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Rapid, Low Level Determination of Silver(I) in Drinking Water by Colorimetric–solid-phase Extraction

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Abstract

A rapid, highly sensitive two-step procedure for the trace analysis of silver(I) is described. The method is based on: (1) the solid-phase extraction (SPE) of silver(I) from a water sample onto a disk impregnated with a silver-selective colorimetric reagent, and (2) the determination of the amount of complexed

analyte extracted by the disk by diffuse reflectance spectroscopy (DRS). This method, called colorimetric–solid-phase extraction (C–SPE), was recently shown effective in determining low concentrations (0.1–5.0 mg/ml) of iodine and iodide in drinking water. This report extends C–SPE to the trace ($\sim 4 \mu\text{g/l}$) level monitoring of silver(I) which is a biocide used on the International Space Station (ISS). The determination relies on the manually driven passage of a water sample through a polystyrene–divinylbenzene disk that has been impregnated with the colorimetric reagent 5-(*p*-dimethylaminobenzylidene) rhodanine (DMABR) and with an additive such as a semi-volatile alcohol (1,2-decanediol) or nonionic surfactant (Brij 30). The amount of concentrated silver(I) is then determined in a few seconds by using a hand-held diffuse reflectance spectrometer, with a total sample workup and readout time of ~ 60 s. Importantly, the additive induces the uptake of water by the disk, which creates a local environment conducive to silver(I) complexation at an extremely high concentration factor (~ 800). There is no detectable reaction between silver(I) and impregnated DMABR in the absence of the additive. This strategy represents an intriguing new dimension for C–SPE in which additives, directly loaded in the disk material, provide a means to manipulate the reactivity of the impregnated reagent.

Keywords

Colorimetric–solid-phase extraction; Diffuse reflectance spectroscopy; 5-(*p*-Dimethylaminobenzylidene) rhodanine

1. Introduction

Space exploration by humans requires maintenance of an adequate drinking water supply. At present, shuttle missions and the International Space Station (ISS) employ iodine (up to 3 mg/l) or silver(I) (up to 0.5 mg/l) as bacterial growth inhibitors. Periodic monitoring of these compounds is therefore required to confirm that their concentrations are held at levels that are sufficient for effective biocidal action, but below those which may affect crew health. Long term exposure to high silver levels can cause argyria [\[1\]](#), whereas extended exposure to high iodine levels may induce thyroid dysfunction [\[2\]](#). To these ends, the testing method must be simple, rapid, and operable in microgravity.

There are a variety of approaches for potentially meeting these needs. One possibility uses reagent-impregnated materials that react with an analyte to produce a colored complex. The most basic version of this approach is based on the immersion of an impregnated strip into a sample and the estimation of the analyte concentration from the intensity of the immobilized colored complex. However, color intensity is not only dependent on analyte concentration but also on the equilibrium constant for complexation and on the immersion time. Equilibrium is sometimes reached only after extended immersion. A recent refinement to this concept couples immobilized reagents and optical fibers, but the time required to reach equilibrium may again be problematic [\[3\]](#).

Another extension of this type of analysis addresses cases in which analytes are present at very low concentrations. This situation dictates use of a preconcentration step in order to achieve the requisite limit of detection. One of the more convenient approaches to meeting this need is solid-phase extraction (SPE), which can achieve concentration factors of 1000 or more [\[4\]](#). In the most used form of SPE, an aqueous sample is first treated with a colorimetric reagent and any requisite solution modifiers (e.g. complexing agents). The resulting complex is then captured upon passage through a small porous disk and quantified by diffuse reflectance spectroscopy (DRS). This strategy has been employed for

determinations of phosphate by the molybdenum blue method [5], uranium(VI) as a thiocyanate complex [6], and cobalt and platinum ions as pyridylazoresorcinol complexes [7]. Preformed complexes of silver and palladium ions [8] and zinc ions [9] have also been preconcentrated on disks impregnated with vinyl pyridine groups.

We recently introduced an intriguing simplification of this methodology: colorimetric–solid-phase extraction (C–SPE) [10]. With C–SPE, a disk is directly impregnated with the colorimetric reagent. The colored complex is therefore formed upon passage of solution through the disk, eliminating sample workup prior to extraction. By using a polystyrene–divinylbenzene disk impregnated with polyvinylpyrrolidone (PVP), we demonstrated that iodine could be exhaustively extracted from aqueous solution as a yellow iodine–PVP complex. The procedure entailed passing a drinking water sample through an impregnated disk by means of a 10 ml syringe attached to a disk holder assembly; the amount of concentrated complex was determined by DRS. The sample workup and readout time totaled only ~60 s, which when coupled with the concentration of the analyte by the disk, yielded an iodine detection limit of 0.05 mg/l.

This paper extends C–SPE to the rapid, trace (~4 µg/l) level monitoring of silver(I), the biocide presently used on ISS. The determination relies on the passage of a sample through a polystyrene–divinylbenzene disk that has been impregnated with the colorimetric reagent 5-(*p*-dimethylaminobenzylidene) rhodanine (DMABR) and an additive such as a semi-volatile alcohol (1,2-decanediol) or nonionic surfactant (Brij 30). The amount of concentrated silver(I) is then determined in only a few seconds by using a hand-held DRS instrument. Importantly, the additive induces the uptake of water by the disk, which creates a local environment conducive to silver(I) complexation at an extremely high concentration factor (~800). There is no detectable reaction between silver(I) and impregnated DMABR in the absence of the additive. This strategy represents an intriguing new dimension for C–SPE in which the presence of additives in the disk provides a means to manipulate the reactivity of the impregnated reagent.

2. Experimental

2.1. Reagents and chemicals

All solutions were prepared with deionized water that was further purified by a NANOpure water purification system (Barnstead).

2.1.1. Standard silver(I) solution

The standard silver stock solution (1000 mg/l) was prepared by dissolving 0.787 g of silver nitrate (Fisher) in 500.0 ml (class A volumetric flask) of water. Standard silver solutions of lower concentrations were then prepared by dilution of this stock.

2.1.2. 5-(*p*-Dimethylaminobenzylidene)rhodanine (DMABR) solution

The DMABR solution used to impregnate the disks was prepared by dissolving 0.02 g of DMABR (Aldrich) in 0.100 l (class A volumetric flask) of a 9:1 methanol/*N,N*-dimethylformamide solution.

2.1.3. 1,2-Decanediol solution

The decanediol solution was prepared by dissolving 3 g of 1,10-decanediol (Aldrich) in 0.100 l of water.

2.1.4. Brij 30 solution

The Brij 30 solution was prepared by dissolving 3 g of Brij 30 (Aldrich) in 0.100 l of water.

2.1.5. C–SPE disks

The extractive phases were made by impregnating 3 M Empore SDB-XC (polystyrene–divinylbenzene) 47 mm extraction disks with DMABR. To start, a disk is mounted on a Millipore Glass Vacuum Filter Holder, with 10 ml of DMABR solution then pulled through the disk by vacuum. Residual solution was removed by vacuum for ~1 min. After ~1 h, 5 ml of the 1,2-decanediol or Brij 30 solution were pulled through the membrane, and residual solution again removed by vacuum. The membrane was then cut into 13 mm disks with a cork borer.

2.2. Instrumentation

A BIK-Gardner color-guide sphere ($d/8^\circ$) DRS (Model LCB-6830) was used to collect the spectral data from the impregnated disks. This hand-held spectrophotometer is small, lightweight, battery operated, and can collect reflectance data over the entire visible spectral range (400–700 nm) in 20 nm increments in only 1.5 s. The resulting spectrum is displayed on the instrument display or downloaded to a computer. The aperture of the instrument enables reflectance readings to be made on a 13 mm diameter disk, which mates to the spectrophotometer through a sample positioner.

2.3. Software

The DRS was interfaced to a computer by a serial cable. Spectra were then transferred to the computer and downloaded to a MS Excel worksheet to plot reflectance data. The data were then transferred to another worksheet to calculate Kubelka–Munk functions and plot calibration curves. The Kubelka–Munk function [11], ($F(R)$), is

$$F(R) = (1 - R)^2 / 2R$$

where R is the absolute diffuse reflectance; $F(R)$ is directly related to the concentration of the complex C by

$$F(R) = \epsilon Cs$$

where ϵ is the absorptivity of the sample, and s the scattering coefficient of the sample surface.

2.4. Extraction procedure and readout of extracted silver(I)

Plastic syringes of differing volumes (10 and 2 ml) were employed to meter known amounts of sample through the 13 mm disks. Each disk, after impregnation, was placed on the support screen on the bottom of a plastic, threaded filter holder (Swinnex Filter Holders; Fisher No. 09-753-10ASX00 0013 00), which was then tightly screwed into the top of the holder. The syringe was connected to the holder via a Luer Lock fitting, and the sample was injected manually throughout the disk; the extraction step required ~0.5 min. After extraction, the holder was separated from the syringe and opened. The membrane was then removed from the holder and mounted on the spectrometer for measuring the change in the diffuse reflectance of the impregnated disk.

3. Results and discussion

3.1. Selection of complexing reagent

Several compounds were examined as complexing agents for the C-SPE determination of silver(I). Dithizone, for example, has been impregnated in paper as its copper dithizonate to form the basis of a sensitive color test for silver(I) [12]. However, DMABR, which is one of the most popular reagents employed in the spectrophotometric determination of silver(I) in solution [13], was selected because of its higher selectivity and sensitivity. DMABR forms a polymeric red-violet precipitate with silver(I) in dilute mineral acid [14]. Complexation with silver(I) occurs by bonding with adjacent -NH and -C=S groups in DMABR. In aqueous solution, the acidity must be carefully controlled or colloidal suspensions will readily form. The higher stability in acidic solution is due to protonation of the dimethylamino group, giving the chelate a net positive charge.

3.2. Conditions for extraction of silver(I)

Unlike most chelating reagents, DMABR is strongly retained by ordinary filter paper and does not detectably elute when washed with water. However, a colored complex is slowly formed when a concentrated aqueous solution of silver(I) is passed through an impregnated disk. This system is therefore unsuitable for our purposes because of its slow kinetics and ensuigly low extraction efficiency.

DMABR is also strongly retained by cellulose phosphate paper. The negatively charged phosphate group holds the reagent by ion-pair interaction with the protonated dimethylamino group. This interaction leaves the heterocyclic ring of DMABR available for complexation with silver(I). C-SPE with DMABR-impregnated cellulose phosphate is extremely sensitive for silver(I). A linear calibration plot of $F(R)$ versus concentration was obtained for 10 ml aqueous samples containing 5–500 $\mu\text{g/l}$ silver(I). Results also showed that the linear range of the analysis could be moved to higher concentrations (i.e. 0.1–1.0 mg/l) by using a smaller sample volume (i.e. 2 ml). Although reasonably satisfactory, these disks had irregular surface, which led to unacceptably poor reproducibility in the DRS measurements.

We also investigated the utility of Empore disks containing cross-linked polystyrene particles, drawing on our success in using this material in our C-SPE determination of iodine [15]. Like the previous two examples, the Empore material strongly retained DMABR upon impregnation. This system, however, did not manifest any detectable color change after passage of an aqueous silver(I) solution. It appears that the polystyrene particles in the disk bind DMABR to such a strong extent that its chelating groups are not free to react with the analyte.

This finding is the second instance in which impregnation markedly degraded the binding capabilities of a reagent. This situation raises two important development issues in C-SPE. The first is identification of the fundamental physical and chemical factors that alter the reactivity of the impregnated material. The second is the creation of approaches for effectively counteracting the influence of impregnation on reactivity. In the case of impregnated DMABR, we hypothesized that a subtle increase in the hydrophilicity at the DMABR-polystyrene interface may “solubilize” the chelate to an extent sufficient to restore its capability to complex silver(I). Tests to explore the merit of this concept were then carried out by treating DMABR-impregnated Empore disks with a 5 ml water-methanol solution containing 30 g/l of 1-decanol. Importantly, the subsequent passage of an aqueous silver(I) solution through the disk induced an instantaneous and exhaustive formation of the purple DMABR-silver(I) complex. This

result indicates that the presence of the additive induces a major enhancement in the reactivity of the immobilized chelate, which supports the general tenant of our hypothesis. That is, the addition of 1-decanol triggers the formation of a more solubilizing intermediary environment that promotes silver(I) complexation.

While improving the binding capability of the impregnated chelate, the incorporation of 1-decanol created a different problem. Impregnated 1-decanol caused considerable resistance to sample flow. In an attempt to reduce flow resistance, but maintain effective chelate solubilization, 1-octanol was substituted for 1-decanol. This change notably reduced the flow resistance, and the silver(I)–DMABR complex formed rapidly and reproducibly. The only disadvantage resulted from the gradual (1–2 days) evaporation of 1-octanol from the disk. As a consequence, fully impregnated disks required refrigeration in a sealed, low volume container until usage in order to ensure effective performance.

As a compromise in viscosity and volatility, 1,2-decanediol was tested as a solubilizer. Disks impregnated with DMABR and a water–methanol mixture containing 1,2-decanediol proved to be a satisfactory solution to both problems. 1,2-Decanediol does not readily vaporize, and is less viscous than 1-decanol. We also found that treatment of a DMABR-impregnated disk with an aqueous solution of the nonionic surfactant Brij 30 performed as well as 1,2-decanediol. Brij 30, however, has the advantage of lower toxicity. Taken together, these results point to an intriguing extension for the development of C–SPE materials in that the chemical composition of the microenvironment can be manipulated through the co-impregnation of solubilizing additives.

The next sections examine details related to how the additive affects the reactivity of the impregnated chelate, and then evaluates the effectiveness of this development as a C–SPE system for the rapid, low level determination of silver(I).

3.3. C–SPE mechanism

Several experiments were carried out to gain insight into how the organic additive alters the reactivity of impregnated DMABR. One investigation characterized each side of a disk by diffuse reflectance infrared spectroscopy after treatment with the 1,2-decanediol solution. These measurements showed that the characteristic peak of the hydroxy group for 1,2-decanediol was stronger on topside of the disk (i.e. the side facing the syringe) than on the bottom side of the disk. In contrast, there was no detectable difference in the two spectra obtained for a disk after passage of a water–methanol solution devoid of 1,2-decanediol. These results confirm that the additive is impregnated in the disk and that more of the additive is impregnated in the top portion of the disk as opposed to the bottom portion of the disk.

Another set of experiments assessed the amount of additive and water loaded into a disk. This study followed the change in the mass of a co-impregnated disk and an as-received disk before and after passage of an aqueous sample. [Table 1](#) summarizes the results of tests when Brij 30 is used as the additive; the same disk was used for all experiments. First, 10 ml of water was passed through the as-received disk, which was then dried for 4 min in a vacuum desiccator. There was no detectable change in the mass of the disk after such treatment. Second, 5 ml of the Brij 30 impregnating solution was passed through the disk, followed by another 4 min of vacuum drying. In this case, a substantial weight gain (60%) was observed, indicative of the uptake of both Brij 30 and water. Third, the disk was then air-dried at 22 °C, and the mass determined at various time intervals. During this time, the mass slowly decreased, but stabilized to a value greater than that of the as-received disk in ~2 h. Since Brij 30 has a

very low volatility, the difference in the mass of the dried and as-received disk is ascribed primarily to Brij 30. A repeat of the cycle yielded a set of mass changes that were similar, but not identical to those found in the first cycle. The observed mass increases roughly correspond to uptakes of 24% by weight in Brij 30 and another 37% by weight in water. Furthermore, the uptake of Brij 30 and water resulted in an increase in the disk thickness by ~18%.

Table 1. Weight of a 45 mm diameter Empore membrane after various treatment

Membrane status	Weight (g)
As is	0.3750
After passage of 10 ml of water (4 min of vacuum)	0.3750
After passage of 5 ml of a 30 ppm solution of Brij 30 (4 min vacuum)	0.6012
Same membrane after 2 h	0.4635
Same membrane after passage of other 10 ml of water (4 min vacuum)	0.6191
Same membrane after other 2 h	0.4634

Diffuse reflectance spectra of a membrane impregnated with DMABR were run after various treatments to obtain more detailed information about the environment within the membrane. The spectra in [Fig. 1](#) show a large increase in reflectance on the upper membrane surface after the membrane has been treated with Brij 30. The increase in reflectance is accompanied by a shift from 470 to 460 nm in the maximum reflectance wavelength. These observations suggest that Brij 30 has effected a change in the environment around the DMABR. However, if the membrane is left standing for 2 h at room temperature, the reflectance decreases and the spectrum is similar to that with no surfactant within the membrane. Passage of 2 ml of water through the membrane restores the spectrum to the higher reflectance level of the original spectrum with Brij 30.

Fig. 1. Reflectance spectra of Empore membranes treated with DMABR.

From these observations, we conclude that the impregnation of the disk by the organic additive is accompanied by the uptake of a large amount of water. The organic additive Brij 30 retained by the membrane results in the uptake of additional water, which in turn results in a much higher diffuse reflectance. The reflectance gradually decreases as the water is slowly lost by evaporation. This interpretation is consistent with the weight-gain data reported in [Table 1](#) and supports the idea that a third phase within the membrane affects the solid-phase extraction.

Prior to treatment with Brij 30 (or with 1,2-decanediol), our system consists of two distinct phases—the aqueous liquid phase and the solid phase formed by spherical cross-linked polystyrene–divinylbenzene particles, all in close proximity and held together by Teflon fibrils within the membrane. A large excess of DMABR solution is added so that impregnation of the membrane is approximately uniform throughout as confirmed by fluorescence microscopy data. The DMABR is retained by strong interaction with the solid polymeric particles. Passage of 10 ml aqueous solution of Brij 30 (30 mg/l) drastically modifies the environment within the membrane disk. In essence, a third phase is created consisting of both water and the liquid surfactant. Interaction of the long-chain alkyl groups and the chains of ethoxy groups most likely hold this liquid in place. Competition of these groups of the surfactant for adsorptive sites on the solid particles may result in the DMABR molecules being retained more by interaction with Brij 30 than by interaction directly with the solid particles. The important practical result of this membrane treatment with Brij 30 or 1,2-decanediol is that mass transfer of an analyte from the aqueous phase to the stationary phase within the membrane and its subsequent complexation are greatly facilitated by the creation of the “third phase” within the membrane.

3.4. Plotting and quantitation

DRS spectra of a disk co-impregnated with DMABR and Brij 30 before and after the passage of 10 ml of a 0.3 mg/l silver(I) solution and of 1 mg/l silver(I) solution are shown in [Fig. 2](#). The evolution of the spectrum with isosbestic point at 510 nm corresponds to the formation of the DMABR–silver(I) complex. However, the spectrum for the complexed and free forms of DMABR are strongly overlapped and poorly resolved.

Fig. 2. Silver(I)–DMABR spectra for different concentration of Ag^+ .

Calibration curves were made after passing both 2 and 10 ml aqueous standards of silver(I) at different concentrations through the co-impregnated disks and measuring the amount of formed complex by DRS. Each standard was injected through three different disks and three measurements were taken for each disk, giving a total of nine determinations for each concentration. The best linearity of plots of $F(R)$ against concentration from 0.05 to 1.0 mg/l was obtained at 580 nm with 10 ml samples (Fig. 3). By working at 540 nm where sensitivity is greater and using 2.0 ml samples, a linear calibration plot was obtained at the very low range of 5–60 $\mu\text{g/l}$ silver(I) (Fig. 4). Under these conditions, the calibration plot levels off at higher concentrations. The detection limit, calculated by adding three times the standard deviation of the blank to the average of the blank is 4 $\mu\text{g/l}$ for the lower range and 40 $\mu\text{g/l}$ for the higher range.

Fig. 3. Silver(I) calibration curve (0.05–1 mg/l range).

Fig. 4. Silver(I) calibration curve (5–60 µg/l range).

3.5. Comparison with alternative method

A simple “immersion” method for the determination of silver(I) was investigated in order to establish a comparative metric for the performance of our C–SPE methodology. To this end, a 13 mm disk was co-impregnated with DMABR and Brij 30 and immersed into 25 ml of a 0.6 mg/l silver(I) solution which was then vigorously stirred. The disk was removed from the solution at fixed time periods and DRS was used to monitor the progression of the color-forming reaction. The results, summarized as a plot of $F(R)$ against immersion time, are presented in [Fig. 5](#). The plot shows a marked change in $F(R)$ as a function of time, with $F(R)$ undergoing an increase in the first 10 min of immersion that is twice that at the end of the next 90 min. Even at 100 min, $F(R)$ is only ~25% (0.044) of that (0.19) measured when 2.0 ml of the same solution are passed a co-impregnated disk. This comparison further demonstrates the merits of C–SPE as a sensitive, easy-to-use analysis technique.

Fig. 5. Reflectance vs. immersion time of a Empore membrane treated with DMABR and Brij 30 in a 0.6 ppm silver(I) aqueous solution.

3.6. Concentration factor

To estimate the concentration factor, a physical picture of the layer formed by the silver(I)–DMABR complex within the disk was obtained by carefully slicing a section of a disk, mounting it on a glass slide, and examining the section by fluorescence microscopy. Fig. 6 shows the resulting photomicrograph after 10 ml of an 80 µg/l silver(I) solution was passed through disk treated with both DMABR and Brij 30. The thickness of the silver(I)–DMABR layer is ~150 µm and the diameter of the disk is 1.0 cm, therefore the volume occupied by the silver complex is estimated at 12 µl. The concentration factor, calculated by dividing the volume of the sample (10 ml) by the volume occupied by the complex in the disk, is ~830. A smaller concentration factor (i.e. 172) was calculated when only 2.0 ml of a more concentrated (0.3 mg/l) silver(I) solution was used. The ability to easily obtain such high concentration factors is a major attribute of C–SPE.

Fig. 6. Fluorescence microscopy image of a section of an Empore membrane treated with DMABR and Brij 30. Exciter filter at 470–480 nm.

3.7. Interference study

The effect of foreign ions on the C–SPE determination of silver(I) was investigated by adding various concentrations of a different anion or cation to a solution of 0.3 mg/l silver(I) (3×10^{-6} M), which was then passed through a co-impregnated disk. The results for 2.0 ml sample injections are summarized in Table 2, which lists the value of $F(R)$ for a blank solution as well as the values of $F(R)$ for solutions with foreign ions present at different concentrations. As expected, anions that form a precipitate or complex with silver(I) interfere strongly. However, carbonate, sulfate, tartrate, citrate and EDTA have no

detectable effect, and the same conclusion applies to low concentrations of copper(II), calcium(II), iron(II), nickel(II), and zinc(II). Although not listed, the $F(R)$ value is unaffected by a pH between 5 and 7; it is, however, somewhat lower outside this range. Nevertheless, an accurate determination of silver(I) in samples outside this pH range may still be possible by buffering the standards and/or the sample at pH between 5 and 7.

Table 2. Interference study—sample: 2 ml of 0.3 ppm silver(I) (3×10^{-6} M)

Added ion	Molarity (M)	$F(R)$	Interference
None		0.10	—
Chloride	3×10^{-4}	0.04	Yes
Bromide	1×10^{-4}	0.02	Yes
Bromide	3×10^{-5}	0.02	Yes
Iodide	4×10^{-5}	0.02	Yes
Carbonate	2×10^{-4}	0.10	No
Sulfate	1×10^{-4}	0.11	No
Thiosulfate	8×10^{-5}	0.01	Yes
Citrate	1×10^{-4}	0.09	No
Tartrate	9×10^{-5}	0.10	No
Copper	6×10^{-6}	0.11	No
Copper	2×10^{-5}	0.11	No
Calcium	2×10^{-3}	0.09	No
Iron	2×10^{-5}	0.10	No
Nickel	2×10^{-5}	0.10	No
Zinc	8×10^{-5}	0.11	No

3.8. Analysis of ISS water samples

The reliability of our method for determining silver(I) was tested by analyzing several different types of space water, including those from ISS and recent shuttle missions, water sampled prior to delivery by Russian Progress Vehicle to the ISS (i.e. Korolev water), and a water-based coolant used in the internal thermal control system of ISS. The results are summarized in [Table 3](#), which lists the total silver levels determined by using inductively coupled plasma mass spectrometry (ICP-MS) [16]. The C-SPE data are generally lower but consistent with the ICP-MS results, except for the Korolev ground water sample.

Since for this sample, the silver was added in solution by an electrolytic method instead of by dissolution of silver fluoride, we suspect that the much larger concentration determined by ICP-MS reflects the presence of silver(I) as well as colloidal and other forms of silver. An ICP-MS analysis of an aliquot of the sample after passage through a 0.45 μm filter yielded a total silver level of 121 $\mu\text{g/l}$, which is in much closer agreement to our result with C-SPE.

Table 3. Analysis of spacecraft water samples by C-SPE and ICP-MS at the Johnson Space Center, Wyle Water Quality Laboratories

Sample	SPE volume (ml)	C-SPE result (ppb)	ICP-MS result (ppb)
Leaky technical CWC	2	252	268
7A potable CWC	2	404	458
Korolev ground supply	2	143	357
Korolev ground supply	10	135	357
7A.1 SRV-K cold	2	≤ 50	15
7A.1 SRV-K cold	10	≤ 5	15
7A SRV-K cold	2	≤ 50	7
7A SRV-K cold	10	6	7
6A SRV-K hot	2	≤ 50	10
6A SRV-K hot	10	≤ 5	10
7A.1 SRV-K hot	2	≤ 50	25
7A.1 SRV-K hot	10	6	25
ITCS coolant, WAFL	1	1120	1260

4. Conclusions

C-SPE provides a quick (~ 60 s) reliable way to determine silver(I) in water samples down to concentrations as low as 5 $\mu\text{g/l}$, drawing primarily on a large concentration factor (~ 820). The hardware employed is compact and easy-to-use, which is ideal for use in both spacecraft water quality monitoring and for numerous ground-based applications. Moreover, the development of the Ag^+ method has added a new dimension in C-SPE: the use of additives in the disk material to manipulate the reactivity of the impregnated reagent. Indeed, preliminary tests, which will be reported elsewhere, have also demonstrated that the method also functions effectively in zero-G simulations.

The work herein also yields further insight into the SPE mechanism in that a resin-loaded membrane impregnated with DMABR must also be pretreated by a semi-volatile alcohol or a nonionic surfactant such as Brij 30 in order for rapid complexation of silver(I) to occur.

Additional applications are to be anticipated. All that is required is a chemical system in which a selected analyte is exhaustively extracted onto a membrane in a form that permits a spectroscopic measurement. We speculate that it may also be possible to improve mass transfer kinetics in HPLC or in ion chromatography by use of similar pretreatment of the column packing.

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