up to twelve; (b) 72 mM polyphosphate, i.e. the polyphosphate concentration of the most concentrated CdS sol was kept constant in all diluted samples; (c) 72 mM polyphosphate–24 mM perchloric acid, i.e. the electrolyte concentration of the most concentrate CdS sol is kept constant in all diluted samples.

The results under standard chromatographic conditions are shown in Fig. 5. Compared to series (a) with a change of all concentrations, the constant polyphosphate content (curve b) did not essentially change the situation, because polyphosphate forms complexes with the particles and thus stabilises them [12]. However, the constant perchloric acid concentration led to an increased adsorption of colloidal CdS. The al-

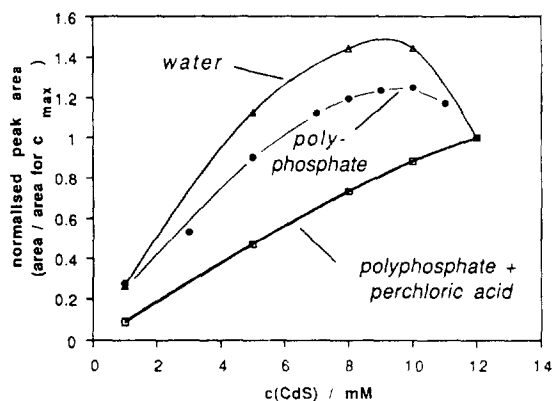


Fig. 5. SEC of a 12 mM CdS sol stepwise diluted with (a) water ( $\Delta$ ), (b) 72 mM polyphosphate ( $\bullet$ ), or (c) 72 mM polyphosphate–24 mM perchloric acid ( $\square$ ) solutions. Normalised CdS peak area (referring to the peak area of the undiluted original sample).

most linear curve *c* indicates an adsorption proportional to the particle concentration. This result was in accordance with previous stationary experiments studying the adsorption of ferric oxide or arsenic trisulfide sols on silica. Also Freundlich et al. [17] and Buzágh et al. [18] described the independence of adsorption on particle concentration as long as the electrolyte content was constant. It is worth mentioning that all CdS peaks of series *c* had the same retention time and very broad half widths just as the highest of series *a*. Obviously the electrolytes, in the present case especially the perchloric acid, were responsible for the loss of CdS particles. The concentration of the particles themselves had only a relatively small effect on the adsorption. Anyhow, the astonishing point about the chromatography was that the electrolytes in the sample had such a strong effect, although they were separated immediately from the particles by the SEC mechanism because these ions are comparatively very small. The adsorption can only take place in the very first part of the column. It should be stressed that all injected solutions were clear without any flocculation. However, it seems reasonable that the colloid in the sample has already been (at least partially) destabilized by the electrolyte environment.

### 3.2. Elution times

In SEC of organic polymers concentration effects are well studied. Several reasons for these effects have been discussed [11,19–22]: hydrodynamic volume contraction, frictional forces, viscosity phenomena and secondary exclusion, i.e. the analyte itself consumes space in the pores and thus reduces the accessible volume. Janca [20] found a relative increase of the elution volumes of about 5% for polystyrenes with a molar mass of 498 000 and 867 000, when the concentration was varied between 0.005% and 0.1% (w/v). In the consideration of inorganic colloids again the two cases have to be distinguished:

(A) When both the particle and the electrolyte concentration varied in parallel (upon dilution in water), the elution times  $t_e$  were constant at 3.16 min below a concentration of 5 mM CdS and increased up to 3.31 min at a concentration of 12.5 mM, i.e. an increase of ca. 5%, (Fig. 6, left, curve b; please note the expanded time scale!). The calibration on this column combination was established by electron microscopy with CdS concentrations not higher than 1 mM (compare [3]). After conversion of the equation for the calibration line (Eq. 2) to the exponential form (Eq. 3) diameters could be calculated.

$$\log d = -0.734t_e + 3.558 \quad (2)$$

$$d = 3612 \cdot 10^{-0.734t_e} \quad (3)$$

Thus the two above mentioned elution times of the different sample concentrations correspond to diameters,  $d$ , between 17.26 nm and 13.40 nm (Fig. 6, right part). The difference  $\Delta d$  was 3.86 nm.

Within the possible concentration range no differences in viscosity between the sols and pure water could be measured with an Ubbelohde viscosimeter. Therefore changes in viscosity can be neglected for inorganic colloids. One could argue that the shift was only due to the enhanced adsorption discussed in the previous section. That could be proofed by using a Nucleosil 120  $C_4$  column (5  $\mu\text{m}$ , 250  $\times$  4 mm I.D.) instead of the Nucleosil 500  $C_4$  and 1000  $C_4$  (7  $\mu\text{m}$ , 120  $\times$  4

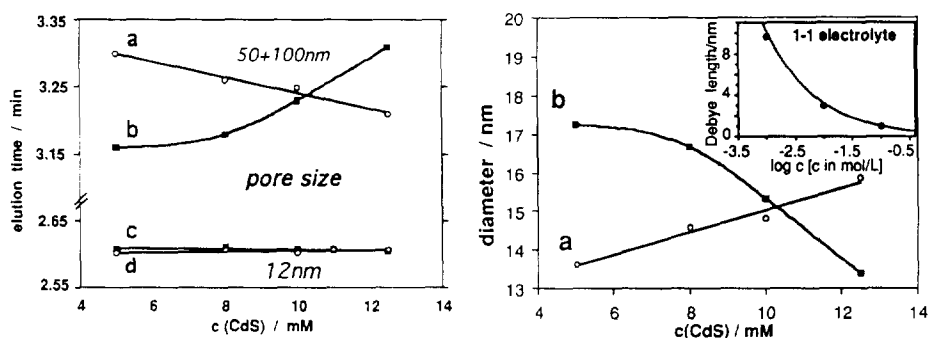


Fig. 6. SEC of a 12 mM CdS sol stepwise diluted with water (■) or 72 mM polyphosphate–24 mM perchloric acid (○) solution, respectively. Left part: Elution time as a function of the CdS concentration. Curves a and b: chromatographic standard conditions. For comparison all samples were also injected on a Nucleosil 120 C<sub>4</sub> column, 250 × 4 mm I.D. (curves c and d). Right part: Average particle diameters corresponding to curves a and b in the left part calculated from the calibration Eq. 3 as a function of the CdS concentration. Insert: Debye length as a function of the concentration of an 1–1 electrolyte according to the Debye–Hückel model.

mm I.D. each), i.e. the same material with small pore size, where adsorption should be dominant and any SEC mechanism negligible in this size regime (Fig. 6, left, curves c and d). Only 5- $\mu$ m material was available here; however, the larger specific surface was a compensation for the inaccessible surface inside the pores. Indeed no shift in elution time was observed, indicating that adsorption was not responsible at all for this concentration effect on elution time. However, it is important with respect to the SEC method to stress that generally no preferential adsorption of larger particles was found, which would also explain such a shift. This was shown by the reinjection of collected effluat as well as by sequential injection (see next section).

However, there is another, and probably the most important reason for the shift in elution time in question. An electrical double layer is formed at any charged interface between a solid and a liquid containing electrolytes by attraction of oppositely charged ions towards the surface. The thickness of this layer is dependent on the electrolyte concentration in the solution. The double layer is quite rigid and cannot easily be penetrated, neither by charged nor by neutral species [15]. For coiled, charged organic polymers, such as proteins, Potschka found a similar behaviour of the elution times [15]; thus again there is a parallel with colloidal inorganic par-

ticles, where the interface is really obvious. Therefore the thickness of the double layer has to be taken into account when the effective diameter of a colloidal particle is considered in SEC. However, this thickness depends strongly on the bulk electrolyte valency and concentration, because at higher electrolyte density the potential drops down much faster. The Debye–Hückel model for the diffuse double layer describes the potential  $\Psi$  as a function of the distance  $x$ . In the case of the CdS sols we mainly have to consider perchloric acid as electrolyte, i.e. a 1–1 electrolyte, because the complex formation between polyphosphate and the particles has only minute effects as shown in the previous section. The Debye length  $\kappa^{-1}$  represents that distance  $x$  from the interface, at which the double layer potential  $\Psi$  has dropped down to the value  $\Psi_0/e$ , where  $\Psi_0$  is the potential directly at the interface. The insert in the right part of Fig. 6 shows the Debye length  $\kappa^{-1}$  versus the logarithm of the concentration for a 1–1 electrolyte according to the Debye–Hückel approximation (modified from the data of Hiemenz [23]). In SEC, the shift in elution time took place between 5 mM and 12 mM CdS. This corresponded to 10 mM and 24 mM perchloric acid according to Eq. 1. In that range  $\kappa^{-1}$  decreases from 3 nm to 2 nm, i.e. by a difference  $\Delta(\kappa^{-1}) = 1.0$  nm. This was approximately a quarter of the

measured  $\Delta d$ . However, these calculations can present no more than an estimation because in chromatography we have a steady dilution of the sample and thus varying concentrations. Thus one should expect no more than the right order of magnitude.

(B) When only the concentration of the particles was varied and that of the electrolytes was kept constant, the effect on elution time was opposite (Fig. 6, left, curve b). Here the elution time decreased somewhat with increasing concentration. For the discussion of secondary exclusion the particle concentration  $c_p$  has to be considered. From the elution time  $t_e = 3.16$  min a weight average diameter  $d_w = 17.3$  nm was obtained by means of the calibration. Assuming the particles to be spherical, the volume of one particle was  $V_p = 2711$  nm<sup>3</sup>. With the volume of a CdS unit cell  $V_u = 0.049$  nm<sup>3</sup> a number of unit cells per particle  $n = 55\,300$  was calculated. In the case of the highest used CdS concentration  $c(\text{CdS}) = 12$  mM the CdS particle concentration was  $c_p = 1.3 \cdot 10^{18}$  l<sup>-1</sup>, or in other words one particle in a volume  $V = 7.5 \cdot 10^5$  nm<sup>3</sup>, i.e. 277-fold its own volume. If two Debye lengths of 2 nm are added to  $d_w$ , the effective diameter would be  $d_{\text{eff}} = 17.3$  nm + 4 nm = 21.3 nm and the effective particle volume  $V_{p,\text{eff}} = 5060$  nm<sup>3</sup>, i.e. still one particle in 148-fold its own effective volume. Under these circumstances secondary exclusion should not be very pronounced. Therefore decrease in elution time at high concentration must be explained in terms of partial, weak and reversible agglomeration. Due to dilution during the run through the separation column later disintegration takes place. That is why the decrease in elution time does not correlate to a dimer diameter.

### 3.3. Memory effect

In this section an effect is described which is generally referred to as conditioning. Because in particle chromatography this effect is extraordinarily pronounced and because it is closely related to the previously discussed recovery problem, it should be briefly demonstrated. When the chromatographic signal was greatly

amplified, it was observed that the “baseline” after the colloidal peak was somewhat higher than the initial one. This led to the conclusion that at least a certain portion of the adsorbed CdS was not completely irreversibly adsorbed on the surface of the stationary phase and that it desorbed only very slowly. Injections of pure methanol–water mixtures after several CdS separations wetted the  $C_4$ -phase and led to enhanced desorption, as indicated by the peak, which showed a typical CdS spectrum in the diode-array detector. The area of this “CdS peak” decreased exponentially with the number of methanol injections. After these observations it remained to be investigated whether a stationary phase which was “modified” by adsorbed particles had a different adsorptivity than uncovered fresh material. For this purpose the same 10 mM CdS sol was injected five times after exactly the same intervals (10 min) by an autosampler. Indeed the peak area increased with the number of injections by ca. 10% and reached a plateau after the fifth injection (Fig. 7, inset). Two points were evident:

- (1) The adsorption activity of a stationary phase already covered by CdS was lower than that of an uncovered one.
- (2) The desorption of CdS from the silica

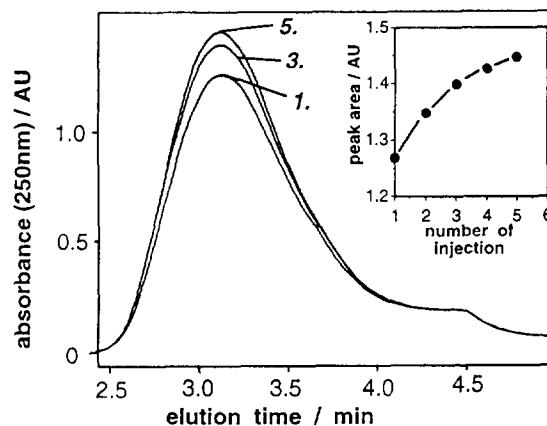


Fig. 7. Memory effect of the column. The same 10 mM CdS sol was injected five times in a 10 min interval (standard condition). Overlay plot of the 1st, 3rd and 5th chromatograms. Inset: CdS peak area as function of the number of injection. (Details in the text).

surface was much slower than the time of one run (5 min).

After five 20- $\mu$ l injections the small initial part of the column bed was covered by CdS, and in this section of the column particles and electrolytes of the sample were not yet completely separated. It can be said that for a certain time the column has a memory of the previous runs, which was lost after careful purging. Fig. 7 shows also that the elution time was constant during the whole series, which excluded any preferential adsorption of particles of one particular size.

The memory effect could also be demonstrated by the experiments shown in Fig. 8. A dilution series of CdS colloids with constant electrolyte content was injected twice, once in increasing order of concentration, and once in decreasing order of concentration. Between both series the column was purged extensively. It is obvious that a sample showed a smaller peak when it was injected on a rather fresh, uncovered clean column surface "with no mem-

ory". At the end of a series the peak was clearly larger. This effect was most pronounced for the most diluted sample, because the loss (ca. 50%) was high compared with the absolute amount of sample.

#### 4. Conclusions

The concentration range for proper SEC of colloidal cadmium sulfide particles has been defined. It has been shown that in the normal concentration range of inorganic sols up to 5 mM the chromatographic behaviour of colloidal cadmium sulfide is quite normal. Above that concentration a dramatic increase of absorption takes place which is mainly caused by the accompanying, and also more concentrated, electrolytes. A remarkably decreased recovery as well as an increase in elution times were found. The changing thickness of the electrical double layer was the main reason for these phenomena. Generally, attention should be paid to the large influence of the electrolytes in the sample, and even more so, in the eluent. Retardation and peak broadening could result in incorrect size distributions. Therefore sol concentrations above 5 mM should be diluted with pure solvent. Increasing particle concentrations with constant electrolyte content gave almost proportional peak areas, but slightly shorter elution times, which is interpreted as weak aggregation.

With respect to concentration effects colloidal inorganic particles behave completely different from neutral organic polymers, but resemble charged polymers such as proteins.

The memory effect of the column was due to a layer of particles on the surface of the stationary phase. If there is a necessity to obtain exact results for particle concentration, one has to work with an already saturated column. However, when SEC is used, generally the main interest is the size distribution, i.e. only the relative amounts of species with different sizes, and fortunately no preferential loss of particular particle sizes was observed here. Therefore the results were not affected by a memory effect.

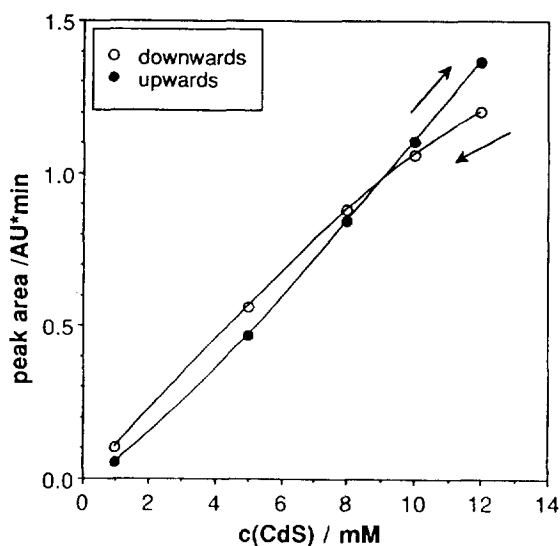


Fig. 8. Memory effect of the column. SEC of a 12 mM CdS sol stepwise diluted with a 2 mM polyphosphate–24 mM perchloric acid solution (standard condition). Order of injection: increasing concentration (●); decreasing concentration (○). Between both series the column was purged extensively. Peak area as a function of CdS concentration.



## Acknowledgement

The authors wish to thank Ms. M. Michalczik for the help with the laboratory work.

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