

Analysis of colloidal particles

V[☆]. Size-exclusion chromatography of colloidal semiconductor particles

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Abstract

An HPLC technique for the size determination of colloidal cadmium sulphide and zinc sulphide in a diameter range from 20 down to 2 nm using silica with pore sizes from 30 to 100 nm is described. The growth of the particles during the run was suppressed by the addition of stabilizers to the eluent and by the use of reversed-phase silica as the stationary phase for inorganic stabilizers. The calibration of the column sets by electron microscopy resulted in a linear relationship between the logarithm of the particle diameter and the elution time. The analysis was carried out within 4–10 min. The lateral resolution lay between 1.3% for larger particles and 1.9% for smaller particles. Below a diameter of 13 nm these values were better than those found from electron microscopy. From the comparison of the calibration lines for various colloidal materials, the differences in their electrical double layers could be estimated. The limitations of the method are discussed and the size-exclusion chromatographic and electron microscopic methods are compared.

1. Introduction

A new branch of colloid chemistry has arisen during the last 10 years resulting from numerous investigations of the photochemistry, radiation chemistry and electrochemistry of nanometre-sized semiconductor and metal particles [5,6]. In the presence of suitable stabilizers, such as polyphosphate and poly(vinyl alcohol), and under optimized conditions, aqueous sols could be prepared with particle diameters down to 1.3 nm [3]. When long-chain alkane thiols were used for the stabilization, the thiol groups were strongly bound to the surface of the inorganic

particles, and as a result they are soluble in organic solvents such as tetrahydrofuran and cyclohexane [7]. These nanoparticles show many interesting phenomena, *e.g.*, size quantization effects (*Q*-effects) in optical absorption and fluorescence spectra.

Colloidal semiconductors are of interest for their possible use of solar energy and in micro-electronic devices. Because of their extraordinary properties, nanoparticles are a very important topic for basic physico-chemical research. For these studies, a knowledge of the size and size distribution of the colloidal particles is very important. Electron microscopy (ELMI) is a good but time-consuming method with respect to particle instability and tedious evaluation [8]. Because many colloidal particles grow in spite of

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* For Parts I–IV, see refs. 1–4, respectively.

being stabilized, it was necessary to find a more rapid method.

Size-exclusion chromatography (SEC) seemed to be a promising alternative. It is widely used for the molar mass determination of organic polymers. In the past also many papers have been published dealing with the analysis of latexes [9], but only a very few on suspensions of solid inorganic particles, *e.g.*, silica and aluminosilicate, which are generally stable colloids [10,11]. This might be due to the fact that many nanometre-sized materials were developed only recently and with SEC they often cause severe problems with stability and absorption. Very recently gold sols have been proposed for the characterization of low-pressure LC columns [12].

Our studies on the SEC of inorganic nanoparticles began with low-pressure chromatography on Sephacryl gels [1]. The work continued with HPLC because of higher resolution and shorter analysis times [2,3]. The latter is extremely important for rapidly growing colloidal species. Previous papers published in physico-chemical journals have described the applications of SEC for colloidal chemists, such as studies of growth mechanisms, of the size-dependent optical spectra in metal sols [4], in semiconductor sols, of magic agglomeration numbers [2] and the preparation of colloids inside an HPLC column [3]. This paper deals with chromatographic aspects of the separation of unstable semiconductor particles by SEC. The method development was carried out with colloidal cadmium sulphide, as it is one of the best known semiconducting materials. The method also was applied to zinc sulphide. In the future, the rigid, non-swelling, non-shrinking, solid particles might also assist in understanding by comparison phenomena of the SEC of organic polymer coils.

2. Experimental

2.1. HPLC conditions

The equipment consisted of a Merck–Hitachi L 6000 pump and a Merck–Hitachi L4200 UV–

Vis detector operating at 250 nm or a Waters Model 990 diode-array detector and a Knauer electrically driven injection valve with a 20- μ l sample loop. For aqueous colloids a set of two 125 mm \times 4 mm I.D. Knauer columns were used in most instances, the first packed with Nucleosil 500 C₄ (7 μ m) and the second with Nucleosil 1000 C₄ (7 μ m) from Macherey–Nagel, and in some instances a set of two 250-mm columns containing Nucleosil 300 C₁₈ (5 μ m, 5.6 mm I.D.) and Nucleosil 500 C₁₈ (5 μ m, 4 mm I.D.). The mobile phase was an aqueous solution of 1 mM sodium polyphosphate [based on the formula Na₆(PO₃)₆; Riedel-de Haën] and 1 mM Cd(ClO₄)₂ (Ventron) for CdS colloids and Zn(ClO₄)₂ (Ventron) for ZnS colloids. CdS colloids stabilized with dodecanethiol were analysed on Nucleosil 500 (7 μ m) and Nucleosil 1000 (7 μ m) columns, the eluent being 1 mM Cd(ClO₄)₂–1 mM C₁₂H₂₅SH in tetrahydrofuran. The flow-rate was 0.5 ml/min under all conditions. Data collection was carried out with either a Bruker Chromstar system or a Waters Model 990 system.

2.2. Preparation of colloidal metal sulphides

Hydrogen sulphide gas or aqueous sodium hydrogensulphide solution was injected through a septum into an aqueous Cd(ClO₄)₂ or Zn(ClO₄)₂ and sodium polyphosphate solution (1 mM each), through which nitrogen had been bubbled for 10 min. After shaking, the solution was used. The particle size was controlled by the amount of sulphide and by the pH value [6]. CdS sols with an organic stabilizer were prepared as follows: Cd(ClO₄)₂ (1 mM) and C₁₂H₂₅SH (0.1 mM–1 M) were dissolved in tetrahydrofuran, and after evacuation and bubbling with nitrogen, hydrogen gas was injected (0.2 mM).

2.3. Electron microscopy

A small drop of sample was adsorbed on the copper grids coated with a 50-Å thick carbon support film. After a contact time of 10 s the fluid was blotted off. The grids were dried under argon and examined in a Philips CM 12 transmission electron microscope with an acceleration

voltage of 120 kV. The microscope was equipped with a supertwin lens and an EDAX detector. For imaging, axial illumination was used in addition to the “nanoprobe mode” with a beam spot size of 1.5 nm, to permit the diffraction of the individual clusters. All images were made under conditions of minimum phase contrast artefacts with magnifications of 120 000 and 430 000 \times .

3. Results and discussion

3.1. Stationary phase

Colloids cannot exist in the presence of high salt concentrations in the eluent as a means of reducing adsorption. Increasing ionic strength would lead to adsorption of ions on the charged surface of the particles. This diminishes the stabilizing net charge and thereby the repelling forces. Coagulation and finally precipitation can occur. Therefore, stationary phases with low

adsorption power had to be applied. In fact, the C₄-modified silica gave better resolution than the unmodified silica because the silanol groups which cause polar interactions were substantially shielded. For particles with diameters between 2 and 20 nm two columns in series with pore sizes of 50 and 100 nm, respectively, were used. These large pores were essential. Obviously the effective size of the particles was much larger. It included the electrical double layer, which was formed at the solid–liquid interface, when particles were charged, and opposite ions were localized at a certain distance from the surface. Also electrical interactions between colloidal particles and the surface of the stationary phase have to be considered. When both carried charges of the same sign, the resulting repulsion reduced the accessible pore volume.

The results for four aqueous cadmium sulphide sols stabilized with polyphosphate are shown in Fig. 1: on the left-hand side the electron micrographs and the corresponding size

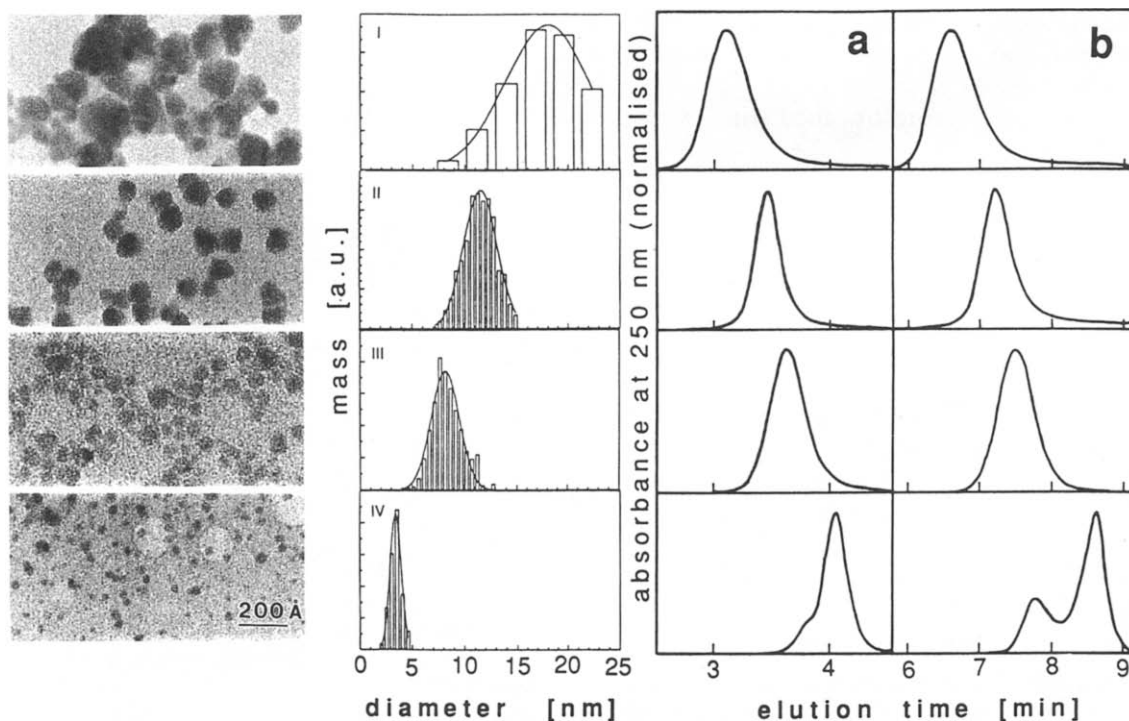


Fig. 1. Four aqueous CdS sols of different particle sizes (stabilizer polyphosphate). Left, electron micrographs and corresponding mass-based size distributions from ELMI; right, SEC separations (a) on Nucleosil 500 C₄ + Nucleosil 1000 C₄ (length each 120 mm) and (b) on Nucleosil 300 C₁₈ + Nucleosil 500 C₁₈ (length each 250 mm). Eluent for both series, 1 mM Cd(ClO₄)₂–1 mM polyphosphate; for further details, see Experimental.

distributions from ELMI and in the middle part the chromatograms obtained on two C_4 -modified silica columns as described under Experimental. The shift of the retention time was inversely related to the change in particle size. Later it was revealed that very small particles (below 2 nm), which do not absorb light in the visible range, grew during the run through the column, whereas no change took place within the same material when it was not injected on to the column. This growth was evident on inspection of the optical absorption spectra before and after the run (Fig. 2). The maximum at 275 nm had shifted to 305 nm after the passage through the column. The onset of absorption shifted towards longer wavelengths. According to the Q -effect, such a red shift takes place when the particle size increases. It is due to the decreasing energy gap between the valence band and the conductivity band. Therefore, in the actual case of the surface of the stationary phase, probably the remaining active silanol groups catalysed the growth of the particles. C_{18} -modified silica, where the silanol groups are better shielded by the larger hydrophilic layer, did not show this undesirable catalytic effect

The best results were obtained with two col-

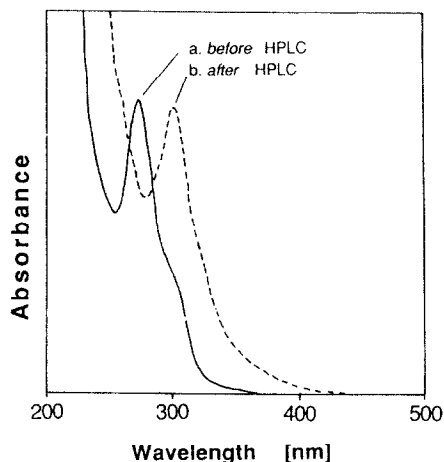


Fig. 2. Normalized optical absorption spectra of an aqueous CdS sol (stabilizer polyphosphate), containing very small particles (mean diameter of the original sample 1.3 nm). (a) Original sample; (b) collected effluent from Nucleosil 500 C_4 + Nucleosil 1000 C_4 .

umns (length of each 250 mm) with 30 and 50 nm pore size (Fig. 1, right). Further, the resolution was enhanced especially in the smaller diameter range so that the two populations in sample IV were better separated. The minor population of larger particles was invisible in the electron microscope (see below). When cadmium sulphide stabilized with organic substances such as long-chain alkanethiols was to be analysed, unmodified silica was preferred, in order to avoid a mixed SEC-reversed-phase mechanism. The surface of these particles is very hydrophobic so that adsorption does not play the same role as in the previous cases. It is worth mentioning that alterations of the colloids by the chromatographic process were also ruled out by reinjection experiments where no changes in the elution times were observed.

3.2. Mobile phase

Four normalized chromatograms of the same aqueous CdS sol stabilized with polyphosphate are shown in Fig. 3. It was injected on to the

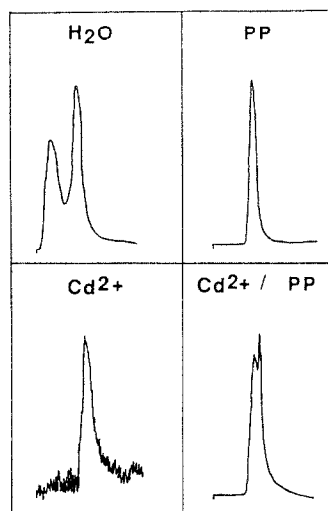


Fig. 3. Optimization of the eluent. Chromatograms of the same aqueous CdS sol (stabilizer polyphosphate) on Nucleosil 500 C_4 + Nucleosil 1000 C_4 with four different eluent compositions: water, water-1 mM polyphosphate (PP), water-1 mM $Cd(ClO_4)_2$ and water-1 mM $Cd(ClO_4)_2$ -1 mM polyphosphate. Only the time range between 2.5 and 4.7 min is shown.

same C₄-modified silica columns (pore size 50 and 100 nm) but utilizing different eluents: pure water, water containing polyphosphate or cadmium perchlorate or polyphosphate plus cadmium perchlorate. The cadmium salt alone led to irreversible and almost complete adsorption of the colloidal material (evident from the high noise level). As already mentioned, electrolytes in the solution lower the stability of a sol, especially in the absence of a stabilizer. Not only are the repelling forces between the particles themselves reduced, but also between them and all kinds of other surfaces with the same charge. When water without stabilizer was used as the eluent, the weakly bound stabilizer molecules separated from the particles by SEC, because they were smaller. As a result of this loss of stabilizer, many particles had grown, as indicated by the second peak in the chromatogram at earlier elution times. The stabilizer did not appear in the chromatogram, because polyphosphate does not absorb substantially at 250 nm.

The best results with respect to particle stability and resolution were obtained with an eluent containing a 1 mM aqueous solution of both polyphosphate [1 mM based on the formula Na₆(PO₃)₆] and cadmium perchlorate. Under these conditions the particles are always surrounded by the stabilizer and by the cations of the colloid. From sol preparation it is well known that an excess of the metal cations over the precipitating anions (here sulphide) generates smaller particles as opposed to a deficiency, which forms larger particles [6,13]. It seemed to be possible to generalize this eluent composition: solvent of the colloid with 1 mM stabiliser + 1 mM of the cation, from which the sol was generated. This rule worked very well not only for aqueous sulphides of zinc and cadmium stabilized with polyphosphates, but also for cadmium sulphide stabilized with alkanethiols (Fig. 4). In the latter case tetrahydrofuran was chosen, for two reasons: it is an excellent organic solvent for inorganic salts and also its ether group has complex-forming and stabilizing properties as known from the Grignard reactions of metal organic compounds. It should be mentioned that a negative system peak appeared whenever the

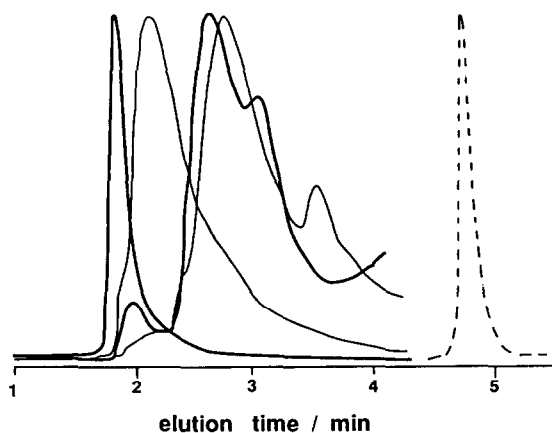


Fig. 4. Chromatograms of four CdS sols (solid lines) of various particle sizes in tetrahydrofuran with dodecanethiol as stabilizer. Columns, Nucleosil 500 + Nucleosil 1000; eluent, 1 mM CdCl₂–1 mM dodecanethiol–tetrahydrofuran. Dashed line, dodecanethiol.

thiol concentration in the sample was lower than in the eluent. This offers a way to calculate the amount of stabilizer bound to the particles.

In another series of experiments, the influence of the stabilizer in SEC was investigated. Cadmium sulphide sols of various sizes prepared in the presence of polyphosphate were injected in both eluents, containing cadmium perchlorate with either polyphosphate or triphosphate. The concentration of the latter was 2 mM so that the content of phosphate units was the same in both mixtures. In all instances the elution time with the triphosphate eluent was significantly shorter (by 10–15%) than the corresponding value with polyphosphate. Growth of particles in the triphosphate eluent, because of its minor stabilizing power, could be ruled out by reinjection of the collected colloid from the triphosphate run in the polyphosphate eluent. No change in elution time was observed in comparison with the original sample also injected in polyphosphate eluent (Fig. 5). Only a large second peak appeared due to triphosphate, which became visible even at 250 nm, because the colloid was very highly diluted after two chromatographic runs and high sensitivity had to be applied.

The reason for the shift in elution time was the change in the electrical double layer when the

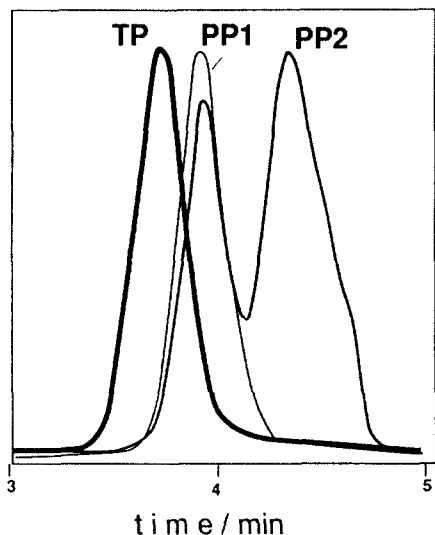


Fig. 5. SEC of an aqueous CdS sol (stabilizer polyphosphate) on Nucleosil 500 C₄ + Nucleosil 1000 C₄. The chromatograms are normalized. PP1: original sample; eluent, 1 mM Cd(ClO₄)₂–1 mM polyphosphate. TP: original sample; eluent, 1 mM Cd(ClO₄)₂–2 mM triphosphate. PP2: collected effluent from TP; eluent, 1 mM Cd(ClO₄)₂–1 mM polyphosphate.

electrolyte, which surrounded the particles, was varied. The used polyphosphate is a polyelectrolyte with a high content of hexamers and higher phosphates. The average negative charge per molecule is at least two times higher than for triphosphate. Therefore, the SEC result is in accordance with the Debye–Hückel model: the double layer thickness decreased exponentially with increasing charge of the electrolyte [14]. This effect can be illustrated by means of Fig. 5 and the calibration of the column discussed in the next section (Fig. 6). A CdS sol with an average size of 2.6 nm has an elution time of 3.93 min in a polyphosphate-containing eluent whereas in triphosphate it is only 3.73 min. This latter value corresponds to 3.9 nm according to the calibration in polyphosphate eluent (see below), *i.e.*, just by exchanging the stabilizer it allowed the particles to appear larger by 1.3 nm or 50%! The order of magnitude seemed reasonable for a change from an 1-6-electrolyte to an 1-3-electrolyte [14].

3.3. Calibration

For the calibration of a column set, relatively monodisperse sols of different particle sizes were prepared. These samples were investigated by transmission electron microscopy. The diameters of a statistically sufficient number of particles (whenever possible more than 300) were measured on the micrographs and the mass distributions of the diameters were constructed (Eq. 1 and Fig. 1):

$$nd^3 = f(d) \quad (1)$$

where n is the number of particles and d the particle diameter.

The mass-based instead of number-based distribution is necessary, because the spectrophotometric detector gives a response proportional to the concentration and therefore also to the mass of material. For the calibration, the logarithm of the diameter is plotted as a function of the elution time as colloidal chemists prefer the more descriptive diameter instead of the molar mass used in polymer chemistry.

Calibration plots are shown in Fig. 6 for the sulphides of cadmium and zinc, respectively, both stabilized with polyphosphate. The experiments of Fig. 6a were obtained on C₄-modified silica with a column length of 2 × 120 mm. The data points for zinc sulphide showed more scattering. The reason is the existence of two different crystal shapes, spherical and brick-like. Form factors would be necessary for a better linear fit. The side ratio of the bricks was about 1:3. For a first approach, two thirds of the long side was used as the size for these crystals when the histograms were constructed for the determination of the average size.

Large differences between the two materials are shown in Fig. 6a: cadmium sulphide particles eluted in cadmium perchlorate–polyphosphate much earlier than zinc sulphide of the same size in zinc perchlorate–polyphosphate. The delay of zinc sulphide was longer for smaller than for larger particles, *e.g.*, 8-nm ZnS corresponded to 3.8-nm CdS and 5-nm ZnS to 0.9-nm CdS, respectively. As described above the electrical

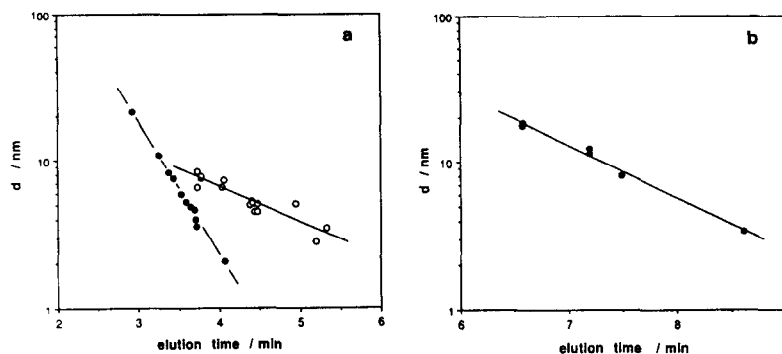


Fig. 6. SEC calibration on Nucleosil. (a) CdS (●) and ZnS (○) on Nucleosil 500 C₄ + Nucleosil 1000 C₄; (b) CdS on Nucleosil 300 C₁₈ + Nucleosil 500 C₁₈. For details, see Experimental part. Eluent, water–1 mM polyphosphate and 1 mM Cd(ClO₄)₂ or Zn(ClO₄)₂, respectively.

double layer is responsible for the differences between size of the solid particle and its effective size. The thickness of this double layer is dependent on the ions in the solution and of course also on the properties of the solid. With data from more materials it might be possible to estimate the relative thickness of the double layers. The effects of eluent components adsorbed on the stationary phase and their possible interactions with the colloids (repulsion or attraction) need further investigation. Consequently, one calibration is valid only for one kind of colloid under well defined conditions including the eluent composition (see above).

In Fig. 6b, the calibration on C₁₈-modified silica with longer columns (2 × 250 mm) is given. As already mentioned, under these conditions much better results were obtained even if in double the time. Nevertheless, the analysis times of 5 and 10 min, respectively, were remarkably short.

3.4. Comparison of SEC and ELMI

Resolution

Two kinds of resolutions have to be considered, as follows.

(1) Lateral resolution or scale resolution: lateral resolution is the term used in electron microscopy, meaning the smallest detectable difference in size, *i.e.*, actually between two

particles in ELMI. It corresponds to the smallest detectable difference in size between two strongly monodisperse sols in SEC. The lateral resolution of the Philips microscope utilized for these experiments is 0.18 nm. In SEC, the standard deviation of the measured size has to be considered. It can be assumed that it is mainly controlled by the uncertainty of the elution time as long as monodisperse samples are taken into account. The standard deviations of the elution time, σ_t , of eight injections of potassium iodide were found to be 0.0099 min (0.22%) for the combination of short 500 C₄ + 1000 C₄ columns and 0.018 min (0.17%) for that of long 300 C₁₈ + 500 C₁₈ columns. In contrast to electron microscopy, the lateral resolution in SEC is a function of the absolute size because of the logarithmic relationship between diameter and elution time. This function is determined from the calibration function in its exponential form (Eq. 2) with the determined relative standard deviation of elution time $\sigma_{t,rel}$. For a range of times t_i and diameters d_i , respectively, the diameters $d_{i+\sigma}$ are calculated. They correspond to the times t_i plus the standard deviation of time σ_{t_i} , which is the product of the time t_i multiplied by the relative standard deviation in % over 100 (Eq. 3).

$$d_i = 8890.3 \cdot 10^{-0.89856t_i} \quad (2)$$

(with d_i in nm and t_i in min);

$$d_{i+\sigma} = 8890.3 \cdot 10^{-0.89856t_i(1+\sigma_{t_{\text{rel}}}/100)} \quad (3)$$

$$\sigma_{d_i} = d_i - d_{i+\sigma} \quad (4)$$

The difference between d_i and $d_{i+\sigma}$ is the standard deviation of the diameter σ_{d_i} at the particular diameter d_i (Eq. 4). Values between 0.07 and 0.24 nm were obtained for SEC in the size range between 2 and 20 nm, corresponding to relative standard deviations between 1.9% and 1.3%. As can be seen from Fig. 7 (top), the values for ELMI were better for larger particles,

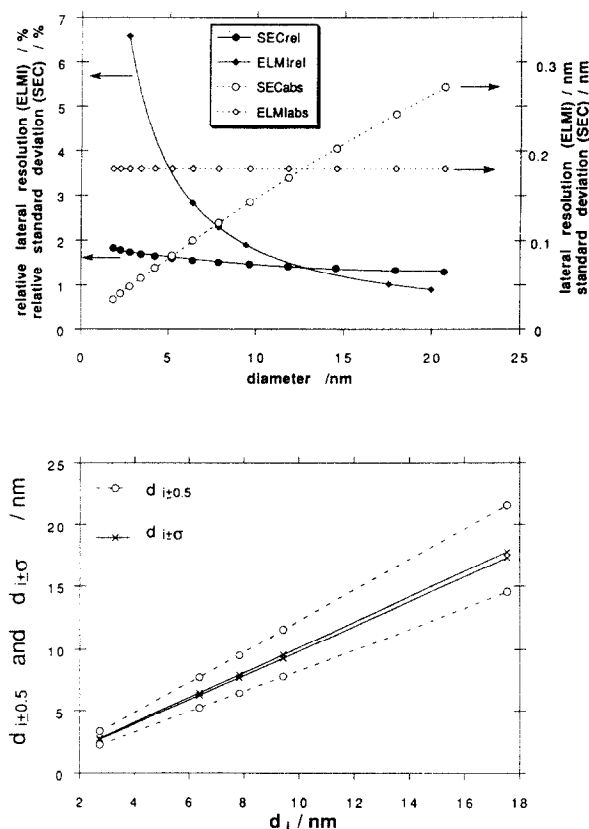


Fig. 7. Resolution of ELMI and SEC as a function of particle diameter. Aqueous CdS sols (stabilizer polyphosphate) on Nucleosil 500 C₄ + Nucleosil 1000 C₄. Top: absolute and relative lateral resolution in ELMI and absolute and relative standard deviation of the measured diameter in SEC as a function of the diameter. Bottom: lateral and separation resolution in SEC as a function of d_i . The full lines enclose the area between $d_{i+\sigma}$ and $d_{i-\sigma}$. The area between the dashed lines is limited by $t_{i+0.5}$ and $t_{i-0.5}$. For further explanation, see text.

but more than three times worse for the smallest particles.

(2) Moreover, the resolution in the chromatographic sense, the separation resolution, has to be considered, *i.e.*, the resolution of two different size populations in *one* sol. Strongly monodisperse colloids were hardly available. Therefore, the peak half-width of potassium iodide was used for this estimation, although as a small ionic compound it had the longest possible elution time and therefore the broadest peak of any monodisperse species. Hence it is the worst case. Its peak width $b_{0.5} = 0.19$ min was transformed into size values in a similar way as before, both for selected elution times t_i and for the times $t_{i+0.5} = t_i + 0.5b_{0.5}$ and $t_{i-0.5} = t_i - 0.5b_{0.5}$ the corresponding diameters $d_{i+0.5}$ and $d_{i-0.5}$ were calculated. In Fig. 7 (bottom), these resulting sizes are plotted against the measured diameters. The area between the full lines represents the uncertainty due to the standard deviation of the elution time. The area between the dashed lines is equivalent to all sizes between the peak half-width. This looks worse than it is for two reasons. First, in practice sols with a size distribution of a few per cent standard deviation do not exist, nor do they occur in one sol with a very close mean size. The typical CdS samples in Fig. 1 have standard deviations in the range 14–23% according to the ELMI results. Second, the earlier a peak eluted the smaller was its peak width, whereas the calculation was carried out with the broadest possible peak width. Theoretically, ELMI should be superior in this respect. However, actually the high energy of the electron beam can lead to radiation damage of the sample itself, so an artificial size distribution is generated and the resolution is decreased, though it is difficult to quantify this effect depending on the material [15].

Statistics and other factors

SEC gives an integral picture of the size distribution with perfect statistics as long as all components elute, whereas the number of counted particles in ELMI is limited. It happened also in ELMI that small particles were completely hidden under larger particles or a

minor population was not observed, at all as in Fig. 1, sample IV, or smaller particles were concentrated in one part of the ELMI support and larger particles in another. All of these effects would deteriorate the statistics for an ELMI size result. Another advantage of SEC is the measurement in solution. The colloids do not lose their solvent, which could cause particle growth.

3.5. Limitations of the method

There are two limitations to the SEC of colloids: too large and too active particles. CdS particles with diameters larger than 20 nm are filtered off by the column. Colloids with very high surface activity such as lead sulphide or silver iodide are irreversibly adsorbed. In such cases it is sometimes successful to work with less fine stationary phases, e.g., 15–25 μm instead of 7 μm material, where the adsorption power and pore volume are more favourable.

4. Conclusions

SEC is a powerful method for the size determination of nanometre-sized colloidal particles. Even unstable colloids can be analysed fairly accurately when the eluent contains a suitable stabilizer. SEC needs electron microscopy once for a calibration. The result is statistically optimum. However, it should be stressed that as for organic polymers, each kind of colloid has its own calibration and optimum conditions including eluent composition. Connection of various detectors will allow easy measurements of various kinds of size-dependent properties. Preparative separations yield very oligodisperse colloids from polydisperse colloids. A paper on this topic is in preparation. Finally, one of the main

benefits of the technique is the speed, which allows the elucidation of growth mechanisms even in cases of very rapidly growing particles.

5. Acknowledgements

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