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Photon correlation spectroscopy (PCS) has been demonstrated as a technique for characterization of the size and size distribution of colloidal species in sea water. Water collected at the Scripps Research Institute in La Jolla, CA, was filtered with Nucleopore membrane filters and the sizes of particles passing through 0.2 μm pore sizes were measured with PCS. The colloids were on the order of 200-500 nm radius. The very low particle concentration made precise analysis of the size distribution and variations very difficult.

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Photon correlation spectroscopy (PCS) has been demonstrated as a technique for characterization of the size and size distribution of colloidal species in sea water. Interest in studies of colloids in sea water has increased in recent years in order to attempt to account for the large amount of "dissolved organic material" (DOM) known to exist. The interest intensified with the discovery, by a new catalytic method, that the quantity of oceanic DOM is perhaps twice the previously accepted amount. The probability that DOM was contained within colloidal species was suggested by studies of humic acid in fresh water with controlled amounts of added salt that showed aggregates of 50-200 nm diameter. Because, even with the new higher estimations of DOM, these colloids would still exist only in extremely low concentration in natural sea water the development of techniques for these measurements is challenging. The support under this ONR support was for a feasibility study in development of PCS as a new technique for such measurements.

Several samples of natural sea water were collected by or supplied to us. Initial studies were performed on samples provided by Dr. Peter Williams of the Scripps Research Institute in La Jolla, CA. These samples were filtered with glass prefilters immediately after collection and they were filtered into dust free scattering cells with 1.0, 0.4, or 0.2 μm pore size Nucleopore filters. PCS measurements of diffusion coefficients of particles in these samples showed very weak signals and with time (over the course of several hours) showed the development of much larger species (~1-20 μm). Poisoning the samples with 10 ppm $HgCl_2$ demonstrated that the larger species were in fact microorganisms which managed to pass through the filter pores and then began to grow. Subsequent samples were all treated by addition of 10 ppm $HgCl_2$ after collection and first filtration with glass fiber prefilters.

Extreme care was necessary to filter the water samples with the 1.0, 0.4, and 0.2 μm Nucleopore filter set prior to scattering measurements. Without filtration samples were much too contaminated with dust and microorganisms to allow any reasonable PCS work. Figures 1 and 2 show representative PCS auto correlation data on samples thus prepared. These particular samples were obtained from Scripps and from a collection from the Santa Monica Bay Pier. The correlation functions appear as single exponentials that can be fit as $G^{(2)} = Ae^{-2\Gamma\tau} + B$ where $\Gamma = Dq^2$ with the scattering wave vector $q = (\frac{4\pi n}{\lambda}) \sin \theta/2$. The diffusion coefficients are converted to hydrodynamic radii by the Stokes-Einstein equation $R_h = \frac{kT}{6\pi\eta D}$. For the purpose of these figures an alternative analysis has been performed with Provencher's inverse Laplace transform CONTIN program. The fitting yields a decay time distribution as shown by the overlaying curves. The data clearly show a fairly narrow single decay. From these relaxation times, diffusion coefficients and then hydrodynamic radii are calculated. Measurements were typically repeated over the course of several hours to insure stability of the particle sizes. These results are shown in Figures 3 and 4 as R_h against time after filtration. The colloids are on the order of 200-500 nm radius. No significant time dependence is observed within the scatter of the data. The variations are quite large however, and are the result of the very low particle concentration which severely limits the precision of the PCS measurements.

There does appear to be a significant difference between the two water sources, with the Santa Monica Bay sample giving larger species. Several samples were collected by Dr. Williams' group at various depths and from various sources at Scripps. We could not establish any consistent dependence of the particle sizes and

these water collection sources. The difference for the Santa Monica Bay water may reflect a local pollution and may not reflect natural bulk oceanic conditions.

The particles observed in the sea water are roughly the same size as has been observed in fresh water. This is perhaps unexpected considering that the DOM concentration is lower by two orders of magnitude than in the fresh water studies.

The use of membrane filtration was necessary to remove contaminating scattering species which are much larger than the typical DOM colloids and would therefore easily overwhelm the scattering intensities. We observed no systematic variation of measured particle size for the 0.2 or 0.5 μm filtered samples. This is reasonable in that colloidal particles can be broken as they are passed through the filters and they then reorganize into their characteristic size very rapidly after the filtration.

We have determined that it is feasible to study colloidal species of DOM in natural sea water by photon correlation spectroscopy. However, the extremely low concentrations of DOM causes the signals to be quite weak and limits detailed interpretation. One possible procedure to improve the measurement precision would be to concentrate the samples by evaporation to increase the concentration. This method has been used for fresh water studies. It is not known what effect this procedure would have on the particle sizes and if one could distinguish any artifacts that may be introduced.

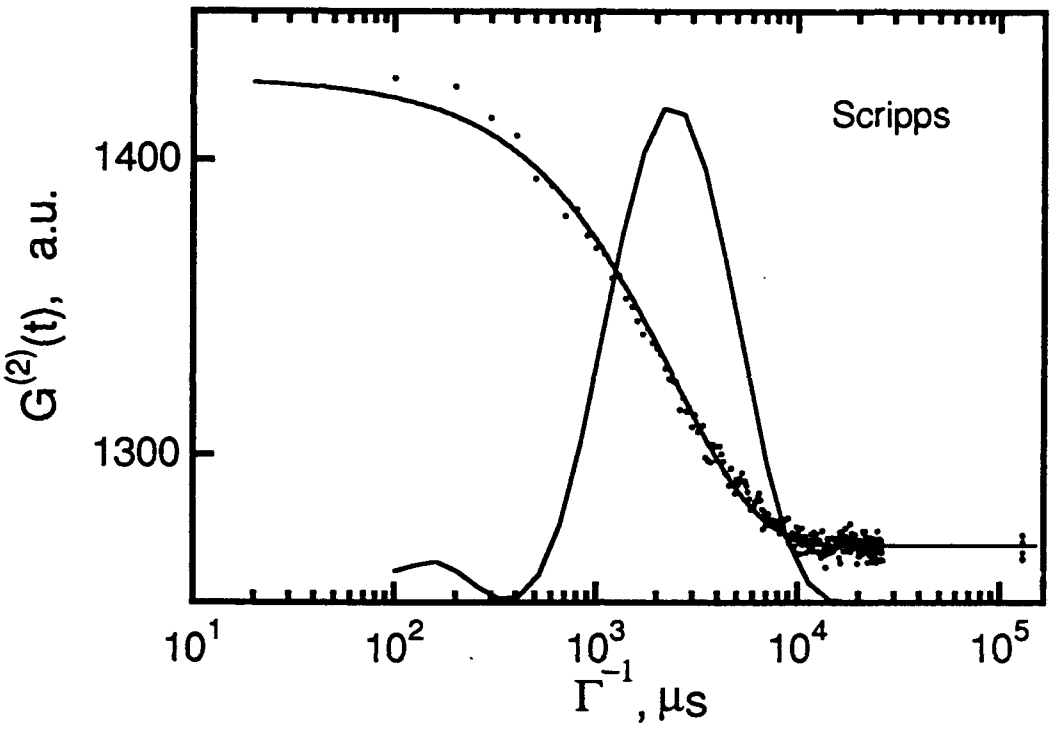
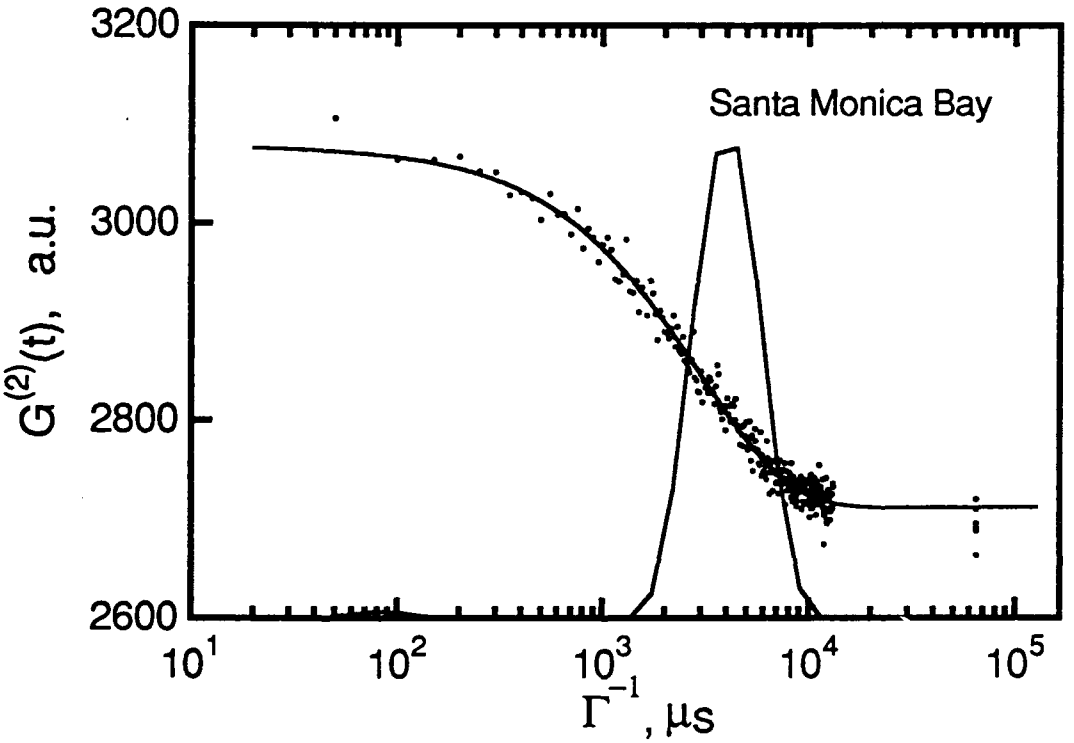


Figure 1



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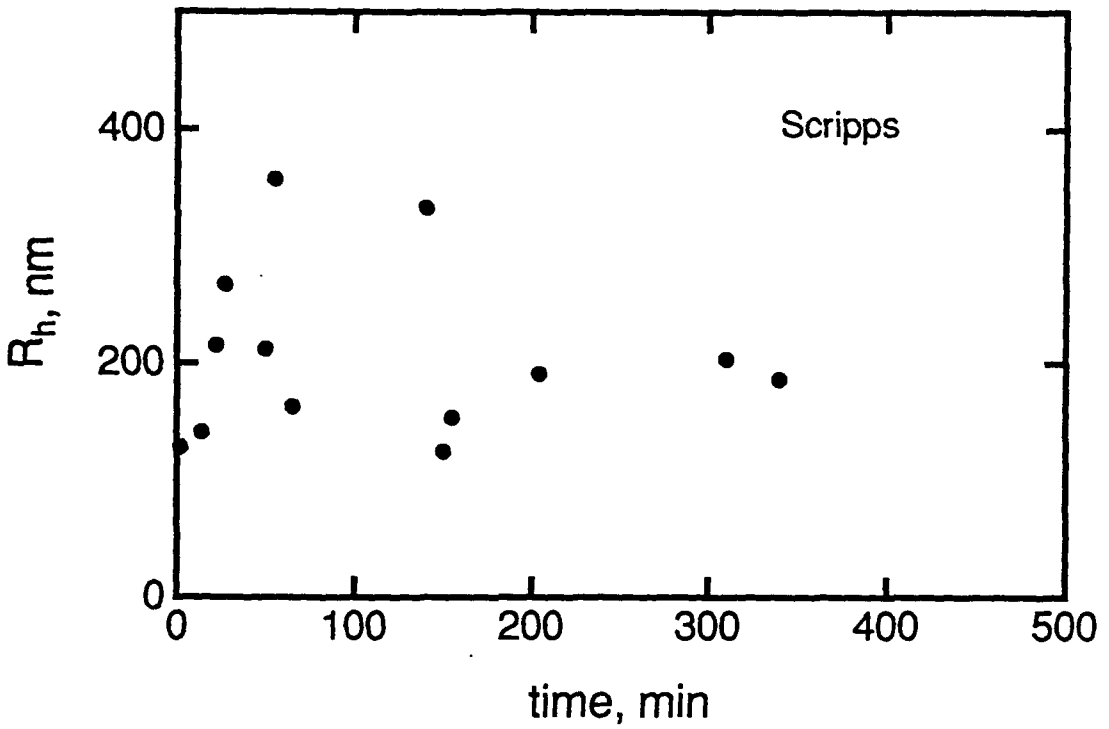

Figure 3

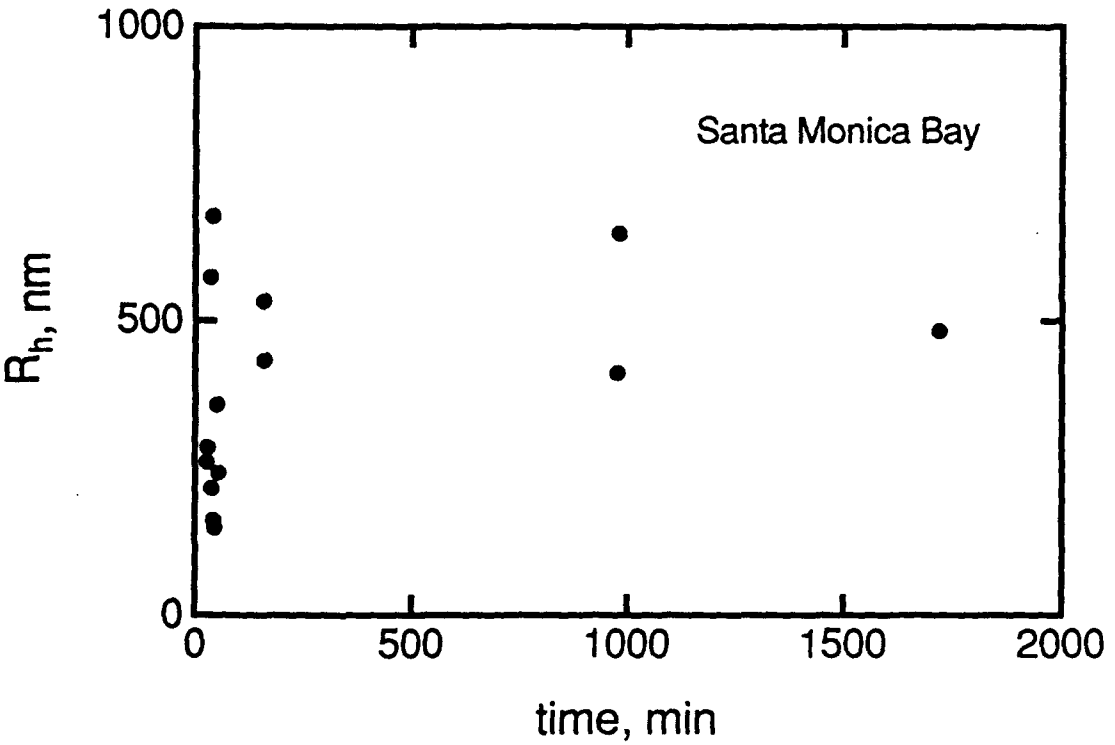

Figure 4