

Microgravity Evaluation of Colorimetric-Solid Phase Extraction for the Measurement of Total I (Iodine, Iodide, and Triiodide) in Spacecraft Drinking Water

Robert J. Lipert and April A. Hill
Iowa State University

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

Daniel B. Gazda, Jeff A. Rutz, John E. Straub,
John R. Schultz, Daniel J. Nolan and James T. Alverson
Wyle Life Sciences Group

J. Torin McCoy
NASA, Johnson Space Center

Copyright © 2008 SAE International

ABSTRACT

We are developing a drinking water test kit based on colorimetric-solid phase extraction (C-SPE) for use onboard the International Space Station (ISS) and on future Lunar and/or Mars missions. C-SPE involves measuring the change in diffuse reflectance of indicator disks following their exposure to a water sample. We previously demonstrated the effectiveness of C-SPE in measuring iodine in microgravity. This analytical method has now been extended to encompass the measurement of total I (i.e., iodine, iodide, and triiodide). This objective was accomplished by introducing an oxidizing agent to convert iodide and triiodide to iodine, which is then measured using the indicator disks previously developed for iodine. We report here the results of a recent series of C-9 microgravity tests of this method. The results demonstrate that C-SPE technology is poised to meet the total I monitoring requirements of the international space program.

INTRODUCTION

The anticipated delivery to the International Space Station (ISS) of the United States water processing assembly (WPA), with its requirement for monitoring the level of biocidal iodine (1 mg/L minimum, 4 mg/L maximum) and total iodine (total I, i.e., iodine, iodide, and triiodide, 6 mg/L maximum) in ISS drinking water,^{1,2} has created an urgent need for an onboard total I test kit. To meet this need, we devised an analytical method

to convert iodide and triiodide to iodine, which can then be measured by colorimetric-solid phase extraction (C-SPE). Our research team has been exploring the development of C-SPE as an approach to meet the biocide monitoring needs of space exploration.³⁻⁷ C-SPE is a spectrophotometric technique based on measuring the change in diffuse reflectance of indicator disks after exposure to a water sample. C-SPE extracts and concentrates analytes on a solid-phase extraction membrane, yielding concentration factors approaching 1000 or more.⁸ A hand-held diffuse reflectance spectrophotometer is used to quantify membrane-bound analytes using the Kubelka-Munk function.⁹⁻¹¹ The Kubelka-Munk function relates the diffuse reflectance of an opaque sample to its absorption coefficient k , and scattering coefficient s , as given by the following equation:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} \quad (1)$$

where $F(R)$ is the Kubelka-Munk function and R is the relative reflectance of the sample (i.e., reflectance measured relative to a nonabsorbing standard). When measuring the reflectance of an absorbing species diluted in a nonabsorbing matrix, relative to the reflectance of the matrix, the absorption coefficient k may be replaced by the product $2.303\epsilon C$, where ϵ is the extinction coefficient and C is the molar concentration.

Then

$$F(R) = \frac{2.303\epsilon C}{s} \quad (2)$$



Documents
Document Sharing Hub

To determine analyte concentrations, spectra are transformed to obtain the value of the Kubelka-Munk function at the appropriate analytical wavelength. This value is then used to quantify the analyte via a standard response curve.

The measurement of iodine by C-SPE uses extraction membranes impregnated with poly(vinylpyrrolidone) (PVP), which serves as the colorimetric reagent.³ Iodine is determined as the yellow iodine-PVP complex. We have also extended our iodine test method to the determination of total I by employing an oxidative pretreatment of the sample solution with Oxone®, a commercially available potassium monopersulfate salt. Oxone® converts iodide and triiodide to iodine, which can then be measured using the indicator disks previously developed for iodine. These disks are insensitive to iodide and triiodide.^{3,6,7}

The oxidative pretreatment step is implemented by filling sample syringes through a reagent cartridge containing Oxone®. Dead space in the reagent cartridge results in the introduction of air into the sample syringe. Previous microgravity testing¹²⁻¹⁴ has shown that air bubbles suspended in water samples can cause uncertainty in precisely knowing the volume of liquid passed through the indicator disks, leading to errors in the determination of analyte concentrations. We report herein the results of a recent series of C-9 experiments designed to evaluate our C-SPE method for total I in microgravity.

The broad goals of these tests were to: (1) evaluate the effectiveness of oxidation of iodide to iodine by Oxone®, introduced by filling a sample syringe through a cartridge containing solid Oxone® in a glass fiber filter matrix; and (2) determine a simple and effective method to remove the air bubbles introduced into the sampling syringe by the reagent cartridge. The achievement of these goals was demonstrated by determining the accuracy and precision of measurements in microgravity of solutions of various iodide concentrations.

To verify the functionality of sample collection procedures and C-SPE test methods in microgravity, analyses for total I were performed using water samples prepared from standard solutions of potassium iodide (KI), which were also analyzed by ground tests using the Leuco Crystal Violet (LCV) method to certify total I concentrations. This process was carried out over a series of four C-9 flights. The following list the objectives of each flight.

Flight 1: Syringe filling and bubble mitigation for total I Analysis of I_2 and $I_2 + KI$ samples

- Evaluate syringe filling strategies for 10.0-mL water sample collection through an Oxone® cartridge.
- Determine a procedure for manual bubble mitigation and expulsion of air and excess sample prior to passing 10.0 mL of bubble-free sample through a C-SPE membrane.

- Evaluate the use of a three-way valve connected to a syringe, sample bag, and waste bag as a means of simplifying sample handling.¹⁵

Flight 2: Test total I analysis as KI

- Use methods developed in Flight 1 to compare ground and flight data from total I analyses.

Flight 3: Refine total I analysis via repetitive tests of single concentration of KI

- Determine if 10.0 mL of sample can be drawn accurately into a syringe through an Oxone® cartridge present in-line between the sample collection bag and syringe by comparing multiple in-flight determinations of a single KI concentration to the certified ground measurement value.
- Evaluate reproducibility of new and existing sample collection and manipulation methods by comparing the results from multiple runs using only one KI concentration.

Flight 4: Evaluate Oxone® introduction and sampling procedures for total I analysis as KI

- Analyze a range of KI concentrations for total I using procedures developed in previous flights.
- Construct calibration curves and determine precision of the method using certified ground analysis concentrations.
- Tabulate results and compare to ground measurements to determine accuracy of the method under microgravity conditions.

The results of these flight experiments illustrate the development of procedures for effectively collecting 10.0-mL bubble-free water samples through an Oxone® cartridge in microgravity, thereby allowing for the in-flight determination of total I.

MATERIALS AND METHODS

INSTRUMENTATION - Both in-flight and ground-based C-SPE measurements were made using BYK Gardner Color Guide spin d/8° diffuse reflectance spectrophotometers. All mass measurements were performed using a calibrated, certified Mettler Toledo model AG205 analytical balance.

IODINE-SENSITIVE MEMBRANES - A solution was prepared by dissolving 14.988 g poly(vinylpyrrolidone) (PVP; MW = 10,000) in 250 mL of 1:1 methanol:water in a 500-mL volumetric flask. The solution was brought to volume with 1:1 methanol:water.

47-mm extraction membrane was placed into a Millipore glass filter holder assembly, and 10.0 mL of the PVP solution was pipetted into the funnel. Next, a vacuum pump was used to apply a pressure differential (~3.5 in Hg) across the membrane to force this solution through the membrane. Once the solution had passed through the membrane, the pressure difference was maximized by setting the vacuum valve to its full-open position for 30 s to remove residual solvent. The prepared membranes were allowed to air dry for ~12 h and stored in Ziploc bags in the dark before being cut into 13-mm disks.

OXONE® GLASS FIBER FILTERS - Oxone® (Aldrich) was used as an oxidizing agent to convert iodide and triiodide to iodine. An Oxone® solution was prepared by weighing 7.4977 g in a weighing boat, transferring to a 25-mL volumetric flask and bringing to volume with DI water. Glass fiber filters (Millipore AP20047000) were placed in 60 × 15 mm (Dia × H) glass Petri dishes, and 1.0 mL of Oxone® solution was pipetted onto the center of each filter to ensure wetting of the entire filter. The dishes containing the treated filters were heated in an oven at 110°C for 2 h, after which the filters were removed and stored in Ziploc bags before being cut into 13-mm reagent chads just prior to use.¹⁶

C-SPE CARTRIDGES - All C-SPE membranes and Oxone® coated glass fiber filters were prepared the day before their corresponding flight. A few hours prior to flight, the PVP-treated membranes and Oxone®-treated filters were cut into 13-mm disks and loaded into separate Swinnex polypropylene cartridges. One end of the filter holder cartridge has a Luer fitting that readily forms a leak-tight connection with a syringe; the opposite end of the cartridge has a slip fit that mates with the sample or waste collection bag. A Teflon gasket contained in the cartridge forms an internal seal and defines the area of the membrane disk exposed to the water sample.

STANDARD SOLUTIONS - A 50-mg/L standard iodide stock solution was prepared by dissolving 0.0696 g KI in deionized water in a volumetric flask and diluting to 1.00 L. The stock solution for iodine and total I was prepared by diluting one ampoule of FIXANAL® standard (Riedel-de Haen, #38060, containing 12.690 g I₂ and 20 g KI) to 1.00 L with deionized water, producing 0.1 N iodine. Working solutions of iodide, iodine, and total I were prepared by appropriate dilutions of the stock with deionized water. The actual solution concentrations of I₂ and total I were certified by the JSC Water and Food Analytical Laboratory using the LCV method.¹⁷

SAMPLE AND WASTE BAGS - A ~72-mL Teflon bag (American Fluoroseal #1P-0072-K) was used to hold the samples. A 1-L Teflon Bag (American Fluoroseal #1PF-0270) was used to collect waste during the sample-passing and membrane-drying steps. A ~12 mL Teflon bag (American Fluoroseal #1P-0012) was used in conjunction with the 3-way valve sampling (Figure 1).



Figure 1. Photograph of the 3-way valve in flight. Syringe has been filled through the Oxone cartridge and the sample bag removed.

MICROGRAVITY WORKBENCH SETUP - The positions of fliers and analytical accessories on and around the flight bench are shown in Figure 2.

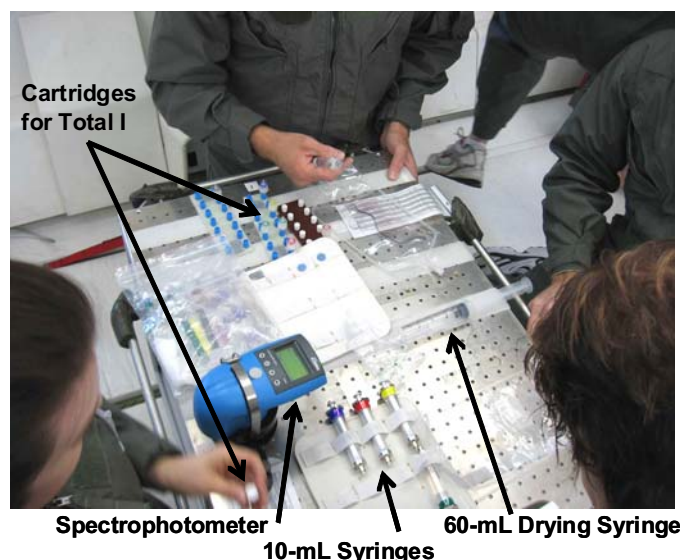


Figure 2. Photograph taken during flight illustrating the layout of the workbench and positioning of four flyers.

PROCEDURES, RESULTS, AND DISCUSSION

GENERAL OBSERVATIONS - All flight experiments were performed aboard NASA's Reduced Gravity Office's C-9 aircraft. Each flight consisted of 4 sets of 10 parabolas (40 total parabolas) that created alternating high gravity and microgravity environments. Efforts were taken to design experiments that could be broken into discrete steps that could be completed in a single microgravity segment.

During the first two flights of this series, challenges were encountered in accurately filling syringes with 10.0 mL of sample through the Oxone filter cartridge during the ~25 s microgravity period of each parabola. Careful reassessment of the test procedures during the third