In-flight Water Quality Monitoring on the International Space Station (ISS): Measuring Biocide Concentrations with Colorimetric Solid Phase Extraction (CSPE)

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The colorimetric water quality monitoring kit (CWQMK) was delivered to the International Space Station (ISS) on STS-128/17A and was initially deployed in September 2009. The kit was flown as a station development test objective (SDTO) experiment to evaluate the acceptability of colorimetric solid phase extraction (CSPE) technology for routine water quality monitoring on the ISS. During the SDTO experiment, water samples from the U.S. water processor assembly (WPA), the U.S. potable water dispenser (PWD), and the Russian system for dispensing ground-supplied water (SVO-ZV) were collected and analyzed with the CWQMK. Samples from the U.S. segment of the ISS were analyzed for molecular iodine, which is the biocide added to water in the WPA. Samples from the SVO-ZV system were analyzed for ionic silver, the biocide used on the Russian segment of the ISS. In all, thirteen in-flight analysis sessions were completed as part of the SDTO experiment. This paper provides an overview of the experiment and reports the results obtained with the CWQMK. The forward plan for certifying the CWQMK as operational hardware and expanding the capabilities of the kit are also discussed.

Nomenclature

CSPE	=	colorimetric solid phase extraction
CWQMK	=	colorimetric water quality monitoring kit
DRS	=	diffuse reflectance spectrophotometer
GFE	=	government furnished equipment
ISS	=	International Space Station
MORD	=	medical operations requirements document
PWD	=	potable water dispenser
SDTO	=	station development test objective
SVO-ZV	=	Russian system for dispensing ground-supplied water

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U.S. = United States
WPA = water processor assembly

I. Introduction

Access to representative water quality data is critical to ensuring that a safe supply of potable water is available to the crew on the International Space Station (ISS). At present time, the vast majority of the water quality data from the environmental control and life support systems on the ISS are obtained by analyzing archive water samples that are collected in flight and returned to the ground. There are several limitations inherent in this archival approach to water quality monitoring, most notably the time lapse between sample collection and ground analysis. Samples collected on orbit must be stored until they can be returned aboard the Shuttle or a Soyuz vehicle. Typical on-orbit storage times for water samples can range from 1 to 4 months, but in certain situations it can be much longer due to launch delays and limited return payload capacity. This time lapse between sampling and analysis precludes implementation of real time adjustments or corrective actions when water does not meet specifications. In most cases, the crew has already consumed the water in question before samples are returned. Sample integrity is also a concern; the storage and transport conditions that archive water samples are subjected to are not ideal and, as a result, the concentrations of certain compounds in the samples may be affected. This can complicate data interpretation and raise questions about whether or not the results from ground analyses are representative of the water quality on orbit.

When Atlantis lands after the final Shuttle mission, there will be a sharp decrease in available return-payload mass which will limit both the volume and total number of environmental samples that can be returned. Following Shuttle retirement, it will no longer be feasible to rely solely on archive water samples to collect water quality data. The majority of analytical instruments used to analyze water samples in ground laboratories are not suitable for deployment in flight. New hardware systems capable of monitoring water quality in flight on the ISS need to be developed to ensure representative water quality data can be collected. The unique operational environment on the ISS and the rigorous safety regulations applied to spaceflight hardware dictate that any water quality monitoring system developed for use in flight possess several key characteristics. “Ideal” water quality monitoring systems must be small, lightweight, reliable, sensitive, provide direct real time readout of results, minimize waste, contain no hazardous materials, meet strict storage and power guidelines, and function effectively in zero gravity. Further, the system must also be rapid and easy to use so that the crew time required for training and operation is minimal.

One technology that embodies many of the characteristics of the ideal water quality monitoring platform for the ISS is colorimetric solid phase extraction (CSPE). CSPE is a sorption-spectrophotometric technique that combines colorimetric reagents, solid-phase extraction, and diffuse reflectance spectroscopy to quantify trace levels of target analytes in water samples. In CSPE, a syringe is used to meter a known volume of sample through an analysis cartridge that contains a membrane disk impregnated with an analyte-specific colorimetric reagent and any additives required to optimize the complexation of the reagent and analyte. As the sample is passed through the analysis cartridge, analytes are selectively extracted and complexed on the membrane. Formation of the analyte-reagent complex causes a detectable change in the color of the membrane disk that is proportional to the analyte concentration. The analyte is then quantified by measuring the color of the membrane disk surface using a hand-held diffuse reflectance spectrophotometer (DRS). This entire process is illustrated in Fig. 1.

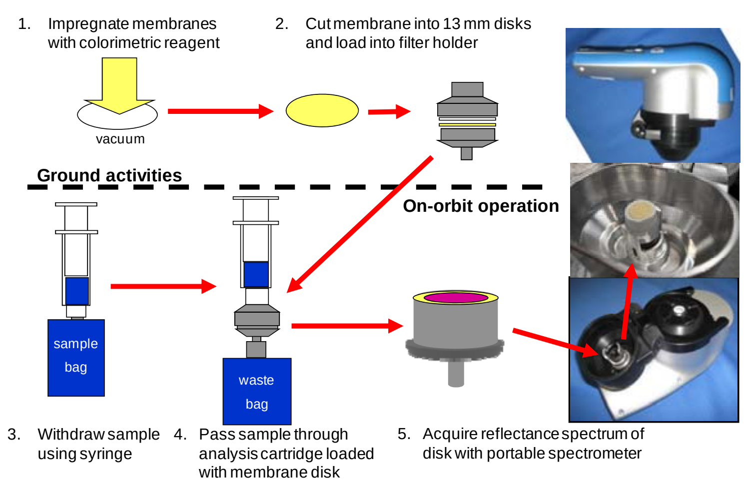

Figure 1. Overview of CSPE process.

An experimental water quality monitoring kit, called the colorimetric water quality monitoring kit (CWQMK), was designed and flown as a station

development test objective (SDTO) experiment to evaluate the suitability of CSPE technology for routine use on the ISS. The experiment, SDTO #15012-U "Near Real-time Water Quality Monitoring Demonstration for ISS Biocides Using Colorimetric Solid Phase Extraction (CSPE)", was launched on STS-128/17A and initially deployed on the ISS in September of 2009. In all, thirteen in-flight analysis sessions were run with the CWQMK as part of the SDTO experiment. This paper provides a summary of the data collected with the CWQMK during the SDTO experiment. Also discussed are the forward plans for certification of the CWQMK as a government furnished equipment (GFE) system and expanding the capabilities of the hardware.

II. Overview of SDTO Experiment

A. Purpose

The primary purpose of the SDTO experiment was to demonstrate the capability to collect in-flight water quality data on the ISS using CSPE technology. This was accomplished by measuring ionic silver (Ag^+) and molecular iodine (I_2) concentrations in ISS water samples on-orbit with the CWQMK. Secondary objectives of the experiment were to evaluate the accuracy and reproducibility of the CSPE methods and to assess the long-term stability of the DRS and consumable items included in the kit (standard solutions and analysis cartridges). A detailed description of the CWQMK hardware and details about how measurements are made was published previously.[1]

B. Analytes

Silver and iodine were selected as test analytes for the SDTO experiment because they are the biocides used in the potable water storage and distribution systems on the ISS. Biocides are added to the potable water systems on spacecraft to inhibit microbial growth. The U.S. uses molecular iodine as the biocide in the water processor assembly (WPA), while the Russian space agency utilizes silver as a biocide in their systems. In both cases, the biocides must be maintained at a level sufficient to control bacterial growth, but low enough to avoid any negative effects on crew health. The presence of high levels of iodine in water can affect thyroid function and cause taste and odor issues that result in diminished water consumption. There are also concerns about long-term consumption of water containing high levels of silver. Ingesting high levels of silver can lead to an irreversible blue-gray discoloration of the skin, a condition known as argyria. As such, ensuring biocides are maintained at safe, effective levels is one application that clearly illustrates the need to develop in-flight water quality monitoring systems to protect the health and safety of spaceflight crews.

In addition to illustrating the need to develop in-flight water quality monitoring systems, evaluation of the CWQMK also served as a first step towards providing hardware to meet an unmet requirement for in-flight monitoring of iodine and total iodine in water samples collected from the US segment of the ISS. The requirements for in-flight water quality assessment on the ISS are listed in the ISS Medical Operations Requirements Document (MORD). Section B of requirement 7.2.2.2 in the MORD contains the list of parameters that should be monitored in water samples collected from the U.S. segment.[2] Based on recommendations from the NASA Aerospace Medicine Board,[3] iodine, iodide, and iodine compounds are included in that list. At present time, no flight-certified hardware exists that is capable of measuring iodine, iodide, or iodine compounds in water samples on orbit.

C. Approach

The capability to use CSPE technology to collect water quality data on the ISS was demonstrated through a combination of in-flight analyses performed with the CWQMK hardware and experiments conducted on the ground. The original plan for the SDTO experiment called for six in-flight analysis sessions. During each in-flight session, ground-supplied standard solutions and water samples collected from different points on the ISS were analyzed with the CWQMK hardware. All water samples were analyzed in triplicate to assess the reproducibility of the CSPE methods. Ground experiments were conducted in parallel with the in-flight analysis sessions to serve as a control for the in-flight analyses. The ground studies were performed with the same standard solutions used in the kit and analysis cartridges that were prepared at the same time as those launched in the CWQMK. The standard solutions were analyzed with standard laboratory methods to assess their stability. The analysis cartridges were exposed to test solutions containing known concentrations of either molecular iodine or ionic silver. The iodine and silver concentrations obtained from the analysis cartridges were compared to results from standard laboratory methods and percent recoveries were calculated for each analyte. The ground experiments were used to assess the stability of the standard solutions and analysis cartridges as well as check for any degradation in performance that occurred as a result of exposure to launch environments and storage conditions on the ISS.

In the U.S. segment, samples were collected from two different points; the U.S. potable water dispenser (PWD) dispensing needle and the PWD auxiliary port. Multiple sampling points were utilized in the U.S. segment because the MORD requires the total iodine concentration in potable water to be < 0.2 mg/L at the point of consumption. Initially, samples for the SDTO experiment were only going to be collected from points of crew consumption, but there were concerns that analysis of samples collected at the dispensing needle would not fully demonstrate the ability to measure iodine concentrations with CSPE because essentially all of the iodine is removed from the water before it reaches the PWD dispensing needle. To ensure that the objectives of the SDTO experiment were being met, the PWD auxiliary port was added as an additional sampling point. The PWD auxiliary port is upstream of the iodine removal hardware in the PWD, so water samples collected from the auxiliary port are expected to contain the nominal biocidal concentration of molecular iodine (1 to 4 mg/L). In the Russian segment, samples were collected from the system for dispensing ground-supplied water (SVO-ZV). Samples from the U.S. segment were analyzed for molecular iodine and samples from the Russian segment were analyzed for ionic silver. The unused portions of the water samples analyzed during each session were temporarily stowed in the CWQMK until they could be returned to ground for laboratory analysis. At the conclusion of each analysis session, data was supposed to be downloaded from the DRS onto the ISS network using an Excel® spreadsheet so that it could be downlinked to the project team on the ground. The CWQMK hardware used during the SDTO experiment is shown in Figure 2.

Figure 2. CWQMK hardware used during the SDTO experiment.

Due to the incomplete data sets collected during the first four in-flight analysis sessions, the decision was made to resupply the CWQMK and extend the SDTO experiment. Nine additional analysis packs were fabricated and delivered to the ISS on STS-131/19A in early 2010. Extending the duration of the SDTO experiment ensured that enough complete data sets were collected in-flight to effectively evaluate CSPE technology.

III. Results

A total of thirteen in-flight analysis sessions were completed with the CWQMK during the SDTO experiment. The plan for the SDTO experiment was to alternate the sampling point in the U.S. segment between the PWD dispensing needle and the PWD auxiliary port. However, due to crew time constraints and delays preparing the procedure for sampling the PWD auxiliary port, only five samples were collected from the auxiliary port. There were also issues downloading spectral data from the DRS during the experiment. Deployment of the software load that contained the data transfer spreadsheets was postponed several times, which prevented data from being downloaded to the ISS network during the first three analysis sessions. Then, during the eleventh analysis session, a communication error between the data transfer spreadsheet and the DRS was reported and no data was downloaded for the remainder of the experiment. When data transfer was not possible, silver and iodine concentrations were still recorded in crew notes and called down to Mission Control. Results obtained during the in-flight sessions and the final results from the parallel ground experiments are discussed below.

A. Results from In-flight Analysis Sessions

Data collected with the CWQMK during the SDTO experiment are summarized in Table 1. Also included in the table are the results obtained from ground analysis of archive samples collected at the same time as the samples analyzed with the CWQMK. While some differences are apparent, most of these are due to an anomalous result from one of the replicate analyses. When these anomalous points are excluded from calculations, the mean results obtained in-flight show excellent agreement with the results obtained using standard laboratory methods. In other instances, information contained in crew notes provides some insight into difficulties encountered during the analysis sessions that could be responsible for the observed differences.

Based on a review of the data collected and information provided by the crew, the two most common issues encountered during the in-flight analysis sessions were both related to procedures. The analysis procedures instruct the crew to analyze each sample in triplicate. However, during several of the sessions, only one analysis was completed on each sample. It is believed that the structure of the procedure led to this oversight as the crew notes

from these activities provided no other explanation. The other issue that occurred most frequently during in-flight analyses related to the target flow rate for iodine analyses. During the first two sessions, the results obtained from analysis of the iodine standard solution were much higher than expected. The iodine concentration measured during the first session was 50% higher than the concentration measured with the standard pre-flight. It is suspected that this resulted from passing the standard solution through the analysis cartridge too slowly. Previous testing has shown that the iodine concentrations measured by CSPE can be affected by the rate at which the sample is passed through the analysis cartridge. If the flow rate is significantly less than the 1 mL/s called out in the procedure the iodine concentration measured in the sample will be higher than the actual concentration. This hypothesis is supported by the fact that the agreement between the ground (1.24 mg/L) and in-flight (1.33 mg/L) results was excellent during the third session, which occurred after the procedures were reformatted to emphasize the target flow rate. Figure 3 show ISS crewmember Nicole Stott conducting an in-flight analysis session with the CWQMK.

Figure 3. ISS crew member performing the second in-flight analysis session with the CWQMK.

Table 1. Results from in-flight analysis sessions and archive samples.

	Concentrations Measured by Session Number (mg/L)												
Solution	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Silver standard	0.404	0.315	0.277	0.236	0.236	0.268	0.537	0.290	0.253	0.205	0.237	0.211	0.136
Sample from SVO-ZV	<0.100	<0.100	<0.100	<0.100	0.397	0.100	0.225	<0.100	<0.100	<0.100	<0.100	<0.100	0.163
	-	<0.100	<0.100	<0.100	0.108	-	0.245	-	<0.100	<0.100	<0.100	<0.100	<0.100
	-	-	<0.100	<0.100	<0.100	-	0.250	-	<0.100	<0.100	<0.100	<0.100	<0.100
Archive from SVO-ZV	0.023	0.081	0.018	0.056	0.069	0.090	0.086	0.125	0.044	0.050	0.060	N/A	0.035
Iodine Standard	2.79	1.95	1.33	1.49	0.32	1.04	1.32	0.90	1.00	0.94	0.36	N/A	N/A
Sample from PWD dispensing needle	<0.20	<0.20	<0.20	-	-	-	<0.20	<0.20	-	<0.20	-	<0.20	<0.20
	-	<0.20	<0.20	-	-	-	1.44	-	-	<0.20	-	<0.20	<0.20
	-	<0.20	-	-	-	-	1.40	-	-	-	-	<0.20	<0.20
Archive from PWD dispensing needle	<0.050	<0.050	<0.050	-	-	-	<0.050	<0.050	-	<0.050	-	<0.050	<0.050
Sample from PWD aux. port	-	-	-	1.04	0.74	0.38	-	-	1.45	-	1.63	-	-
	-	-	-	0.63	0.33	-	-	-	0.74	-	1.69	-	-
	-	-	-	0.63	0.71	-	-	-	0.80	-	1.68	-	-
Archive from PWD aux. port	-	-	-	N/A	1.11	<0.050	-	-	N/A	-	N/A	-	-

B. Results from Ground Experiments

Ground experiments were conducted in parallel with each of the first six in-flight analysis sessions to serve as controls for the in-flight analyses. The final data points for the ground experiments were collected one year after the test articles were prepared. The experiments were used to assess the stability of the standard solutions and analysis cartridges and also to check for any degradation in performance that may have occurred as a result of exposure to the Shuttle launch environment and storage conditions on the ISS. As discussed above, all test articles were prepared at the same time as the original consumable launched in the CWQMK. The standard solutions and analysis cartridges were stored at ambient temperature and protected from direct exposure to light until used.

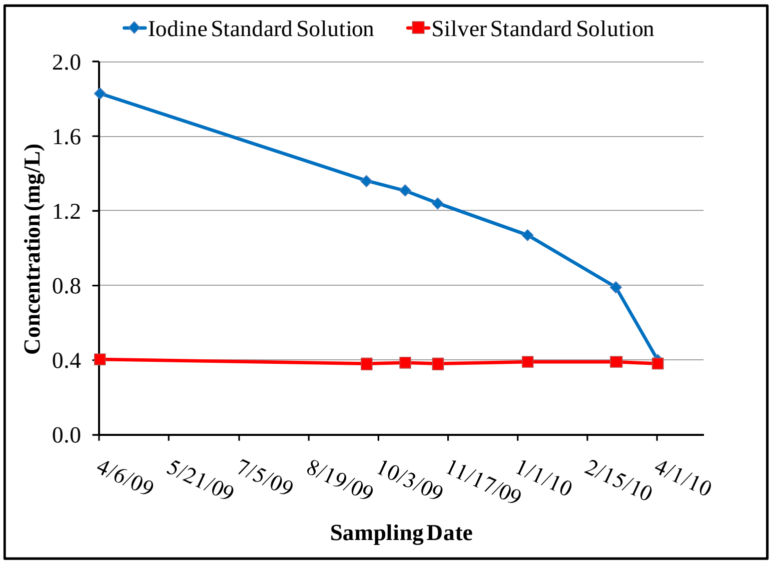

Figure 4. Results from ground experiments performed with the standard solutions launched in the CWQMK.

The results from the stability test of the standard solutions are plotted in Figure 4. Analyses performed when the standard solutions were prepared in April, 2009 showed that the silver standard solution contained 0.403 mg/L of silver and the iodine standard contained 1.83 mg/L of iodine. As shown in the plot, the silver standard is very stable. The measured silver concentrations remained within 5% of the initial concentration measured in the standard solution for 12 months. The iodine standard solution, however, degraded significantly during the course of the ground experiments. By the time the initial in-flight analysis session had occurred, the concentration of iodine in the standard solution had already decreased to 1.36 mg/L. The measured iodine concentration continued to decrease in the subsequent ground experiments, falling to 0.40 mg/L by the end of the study.

The ground experiments also evaluated the stability of the analysis cartridges that were launched in the CWQMK. To accomplish this, analysis cartridges prepared at the same time as those used in the in-flight analyses were exposed to solutions with known silver and iodine concentrations. The silver and iodine concentrations measured with the analysis cartridges were then used to calculate percent recoveries relative to the know concentration. The mean percent recoveries calculated during each set of ground experiments are plotted in Figure 5. All data points in the figure represent mean recovery values calculated from at least three replicate analyses.

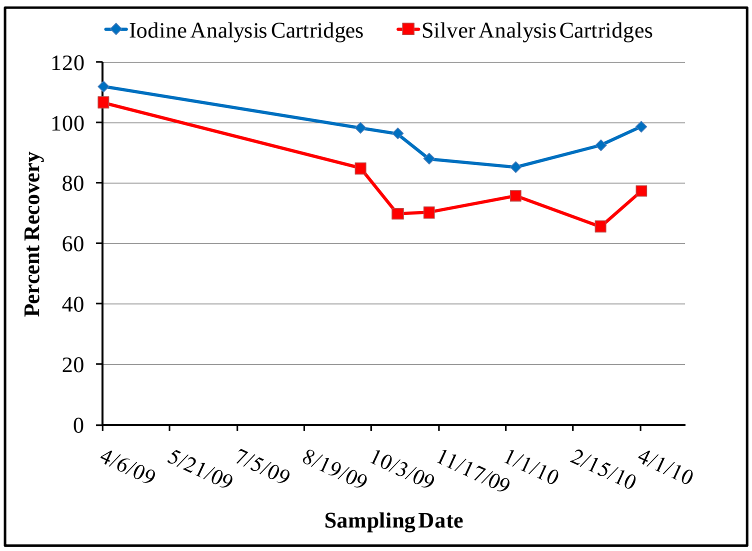

Figure 5. Results from ground experiments performed with silver and iodine analysis cartridges prepared at the same time as those used during in-flight analysis sessions.

The silver analysis cartridges demonstrated a definite decrease in percent recovery as storage times increased in the ground experiments. After the initial decrease in percent recovery, the response of the membranes fluctuated over the remainder of the test but remained between 70% and 75%. The iodine analysis cartridges exhibited similar

behavior, but the decrease in response was not as severe as that observed with the silver cartridges. The percent recoveries were greater than 80% for the entire test.

C. Discussion

The ultimate evaluation of the acceptability of CSPE technology for routine use monitoring water quality on the ISS must be based upon agreement between the results from the in-flight analyses and the ground analyses performed on archive samples. Ideally, this comparison would be made using the same sample (i.e., the unused portion of the sample analyzed in flight would be returned to the ground for analysis), but that was not possible. Due to competition for return manifest space and samples being misplaced, very few of the CWQMK samples were returned. Fortunately, collection of the CWQMK samples was coordinated with the nominal archive sample collection, so the results obtained with the CWQMK can be compared to those obtained with the archive samples to assess the performance of the kit. Overall, the agreement between the in-flight and ground results for the samples from the PWD dispensing needle is very good. The lone exception is the result from the seventh analysis session, which was conducted on April 27, 2010. The results from that sample were much higher than any other sample from the PWD needle. Unfortunately, no crew comments or observations were recorded, so there is no way to explain this anomalous result.

There is general agreement between the in-flight and ground results from the PWD auxiliary port samples in all but one sample (session 6). The one sample that did not contain iodine was one of the CWQMK samples that was returned to ground. It is believed that this sample did contain iodine when collected, but that it degraded during storage on the ISS. The returned sample volume was very low (20 mL), and previous studies have shown that iodine solutions degrade in sample bags with high surface area to volume ratios. Unfortunately, assessing the accuracy of the in-flight measurements is difficult due to the questions about whether or not the auxiliary port and sampling hardware were adequately purged prior to sample collection. This assessment is further complicated because archive samples from the PWD auxiliary port are not normally collected. The result from the eleventh session (July 2010) provided the best opportunity to evaluate the accuracy of measurements made with the CWQMK. This sample was collected after 6 L of water has been flushed from the auxiliary port. The iodine concentration in this sample was measured to be 1.66 mg/L. This is very close to the iodine concentrations measured in the product water samples collected during WPA check out (1.4 mg/L, 1.89 mg/L, and 1.9 mg/L). The result is also in good agreement with a sample of WPA product water collected at the rack interface panel (RIP) two weeks after the in-flight analysis (2.05 mg/L).

The results from in-flight and ground analyses run on the SVO-ZV samples show excellent agreement. Ground analysis of returned samples confirmed that the silver concentration in water collected from the SVO-ZV system was very low. The exception, once again, is the result obtained from the seventh analysis session. Similar to the iodine result, the silver concentration measured during this session was much higher than expected. As discussed above, this is believed to be an anomalous data set, but there is no information available to confirm that belief.

IV. Conclusions and Future Work

Despite the difficulties encountered during the early in-flight analysis sessions, the results obtained during the SDTO experiment clearly demonstrate that CSPE can be used for routine water quality monitoring on the ISS. The hardware provided the capability to measure ionic silver and molecular iodine concentrations in water samples on the ISS. Further, the measurements made with the CWQMK show good agreement with the results from ground analyses, indicating that the in-flight measurements have good accuracy.

Moving forward, the project team is in the process of transitioning the CWQMK to operational hardware. They have been given authorization to proceed with development of a Government Furnished Equipment (GFE) version of the CWQMK that will include the capability to monitor total iodine (sum of iodide, molecular iodine, and triiodide). As part of this effort, they will also be evaluating ways to improve the performance of the existing methods for ionic silver and molecular iodine, such as adjusting the coefficients of the response functions to account for decreases in the response of the analysis cartridges. Once the GFE system is certified, the focus of the project will shift to expanding the capabilities of the CWQMK. This expansion will include other analytes in drinking water and, potentially, analytes in other samples matrices such as urine, coolant, and air.

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