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ABSTRACT

The applicability of light scattering in combination with photon correlation spectroscopy (PCS) for determination of concentration and size distribution of colloidal matter in a deep groundwater was tested *in situ* and on-line at Äspö Hard Rock Laboratory, Oskarshamn, Sweden.

Well-defined reference colloids (sizes predominately in the range 50-500 nm) of Fe_2O_3, $Al(OH)_3$, SiO_2, kaolinite, illite and a high molecular humic acid (Aldrich) in aqueous media were used as model substances for calibration of the PCS instrument (signal vs. concentration). The intensity of scattered light was found to be dependent on the composition of the colloids. The concentration ranges where a quantitative determination of the colloids could be achieved were Fe_2O_3 0.03-2 mg/l, $Al(OH)_3$ 0.1-2 mg/l, SiO_2 0.1-7 mg/l, kaolinite 0.5-10 mg/l, illite 0.5-50 mg/l and humic acid 0.5-75 mg/l.

The colloid concentration in the rather saline groundwater (electrical conductivity of 660 mS/m corresponding to a total concentration of dissolved salts of 3900 mg/l) was below the detection limit for the used PCS equipment which corresponds to a colloid concentration not higher than 0.5 mg/l and probably below 0.1 mg/l according to the measurements on-line and *in situ* at Äspö and in comparison to the calibrations performed with reference colloids.

The results clearly demonstrated that the stability, concentration and composition of a colloidal-size suspended phase in an anoxic groundwater with high content of Fe(II) (0.3 mg/l), like the one in Äspö, is extremely sensitive to exposure to atmospheric conditions during sample handling and preparation. Diffusion of air into the closed measuring cuvette was enough to alter the colloid content significantly within 6 hr. A particle fraction with a size distribution in the range 170-700 nm was formed within 45 minutes when air was allowed to diffuse into the aqueous phase from the air filled upper part of the cuvette. The corresponding time to generate a significant colloid precipitate was less than 1 minute (size distribution range 100-600 nm) when a stream of air (1.5 ml) was bubbled through the water samples. The precipited colloidal phase consisted of a mixture of ferric (hydr)oxide and calcium carbonate in all three cases.

SAMMANFATTNING

Studien har haft till syfte att utvärdera användandet av en ljusspridningsteknik som kombinerades med fotonkorrelationsspektroskopi (PCS) för att bestämma koncentrationen av respektive storleksfördelningen hos kolloidalt material i djupa salina grundvatten. Försöken genomfördes *in situ* och on-line i Äspö Laboratoriet, Oskarshamn.

För att kalibrera PCS-instrumentet (signal vs. koncentration) användes väldefinierade referenskolloider (alla huvudsakligen inom storleksområdet 50-500 nm) bestående av Fe_2O_3, $Al(OH)_3$, SiO_2, kaolinit, illitisk lera samt en högmolekylär humussyra (Aldrich) uppslammade i vatten. Intensiteten hos det från kolloiderna spridda ljuset visade sig vara relaterat till kolloidernas sammansättning, vilket innebär att de koncentrationsintervall inom vilka en kvantitativ bestämning av kolloidhalten kan göras varierar mellan de olika referenskolloiderna. Följande intervall erhölls: Fe_2O_3 0.03-2 mg/l, $Al(OH)_3$ 0.1-2 mg/l, SiO_2 0.1-7 mg/l, kaolinit 0.5-10 mg/l, illit 0.5-50 mg/l och humussyra 0.5-75 mg/l.

Mätningar on-line och *in situ* i det relativt salina grundvattnet i Äspö (elektrisk konduktivitet 660 mS/m vilket motsvarar en totalhalt löst salt om 3900 mg/l) visade att kolloidkoncentrationen var under detektionsgränsen för det använda PCS-instrumentet. Enligt kalibreringarna med referenskolloider motsvaras detta av en kolloidkoncentration lägre än 0.5 mg/l, och troligen även under 0.1 mg/l.

Studien visade dessutom att en suspenderad fast fas, i det kolloidala storleksområdet, i ett anoxiskt grundvatten med hög halt av Fe(II) (0.3 mg/l), som det i Äspö, kan genomgå stora förändringar m a p stabilitet, koncentration och sammansättning om den vid provtagning och eventuell behandling av provet exponeras för atmosfärens förhållanden m a p tryck och temperatur. Exempelvis visade mätningarna att enbart diffusion av luft in i den stängda mätkyvetten under 6 h, var tillräckligt för att signifikant förändra mängden kolloider i provet. När 1.5 ml luft försiktigt trycktes in i överdelen av mätkuvetten kunde en partikelfraktion inom storleksintervallet 170-700 nm observeras efter 45 minuter. Om däremot luften tilläts strömma genom provet, tog det mindre än 1 minut innan en kolloidal fällning erhölls (storleksintervall 100-600 nm). Sammansättning hos det kolloidala fällningen visade sig, i alla tre fallen, vara en blandning mellan järn(hydr)oxid och kalciumkarbonat.

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1 INTRODUCTION

The possible leakage of radionuclides from repositories in the crystalline bedrock similar to that proposed for the future final disposal of high-level radioactive wastes in Sweden, has been suggested to be governed by a numerous of processes including biological and chemical activities (e.g. oxidation/reduction, accumulation), hydrochemical conditions (e.g. pH, salinity, redox potential, complexing anions) as well as interactions with solid phases (colloidal (< 1 µm) and particulate (>1 µm) matter)). The importance of interactions with solid matter has been shown both in well-defined laboratory experiments as well as in field studies (e.g. Benes and Maier, 1980; Stumm and Morgan, 1981; Salomons and Förstner, 1984). Several studies have indicated that transition elements as well as lanthanides and actinides can exist to a high, and sometimes dominating, extent in associations with solid colloidal and particulate matter in natural aquatic systems (see e.g. Hoffmann et al., 1981; Karlsson et al., 1988; Orlandini et al., 1990; Vilks and Degueldre, 1991).

The colloidal phase in natural waters is usually defined as solid matter with a diameter in the range 1 nm to 1 µm. Dominating components and/or surface films are usually oxides and hydroxides of Al, Fe, Mn and Si, clay minerals, Ca- and Ca-Mg-carbonates as well as organic matter (humics) (e.g. Tipping and Cooke, 1982; Tessier et al., 1985; O'Melia, 1989; Vilks et al., 1991). There is, however, only limited information about the size distribution and concentration of the solid matter of colloidal size in natural waters, particularly in groundwaters.

The use of various methods for the characterization of colloidal matter, as well as the limitations of the methods applied in field systems, has recently been summarized in the literature (e.g. Degueldre, 1990; Ledin et al., 1995).

Measurements of mass and size distribution of the solid phase dispersed in groundwater have often been made by gravimetric determination of the fraction retained by filters of different nominal pore sizes, combined with statistical analysis of electron micrographs. Filtration can be considered as a simple straight-forward procedure, but precautions to maintain the original distribution of both dissolved and solid constituents are required e.g. in waters of low redox potential, where an oxidation and gradual precipitation of Fe will take place after exposure to air. On-line filtration of small volumes under an inert atmosphere and at the original temperature of the sample can provide reliable size determinations. However, loss of solid matter and dissolved trace elements by adsorption to the filters must be considered when filters with large surface areas, e.g. ultrafilters and cellulose derivative filters as well as hollow fibres are used (Fan and Gentry, 1978; Salbu et al., 1985). Screen filters (e.g. thin films of polycarbonate) are non-sorbing but suffer from clogging (Karlsson et al., 1994).

Size distributions from scanning or transmission electron microscopy (SEM and TEM) suffer from changes induced during the sample preparation, since the samples (often wet filters and grids) have to be dried. Dehydration of amorphous precipitates can lead to consolidation, and agglomeration of organic macromolecules as well as inorganic colloids may take place when the ionic strength and pH change during drying etc. Instrumental limitations in counting particles below 100 nm with SEM restrict the use of this technique even further (Degueldre et al., 1989). It is therefore important that results obtained with various batch-type techniques can be validated with complementary studies, if possible by using procedures suitable for field work on original water samples. For that purpose, some modified methods have been developed. For instance, new sample preparation procedures have been applied in studies with TEM (Leppard et al., 1990; Perret et al., 1991), where the dehydration of the colloids can be avoided.

Photon correlation spectroscopy (PCS) is a non-destructive technique that requires a minimum of sample treatment. Delgado and Matijevic (1991) stated, that PCS would be preferable compared to electron microscopy, particularly for monodisperse samples, since sample treatment and exposure to the electron beam can alter the composition and size distribution of the colloidal matter. PCS has previously been used for determination of size distribution, in studies of the stability of inorganic colloids (e.g. Novich and Ring, 1984; 1985; Ramsay et al., 1988; Amal et al., 1990; von Gunten and Schneider, 1991; Ledin et al., 1993a), as well as for measurements of the particle character of natural organic macromolecules (Caceci and Billon, 1990; Caceci and Moulin, 1991; Reid et al., 1991) and studies of natural colloidal matter (Billon et al., 1986; Gschwend and Reynolds, 1987; Nicholson and Ramsay, 1990; Rees and Ranville, 1990; Ryan and Gschwend, 1990, Ledin et al., 1993b; Perret et al., 1994) under laboratory conditions. The experience of the technique for studies of natural water colloids *in situ* is limited (Ledin et al., 1994), largely because the instrument requires high voltage and efficient cooling of the laser light source. Also, the possibilities to characterise natural heterogeneous samples (with respect to size distribution, particle geometry as well as elementary and mineral composition) are limited (Weiner, 1991).

The aim of the present study was to evaluate the applicability of light scattering in combination with PCS technique, for continuos on-line measurements *in situ,* of the concentration and size distribution of colloids in groundwater. This would be favourable in a system where precipitation of new solid phases would be difficult to avoid during sampling and storing, as well as during various analytical procedures (e.g. filtration and preconcentration).

2 MATERIALS AND METHODS

Field measurements were performed in the Äspö Hard Rock Laboratory, about 20 km NNE of Oskarshamn, Sweden, at a depth of 75 m. This underground laboratory is being built and operated by the Swedish Nuclear Fuel and Waste Handling Co. (SKB) within the Swedish nuclear waste programme to be used for studies of geology, groundwater flow, rock properties etc. within the crystalline bedrock similar to that proposed for the future final disposal of high-level radioactive waste in Sweden.

Different strategies for sampling of colloids as well as sample treatment were tested. Calibrations of the PCS signal vs. colloid concentration as well as estimates of detection limits were performed in complementary laboratory experiments, using well-defined colloids with size distribution and particle geometry known from examination with SEM.

2.1 PCS EQUIPMENT

Size distribution and concentrations of the colloidal phases in both the laboratory and field samples were estimated by a Brookhaven BI-90 instrument, operated at a fixed scattering angle of 90°. The light source was a 2 W argon-laser (Lexel Co.) operated at a wavelength of 488 nm and with powers of 700-900 mW.

The number of photo counts per seconds (count rate; kcps) that reach the photo multiplier is in principle determined by the number of particles in the scattering volume and can be used for concentration estimates. Unfortunately is the count rate also influenced by the size distribution and composition (refractive index and geometry) of the colloidal phase that limits the applicability in heterogeneous systems.

The size distribution of the colloidal matter is calculated from the temporal fluctuations of the scattered intensity, which are due to the Brownian motion of particles. This is usually achieved through an estimate of the normalized temporal autocorrelation function (ACF) of the scattered intensity. The ACF was in the present study solved by inverse Laplace transform routines with the use of the original instrument software (BI-MSD). General descriptions of the PCS method are given e.g. by Chu (1974), Berne and Pecora (1976) and Rees (1987).

2.1.1 Calibration with reference colloids

Various precipitation procedures were followed for the preparation of colloidal $Al(OH)_3$ (Hiemstra et al., 1987) as well as Fe_2O_3 (Penners and Koopal, 1986). Suspensions of colloidal SiO_2 were prepared by grinding natural crystalline quartz (from Olden, Sweden), kaolinite (from Washington County, Georgia, USA) and illite (from Harwell Borehole, USA) in a vibration mill. The various systems, suspended in Milli-Q water, were allowed to settle in sedimentation funnels (in the dark at 8°C; pH 6) until a fairly monodisperse colloid population with a narrow size distribution was obtained (after four weeks or more). A humic acid (HA; from Aldrich; Na-salt, Cat NoH1, 675-2) was dissolved in 0.005 mol/l $NaClO_4$ at pH 10, dispersed by ultrasonication for 10 minutes and acidified to pH 6. The time for storage of colloidal HA was limited to 48 hr, in order to avoid microbial degradation.

The colloids were sequentially diluted with Milli-Q water (HA with 0.005 mol/l $NaClO_4$), equilibrated for 10 minutes, whereafter the count rate and size distributions were recorded in 6 replicates. Measurements were performed in polystyrene cuvettes closed with plastic caps, which were rinsed several times with Milli-Q water prior use. Absolute concentrations of the colloids (in salt free solutions) were determined gravimetrically after collection in small cups of PTFE.

SEM was used to validate the PCS measurements and to obtain information on the geometry of the colloids. Samples for SEM studies were prepared by filtration of approximately 1 ml colloid through 0.015 µm polycarbonate membrane filters. The filters were dried in a Lamin-air flow cabinet and covered with gold (10 nm) prior to the examination in SEM.

2.2 FIELD SAMPLING AND QUANTIFICATION

2.2.1 General hydrochemistry

The geological and hydrological conditions within the Äspö Hard Rock Laboratory including the current fracture zone are described by Smellie and Laaksoharju (1991) and by Banwart et al. (1992), while the chemical composition of the water at the present sampling date is summarized in Table 2-1. Total concentration of humics was defined as the quantity of dissolved organics adsorbed to an anion exchanger (Sephadex DEAE A-25) according to Pettersson et al. (1989) at the natural pH.

This water is a Na-Cl-dominated highly saline groundwater with a total concentration of dissolved salts of 3900 mg/l. Alkalinity as well as pH are high. Saline groundwaters of similar type are common in the Äspö area (Laaksoharju, 1990a), but otherwise unusual in the granitic bedrock of Sweden (Allard et al., 1983). The element ratios Na/Cl, K/Cl, Mg/Cl, Ca/Cl, Ca/Na and Ca/Mg have the signature of relict Baltic Sea-water, although the high TOC-value indicates significant contributions of waters of younger origin. The redox potentials (-0.10±0.05 V) are higher than generally observed in deep groundwater; more often potentials in the range -0.25 to -0.30 V are recorded (cf. Banwart et al., 1992). The high potentials could reflect a water of mixed origin. A further confirmation of this is the ^{14}C-age of 640 yr., determined from the organic carbon fraction (Pettersson et al., 1993). A saline deep groundwater would otherwise have a ^{14}C-age of 5000-10000 yr. or more. Analytical procedures and a discussion of the sampling programme are presented elsewhere (Nilsson, 1991).

Table 2-1. Groundwater composition at Äspö (sampling hole KR0013B, July 8 1992; Geotab, 1992).

Parameter	Concentration mg/l
Na	848
K	4.0
Mg	61.9
Ca	433
Fe(II)	0.317
Fe(tot)	0.374
Mn	0.28
S(tot)	49.6[a]
F^-[b]	1.6
Cl^-	2130
Br^-	10.7
Si(tot)	7.2
TOC	15
Aquatic humics[b]	15
Alkalinity (as HCO_3^-)	270
Conductivity (mS/m)	660
Eh (V)	-0.1±0.05
pH	7.83

[a] Corresponding to 149 mg/l SO_4^{2-}

[b] Determined in this study.

2.2.2 Colloids

The PCS instrument was installed in the underground tunnel in a caravan modified to a chemical field laboratory and equipped with filters to remove dust from the surronding air. A PTFE tubing connected to a hosing in the bedrock (sampling holes KR0012B, KR0013B and KR0015B) provided groundwater flowing from a fracture zone (at 200-400 ml/minute), thus allowing a continuos water sampling and subsequent analysis in the caravan.

The cuvettes for the PCS instrument were rinsed with Milli-Q water, thoroughly purged with nitrogen, flushed with the flowing groundwater for at least 1 minute (equivalent to 40 cuvette volumes at a water flow of 200 ml/minute) and closed with the plastic cap. The whole procedure was performed in a glove-bag with nitrogen atmosphere (Alfax, quality N60) in order to prevent oxidation of the samples. Formation of ferric hydroxides would otherwise start immediately (cf. Table 2-1 and discussion below). The sealed cuvettes containing the water samples were taken out from the glove-bag and measured by PCS, with repeated measurements after 6 hr and 24 hr, respectively. The cuvettes were not opened between the measurements.

Continuos on-line measurements were performed, using a flow-through cuvette (Figure 2-1) attached directly to the tubing from the rock, in order to minimize contact with atmospheric oxygen, as well as changes in temperature and in the partial pressure of carbon dioxide. The water flow through the cuvette was controlled by a needle valve on the inlet tubing. The water was allowed to flow through the cuvette while placed in measuring position in the PCS instrument, at 10 ml/minute for at least 5 minutes (equivalent to more than 12 cuvette volumes) before the flow was stopped and the PCS measurement began.

After completed measurements on-line the samples from sampling hole KR0013B were exposed to air in various ways: (a) diffusion through the open cannulae into the cuvette; (b) slow bubbling of 1.5 ml air through the sample in the cuvette; and (c) filling the upper part of the cuvette with 1.5 ml air. Samples with Milli-Q water were used as references in order to estimate the impact of particles which were ambient in the air. The size distribution and particle concentrations (given as count rates) were measured during 24 hr for the samples (a)-(c) as well as the references.

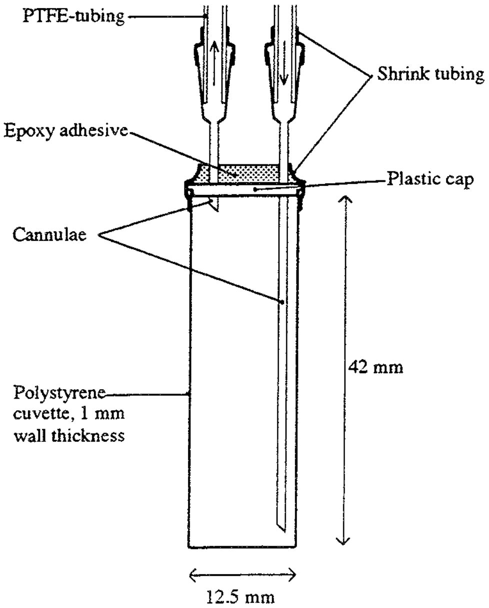


Figure 2-1. Sketch of the flow-through cuvette used in on-line PCS-measurements.

A separate set of groundwater samples were equilibrated with the atmosphere for 72 hr. The particulate matter was collected on 0.015 μm polycarbonate membrane filters that were allowed to clog, washed with 2 ml Milli-Q water in order to minimize the amount of remaining salt and dried in a desiccator followed by gravimetric determination of the mass. The precipitate was digested in a mixture of concentrated sulphuric and nitric acids, followed by dissolution in condensed phosphoric acid. The concentrations of Al, Ca, Fe, Mg, Mn and Si in the solids were determined by AAS. Mineral composition and possible surface coatings of macromolecular organic matter in the precipitate were studied by infrared spectroscopy (FTIR) on a replicate solid sample.

3 RESULTS AND DISCUSSION

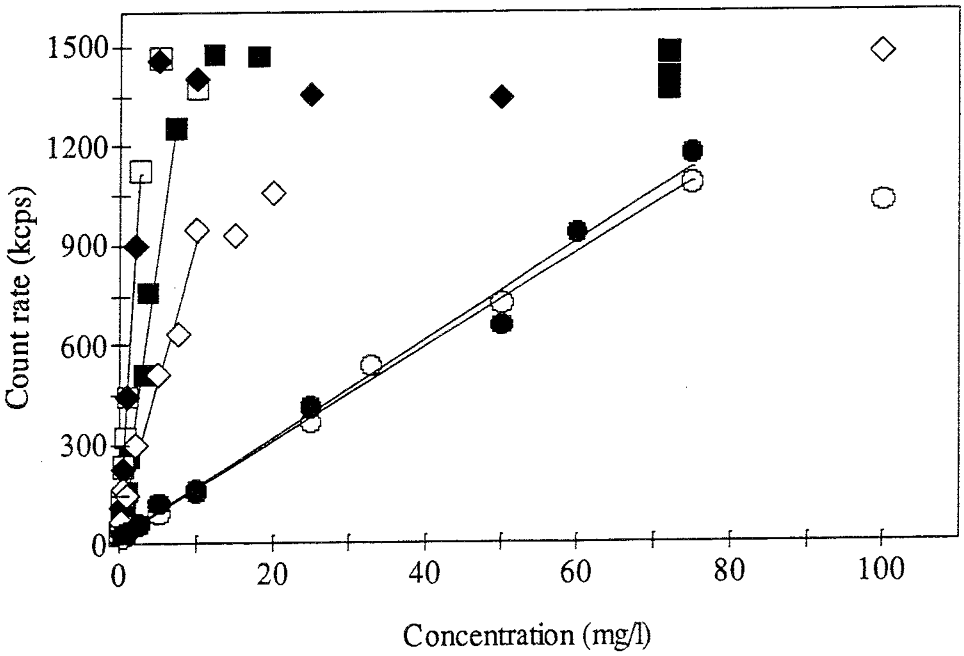
3.1 COLLOIDS

3.1.1 Instrument performance and calibration

The count rate is in principal determined by the number of particles in the scattering volume. A minimum of 100 particles is required (Weiner, 1991), which is equivalent to a count rate above 10 kcps for the PCS equipment used in this study. Other parameters influencing the intensity of the scattered light are e.g. refractive index of the particles as well as their geometric forms.

The count rate was proportional to the colloid concentration, however in concentration ranges that were individual for the materials (Figure 3-1 and Table 3-1). Assessed initial size distributions (Figure 3-2 and Table 3-1) were confirmed from SEM micrographs from which the geometric shapes could be studied (Table 3-1). Examination of HA with SEM indicated a structure where no typical geometries were evident.

Neither the number of particles in the scattering volume (estimated from size distributions, geometry and densities) nor the refractive indices can alone explain the large differences between the colloids, as given by the observed signal to mass relationship. Effects of absorption (particularly HA) and shape (e.g. number of edges and corners) are difficult to estimate.



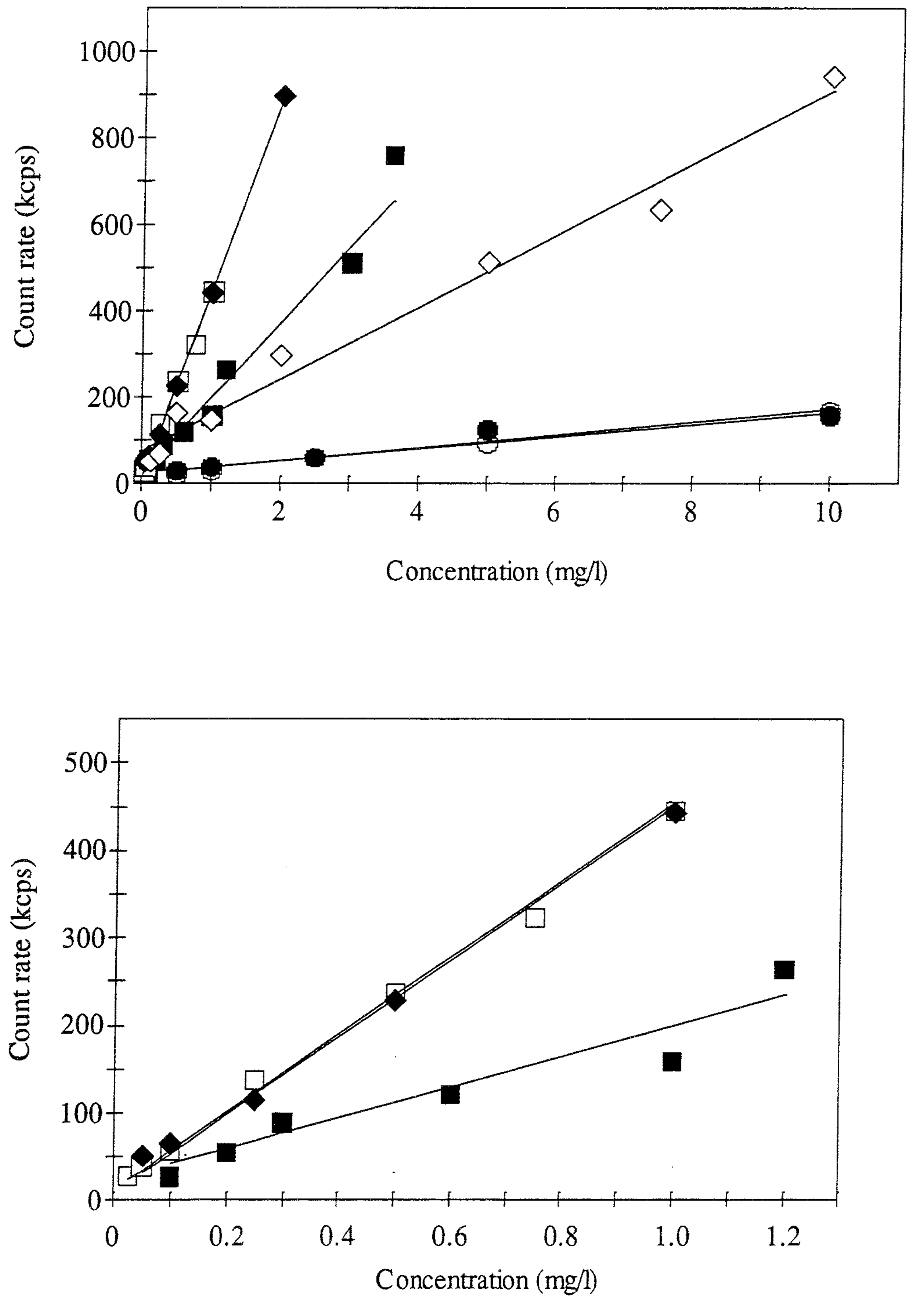


***Figure 3-1**. Relationship between the PCS count rate and the concentration of the reference colloids. □Fe_2O_3; ◆$Al(OH)_3$; ■ SiO_2; ◇ kaolinite; ○ illite; ● humic acid. (a) Concentration range 1-110 mg/l. (b) Concentration range 0-11 mg/l. (c) Concentration range 0-1.3 mg/l.*

Table 3-1. Characteristics of the reference colloids according to the PCS measurements and the SEM micrographs.

Colloidal phase	Concentration range (mg/l)[a]	Initial size distribution (nm)	Geometric shape	Refractive index [b]
Fe_2O_3	0.03-2	10-75	spherical	2.94; 3.22
$Al(OH)_3$	0.1-2	100-325	plates	1.56-1.60
SiO_2	0.1-7	50-300	spherical	1.55
Kaolinite	0.5-10	115-350	plates	1.55-1.57
Illite	0.5-50	50-400	plates	1.54-1.57
Humic acid [c]	0.5-75	70-250	not determinable	

[a] Range where the concentration is proportional to the count rate.
[b] From Handbook of Chemistry and Physics, 1983-84.
[c] From Aldrich, soil origin.

3.1.2 Field measurements

Samples from all three sampling holes (KR0012B, KR0013B and KR0015B) prepared in the glove-bag as well as measurements performed on-line had initial count rates below the detection limit of this instrumental set-up (10 kcps). Thus the PCS equipment was not sensitive enough to measure the low colloid concentrations found in the present saline groundwater. It indicates, however, an upper limit which is similar to or even lower than reported with other available methods. According to the calibrations of the instrument with reference colloids the measured count rates correspond to colloid concentrations less than 0.5 mg/l, assuming inorganic colloids consisting of kaolinite and illite (plates, in the size range 50-400 nm) or organic colloids with HA (amorphous structure, in the size range 70-250 nm) as the main component. If a dominating original colloidal fraction of SiO_2 or $Al(OH)_3$ (particles which are spherical and plates, respectively, in the size range 50-325 nm) is assumed the corresponding concentrations would be less than 0.1 mg/l, while iron as main constituent (spherical particles of sizes below 75 nm) would indicate even lower concentrations (<0.03 mg/l). These results illustrate that a calibration of the instrument requires careful phase analysis or calibrations performed with natural colloidal matter collected at the field site of interest when using the PCS technique for estimation of concentrations of the colloidal matter in field samples (cf. Ledin et al., 1993b).

These results illustrate the limits of the method in general, however they can be compared to studies performed in various groundwaters using other methods for the determination of the colloid concentrations. Laaksoharju (1990b) assessed that the concentration of colloids in deep Swedish granitic groundwaters is below 0.4 mg/l. This concentration level was estimated from elementary analysis of groundwater particles collected on filters, combined with calculated saturation indices as indications of probable particle compositions. In a subsurface fracture in granitic rock at Grimsel Test Site, Switzerland, Degueldre et al. (1989) estimated the colloid concentration (size range of 100-1000 nm) to 0.2 mg/l inorganic colloids or 0.1 mg/l organic colloids. Miekeley et al. (1991) reported inorganic colloid concentrations (<450 nm) of less than 1 mg/l in

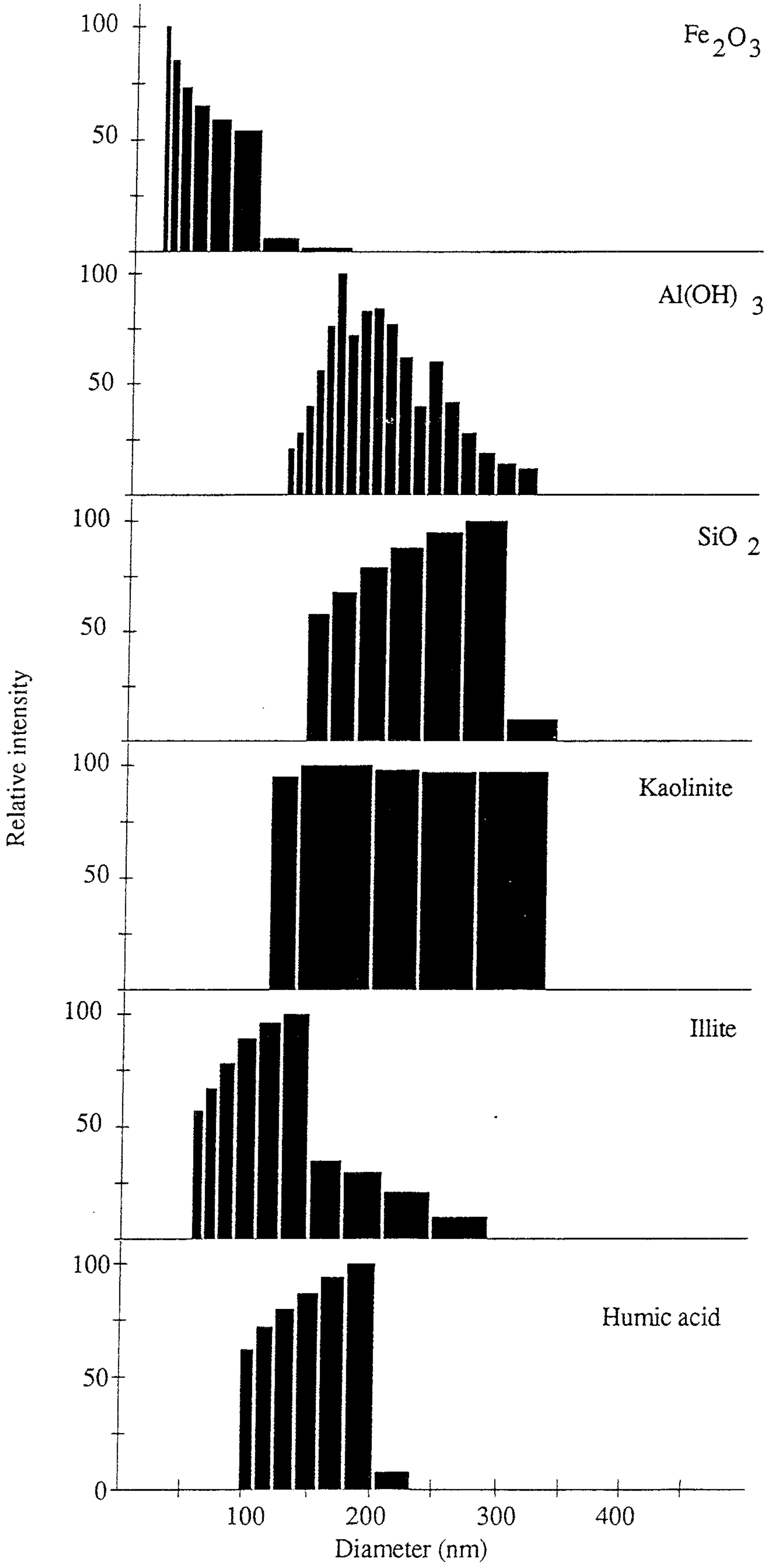


Figure 3-2. Typical size distribution histograms for the reference colloids (pH 6.0± 0.5).

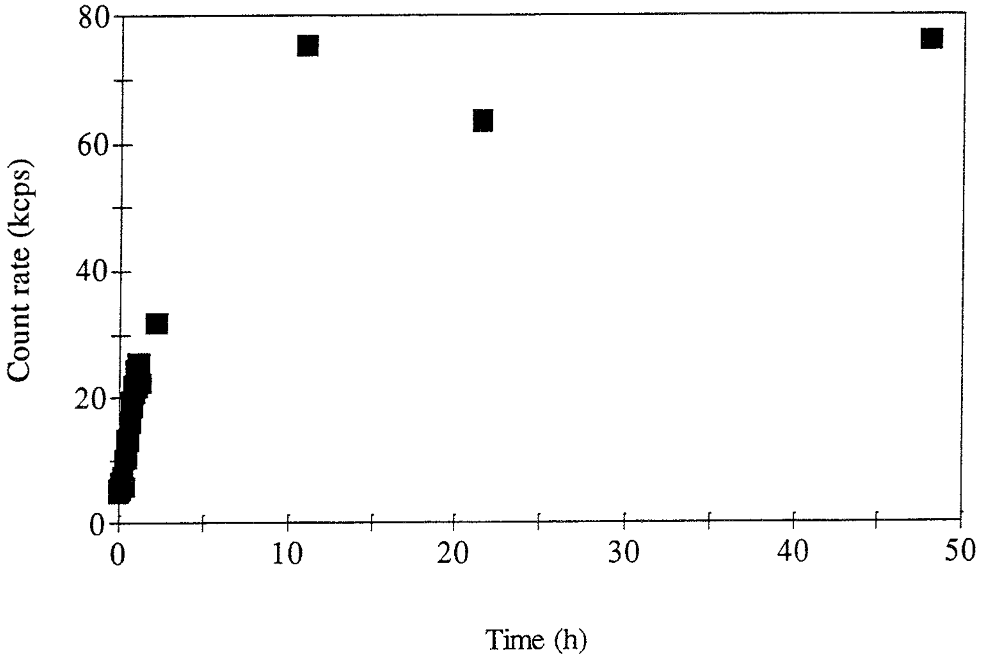
waters from Osamu Utsumi mine and Morro de Ferro analogue study sites, Pocos de Caldas, Brazil. The estimates by Degueldre et al. and by Miekeley et al. were largely based on SEM analyses of particles collected on filters assuming, that the colloids were either organic (density of 1 mg/cm^3) or inorganic (density of about 2 mg/cm^3).

3.1.3 Formation of colloidal particles after exposure to air.

A particle fraction was formed in the cuvettes filled and closed in the glove-bag within 6 hr with an average of 210 nm, a size distribution in the range 125-385 nm and a total concentration corresponding to a count rate of 80 kcps. The count rate was constant 18 hr later, while an increase in the average diameter to 1280 nm was observed (size distributions were not determined because of the limitations in the present procedure to solve the auto-correlation function when the samples contain particles with diameters larger than 1000 nm).

The growth of colloids by the exposure to air was further observed in the flow-through cell (Figure 2-1). A colloidal fraction was formed in the cell within 1 hr and reached a maximum in count rate of 70 kcps after 11 hr in the experiment where 1.5 ml air was introduced in the upper part of the cuvette prior the first measurement (Figure 3-3a). A corresponding increase in particle size was evident (Figure 3-3b), where a maximum average diameter of 2800 nm was indicated. The formation of a solid precipitate as a function of time and air exposure in the samples is further illustrated in Figure 3-4. A colloidal fraction within the size range of 100-600 nm (average diameter of 380 nm) at a count rate of around 20 kcps could be detected already within 1 minute in samples where air was bubbled through the water. Under conditions where the air was allowed to diffuse into the aqueous phase the corresponding time to reach a count rate of 20 kcps was ca 40 minutes, and the corresponding measured size distribution was in the range 170-700 nm (average diameter of 500 nm). Thus, regardless of how air was introduced in the sample, a precipitate of a solid phase was initiated in a matter of hours. Measurements in Milli-Q water (mean count rate of 9 kcps) ascertained that the colloids found in the samples were not an artefact due to contamination with particles from the air.

The formation of a colloidal particle fraction is further illustrated by the size distribution histograms in Figure 3-5, which cover 90% of the "intensity-weighed" colloid population. A shift towards a dominance of the smaller sizes for fresh colloids, having an over-all size range below 150-200 nm is observed in Figure 3-5a. This is in accordance with the results of Degueldre et al. (1989) and Miekeley et al. (1991) who found from SEM micrographs that the colloid population followed an exponential distribution, with larger numbers of particles in the smaller size ranges. There are general limitations in the estimation of size distributions by PCS technique in samples with polydisperse colloid populations, since the intensity of the light scattered from larger particles is higher than the corresponding intensities from the same number of small particles. The intensity is proportional to the sixth power of particle radius for spherical particles which will result in a masking effect of particles with smaller diameters and a calculated size distribution may underestimate the smallest size fractions. This can be the reason for the discrepancy between the size distribution given in Figure 3-5a for a particle population with low polydispersity and Figure 3-5b and c, for samples of higher polydispersity. The discrepancy between the calculated average diameters and the size distribution range



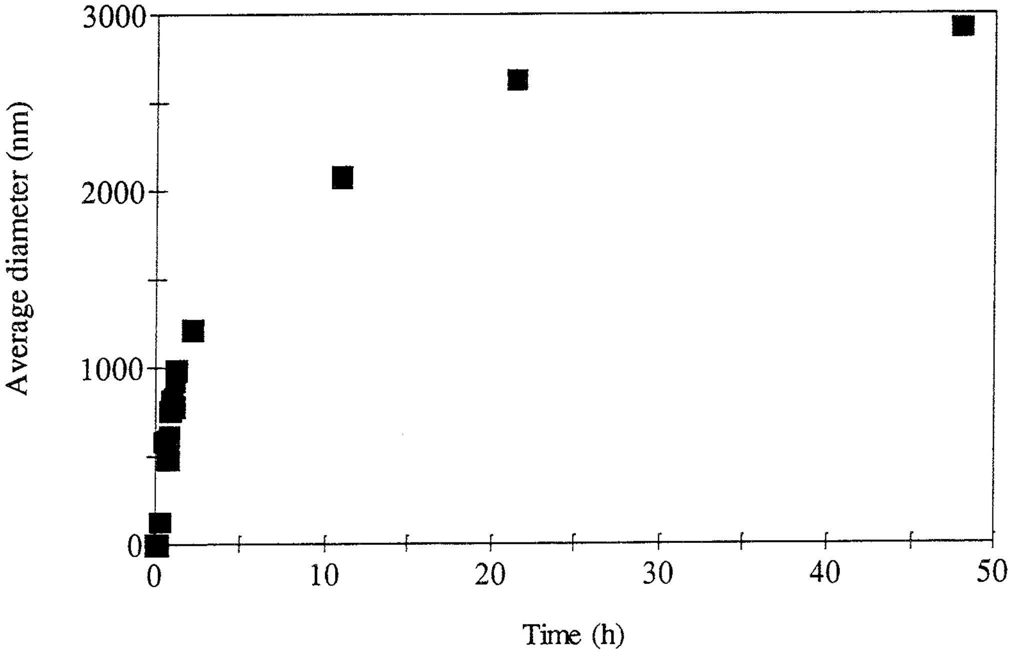
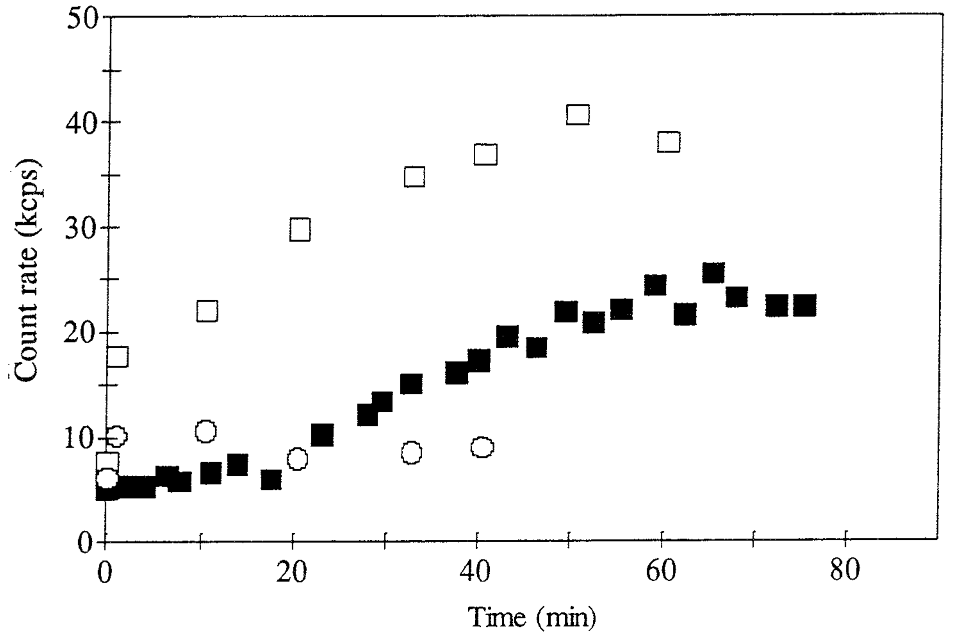


***Figure 3-3**. Results from PCS measurements for groundwater from Äspö Hard Rock Laboratory measured in the flow-through cuvette. 1.5 ml air was added in the top of the cuvette after the initial measurements at t=0. (a) Count rate. (b) Average diameter.*



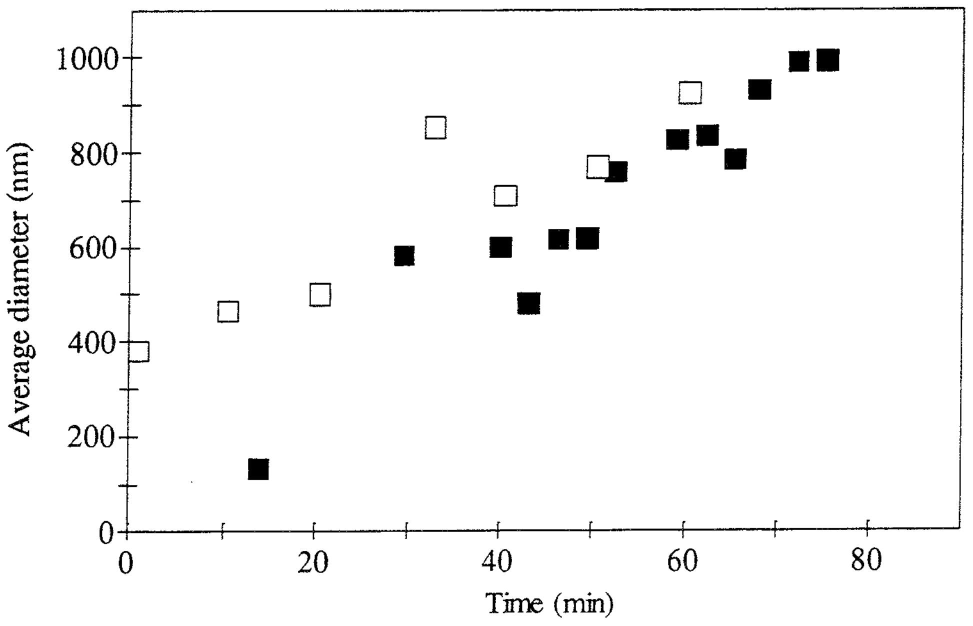


Figure 3-4*. Results from PCS measurements for groundwater from Äspö Hard Rock Laboratory measured in the flow-through cuvette. ■ Addition of 1.5 ml air in the top of the cuvette; □ slowly bubbling of 1.5 ml air every 10th minute; ○ Milli-Q water; slowly bubbling 1.5 ml air every 10th minute. (a) Count rate. (b) Average diameter.*

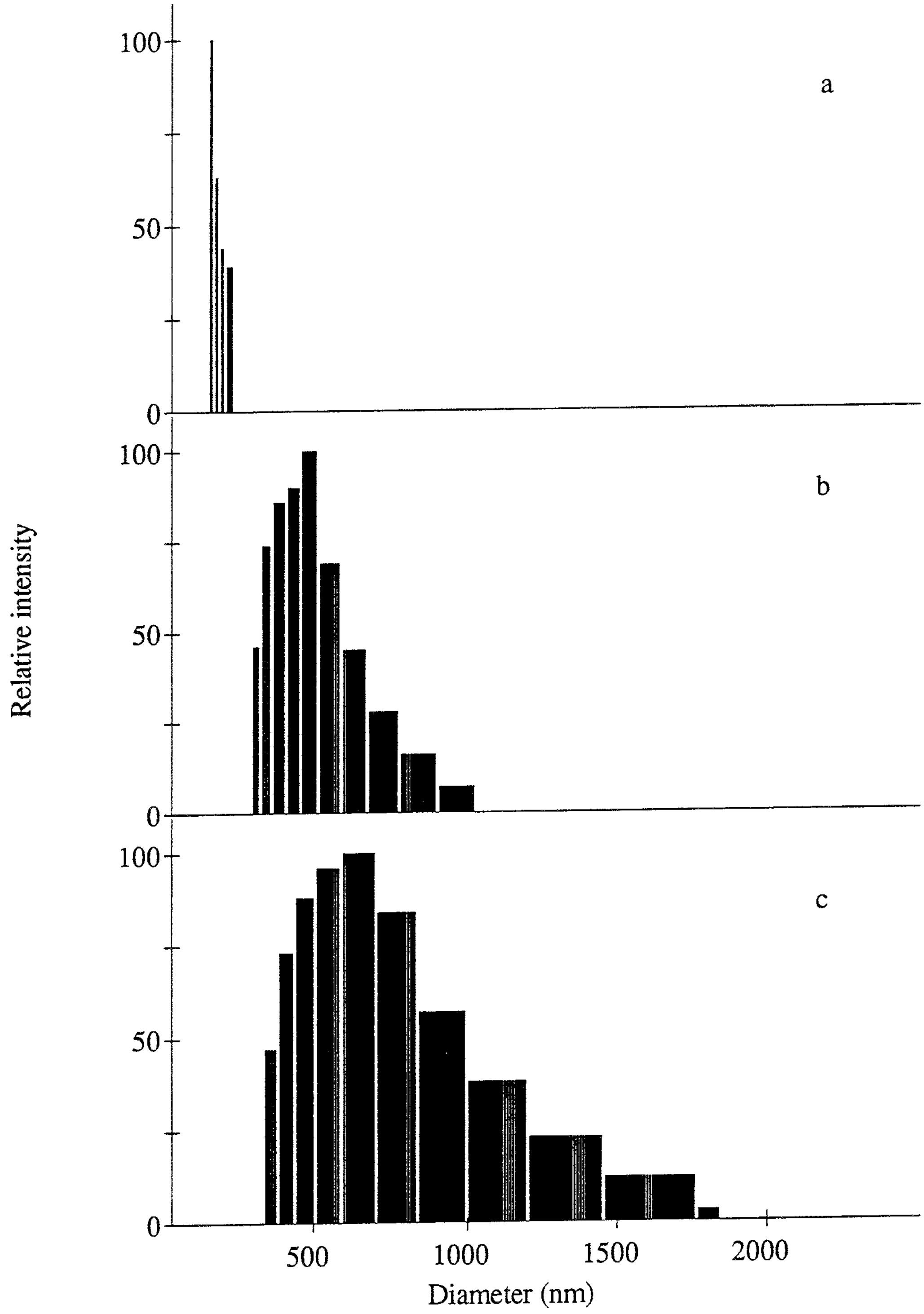


***Figure 3-5**. Size distribution histograms for colloids formed in the groundwater samples after the addition of 1.5 ml air at t=0 (includes 90% of the "intensity-weighed" population). (a) t=14 min; average diameter 131 nm. (b) t=30 min; average diameter 582 nm. (c) t=75 min; average diameter 992 nm.*

reflects the same effect. A minor fraction (less than 10%) of the particles is larger than 400 nm in Figure 3-5a; these rather few particles will increase the apparent average diameter. It would generally be preferable to filter highly dispersed field samples in order to remove the largest size fraction. This is, however, not easily done in the present system, where the formation of new particles due to precipitation is so quickly initiated. Furthermore, the ACF is based on the assumption that all particles are spherical, which is not the case for most natural systems. This fact further limits the accuracy in the evaluation of the true size distribution.

Determination of the major cationic elements in the precipitates gave a composition of 21% Fe, 9% Ca, 3% Si, 3% Mg, 1% Al and 1% Mn (dry weight). Spectra from FTIR indicated the presence of organics, notably aquatic humics, in the solid matter although the absolute content of organic carbon was not determined (Figure 3-6). It was not possible to identify any carbonate minerals or ordered ferric hydrous oxide phases from the FTIR spectra.

Calculations of saturation indices were made with the geochemical model PHREEQE (Parkhurst et al., 1984) using the analytical input data from Table 2-1. The effects of equilibration with atmospheric pressures of oxygen (log pO_2=-0.7) and carbon dioxide (log pCO_2=-3.2) were assessed in terms of changes in saturation indices. The results indicate that the original water in the bedrock was oversaturated with respect to Ca-Mg-carbonates (calcite, aragonite, dolomite; Table 3-2) and possibly also iron oxides (hematite and goethite; Table 3-2).

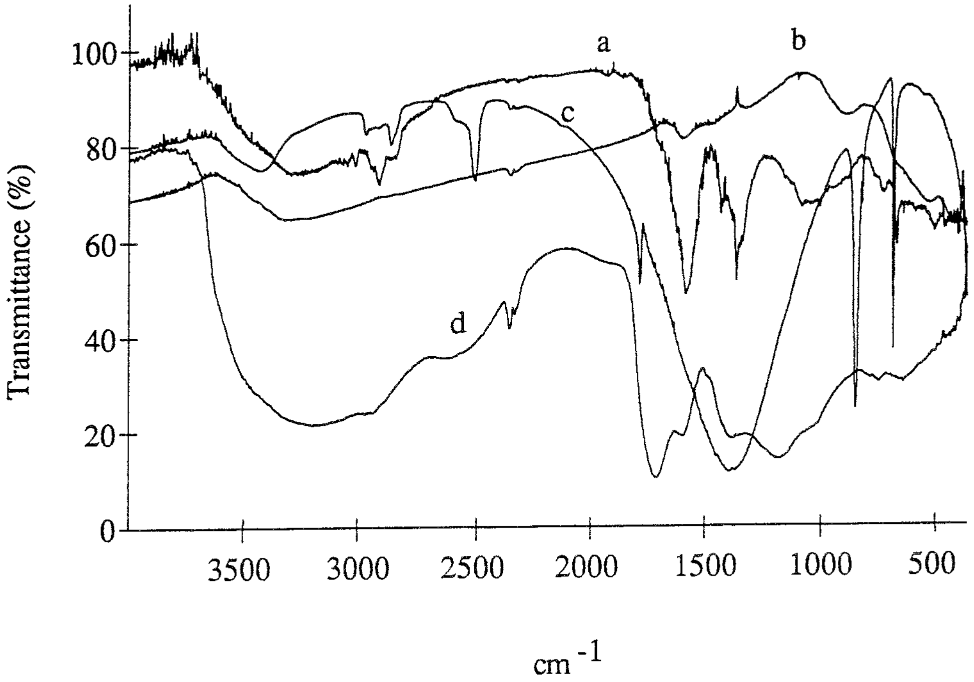


Figure 3-6. FTIR spectra of the precipitated solids in aerated water from Äspö Hard Rock Laboratory and three reference materials. (a)Äspö colloids. (b)$Fe(OH)_3$. (c)$CaCO_3$. (d) FA.

The system was close to equilibrium with respect to fluorite, siderite and quartz but undersaturated with respect to amorphous ferric hydroxide. If a pe of -4.7 is assumed (representing a hematite/magnetite equilibrium) only the carbonates, as well as pyrite, would be expected to be oversaturated. A precipitation of carbonates and various ferric hydrous oxides would therefore be expected in both cases after exposure to air. The composition of the solid precipitate was assessed, assuming the formation of $Fe(OH)_3$, SiO_2(am), $Al(OH)_3$, $CaCO_3$, $(Ca,Mg)CO_3$ and MnO_2 (Figure 3-7), based on the chemical analysis and the calculated saturation indices. Organic components were assumed to be the major component in the remaining fraction required for mass balance, but it can not be concluded whether the organic constituents are components of the solid phase or just retained by the filter through adsorption to inorganic solids that are clogging the pores or electrostatic attraction by the filter.

The results clearly illustrate, however, the impact of two important phenomena induced by aeration of the water samples: (a) formation of colloids by precipitation of predominantly ferric hydroxides as well as carbonates and (b) adsorption or coprecipitation of macromolecular organic matter.

Table 3-2. Calculated saturation indices using PHREEQE for a water with composition according to Table 2-1.

log (SI)[a]	A	B	C	D
Calcite	1.08	0.97	1.45	0.49
Aragonite	0.93	0.82	1.29	0.33
Dolomite	1.68	1.45	2.18	0.26
Siderite	-0.02	-2.63	-11.81	-11.67
Rhodochrosite	-0.35	-0.46	-0.20	-0.96
Gypsum	-1.15	-1.87	-1.10	-1.09
Anhydrite	-1.36	-2.09	-1.50	-1.49
Hydroxyapatite	0.26	0.32	1.40	-0.34
Fluorite	0.09	0.10	0.31	0.31
Chalcedon	-0.39	-0.39	-0.21	-0.21
Quartz	0.09	0.09	0.33	0.33
Gibbsite	-0.15	-0.14	-0.29	-0.16
Kaolinite	0.33	0.33	0.30	0.56
Sepiolite	-2.42	-2.39	-1.02	-2.92
Hematite	8.62	-0.73	18.34	18.63
Goethite	1.82	-2.86	6.71	6.86
Ferrihydrite	-2.58	-7.26	2.87	3.02
Pyrite	-16.32	10.51	-258.53	-256.45

a Saturation index (SI), assuming equilibrium and
A: pe=-2.5 corresponding to measured values (Geotab, 1992)
B: pe=-4.7 corresponding to a system in equilibrium with hematite/magnetite
C: Original pe=-2.5; final conditions representing a system in equilibrium with atmospheric (O_2 and CO_2)
D: Original pe=-4.7 ; final conditions as in C.

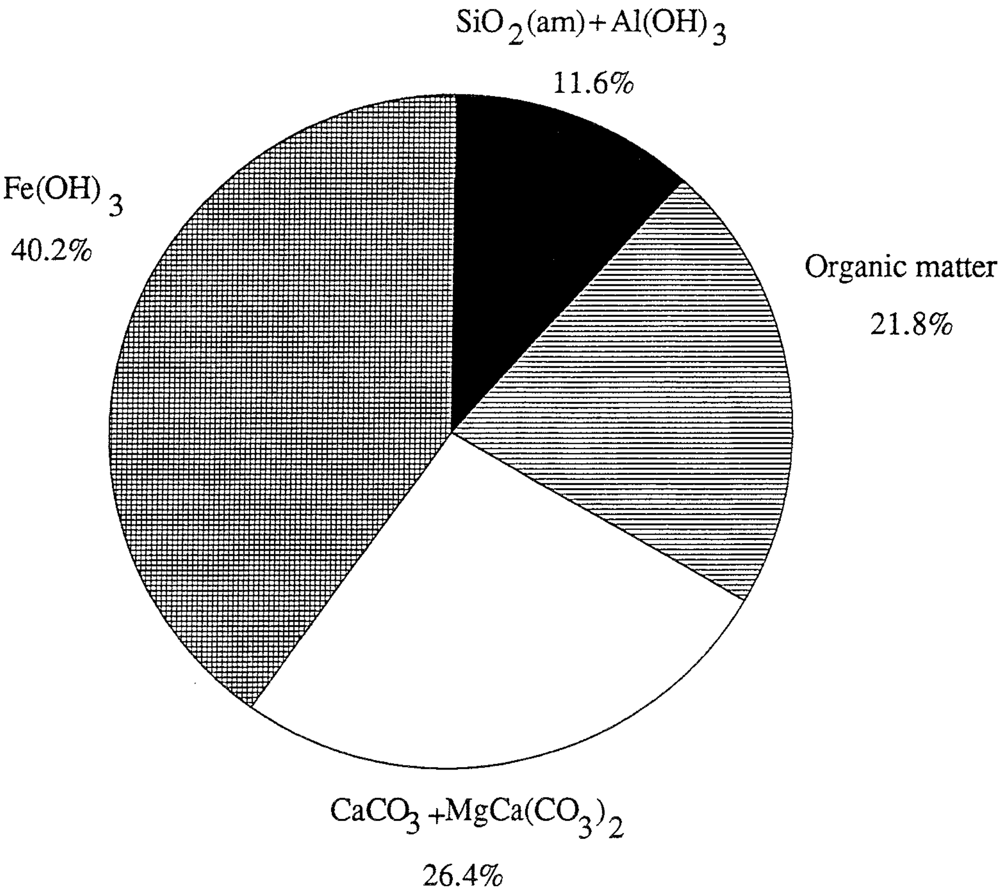


***Figure 3-7**. Assessed dominating phases in solids retained by 0.015 μ m polycarbonate membrane filters (after contact with air for 72h).*

4 CONCLUSIONS

The following general conclusions can be drawn:

The measured count rate was proportional to the colloid concentration in the concentration ranges 0.03-2 mg/l, 0.1-2 mg/l, 0.1-7 mg/l, 0.5-10 mg/l, 0.5-50 mg/l and 0.5-75 mg/l for Fe_2O_3, $Al(OH)_3$, SiO_2, kaolinite, illite and a high molecular weight humic acid, respectively. Thus, it is in principle feasible to perform non-disturbing direct measurements of size distribution as well as concentrations down to at least 0.5 mg/l or even lower (down to 0.1 mg/l for Al- and Si-colloids; down to 0.03 mg/l for homogeneous Fe-colloid systems), providing that the phase composition is known.

Great precaution is, however, needed when the PCS technique is used for measurements of colloid concentrations in heterogeneous systems, like most natural waters. The results can be totally erroneous if the calibration is performed with improper reference colloids. Consequently, accurate determinations of the colloid concentrations with PCS technique require in principle a detailed knowledge of the mineralogic composition of the colloids or possibly even a calibration of the instrument with natural colloidal matter from the specific field area.

The PCS technique can be adapted for direct measurements *in situ* and on-line with a minimum of disturbing sample treatment or storage which is preferable in samples where precipitation of new solid phases would occur otherwise. There is probably no other technique that could be used for quantitative non-interacting characterization of colloids (concentration as well as size distribution) at these concentration levels, in field systems.

The upper colloid concentration can be assessed in waters with extremely low colloidal content, e.g. deep groundwaters. Since the detection limit of 0.5 mg/l or below is at least as good as what is achieved with other techniques and with the advantage of a minimum of undesired side-reactions.

Changes in the partial pressures of O_2 and CO_2 during the analysis of the samples from a deep groundwater like the one in Äspö may very fast (within a few minutes) both increase the quantity of colloidal matter as well as change the composition and the size distribution.

5 ACKNOWLEDGEMENTS

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