

Solid Phase Extraction Mechanistic Studies of the Ag(I)-DMABR Complex: Improving Efficiency of the C-SPE Standard Method of Analysis

Lorraine M. Siperko and Marc D. Porter
University of Utah

Robert J. Lipert
Iowa State University

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ABSTRACT

Aqueous silver(I) is added at trace levels (0.1 – 1.0 mg/L) to spacecraft potable water as a biocide. Development of a method that can be deployed on orbit and in future Lunar and Mars missions is therefore central to maintenance of safe drinking water and crew health. To address this need, our laboratory has created an analytical technique that couples a selective sorption process based on solid phase extraction (SPE) with the quantitative measurement of the extract by a hand-held diffuse reflection spectrophotometer. This technique, referred to as colorimetric-solid phase extraction (C-SPE), enables the low level detection (limit of detection ~5 ppb) of silver(I) by metering 1.0 mL of a water sample through a reagent-impregnated (i.e., 5-(*p*-dimethyl-aminobenzylidene)rhodanine, DMABR) SPE membrane. The total workup time for the analysis is only 60-90 s. Moreover, the effectiveness of this method has been demonstrated by microgravity simulations through comparisons to concurrent ground-based analyses of companion samples.

In keeping with the mission of our research, we are constantly refining the efficiency and effectiveness of our methodology. One pressing problem when using C-SPE in a microgravity environment is the presence of dispersed air bubbles that can lead to errors in exact measurement of sampling volumes. Our current protocol requires the withdrawal of more than the specified volume of analyte into a syringe and swinging the syringe in an arc to force the entrapped air to the tip. The air and excess sample are expelled into a waste container before ejecting the analyte through the extraction cartridge. The ideal situation would involve filling a syringe without concern for the exact sample volume, and this can be accomplished by applying the principles of negligible depletion (ND) in conjunction with C-SPE measurements. To determine if current C-SPE

protocols could be manipulated to our advantage, a series of experiments were performed to gain a fuller understanding of the role of DMABR in complexing silver(I). Currently used SPE membranes were found to be highly efficient for retaining DMABR, suggesting that reagent loadings may be reduced without compromising extraction performance, posing the potential to adjust the amount of reagent in a membrane to manipulate ND volumes.

INTRODUCTION

The fundamental importance of safe drinking water to the survival of humans in the isolated environment of space invokes a critical need for rapid, reliable monitoring of levels of biocidal agents used to arrest microbial growth in potable water. The ability to accomplish such a task on board the International Space Station (ISS) requires development of a method that is selective and sufficiently sensitive to detect such analytes at low concentrations. The method must also be capable of operation in microgravity and be appropriately rapid to minimize crew time, which is at a premium due to the many pressing demands of flight. User-friendly, small and lightweight technology that meets all the requirements of water quality monitoring in a space environment will facilitate real-time correction protocols to be put in place for rapid response in compromising situations.

Our laboratory has developed colorimetric-solid phase extraction (C-SPE) methodology to monitor heavy metals (nickel(II), chromium(VI), copper(II), iron(III)) in addition to the biocides iodine (I₂) and silver(I).¹⁻⁴ The latter two have been tested in microgravity (KC-135, C-9 flights) and have shown a strong correlation of the data between flight and ground-based analyses, demonstrating the potential for the use of C-SPE methodologies in space. However, a persistent problem

associated with analyses in simulated space environments is the occurrence of air bubbles entrapped in a liquid sample. This situation limits the ability to meter a precise volume of sample through the extraction disk and can ultimately compromise the reliability of the analysis. To overcome such a limitation, protocols for C-SPE determinations to be used under microgravity conditions must be adjusted, a process that entails reconsideration of several steps in the analytical process.

EXPERIMENTAL

REAGENTS AND CHEMICALS

All solutions were prepared daily with deionized water that was purified by a Millipore Milli-Q Water purification system.

Silver(I) solutions. A 10.0 ppm stock solution was prepared by dilution of an appropriate volume of silver(I) atomic absorption standard solution (983 $\mu\text{g/mL}$ silver(I) in 1% (w/w) nitric acid (HNO_3), Aldrich). More dilute silver(I) solutions were prepared from aliquots of the stock solution.

5-4(Dimethylaminobenzylidene)rhodanine (DMABR) solution. A stock solution used to impregnate the membranes was prepared by dissolving 0.0885 g DMABR (Aldrich) in 100.0 mL of methanol:dimethylformamide (MeOH:DMF) at a ratio of 9:1.

DMABR-impregnated membranes. C-SPE membranes (EmporeTM SDB-XC 47-mm extraction membranes (3M)) were mounted on a vacuum filter holder and impregnated by applying 10.0 mL DMABR from varied dilutions of the stock solution. Next, 5.0 mL aqueous 3% Brij 30 surfactant (Fluka) were added to the impregnated membrane. The concentration of each solution was determined spectrophotometrically from diluted samples. The effluent from each membrane was recovered in 10 mL DMF + 10 mL MeOH, which was diluted 1/20 for spectrophotometric determination of DMABR concentration. Membrane retention was determined by the difference between the amount of DMABR present in the influent and effluent solutions.

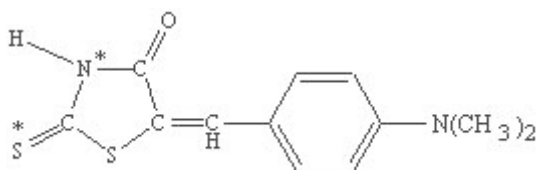


Figure 1: Structure of 5-(*p*-dimethyl-aminobenzylidene)-rhodanine (DMABR). There are two possible sites on each DMABR molecule for interaction with silver(I), i.e., nitrogen and the adjacent sulfur on the ring (*).

It should be noted that, without the presence of Brij 30 ($\text{H}_3\text{C}-(\text{CH}_2)_{11}-(\text{OCH}_2)_n-\text{OH}$), silver(I) does not form a

complex with DMABR impregnated in the membrane. We attribute the facilitation of complexation to a membrane swelling effect of the surfactant and retention of water, which permits the analyte to pass through the membrane more readily. Thus, complexation takes place due to the ability of the reagent, in the presence of surfactant, to more easily form structural conformations that could facilitate silver(I)-DMABR interaction.

C-SPE extraction cartridges. Impregnated membranes were cut into 13-mm disks which were placed on top of a support screen located in the bottom half of Swinnex polypropylene filter holders (Fisher No. 09-753–10ASX00 0013 00). The holders were then assembled by sealing the disks tightly against silicone gaskets located in the top half of the holders. A specified volume of silver(I) was metered into a syringe and ejected through the extraction cartridge. The disk was dried by forcing 60-mL of air through the cartridge with a syringe. The cartridge was disassembled and the reflectance spectrum of the complexed disk was obtained.

INSTRUMENTATION

UV-Vis Spectrophotometer. All absorbance spectra were collected with a Hewlett-Packard model 8453 UV-Vis spectrophotometer that accommodated 1.00 cm pathlength quartz cuvette sample holders. ChemStation software acquired the data, which were later plotted after incorporating into a worksheet. The wavelength of maximum absorbance (λ_{max}) of the complex in solution was determined to be 463 nm. Solution concentrations for retention studies were calculated using a molar absorptivity (ϵ_{DMABR}) of $40106 \text{ cm}^{-1}\text{M}^{-1}$, which was determined experimentally.

Diffuse Reflectance Spectrophotometer. A BYK-Gardner (CB-6834 Spectro Guide Sphere) diffuse reflectance spectrophotometer was used to collect spectral data of the impregnated disks before and after extraction and complexation of the analyte. The small, lightweight, battery operated spectrophotometer has a spectral range of 400 – 700 nm with 10-nm resolution. The instrument's aperture is such that reflectance measurements can be read from the 13-mm cartridge disks, which mate to the spectrophotometer through a sample positioner. To ensure use of the most effective analytical wavelength, reflectance values were acquired at $580 \pm 10 \text{ nm}$ for the Ag(I)-DMABR complex and at $470 \pm 10 \text{ nm}$ for the reagent-impregnated membrane.

DATA ANALYSIS AND SOFTWARE

The spectra were downloaded to a personal computer and analyzed using a version of BYK-Gardner QC-Link software to calculate the Kubelka-Munk (K-M) function and to plot calibration curves. The functional basis for C-SPE lies in the fact that the concentration of analyte in solution is determined by comparing the reflectance intensity of the complex formed on the extraction disk to that of a calibration curve constructed from intensities obtained from a set of disks exposed to a series of