TOC Calibration Method for Exploration Application

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Total organic carbon (TOC) is the amount of carbon associated with organic compounds in solution and is often used as a non-specific indicator for water quality or cleanness. Currently, the Total Organic Carbon Analyzer (TOCA) is being used onboard the International Space Station (ISS) for water recovery system process control. An exploration-class TOCA is now being developed to close the technology gaps between the State-of-the-Art ISS TOCA and the emerging requirements of future exploration missions. One of the technical gaps for an exploration TOC analyzer is the development of suitable methods for on-orbit calibration. While the ISS TOCA uses pre-packaged ground-supplied TOC calibration standards, there is limited stability data. Other options include preparing calibration standards in space, which can be challenging due to the lack of low TOC reagent water. This paper explores the practice of the standard addition method and passive dosing approaches as potential solutions to overcome this problem.

Nomenclature

DI = deionized
ECLSS = Environmental Control and Life Support System
ISS = International Space Station
KSC = Kennedy Space Center
L = liter
LSS = Life Support Systems
MCO = Mars Campaign Office
min = minute
mL = milliliter
mm = millimeter
mol = moles
NASA = National Aeronautics and Space Administration
ppb = part per billion
ppm = part per million
PT = pressure transducer
SOA = the State-of-the-Art
TOC = total organic carbon
TOCA = Total Organic Carbon Analyzer
TRL = technology readiness level
µm = micrometer

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I. Introduction

TOTAL organic carbon (TOC) is the amount of carbon associated with organic compounds in solution and is often used as a non-specific indicator for water quality or cleanness. Currently, the Total Organic Carbon Analyzer (TOCA) is being used onboard the International Space Station (ISS) for water recovery system process control. An exploration-class TOCA, referred to as MiniTOCA, is now being developed by the Mars Campaign Office (MCO) Life Support Systems (LSS) Project to close the technology gaps between the State-of-the-Art (SOA) ISS TOCA and the emerging requirements of future exploration missions.[1,2,3,4,5]

One technical gap for an exploration TOC analyzer is the development of suitable methods for on-orbit calibration. While the ISS TOCA uses pre-packaged ground-supplied TOC calibration standards, there is limited stability data when storing the standards beyond 18 months. Meanwhile, a component shelf life longer than three years is required for exploration missions. In addition to solution stability, there is an issue with the additional consumable mass needed to fly the calibration standards in a fully hydrated pre-packaged format.

This paper summarizes the ongoing development of a calibration method for an exploration class TOC analyzer.

II. Background

A preliminary trade study of concepts for providing on-orbit TOC calibration standards was conducted. Four concepts were considered and compared: (1) Ground-filled pre-package TOC standards, (2) On-orbit dilution of concentrated liquid or solid TOC reagent, (3) Development of a packed bed organic desorber or passive dosing device; and (4) Carbon dioxide (CO_2) gas standards for standalone calibration of the TOC detector. These concepts are briefly described, along with their perceived advantages and disadvantages.

Concept 1, Ground-filled TOC standards: This concept is the current state-of-the-art for on-orbit TOCA calibration. For this concept, TOC standards are made on the ground and flown for use in orbit in pre-packaged bags. This concept was selected as the near-term solution for meeting the timeline and objectives of the miniTOCA Technology Demonstration on the ISS. The miniTOCA project aims to optimize the ground-filled TOC standard preparation method and to meet a calibration standard stability requirement for long-duration missions for up to 3 years.

Concept 2, Dilution of a TOC concentrate or solid: This concept involves flying a pre-packaged liquid concentrate or solid form of the reagent in which low TOC water could be added in the proper preproportion to create a TOC standard on-orbit. This concept is being considered with interest due to its simplicity and potential improvements in stability and mass savings over Concept 1. The only identified challenge is that these types of calibration techniques generally will require a means of generating low TOC water or compensating for background TOC to achieve a reliable calibration method due to the lack of low TOC diluent on orbit.

Concept 3, Packed bed doser: For this concept, water is passed through a matrix containing a solid TOC standard that is released into the passing water to create a TOC standard solution, generally through a desorption or dissolution process. This concept is particularly interesting because it lends itself well to system automation. However, the main challenges with these systems are the relatively low technology readiness level (TRL), the potential for added system complexity, and a general lack of experience with such systems in flight. In addition, it also requires low TOC water, similar to Concept 2.

Concept 4, Gas standards: This concept considers using compressed CO_2 to perform standalone calibration of the TOC detector system. However, this does not account for system variations beyond the detector performance, such as changes in organic carbon oxidation performance or CO_2 transport efficiencies, and thus does not provide a system-level calibration.

While Concept 1 is attractive due to its flight heritage and simplicity, it might be the most mass-intensive of the concepts. The standards must be flown in their fully hydrated form to cover the entire mission duration. Typical off-the-shelf TOC standards have a shelf life of less than a year;[6] higher concentration standards can have a longer shelf life before the container is opened, but they have a relatively short expiration period after that. As the desired range of TOC calibration standards is below 10 ppm, the 3-year shelf life for ready-made solutions may be challenging.

Similarly, the miniTOCA project also plans to investigate Concept 2 as a potential long-term solution. However, challenges remain associated with measuring the proper amounts of water and the lack of a low TOC reagent water diluent. Presently, work on Concept 2 remains limited.

There remains significant interest in Concept 3. Based on this approach's overall low TRL, the team dedicated more upfront development effort to understanding its feasibility. Based on work at the Kennedy Space Center (KSC) on the passive dosing technology[7,8] an opportunity was identified for the KSC team to lead an effort in the feasibility investigation for Concept 3.

In addition, because both Concepts 2 and 3 require considerations for the lack of high-purity reagent water, a literature review was carried out to identify a solution to address this issue.

This paper describes the development of a passive packed bed doser using a flow-through cell and the development of a calibration method using the standard addition approach.

III. Packed Bed Doser: Design and Building

Based on MiniTOCA design requirements, the targeted measurement range will be 1 to 10 ppm TOC, with a more desirable range between 0.25 to 10 ppm TOC; the measurement accuracy should be better than 25%, while the precision should be better than 25%, and preferably better than 10%.[1] The MiniTOCA's sampling flow rate is controlled at 0.4mL/min. Thus, the TOC passive doser should achieve a relatively stable effluent TOC concentration in the target calibration range (0.25 to 10 ppb) at this flow rate. In addition, the current pump in the MiniTOCA design limits the allowable pressure drop over the doser, preferably no greater than 0.25 psi.

To achieve this, we decided that the concept design should meet the following requirements: (1) a packed bed filled with a solid TOC standard material with a constant surface area and a low solubility, (2) built from materials that do not leach TOC.

A. Surface Area

Because the dosing is achieved through the dissolution of the standard material, the dosing rate (the dissolution rate) is related to the properties of the solid solute (the standard material) and the solvent (water), as described by Noyes-Whitney equation: [9,10]

$$Dissolution\ rate = \frac{dm}{dt} = A\frac{D}{d}(C_s - C_b) \qquad (1)$$

Where: $\frac{dm}{dt}$ = dissolution rate, kg/s, the rate of transfer of mass from the solid solvent to the solution.

A = the area of the solid exposed to the solvent, m^2.

C_s = the solubility, the saturation concentration of the solid in the medium, kg/m^3.

C_b = the concentration of the solid in the bulk medium, kg/m^3.

D = the diffusion coefficient of the solid in the medium, m^2/s.

d = the width of the diffusion boundary layer, m.

The Noyes-Whiney equation demonstrates the effect of the surface area on the dissolution rate. Based on our experience with passive dosing technology, the stability of the solid surface area is one of the most critical design elements to ensure a stable dosing rate. Also, the total surface area can change as the particle size changes over time, potentially leading to bed channeling and resulting in efficiency or system failure losses. Thus, to use these solid-phase calibration standards, it is critical to consider these factors in the design and to demonstrate their useful life span.

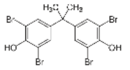
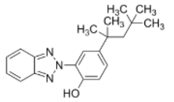
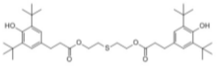
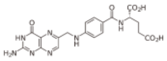
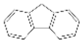
To achieve a stable surface area, we first considered the AgFoam approach,[8] using a polymer foam matrix to hold the solute particles in place and provide a stable surface area. However, the polymer foam can contribute a small amount of TOC (about 50 ppb) even after cleaning. Thus, it is not ideal for TOC calibration at an ultra-low TOC level. Further literature reviews were carried out to identify possible technical solutions to provide a stable surface area of the TOC standard particles.[11,12,13,14] As this is a low TRL technology, only one reference was found on solid TOC standard dosing, which uses solid particles directly in the packed bed.[14] This verifies the packed bed doser concept without providing insight into the stable surface area design, and the TOC level in the effluent shows some small variation for the 600 mL of water dosed. However, some references for a different application[12] show that saturated solutions of low solubility compounds can be prepared by packing columns with glass beads coated with these compounds using a rotary evaporator and then flowing water through at a relatively low flow rate (0.1 to 5 mL/min).[12]

With these potential techniques in mind, we have decided to build a flow-through cell by filling a stainless steel column with small glass beads coated with an organic compound of low solubility.

B. Material Selection for TOC Standards

The ideal measurement range of MiniTOCA is 0.25 to 10 ppm TOC. Some compounds with low TOC solubility were considered to be used as the calibration standard materials for this range. We used AqSolDB, a curated solubility reference database,[15] to down-select the low TOC standard compounds with solubilities at or below 1 ppm. The unit of the solubility data, available in Log Solubitiy (LogS) with solubility in moles per liter (mol/L), were converted into ppm concentrations. The list of compounds with solubilities ranging from 1 to 2 ppm were compiled. All hazardous chemicals were eliminated, and the final downselection was made based on the physical properties of the materials, e.g., melting point and odor, as well as the availability of each product. Five compounds were identified at the end of the assessment, as shown in Table 1. The materials were purchased and tested for their TOC level at saturation.

Table 1. The list of compounds selected for the initial screening test of low TOC standard materials.

Name	Structure	ppm	Note	CAS
Tetrabromo-bisphenol-A		1.1	Flame retardant	79-94-7
Octrizole		1	fragrance, air freshener, light stabilizer.	3147-75-9
Irganox 1035 (BASF)		1	Lubricants, auto refrigerant, thermal stabilizer, phenolic antioxidant	41484-35-9
folic acid		1.6	vitamin B9, drug	59-30-3
fluorene		2	precursor to other fluorene comps. Violet fluorescence.	86-73-7

Among the TOC reagents, Irganox 1035, 2,2'-thiodiethylene bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], was selected for further evaluation. The initial tests showed this compound's saturation TOC value to be below 1 ppm. Note that the TOC values of the initial tests are likely affected by the presence of impurities.

C. Material Selection for the Packed Bed Components

In the packed bed flow-through cell, the only source of TOC should be the standard itself. All other components of the cell and the test setup should not contribute TOC. While this seems obvious in concept, the cleanliness requirement on a low TOC hardware and test setup can initially be challenging in practice.

After some preliminary tests, it became clear that the packed bed should be built from materials completely free of organic carbon, such as stainless steel and glass.

While the stainless steel flow-through cell was being built, a first-generation plastic prototype was used to conduct preliminary tests to evaluate pressure drop, flow rate effect, and test setups.

1. The first-generation plastic prototype

The first generation plastic prototype flowthrough cell was built using Irganox 1035 particles and a Cole-Parmer TELOS® dry loading cartridge.[16] The cartridge had a 12-gram bed mass with 20µm frits at the top and bottom. The cartridge featured luer-lok® inlet and luer-slip outlet fittings. Glass beads, 710-1,180 µm, were used as the packed bed substrate upon which the TOC materials were coated. The standard particles were mixed with glass beads for the early prototype. Glass wool was used between the frits and the glass beads to provide additional containment.

A control cell was assembled using the same process but without the TOC standard material.

Figure 1. The first-generation plastic-packed bed cell is built with a TELOS cartridge, glass beads, and quartz wool.

2. *Stainless Steel Prototype*

The next prototype was built using stainless steel 316L tri-clamp fittings, tubing, adaptors, and valves, using the following list of materials (with descriptions and counts).

- Gasket w/ Steel Mesh (2 each)
- 316 Stainless Steel Column (2" Diameter, 6" Length, ~270mL Volume, 1 each)
- 316 SS Thermometer Caps (2" to 1/4" NPT, 2 each)
- 304 SS Tri-Clamps (2", 2 each)
- 316 SS 1/8" Compression Fitting to 1/4" NPT Adaptors
- 316 SS 1/8" Compression Fitting to 1/8" NPT Adaptors
- 316 SS 1/8" Compression Fitting to Male Luer Lock
- 316 SS 1/8" NPT Needle Valve
- 316 SS 1/8" Steel Tubing

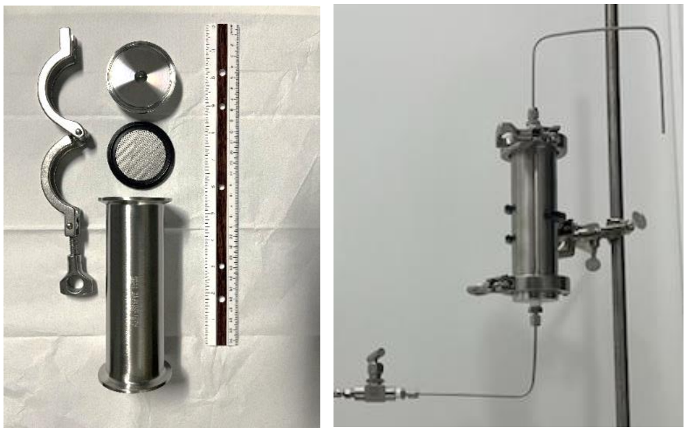


Figure 2. The parts and the assembled stainless steel prototype cell.

After the initial cleaning and testing, the gaskets were recognized as TOC sources, and stainless steel O-ring and Teflon replacements were identified.

IV. On-orbit Calibration Method Development

A typical TOC calibration method requires high-purity, practically TOC-free water for TOC standard preparation and serving as a blank standard to count for the background signal. Such water is not readily available in orbit. A potential solution is to use a water purifier cartridge, such as the Activated Carbon Ion Exchange (ACTEX) filter currently used on the ISS. While this should provide effluent with TOC below 50 µg/L (ppb), it will add some complexity and consumables. Here, we propose an alternative on-orbit TOC calibration method: the standard addition calibration, combined with background correction using a recirculation-generated system blank.

1. Linear Regression Calibration Model

The miniTOCA instrument has been shown to fit a linear regression model to accomplish system calibration. The detector's response is linearly correlated to sample concentration for this model. By measuring calibration standards over the established range of the instrument, a linear regression analysis can be performed to establish a generalized straight-line expression:

$$Y = mX + b \tag{2}$$

In this case, Y is the area under the detector signal response (peak height or area under curve), X is the TOC concentration in water, m is the slope of the linear regression line, and b is the intercept. Once the best fit of the data is determined, the equation can be used to back-calculate the concentration of an unknown sample based on the system measurement and response.

While some nuances exist to the specific calibration method for the miniTOCA instrument, proper linear regression calibration requires establishing a known and stable system blank. In general, the system blank refers to any contribution to the instrumental response not associated with the sample analyte being measured. These can include noise or bias in the system that affects the detector response or even TOC contributions from sources other than the sample, e.g., system-level contamination of the instrument. When these effects are insignificant, they can be accounted for by using “TOC-free” water as a blank (zero TOC) standard and the reagent diluent to prepare other standards.

2. Calibration Considerations Without High Purity Reagent Water

However, there is no readily available high-purity reagent water onboard the ISS, and there are no current plans to supply such a source in future exploration vehicles. At present, the cleanest water available is the spacecraft's potable water supply. Unfortunately, it is also the sample of interest; its TOC must be measured. Thus, it is not “TOC-free.”

Again, Concept 2 and Concept 3 share the challenge of a lack of high-purity reagent water for calibration standard preparation. To solve this problem, a quick literature review was carried out. It was determined that combining the standard addition method and system recirculation could be a consumable-free alternative to the high-purity water calibration requirement.

3. Considering the Application of the Standard Addition Method For On-board Calibration

It was determined that the standard addition method, which has been used for TOC analyzer calibration,[17] could solve this challenge. When this method is used, the standard is added directly to the aliquots of the analyzed sample. It is a method to address the matrix effect (or matrix interferences), which can make the traditional calibration curve approaches ineffective. The standard addition method is relatively well-known for calibration and measurement verification. It is often the recommended method for measuring the TOC values of the reagent blanks, such as that of the reagent acids used for analysis.

The method can potentially be adopted here to obtain the slope of the calibration curve without using high-purity reagent water. Experimentally, equal volumes of the sample water, with unknown TOC concentration (x), are taken and “spiked” with known and different amounts of the TOC standard materials so that their TOC concentrations are x+A, x+B, and x+C. These spiked solutions are measured, and the corresponding signals are Y_{x+A}, Y_{x+B}, and Y_{x+C}. The slope of the calibration curve can be calculated as follows:

$$m = \frac{dY}{dX} = \frac{Y_{x+B} - Y_{x+A}}{(x+B)-(x+A)} = \frac{Y_{x+B} - Y_{x+A}}{B-A} \tag{3}$$

The slope can also be obtained by plotting the signals of the spiked samples (Y_{x+A}, Y_{x+B}, and Y_{x+C}) against the amount of the TOC materials spiked (A, B, and C) and then using linear regression to obtain the slope value *m*.

This approach has been tested, and it was demonstrated that the standard addition method can be used to calculate the slope of the calibration curves.

4. Considering the Application of an Instrument Blank Using a Recirculation Method[17]

As mentioned above, the slope of the linear calibration curve *m* can be obtained using the standard addition method but not the intercept b. However, this could be "good enough" when the calibration curve's intercept is considered negligibly small. That is usually the case when the sample TOC level is above 1 ppm.

However, for low TOC water samples, the calibration curve's intercept or the positive signal for the blank value can not be ignored for accurate measurements.

The positive signal (usually an area value) reflects the blank value, which can be the sum of several contributing factors:

- Blank value of the instrument
- Reagent impurity
- Blank value of the standard (ultrapure water)
- Contaminations from the environment (dust, contaminations on the glassware, etc.)

While minimizing environmental contamination to an acceptable level is not trivial, it is possible through painstaking best practices. The impact of the impurity associated with the reagent chemicals and the reagent water can be eliminated or minimized using the standard addition method. However, the instrument's blank value needs a different solution.

After best controlling the sources of environmental contamination, the instrument blank value can be obtained by carrying out an automatic analysis of circulating ultrapure water or the cleanest water sample available. This re-circulation of the water sample through the analysis process will eventually reduce the TOC level of the sample to such a low level that it essentially contains no TOC, and the final determined area or signal corresponds to the actual instrument blank value. This is also the intercept of the calibration curve. The MiniTOCA team has verified this method using their prototype TOC analyzer.

V. Preliminary Tests: Experimental

A. Pressure Drop

The initial pressure drop evaluation was done using the first-generation plastic prototype. The pressure drop over the cell was measured at different flow rates, with two pressure sensors connected to the cell, one located upstream and the other downstream. The pressure sensors are Setra systems 0-10 psi range pressure transducers, with accuracy at 0.25% of the entire pressure range, i.e. 0.025 psi. A peristaltic pump was used to control the flow rates.

B. Flow-Through Testing of the Plastic TOC Prototype Packed Bed

1. Flow Rate Effects at 5, 10, 12 mL/min

Planned operational flow rates for the miniTOC analyzer will be around 0.4ml/min. To test the effect of the flow rate, initial testing was performed at 12, 10, and 5 mL/min. In these experiments, flow rates were controlled using MasterFlex peristaltic pumps. DI water was pumped through the control and standard test cells, the effluent was collected into TOC sample bottles, and the TOC levels were analyzed using an Anatel PAT 700 TOC Analyzer (Beckman Coulter) with a built-in 4-bottle grab-sample analyzer.

2. Flow-Through Test at Targeted Flow Rate of 0.4mL/min

A syringe pump was used for the low flow rate operational test at 0.4 mL/min test (see Figure 4). A plastic syringe was initially used, and glass and stainless steel syringes were tested as low-TOC leaching alternatives. The plastic syringe was tested first and replaced by the glass syringes soon after, as the plastic syringe would contribute an appreciable amount of TOC to the test.

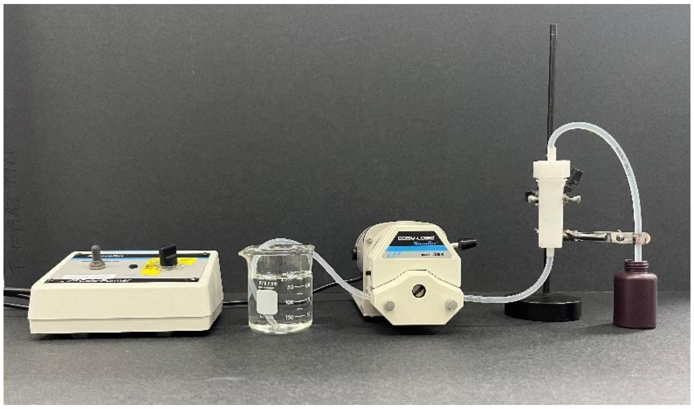


Figure 3. The flow through test setups at higher flow rates.

For testing, a syringe was filled with deionized water (DI), which was used as the influent supply to the cartridge. A similar syringe was filled with DI water, serving as the control of the test, and was repeated for each sample bottle. The sample collection was almost continuous, one right after another, as it took a few hours to collect samples at the low 0.4mL/min flow rate. The syringes were cleaned before each use: washed with soapy water, rinsed with tap water, and rinsed with DI water at least three times at each step.

Figure 4. The flow-through test setup at 0.4 mL/min with a glass syringe. The insert image shows both the plastic syringe and the glass syringe.

VI. Preliminary Test: Results and Discussion

A. Pressure Drop

Figure 5 shows the reading of the pressure transducers located before and after the flow-through cell, PT1 and PT2, respectively. The difference between the two readings reflects the pressure drop.

Using a peristaltic pump to control the flow rates precisely at the slow target flow rate (0.4 mL/min) was difficult. Four flow rates were tested: 0.15, 2.5, 12, and 20 mL/min; the corresponding pressure drop values were about 0.07, 0.1, 0.18, and 0.26 psi. Based on these results, the pressure drop at 0.4 mL/min can be estimated at below 0.1 psi. While the first-generation flow-through cell meets the pressure drop requirement, the same test has to be done for each prototype and the final design.

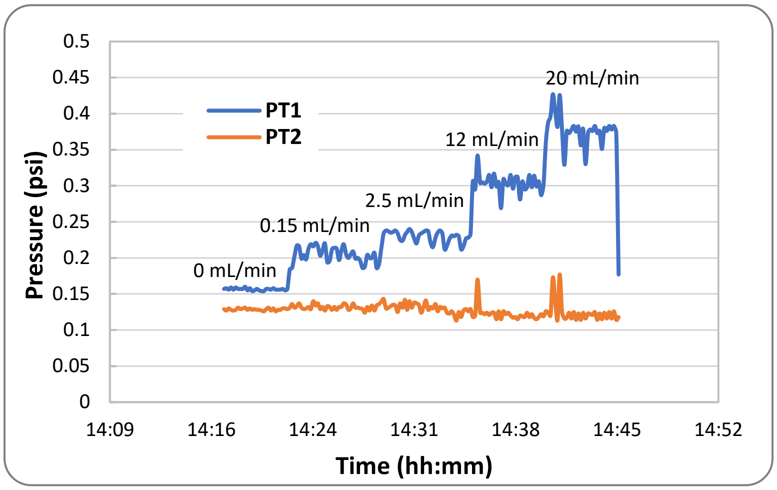


Figure 5. Pressure drops over TOC standard cell at various flow rates.

B. Flow-Through Testing of the Plastic TOC Prototype Packed Bed

1. 5, 10, 12 mL/min: Control Cell

The input DI water and 6 effluent samples were collected for a typical test, and their TOC concentrations were measured. The TOC increase values were calculated for the first bottle of effluent (Bottle 1-DI) and the average of bottles 2 to 6 (Bottle Average-DI). They were plotted against the flow rates and the soak time.

These results are for the control cell, so the expected TOC dosing levels from the glass beads and the column were expected to be zero or at very low ppb levels. However, the parts used to build the control column were only washed with soapy water and rinsed by DI (more than three times).

Figure 6 shows the average TOC level of DI-corrected Bottles 2 to 6 as a function of flow rate. The flow rate effect on the TOC release is not very clear. At the end of the test, the average TOC increase was around 20 ppb.

Figure 7 shows the increase in the TOC level of Bottle 1 plotted against the soak time between tests. It was observed that the longer the soak time between tests, the higher the level of the TOC released. It is clear that even at the end of the test, the cell still leaches TOC, especially after allowing the system to soak.

These data indicate that more rigorous cleaning is needed or the cell materials should be changed, possibly both.

2. 5 and 10 mL/min: Standard Cell

Based on the results from the control cell, the parts used to build the standard cell were more rigorously cleaned to prevent contamination. These parts were washed three times with soapy water, rinsed with tap water, and rinsed twice with DI water. Then, each part was submerged in DI water and sonicated for 30 minutes. This process was repeated three times while measuring the TOC level of the DI water bath to ensure all the parts were clean.

Similar to the control cell test, the TOC level of Bottle 1 is always higher than the rest of the samples, reflecting the higher TOC level of the water due to a long soak between tests.

The input DI water and 4 effluent samples were collected, and their TOC concentrations were measured. The TOC increases were calculated for the first bottle of effluent (Bottle1-DI) and the average of bottles 2 to 4 (Bottle Ave -DI). They were plotted against the flow rate and the soak time.

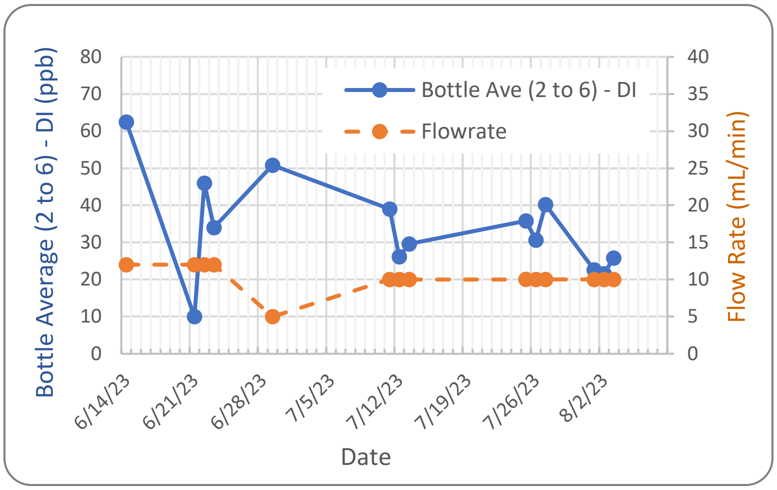


Figure 6. Control cell test results: the average TOC increase of samples 2 to 6.

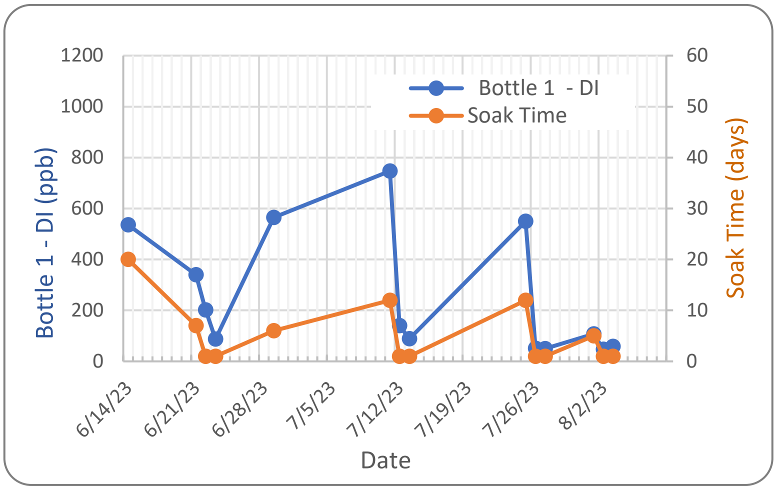


Figure 7. Control cell test results: the TOC level of Bottle 1 minus DI input.

Figure 8 shows the average TOC level of DI-corrected Bottles 2 to 4 versus flow rate. After testing at 10 mL/min and observing a decrease in the TOC levels, the flow rate was reduced to 5 mL/min. The 5 mL/min results showed an initial increase in TOC followed by a gradual decrease. At the end of the test, the average TOC increase was around 20 to 30 ppb.

Figure 9 shows the TOC increase of Bottle 1 and the soak time between tests. Similar to the trend of the control cell, the longer the soak time, the higher the TOC in sample Bottle 1. In addition, the trend for the average TOC increase of samples 2 through 4 is also plotted at a 10-time multiple value. It can be seen that soak time between tests heavily impacts the TOC level of the first sample and also influences the average TOC of the following samples.

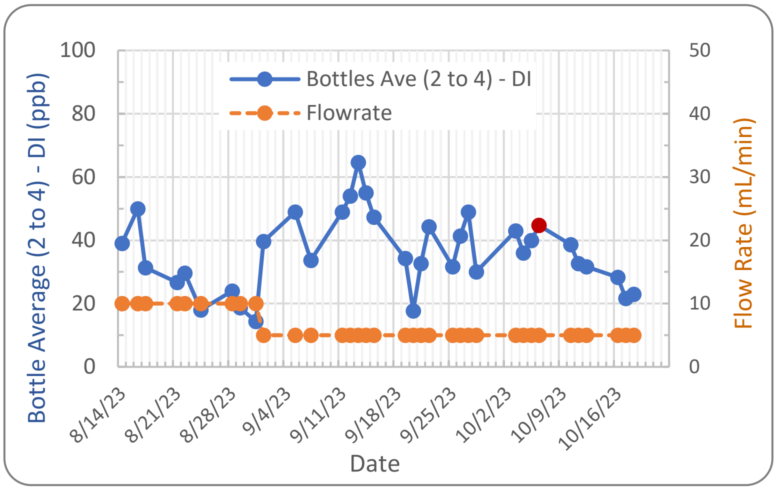


Figure 8. TOC standard cell results: the average TOC level increase of samples 2 to 4.

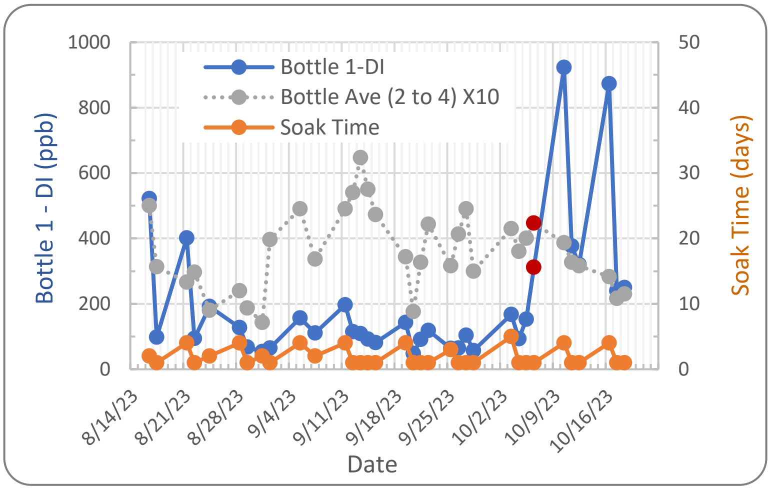


Figure 9. TOC standard cell results: the TOC level of bottle 1 minus DI input.

As the standard cell was cleaned before assembly, it was expected that after some initial testing, the TOC would level off for a given flow rate, but it continued to trend down. Such trends indicate that cell material also contributes to TOC over time.

To better observe the trends and reduce the soak time effect on samples 2 to 4, a change was made to the test setup on 10/06. During the time between tests, the test cell was isolated from the rest of the test system by clamping closed the cell inlet and outlet tubing so that TOC leaching during soak would only affect the cell volume, which would be flushed out in Bottle 1. This resulted in an increase in the TOC level of Bottle 1, but also a more apparent trend in the bottle averaged TOC of samples 2 to 4. Ultimately, the average TOC decreased further until about 20 ppb. This can be observed in Figure 8 and Figure 9, where the 10/06 data points, the start of implementing cell isolation, have been highlighted with red circles.

It was concluded that the plastic cell continued to contribute to the TOC level in the effluent, even though all parts of the cell were cleaned before use.

3. *Flow through Test at Targeted Flow Rate (0.4mL/min)FS*

The result of the flow-through test of the plastic standard cell at 0.4 mL/min is shown in Figure 10. The sample (S) is the effluent sample, while DI (D) is the TOC contribution from the input DI water.

As the test results at higher flow rates show, the first sample reflects the TOC accumulation during the soak time between tests, which usually has a higher TOC level than the other samples.

After the initial test with the plastic syringe, it was clear that it contributed a high amount of TOC to the effluent, so it was replaced by the glass syringe on 11/29.

Figure 10 shows the TOC increase in Bottle 1, Bottles 2 to 4 average, and the soak times between test runs. At a low flow rate, the effluent TOC level is higher at the end of the test, around 100 ppb. However, as shown in the higher flow rate test results, the sample TOC level is still affected by the soak time, indicated in the TOC level of sample 1 and reflected in samples 2 to 4.

Two TOC sources contribute to the TOC in the effluent samples: the standard material and the plastic cell itself. The former should only increase till it reaches its saturation point, while the latter could continue to rise with time. Based on our observation, the soak behavior dominates the latter, as indicated by the flow-through test at higher flow rates.

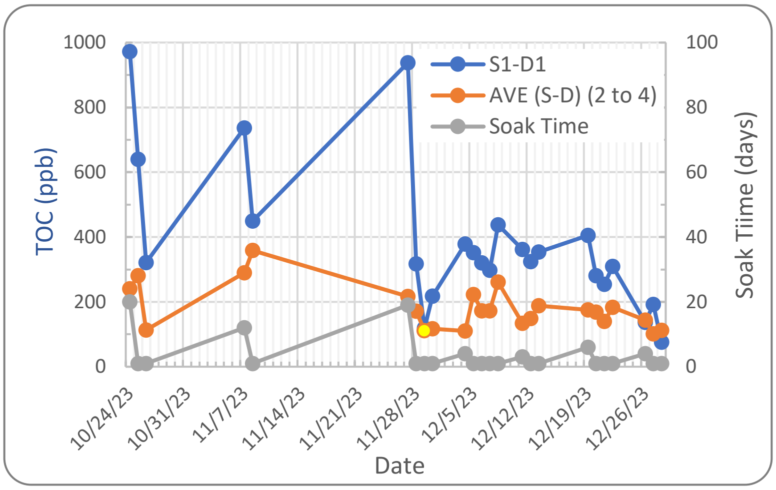


Figure 10. The result of the plastic standard cell's flow-through test at 0.4ml/min.

The plastic flow-through cell showed some flow rate effect. In general, the slower the flow rate, the higher the TOC dosing concentrations. However, the most important lesson learned is to avoid the TOC contribution for cell components. Each cell component must be cleaned thoroughly and soaked for at least days to verify no TOC leaching. This was carried out for the stainless steel cell after it was built.

VII. Summary

In summary, a passive dosing device has been proposed as a potential online calibration standard method based on Concept 3 for a packed bed organic desorption/dissolution device. A first-generation prototype was developed using TOC standard material particles with low solubility packed in a commercially available polymer column. The prototype was built and tested to understand the effects of TOC release as a function of flow rates and to optimize the system further. Based on the initial testing results, the second-generation prototype device was built with a stainless steel column to eliminate potential TOC leaching from the cell components. Testing of the stainless system is ongoing. In addition, a potential method for calibration of the future exploration-class TOCA instrument was identified for possible use in on-orbit TOC calibration when ultrapure reagent water is not readily available. This method would include the standard addition method to determine the slope of the calibration curve and a sample re-circulation method to determine the intercept.

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References

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[1] Morrison, C., McPhail C., Schumacher S., Callahan, M., and Pensinger, S., “Considerations for Development of a Total Organic Carbon Analyzer for Exploration Missions,” ICES-2018-185, 48th International Conference on Environmental Systems, 8-12 July 2018, Albuquerque, New Mexico.

[2] Morrison, C., McPhail C., Callahan, M., and Pensinger, S., “Concepts of a Total Organic Carbon Analyzer for Exploration Missions,” ICES-2019-254, 49th International Conference on Environmental Systems, 7-11 July 2019, Boston, Massachusetts.

[3] Winiberg, F. A.F., Christensen, L., Kale, M., Jones, A., and Morrison, C., “Miniature TOC Analyzer using Tunable Laser Spectroscopy and Combustion,” ICES-2020-239, 50th International Conference on Environmental Systems.

[4] Gonzalez, M., Lopez, V., Winiberg, F., Christensen, L., Noell, A., Kidd, R., Homer, M.L., Fridosy, S., Darrach, M., Morrison, C., and Callahan M., “Photocatalytic Oxidation using TiO_2 and UV for Total Organic Carbon Analysis of Water,” ICES-2020-67, 50th International Conference on Environmental Systems.

[5] Morrison, C., To, J., Noell, A., and Callahan, M., “Selection of a Total Organic Carbon Analyzer System for Exploration Missions,” ICES-2020-398, 50th International Conference on Environmental Systems.

[6] https://www.sigmaaldrich.com/US/en/specification-sheet/SIAL/94450

[7] Irwin, T., Li, W., Buhrow, J., Calle, L., and Callahan, M., “Silver Foam as Long-Term Passive Biocide for Potable Water Systems,” 49th International Conference on Environmental Systems, ICES-2019-272, 7-11 July 2019, Boston, Massachusetts.

[8] Irwin, T., Li, W., Diaz, A., Calle, L., and Callahan, M., “Silver Foam: A Novel Approach for Long-Term Passive Dosing of Biocide in Spacecraft Potable Water Systems – Update 2022,” 51st International Conference on Environmental Systems, ICES2022-097, 10-14 July 2022, St. Paul, Minnesota.

[9] Noyes A. A, Whitney W. R., “The rate of solution of solid substances in their own solutions,” *Journal of the American Chemistry Society*, Vol. 19, No. 12, 1897, pp. 930-934.

[10] Dokoumetzidis A. and Macheras P., “A century of dissolution research: from Noyes and Whitney to the Biopharmaceutics Classification System,” *The International Journal of Pharmaceutics,* Vol. 321, No. 1, 2006, pp.1-11.

[11] EPA Product Properties Test Guidelines OPPTS 830.7860 Water Solubility (Generator Column method), EPA 712-C-96-042, August 1996, https://www.regulations.gov/document/EPA-HQ-OPPT-2009-0151-0035

[12] May, W. E., and Wasik, S. E., “Determination of the Aqueous Solubility of Poluunuclear Aromatic Hydrocarbons by a Coupled Column Liquid Chromatographic Techniques,” *Analytical Chemistry*, Vol 50, No. 1, 1978, pp.175-179.

[13] Birch, H., Redman, A. D., Letinski, D. J., Lyon, D. Y., and Mayer, P., “Determining the water solubility of difficult-to-test substances: A tutorial review,” *Analytica Chimica Acta*, Vol. 1086, 2019, pp.16-28.

[14] Jolly, C. (2012). Total organic carbon (TOC) and total inorganic carbon (TIC) calibration system, US Patent No. 5,312,756, U.S. Patent and Trademark Office. https://ppubs.uspto.gov/pubwebapp/

[15] Sorkun, M.C., Khetan, A., and Er, S, “AqSolDB, a curated reference set of aqueous solubility and 2D descriptors for a diverse set of compounds,” *Scientific Data*, Vol 6, 2019, Article number 143. https://doi.org/10.1038/s41597-019-0151-1

[16] https://www.coleparmer.com/i/cole-parmer-telos-dry-loading-cartridge-20-m-frit-slip-tip-12-g-20-pk/0647555

[17] Shimadzu TOC Application Handbook, www.shimadzu.eu.com/sites/shimadzu.seg/files/toc_application_handbook4_18a.pdf