Dissolved and Colloidal Ag in Natural Waters – Analytical Aspects

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Abstract

A series of laboratory experiments were conducted to better understand and illustrate the possible occurrence of artifacts during water sampling, sample storage, sample digestion, and preconcentration. Silver in solution tended to sorb onto the walls of sample bottles regardless of the bottle composition even when utilizing a conventional sample acidification (2 mL HNO₃/L of water) method. However, using a combination of sonification and UV-irradiation, sorbed Ag could be released back into the water. Such a digestion procedure was also a necessary step for colloidal samples before extraction. We also found that more than 30% of the conventionally defined “dissolved” Ag (≤0.45μm) in fresh and marine waters was retained by a 0.1μm filter.

Introduction

Chemical and phase speciation of trace elements is key to understanding the factors controlling their biogeochemical cycling within natural aquatic systems. The fate of trace metals, such as Ag, in aquatic environments is dependent, to a large extent, on the energetics of heterogeneous reactions. Bioavailable solution species often react on surfaces of heterogeneous particulate phases, which include aggregates of organic matter, the oxyhydroxides or sulfides of Fe and Mn, clay minerals, or carbonates, of diameters ranging from nanometers to tens of micrometers. Each of these phases act as sites for sorption/desorption, proton and electron exchange, or photochemical reactions. In most cases, the bioavailability and toxicity of trace metals are enhanced when metals exist predominately as true solution phase species. However, the difference between beneficial and toxic concentrations even, of required trace metals in aquatic environments is often very small.

Silver is often introduced into the aquatic environment from municipal and industrial water treatment plants receiving liquid wastes from the photographic industry. Thereafter, Ag has the potential to be a major urban pollution indicator. In here, a series of experiments were conducted to better understand the proper methods for sampling, storing and analyzing of water samples for “dissolved” Ag.
Methodologies and Approaches

"State-of-the-art" ultraclean techniques were used during all stages of sample collection, transport, handling, processing and analysis (Wen et al, 1996). Two ultraclean CFUF systems (AMICON, S10N1 and Miniplate-3) were used for Ag phase speciation studies. A specially constructed UV-irradiation chamber was used for the digestion of all samples. Radiotracer (110mAg) and a well-type high purity Ge detector interfaced with a Canberra Series 100 multichannel analyzer were used for the sample storage experiments. A modified solvent extraction procedure (Bruland et al., 1985) was used for preconcentration, while a PE5100 Perkin Elmer GF-AAS with Zeeman correction were used for the analysis of Ag in total dissolved, ultrafiltrate and retentate samples.

For the bottle adsorption and storage experiments, radioactive 110m Ag was added to filtered (≤0.45µm) sample waters (DDW, tapwater, unacidified and acidified river water) contained in a Teflon bottle. During a two-month storage period, time series subsamples were taken and gamma counted. After storage, the unacidified samples were acidified (2ml conc. HNO3 per 1 L of sample) and subsamples gamma counted, after which time all samples were ultrasonicated for 1 hour at 60°C and gamma counted again, and finally UV irradiated for 24 hours and gamma counted. For the storage experiment, with natural filtered water samples (<0.45µm) collected from a Colorado river site down stream from a waste water effluent had been used for the adsorption study. First, two samples were extracted immediately after collection. Second, two samples were acidified in the field immediately after collection, and extracted in the laboratory. Third, two samples were acidified and extracted in the laboratory after 3 months. Fourth, 4 samples collected in a 2 L TEFLOW bottles were ultrasonicated and UV digested in the laboratory after 3 months, and extracted. Fifth, 4 samples collected in a 2 L TEFLOW bottle were acidified, ultrasonicated, and UV digested in the laboratory only after 3 months and then extracted. Two different types of colloidal solutions (≥1kDa CFUF retentate), Trinity river (S=0) and Galveston Bay water (S=30) were used for a test study of the importance of a proper digestion procedure before sample preconcentration. The Trinity River filtered (≤0.45µm) water had a colloidal organic carbon (COC) concentration of 3.4 mg/L at that time, while the surface water sample from the Gulf of Mexico had a COC content of 1.1 mg/L.

Results and Discussions

Results of sample storage experiments, for both radioactive and stable Ag, are shown in
Figure 1 and 2. Results indicate that all samples waters with $^{110m}$Ag spiked without acidification sustained a great loss to the bottle walls in less than 24 hours, however even with acidified samples, some $^{110m}$Ag still adsorbed onto the bottle walls (Figure 1). After the sample waters were acidified again, there was no significant desorption of previously sorbed $^{110m}$Ag back into the solution, even after a sonification procedure was applied. However, after UV irradiation of the sample water, 100% recovery was consistently achieved (Figure 1).

For the natural water storage experiment, we had found that in-situ extraction or in-situ acidification resulted in identical Ag concentrations (Figure 2). Even if samples were not acidified immediately, after three months, all the Ag can be recovered with a proper acidification and UV-irradiation method (Figure 2).

For the proposed digestion protocol for colloidal sample waters, samples processed without a UV-digestion procedure usually exhibited considerably lower recovery even with acidification and sonification (Figure 3). These results clearly demonstrate that UV-irradiation is the most effective and convenient water sample digestion method.

Using ultraclean cross flow ultrafiltration, we were previously able to demonstrate that 15-70% of the conventionally defined “dissolved ($\leq 0.45\mu m$)” Ag was actually bound to a colloidal phase in river waters and estuarine waters of Texas (Wen et al., 1997). We found that this was also true for river waters of Colorado. Only 10 to 40% of the “dissolved($\leq 0.45\mu m$)” Ag was in fractions smaller than 3kDa. A major fraction of the Ag was bound to colloidal organic matter.

Conclusions

Results from sample storage experiments using both radioactive and stable Ag indicate that even with acidified samples, some Ag will be adsorbed onto Teflon bottle walls. However, by UV irradiating the sample water, 100% recovery was consistently achieved. Also, we found that the UV-irradiation digestion method was required for Ag analysis in concentrated colloidal solutions. In natural waters from widely different geographical regions, we found that 5-90% of the conventionally defined “dissolved” Ag is actually bound to a colloidal phase, and not present in ionic forms. Thus, the use of CFUF is important to reveal the phase speciation of Ag in natural waters.

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References


Figure 1

Diagram showing the adsorption/reaction time (day) vs. activity (cpm) for DI water, Tap Water, Colorado River water, and Colorado River water (acidified).
Figure 2

- Acidified, UV-irradiated & extracted in lab (E)
- UV-irradiated & extracted in lab (D)
- Acidified & extracted in lab (C)
- In-situ acidification, UV-irradiated & extracted in lab (B)
- In-situ acidification & extraction (A)

Concentration (ng/L)
Figure 3

- FW Colloid
- SW Colloid

Concentration (ng/L)

Unacidified  Acidified & Sonicated  Acidified, sonicated and UV-irradiated