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On-line determination of silver in natural waters by inductively-coupled plasma mass spectrometry: Influence of organic matter

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Abstract

We investigated interference effects on the analysis of silver in estuarine and oceanic waters using on-line high resolution inductively coupled plasma mass spectrometry (ICP-MS). A mini-column packed with a strong anion exchange resin (Dowex 1-X8) was used in a flow-injection system to separate and concentrate silver from the saline samples prior to on-line determination by ICP-MS. A series of analyses showed the concentrations of silver measured in San Francisco Bay estuary and the North Pacific that had been acidified (pH < 2) and stored for periods of 1–2 years were 10–70% lower than those measured in aliquots of those samples after ultraviolet (UV) irradiation. Additional silver released after UV irradiation of the estuarine waters, but not the ocean waters, was positively correlated ($r = 0.77$, simple linear correlation) with chlorophyll-*a* concentrations, but not with dissolved organic carbon (DOC) concentrations. Spatial distributions of chlorophyll-*a* and UV-released silver also exhibited similar patterns along a salinity gradient in the San Francisco Bay estuary, suggesting an in situ biogenic source of the interferent for the silver measurements.

Keywords: San Francisco Bay; Estuaries; Silver; ICP-MS; North Pacific Ocean; UV oxidation; Flocculation

1. Introduction

Silver has long been used as a geochemical tracer of wastewater discharges in receiving waters (Benoit et al., 1994; Sanudo-Wilhelmy and Flegal, 1992; Smith and Flegal, 1993) and, more recently, as a tracer of atmospheric contamination from fossil fuel combustion in oceanic waters (Ranville and Flegal, 2005). These tracer studies require pM measurements of silver in complex matrices, including estuarine and oceanic waters that can contain as much as 3% total dissolved solids (Flegal et al., 1995; Smith and Flegal, 1993; Zhang et al., 2001). Those low concentrations of silver, combined with relatively high (mM) concentrations of alkali and alkaline earth ions, make direct determination of trace silver levels in saline matrices very challenging—even with the most sensitive analytical methods currently available. Consequently, it is best to both isolate silver from those interferents and pre-concentrate it prior to instrumental analysis.

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One technique to pre-concentrate and separate silver from complex matrices is solvent extraction. For example, a combination of ammonium 1-pyrrolidinedithiocarbamate and diethyldithiocarbamate (APDC/DDC) has proven reliable and has been widely used for the extraction of silver, and several other trace metals, from saline waters prior to analysis by either graphite furnace atomic absorption spectrometry, GFAAS (Bruland et al., 1979; Rivera-Duarte et al., 1999; Smith and Flegal, 1993; Wen et al., 2002), or high resolution inductively coupled plasma mass spectrometry, ICP-MS (Ndung'u et al., 2001). But solvent extraction methods are labor intensive, use relatively large quantities of chlorinated organic solvents, and are difficult to automate.

Consequently, solvent extraction techniques are being replaced by ion exchange resins for many trace element concentration measurements, including those of silver. The resins are more adaptable to automation because they can be easily packed in mini-columns and incorporated in flow-injection (FI) systems. In addition, FI systems can be coupled on-line to sensitive instrumental detectors, such as high resolution ICP-MS, allowing all three analytical steps of separation, pre-concentration, and final analysis to be conducted on-line (Barriada et al., 2003; Yang and Sturgeon, 2002).

In spite of the recent increase in the use of ion exchange resins for trace metal pre-concentration and separation prior to on-line or off-line analysis of trace element concentrations, only a few studies have rigorously investigated the effect of dissolved organic matter (DOM) on the performance of resins in the determination of total dissolved (<0.4 μm) trace metal concentrations in natural waters. But such studies are still necessary because DOM is an integral constituent of most natural waters and has a demonstrated trace metal binding capacity, which has the potential to interfere with resin preconcentrations (Mackey et al., 1997). That potential interference was recently demonstrated in a detailed investigation of the performance of an on-line ion exchange-based method for the analysis of total dissolved trace metal cations in the San Francisco Bay estuary, which showed that up to 13% of the copper and 20% of the cobalt were relatively strongly complexed to organics in those waters and unavailable for uptake by a cation exchange resin unless UV radiation was used to decompose organic matter prior to the extraction (Ndung'u et al., 2003).

That report (Ndung'u et al., 2003) specifically did not include silver measurements because the iminodiacetate-based cation exchange chelating resin (Toyopearl™) used in the extractions was found to be unsuitable (i.e., not quantitative) for silver. This limitation was tentatively attributed to the speciation of silver in marine waters, which is dominated by chloride complexation (Miller and Bruland, 1995). Those silver-chloride complexes, which are predominantly negatively charged, have a high affinity for anion exchange resins; and that limits the applicability of those resins in silver extractions from saline waters.

However, Yang and Sturgeon (2002) and Barriada et al. (2003) recently reported the use of an anion exchange resin (Dowex™ 1-X8) to extract silver from National Research Council of Canada (NRCC) marine water certified reference material (CRM) for estuarine water (SLEW-3) and coastal sea water (CASS-4) and oceanic waters from the northeast Atlantic, prior to on-line ICP-MS analysis. Also recently, Wen et al. (2002) investigated the effects of DOM on the analysis of dissolved silver in different natural waters. They found that it was necessary to UV irradiate and ultrasonicate acidified natural water samples in order to eliminate DOM interferences prior to silver extraction and analysis using APDC/DDC and GFAAS.

Therefore, we investigated the effects of DOM on the performance of the on-line anion exchange resin method (FI-ICP-MS) for silver measurements. We analyzed dissolved silver in estuarine (San Francisco Bay) and oceanic (North Pacific) waters, as well as in comparable estuarine (SLEW-3) and marine (CASS-4) certified reference materials, and demonstrated the effectiveness of batch UV digestion of estuarine and oceanic waters for those measurements. The San Francisco Bay samples had a wide range in DOM and salinity. Those samples included relatively fresh waters from the northern reach of the estuary (North Bay), which is impacted by natural and agricultural DOM from the Sacramento and San Joaquin rivers that drain California's Central Valley, and relatively saline waters from the southern reach of the estuary (South Bay), which is impacted by industrial and urban DOM from point source discharges and surface runoff from much more local sources of the San Francisco Bay area megalopolis. The North Pacific samples were from surface transects and vertical profiles in the North Pacific. Those oceanic waters also had a relatively wide range in DOM, but a much more limited range in salinity.

2. Experimental

2.1. Samples

San Francisco Bay estuary surface water samples were collected between February 2001 (winter) and